Phase formation, thermal stability and mechanical behaviour of TiCu-based alloys

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Piter Gargarella
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Referee 1: Prof. Dr. Jürgen Eckert (TU Dresden, IFW Dresden)

Referee 2: Prof. Dr. Walter J. Botta Filho (DEMa/UFSCar, Brazil)
Abstract

The large elastic limit, the strength close to the theoretical limit, the excellent magnetic properties and good corrosion resistance of bulk metallic glasses (BMGs) make them promising for several applications such as micro-geared motor parts, pressure sensors, Coriolis flow meters, power inductors and coating materials [1]. The main limitation of these materials is their reduced macroscopic ductility at room temperature, resulting from an inhomogeneous deformation concentrated in narrow shear bands.

The poor ductility can be overcome by the incorporation of a ductile second phase in the glassy matrix to form composites, which exhibit a better balance between strength and ductility. Different types of BMG composites have been developed to date [2] but considerable plastic strain during tensile or bending tests has been only obtained for composites with in-situ formation of the second phase during solidification [3, 4].

Among these in-situ formed composites, significant tensile ductility has been only observed for two types of alloys so far: TiZrBe-based and CuZr-based BMG composites. The former precipitate dendrites of the cubic β-(Ti,Zr) phase in the glass matrix, whereas the latter combine spherical precipitates of the cubic B2-CuZr shape memory phase within the glass. The CuZr-based BMG composites have certain advantages over the TiZrBe-based composites such as the absence of Be, which is a toxic element, and exhibit a strong work-hardening behaviour linked to the presence of the shape memory phase.

This concept of “shape memory” BMG composites has been only applied to CuZr-based alloys so far. It is worth investigating if such a concept can be also used to enhance the plasticity of other BMGs. Additionally, the correlation between microstructure, phase formation and mechanical properties of these composites is still not fully understood, especially the role of the precipitates regarding shear band multiplication as well as the stress distribution in the glassy matrix, which should be significantly influenced by the precipitates.

The aim of the present work is to develop a new family of shape memory bulk metallic glass composites in order to extend the concept initially developed for CuZr-based alloys. Their thermal and mechanical properties shall be correlated with the microstructure
and phase formation in order to gain a deeper understanding of the fundamental deformation mechanisms and thermal behaviour.

A candidate to form new shape memory BMG composites is the pseudo-binary TiCu-TiNi system because bulk glassy samples with a critical casting thickness of around 1 mm have been obtained [5] in the compositional region where the cubic shape memory phase, B2-TiNi, precipitates [6]. This phase undergoes a martensitic transformation to the orthorhombic B19-TiNi during cooling at around 325 K [7]. The B2- and B19-TiNi exhibit an extensive deformation at room temperature up to 30% during tensile loading [7].

Compositions in the Ti-Cu, Ti-Cu-Ni, Ti-Cu-Ni-Zr, Ti-Cu-Ni-Zr-(Si) and Ti-Cu-Ni-Co systems were selected based on literature data and on a recently proposed $\lambda + \Delta h^{1/2}$ criterion, which considers the effect of atomic size mismatch between the elements and their electronic interaction [8]. Samples were then produced by melt spinning (ribbons) and Cu-mould suction casting (rods and plates).

The investigation started in the Ti-Cu system. A low glass-forming ability (GFA) was observed with formation of amorphous phase only in micrometer-thick ribbons and the results showed that the best glass former is located around Ti$_{50}$Cu$_{50}$.

Considering that the GFA of the binary alloys can be further improved with additions of Ni [9], new Ti-Cu-Ni shape memory BMG composites were then developed in which the orthorhombic Ti(Ni,Cu) martensite precipitates in the glassy matrix. These alloys exhibit a high yield strength combined with large fracture strain and the precipitates show a reversible martensitic transformation from B19 to B2-type structure at a critical temperature around 320 K (during heating).

The amorphous matrix stabilizes the high-temperature phase (B2 phase), which causes different transformation temperatures depending on whether the precipitates are partially or completely embedded in the glassy matrix. The deformation starts in the softer, crystalline phase, which generates a heterogeneous stress distribution in the glassy matrix and causes the formation of multiple shear bands. The precipitates also have the important function to block the fast movement of shear bands and hence retard fracture.
However, the size of such composites is limited to 1 mm diameter rods because of their low GFA, which can be further improved by adding CuZr. New Ti-Cu-Ni-Zr composites with diameter ranging from 2 to 3 mm were developed, which consist mainly of spherical precipitates of the cubic B2-(Ti,Zr)(Cu,Ni) and the glassy phase. The interrelation between composite strength and volume fraction of B2 phase was analysed in detail, which follows the rule of mixture for values lower than 30 vol.% or the load-bearing model for higher values. The fracture strain is also affected by the volume fraction of the respective phases with a maximum observed around 30 vol.% of B2 phase, which agrees with the prediction given by the three-body element model. It was observed that the cubic B2 phase undergoes a martensitic transformation during deformation, resulting in a strong work hardening and a high fracture stress of these alloys.

The GFA of the Ti-Cu-based alloys can be further increased by minor additions of Si. A maximum GFA is observed for additions of 1 and 0.5 at.% Si to binary Ti-Cu or quaternary Ti-Cu-Ni-Zr alloys, respectively. This optimum GFA results from the formation of a lower amount of highly stable Ti$_5$Si$_3$ precipitates, which act as nuclei for other crystalline phases, and the increased stability of the liquid and the supercooled liquid. The addition of Co has the opposite effect. It drastically decreases the GFA of Ti-Cu-Ni alloys and both the martensitic transformation temperature and their mechanical behaviour seem to correlate with the number and concentration of valence electrons of the B2 phase. The transformation temperature decreases by increasing the concentration of valence electrons.

An excellent combination of high yield strength and large fracture strain occurs for Ti-Cu-Ni-Zr and Ti-Cu-Ni-Zr-Si alloys with a relatively low amount of CuZr, with a fracture strain in compression almost two times larger than the one usually observed for CuZr-based composites. For instance, the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ alloy exhibit a yield strength of 1490±50 MPa combined with 23.7±0.5% of plastic strain. However, a reduced ductility was found for the CuZr-richer Ti-Cu-Ni-Zr compositions, which results from the precipitation of the brittle Cu$_2$TiZr phase in the glassy matrix.
The present study extends the concept of “shape memory BMG matrix composites” originally developed for CuZr-based alloys and delivers important insights into the correlation between phase formation and mechanical properties of this new family of high-strength TiCu-based alloys, which upon further optimization might be promising candidates for high-performance applications such as flow meters, sensors and micro- and mm-sized gears.
Zusammenfassung


Das Konzept, massive metallische Formgedächtnis-Glas-Matrix-Komposite herzustellen, um die mechanischen Eigenschaften zu optimieren, wurde bisher nur auf CuZr-Basislegierungen angewandt. Es soll mittels dieser Arbeit nun erforscht werden, ob dieses Konzept auf andere massive metallische Gläser übertragbar ist. Des Weiteren ist der
Zusammenhang zwischen Gefüge, Phasenbildung und mechanischen Eigenschaften der Komposite noch nicht vollständig verstanden, insbesondere die Rolle der Ausscheidungen in Bezug auf die Scherbandbildung und die Spannungsverteilung in der Glas-Matrix.


Die hier erzeugten Ti-Cu, Ti-Cu-Ni, Ti-Cu-Ni-Zr, Ti-Cu-Ni-Zr-(Si) und Ti-Cu-Ni-Co-Legierungen basieren auf Literaturangaben und Vorhersagen bezüglich der Glasbildungsfähigkeit in diesen Systemen mittels λ+Δh^{1/2}-Kriterium, welches die Auswirkungen der Atomgrößenunterschiede der Elemente und deren elektronische Wechselwirkung einbezieht. Die Proben wurden im Schmelzspinnverfahren (Bänder) und mittels Saugguss in einer Cu-Kokille (Stäbe und Bleche) hergestellt.


Die Glasbildungsfähigkeit von binären Legierungen kann durch die Zugabe von Ni weiter verbessert werden. Dies führte innerhalb dieser Arbeit zur Entwicklung neuer Ti-


Die Glasbildungsfähigkeit von TiCu-Basislegierungen kann im Gegenzug weiterhin durch geringe Si-Zusätze gesteigert werden. Hierbei tritt jeweils ein Maximum bei Zusätzen von 1 und 0,5 at-% Si zu binären Ti-Cu- oder zu quaternären Ti-Cu-Ni-Zr-Legierung auf. Das Optimum der Glasbildungsfähigkeit ist das Ergebnis sowohl eines geringeren Anteils

Eine ausgezeichnete Kombination von hoher Streckgrenze und Bruchdehnung tritt für die Legierungen Ti-Cu-Ni-Zr und Ti-Cu-Ni-Zr-Si mit einem relativ geringen CuZr-Anteil auf. Die Bruchdehnung unter Druck ist fast zweimal höher als es für CuZr-Basis-Komposite gewöhnlich beobachtet worden ist. Die Legierung Ti₄₅Cu₃₉Ni₁₁Zr₅ zeigt beispielsweise eine Streckgrenze von 1490±50 MPa in Kombination mit einer plastischen Dehnung von 23,7±0,5%. Für die CuZr-reicheren Ti-Cu-Ni-Zr Zusammensetzungen wurde jedoch eine geringere Duktilität festgestellt, was das Resultat spröder Cu₂TiZr-Ausscheidungen in der Glas-Matrix ist.

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1 Introduction and motivation

The absence of lattice defects such as dislocations and grain boundaries yields the higher strength and larger elastic limit of metallic glasses when compared with their crystalline counterparts [10]. Despite of these interesting properties, they are still barely used in structural applications because of a limited deformability at room temperature. A better compromise between strength and ductility can be obtained when a soft secondary phase precipitates in the glassy matrix [11]. Excellent mechanical properties were obtained for TiZrBe-based bulk metallic glass composites for instance, which form dendrites of the soft β-(Ti,Zr) phase in the glass matrix, with yield strength of around 1600 MPa and elongation up to 10% [12, 13]. These alloys, however, have two major disadvantages linked with the presence of the toxic element Be and, in addition, they exhibit a work-softening behaviour, unwanted in structural applications.

More recently, new, Be-free CuZr-based bulk metallic glass (BMG) composites were obtained in which the cubic B2-CuZr phase polymorphically precipitates in the glassy matrix [4, 14]. Due to the shape memory characteristics of this cubic phase [15] this new class of composites has been named “shape memory bulk metallic glass composites” [16]. They also exhibit a high strength combined with a large ductility and more importantly, show strong work-hardening behaviour originating from a stress-induced martensitic transformation within the precipitates from a cubic B2 to monoclinic B19-type structure during deformation. However, so far the concept of “shape memory BMG matrix composites” has been only proven for CuZr-based alloys and an extension is vital to prove the universality of this concept.

Moreover, the correlation between microstructure, phase formation and mechanical properties of these composites is still not completely understood, especially the role of the precipitates regarding the shear band multiplication and the stress distribution in the glassy matrix, which should be significantly influenced by the precipitates and the relation between spacing of the precipitates and the critical crack length of the amorphous phase (minimum crack length to fracture the material). These B2-CuZr precipitates seem to control the deformability of the composites [14], which usually exhibit a fracture strain only slightly
larger than the observed for a pure B2-CuZr sample (around 10% in compression [14]). The search for new composites, which incorporate a shape memory phase with larger plasticity, is the key to improve the mechanical behaviour of this new class of BMG composites.

One promising candidate to produce new shape memory bulk metallic glass composites is the Ti-Cu-Ni system. Bulk glassy samples with a critical casting thickness of around 1 mm have been reported in the pseudo-binary TiCu-TiNi system [5]. The cubic B2-TiNi phase is thermodynamically stable in a large compositional range up to 32 at.% Cu and undergoes martensitic transformation to the orthorhombic B19 or monoclinic B19’ phase depending on composition [7]. B2- and B19’-TiNi exhibit an extensive deformation at room temperature up to 30% during tensile loading [7]. The possibility to incorporate these soft and ductile phases into a glassy matrix opens a window for the development of bulk metallic glass composites with advanced mechanical properties. Additionally, the TiNi intermetallic is well known for its excellent shape memory properties with large shape recovery and superelastic behaviour [7]. New BMG composites with good shape memory properties could be obtained, which may be useful in functional and structural applications.

The present work aims to develop a new family of TiCuNi-based shape memory BMG matrix composites with high strength and large deformability and to correlate properties, microstructure and phase formation. The concept developed for CuZr-based alloys should be confirmed for this new family of alloys.

Some fundamental aspects about BMGs and their deformation behaviour, the formation and properties of BMG composites with emphasis on shape memory BMG composites and an overview of the phase formation in TiCuNi-based systems are given in chapter 2. Details of the experimental procedure of samples preparation and their characterization are described in chapter 3.

Chapters 4 to 9 show the results obtained in this thesis, starting with the investigation of the glass-forming ability (GFA) in the binary Ti-Cu system (chapter 4) with the help of the $\lambda + \Delta h^{\frac{1}{2}}$ and the $\gamma^*$ amorphization criteria. The former considers the effect of atomic size mismatch between the elements and their electronic interaction [8] and the latter considers the difference between the formation enthalpies of amorphous and
intermetallic phases [17] (more details will be given in section 2). The Ti-Cu system is the basis for the development of several TiCu-rich bulk metallic glasses [9, 18-23] and a detailed study was carried out in order to reveal the full potential of this system by understanding its GFA before expanding the search to multi-component systems. In order to precipitate the B2 or B19 TiNi phase in the glassy matrix, additions of Ni are necessary.

Additions of 7 to 10 at.% Ni already allows the formation of bulk metallic glass composites with precipitation of the B19 phase during cooling. The correlation between phase formation, thermal stability and mechanical properties of these novel Ti-Cu-Ni shape memory bulk metallic glass composites is discussed in chapter 5. The thermal evolution during heating of two Ti-Cu-Ni metallic glasses is shown in chapter 6, especially concerning the correlation between phase formation and microstructure obtained during crystallization with the occurrence of martensitic transformation.

The improvement of the GFA of Ti-Cu-Ni alloys with additions of CuZr and Si was also investigated. Their effect on the phase formation and the mechanical behaviour is described in detail in chapters 7 and 8, respectively. Chapter 9 shows the influence of Co additions on the phase formation, the thermal stability and the mechanical behaviour of Ti-Cu-Ni alloys, with a focus on the influence of the chemical composition of the B2 phase on the martensitic transformation and the mechanical properties. The findings are discussed based on the number and concentration of valence electrons in the B2 phase.
2 Fundamentals

2.1 Bulk metallic glasses

Although some references date back the formation of the first amorphous metals already to the 1840s [24], it was just in the first half of the 20th century after the discovery of the X-ray diffraction method that their formation was confirmed [24]. They were first obtained by vapour quenching or electro-deposition methods [24, 25]. Another important step forward was made at the Caltech lab of professor Pol Duwez in 1960 [26] when an Au-Si alloy was vitrified by cooling from the liquid state using a novel technique called splat cooling [27]. Since then, metallic glasses have been extensively studied and several new compositions and processing techniques were developed, with applications ranging from structural parts in miniaturized motors and precision machinery to sensors and flow meters, protective coatings and highly efficient transformers [1, 28]. In the following, the main aspects about the atomic structure of metallic glasses, glass-forming ability of metallic melts and glass transition will be briefly mentioned.

Atomic structure of metallic glasses

A glassy state can be obtained (in principle) in all kinds of materials independent of the atomic bonding nature but their glass-forming ability (GFA) varies widely [24]. They are commonly described as “frozen” liquids as they do not flow on practically relevant time scales and thus can be considered to be solid for all applications. Since the pioneering work of Bernal et al. [29], it has been demonstrated that dense packing is a common feature of the atomic structure of metallic glasses [30]. It is impressive that although these materials have a complete absence of long-range order, they possess a density just slightly lower (less than 0.5%) than the corresponding crystalline alloys [31]. Another feature of the glassy structure is that they form local atomic configurations, which are generally completely different from the corresponding equilibrium phases. Frank [32] suggested that the barrier for homogeneous nucleation in undercooled liquids occurs as a result of the formation of local icosahedral ordering, which shows high atomic packing and is incompatible with the crystalline structure of the equilibrium phases. Recent works using containerless processing
have confirmed Frank’s hypothesis for Ti-Zr-Ni alloys [33]. Simulations have also shown that icosahedral order rises during cooling of Cu-Zr metallic glasses towards the glass transition, which is associated with an increasing viscosity [34]. This icosahedral ordering seems to be predominant in metal-metal-type alloys as Ti-Cu-based metallic glasses [1, 35].

The structure of metallic glasses can be described by local atomic units (clusters), which are connected in different ways (face-, edge- or vertices-sharing) and thus yield a configuration lacking long-range order and translational symmetry. These clusters in turn can be depicted by means of the solute-centred model: solvent atoms form coordination shells around a central solute atom giving rise to a quasi-equivalent short-range order inherited from the liquid state [36, 37]. Figure 2.1 shows that despite the absence of long-range order, different metallic glasses form different local units. Specific size ratios between the solvent atom in the centre and the solvent atoms around it determine how many solute atoms fit into the different coordination shells [30]. For instance, Ni$_{81}$B$_{19}$, Ni$_{80}$P$_{20}$, Zr$_{84}$Pt$_{16}$ and Ni$_{63}$Nb$_{37}$ metallic glasses form two dominant coordination shells represented by different polyhedra as shown in Figure 2.1. These clusters are connected in different ways depending on composition, atomic size and chemical affinity between the elements [36] and form the second level of the structural hierarchy named medium-range order.
Figure 2.1 – Coordination number (CN) distribution of the solute atoms in different metallic glasses. Two dominant CNs are formed in each alloy. The polyhedra shown in the bottom part of the figure correspond to these different CN. Taken from ref. [36].

Miracle [38] proposed a structural model based on an efficient packing of solute-centred atomic clusters (ECP model). As shown in Figure 2.2, icosahedral solute-centred clusters composed of α solute and Ω solvent atoms are arranged in a face-centred-cubic lattice [38] (in the case of metal-metalloid glasses, a simple cubic packing scheme is preferred [39]). As a consequence, tetrahedral and octahedral interstices are formed, giving rise to two topologically distinct atomic positions (named β and γ, respectively, Figure 2.2). This medium-range order extents only up to a few cluster diameters as a result of atomic relaxations and internal strains [39]. The model considers that the solute-centred clusters are formed just by a first coordination shell of solute atoms, there is no orientational order among these clusters and all solutes have a specific atomic size ratio with the solvent in order to have an efficient packing [30, 38]. The ECP model has been refined over the years and an impressive agreement with experimental data has been obtained [38-40], especially concerning density [40].
Sheng et al. [36] used reverse Monte Carlo simulations based on experimental X-ray diffraction and absorption data, as well as ab initio simulations to solve the short- and medium-range order of binary glasses and they found that not just a specific coordination number occurs but a range of different quasi-equivalent clusters (Figure 2.1), allowing a larger flexibility to pack more efficiently the atoms without the need of a specific lattice [37]. In contrast to the ECP model prediction, they found that the medium-range order consists of an icosahedral arrangement of clusters with about 12 neighbouring clusters. The short- and medium-range order of a Zr-Ni metallic glass have been recently observed by nanobeam electron diffraction combined with ab initio molecular dynamics simulation [41].

The actual challenge in structural analyses of metallic glasses is to unravel how the clusters are connected and to find common rules or trends, which can be used to predict the medium-range order and to correlate the atomic structure with macroscopic properties, for instance with the mechanical performance. As one example, Ma et al. [42] have shown that both Young’s modulus and shear modulus of metallic glasses are defined by the solvent-rich configurations among bonded atomic clusters and proved the important role of medium-range order for the mechanical properties of glassy alloys.

**Glass-forming ability of metallic melts**

For many years it was believed that glassy metals could be produced only by applying extremely high cooling rates as obtained using melt-spinning \((10^4 - 10^6 \text{ K/s [43-45]})\) and splat cooling \((\text{up to } 10^{10} \text{ K/s [46]})\) because of the flexible non-directional nature of
metallic bonds, which allows fast rearrangements at high temperatures. The easiness of
crystallization is proved by the low nucleation barrier and high growth rate of critical nuclei
during homogeneous nucleation [47]. Nevertheless after the mid-1970s [23], new
compositions were discovered with the ability to bypass crystallization during cooling and to
undergo a glass transition under relatively low cooling rates down to 0.067 K/s [35], forming
the so-called “bulk” metallic glasses. Samples with typical dimensions in the centimeter
regime were obtained in Pd-, Zr-, Cu-, Mg-, RE-, Fe-, Co-, Ti-, Ca-, Pt-based systems [35].

The tendency for glass formation is related to a high stability of the liquid phase and
sluggish solidification kinetics of the competing crystalline phase(s) [48]. The liquid’s
stability is enhanced by a high atomic packing of atoms [38] and a large negative enthalpy of
mixing between the main elements [49] whereas a solidification process with the
simultaneous formation of different phases and polymorphs [50] associated with slow
crystal grow [51] favours glass formation.

Several criteria were proposed to evaluate the glass-forming ability (GFA) based on
the glass transition, liquidus and crystallization temperatures (\(T_g\), \(T_l\) and \(T_x\), respectively) of
the metallic glasses [52]. The three most commonly used are \(T_{rg} (=T_g/T_l)\) [53], \(\Delta T_x (=T_x-T_g)\)
[49] and \(\gamma (=T_x/(T_g+T_l))\) [48]. The latter was further refined to \(\gamma_m (=2T_x-T_g)/T_l\). The
crystallization is thermodynamically possible below the liquidus temperature and is
kinetically hindered below the glass-transition temperature. The first parameter, \(T_{rg}\),
suggests that the gap between them should be minimized in order to favour glass formation
[35]. Nevertheless, a better description of the GFA was observed for combinations of the
three characteristic temperatures [52, 54]. The crystallization temperature should be also
considered because it tells how stable the supercooled liquid is when compared with the
crystalline phases. Guo et al. [52] evaluated many thermal criteria using statistical and
physical considerations and found that the best indicator is the \(\gamma_m\) criterion [55].
Considering that they make use of thermal properties of the glassy state, they cannot
predict new compositions \textit{a priori}.

Additional to these thermal parameters, empirical rules have been widely used [49,
56] to assess the tendency of a melt to vitrify, i.e. (1) the alloy composition should consist of
three or more chemical elements, (2) the difference in atomic size between these elements should be more than 12%, (3) a negative heat of mixing should occur between the main elements and (4) the composition needs to be close to a deep eutectic where the liquid phase has high thermal stability. These rules do not strictly apply in many cases since new bulk metallic glasses have been discovered in some binary systems [57-61], in compositions far from the eutectic points [59, 62-65] and in alloys where the addition of elements with a positive heat of mixing can induce phase separation and surprisingly improve the GFA [66].

Although the empirical rules are very helpful in selecting new glass-forming compositions, they lack the precision to determine alloys with maximum GFA. The development of an accurate predictive criterion based on fundamental properties of the elements such as atomic size and electronic structure is of utmost importance because new metallic glasses and composites could be developed with better mechanical properties and maximum size. Many predictive criteria have been proposed along the years based on electronic structure [67], the formation enthalpy of amorphous and crystalline phases [17, 68], topological instability or destabilization of the host crystalline lattice [69-71], the electronegativity difference [69, 72-74], calculation of the liquidus temperature based on the CALPHAD technique [68] and structural models [38, 68, 75]. However, none of these criteria proved to have a universal applicability and current research is devoted to combining different criteria to refine and improve their predictability and to obtain a better agreement with experimental data [68, 72, 76].

Among these predictive criteria the thermodynamic parameter, $\gamma^*$, has been successfully used to predict the GFA in many systems as Cu–Zr [17], Cu–Hf [77], Ni–Ta [60], Ni–Nb [61], Ni–Ti [78] and Al–La [79]. It was proposed by Xia et al. [17, 61, 77] and considers the driving force of amorphization ($\Delta H_{\text{amor}}$) and the resistance to crystallization ($\Delta H_{\text{inter}} - \Delta H_{\text{amor}}$). The thermodynamic parameter ($\gamma^*$) is expressed as follows:

$$\gamma^* = \frac{\Delta H_{\text{amor}}}{\Delta H_{\text{inter}} - \Delta H_{\text{amor}}}, \quad (2.1)$$

where $\Delta H_{\text{amor}}$ and $\Delta H_{\text{inter}}$ are the formation enthalpies of amorphous and intermetallic phases according to Miedema’s model, respectively [80, 81]. The interface enthalpy
between the constituent elements, the shear and bulk moduli and the melting temperature as well as the molar volume of each element are included in the calculations (more details about the enthalpy calculations can be found in references [17, 61]). Larger \( \gamma^* \) values indicate compositions with higher glass-forming ability.

Another predictive criterion is the recently proposed \( \lambda + (\Delta h)^{1/2} \) criterion [8]. It combines the effect of atomic size mismatch between elements given by the \( \lambda \) parameter [82] with the influence of their electronic structure taken into account by the \( \Delta h \) parameter [83]. The \( \lambda \) parameter was first proposed by Egami and Waseda [82] to determine the minimum solute concentration in a binary alloy system, which causes the topological instability of the respective solid solution and thus leads to the formation of amorphous phase during rapid solidification instead. This parameter was further extended to predict the crystallization behaviour of Al-based alloys [70] and to predict new amorphous compositions in multi-component systems [69, 84] by trying to avoid compositional fields associated with primary crystallization. The \( \lambda \) parameter can be calculated using the following equation:

\[
\lambda = \sum c_i \left| \frac{r_i^3}{\sum n_j r_j^3} - 1 \right|, \tag{2.2}
\]

where \( c_i \) and \( r_i \) are the molar fraction and atomic radius of the solute element \( i \), respectively, and \( n_j \) and \( r_j \) are the amount and atomic radius of each element \( j \) in the host compound, respectively.

Let us consider two adjacent phases in a binary phase diagram, i.e. an A-rich and a B-rich phase: the addition of B to the A-rich phase as well as the addition of A to the B-rich phase destabilizes each crystalline phase. At a certain composition the topological instability of both phases, or likewise their \( \lambda \) values coincide, and this point corresponds to the maximum topological instability in the compositional region between them. For this composition vitrification should be easiest. Based on this assumption and considering all equilibrium phases, a \( \lambda \) plot is built.

As indicated by the empirical rules proposed by Inoue et al. [49], a negative enthalpy of mixing between the main elements of an alloy favours glass formation [49]. It relates
directly to the electronic interactions between the constituent elements [85] and hence they should be taken into account to indicate the GFA of the metallic system. In order to improve the predictability of the $\lambda$ criterion, Oliveira et al. [8] combined the $\lambda$ criterion with a recently proposed electronic parameter, $\Delta h$ [83]. The $\Delta h$ parameter describes the contribution of the work function difference ($\Delta \phi$) and the electron density difference at the Wigner-Seitz cell boundary ($\Delta n_{ws}$) in a simplified Miedema’s equation for calculation of the formation enthalpy [80]:

$$\Delta h = (\Delta \phi)^2 - 5.7 (\Delta n_{ws}^{1/3})^2. \quad (2.3)$$

$\Delta \phi$ and $\Delta n_{ws}$ correlate with the surface concentration of atoms ($S_i$) in a random packing of neighbours around a central atom as follows [83]:

$$\Delta \phi = \sum X_i \left( \sum S_j |\phi_i - \phi_j| \right), \quad (2.4)$$

$$\Delta n_{ws}^{1/3} = \sum X_i \left( \sum S_j |n_i^{1/3} - n_j^{1/3}| \right), \quad (2.5)$$

$$S_i = \frac{X_j r_j^2}{\sum X_j r_j^2}, \quad (2.6)$$

where $X$, $r$, $\phi$ and $n$ are the atomic fraction, atomic radius, work function and electron density of different elements $i$ and $j$, respectively. A larger $\Delta h$ value gives a higher formation enthalpy, which refers to a higher GFA. The best combination between $\lambda$ and the $\Delta h$ criteria was determined to be $\lambda +(\Delta h)^{1/2}$ by means of linear and nonlinear multiple regressions. This combination showed a linear correlation coefficient of 0.76 with the critical cooling rate for amorphization of 68 alloys from 30 different metallic systems [8].

**Glass transition**

A metallic liquid vitrifies by applying a sufficiently fast cooling rate in such way that crystallization is avoided. Although the driving force for crystallization increases by decreasing the temperature, the diffusion rate has an opposite trend [86]. After a critical temperature known as the glass transition temperature, the undercooled liquid metal cannot rearrange at the available time giving by the cooling rate and its viscosity increases.
sharply up to $10^{13}$ Poise and the material starts to behave like a solid [87]. The dependence of the viscosity with temperature is given by the Vogel-Tammann-Fulcher equation [88-90]:

$$\eta = Ae^{-\frac{B}{(T-T_0)}}$$  \hspace{1cm} (2.7)

where $A$ and $B$ are temperature-independent constants, $\eta$ is viscosity and $T$ is temperature. Adam and Gibbs suggested that the kinetic slowdown when approaching the glass transition temperature involves cooperatively rearranging regions (CRRs) [91]. The number of particles in CRRs are inversely proportional to the liquid’s configurational entropy relative to that of the crystal ($\Delta S_{\text{conf}}(T)$) and the time for the CRR rearrangement depends exponentially on its size. Considering this, they proposed a simple relation that links the thermodynamics and kinetics of the glass transition [87, 91]:

$$\tau(T) = \tau_0 e^{-\frac{C}{\Delta S_{\text{conf}}(T)}}$$  \hspace{1cm} (2.8)

where $\tau_0$ and $C$ are constants and $\tau$ is the relaxation time, which is directly proportional to the viscosity considering the Maxwell relation $\tau(T) = \frac{G_{\infty}}{\eta(T)}$ and assuming that the instantaneous shear modulus $G_{\infty}$ is temperature-independent. According to equations 2.7 and 2.8, the viscous-slow down near the glass transition occurs as a result of the decreasing in the number of configurations that the system is able to sample given by $\Delta S_{\text{conf}}(T)$.

Figure 2.3 gives the variation of the volume and enthalpy of the liquid phase with temperature. During formation of a metallic glass, the volume and enthalpy of the liquid decrease linearly with temperature down to the glass transition which causes a continuous change in this linear fashion. In contrast, the transition of liquid to crystal shows an abrupt change in these properties, characteristic of a first-order transition [93]. The glass transition temperature of two glasses, a and b, solidified under a lower and a higher cooling rate, respectively, is shown in the figure by $T_{ga}$ and $T_{gb}$. It demonstrates that the glass transition is dependent on the cooling rate applied during sample preparation and shows that the glass transition actually occurs over a temperature range. A higher cooling rate gives rise to a higher glass transition temperature [87], which confirms its kinetic nature. The faster a
liquid is cooled, the shorter the time available for rearrangements at a certain temperature, which increases the glass transition temperature (Figure 2.3). For a more complete description of glass transition, the reader is referred to two reviews of Debenedetti and Stillinger [87, 94].

2.2 Deformation behaviour of bulk metallic glasses

The absence of defects found in crystalline lattices like dislocations and grain boundaries is responsible for the high strength of metallic glasses, which is much closer to the theoretical limit [28]. Linked with the higher strength is the larger elastic strain metallic glasses can bear compared with their crystalline counterparts. Metallic glasses exhibit almost no plastic deformation during tensile loading at room temperature and lack a clear work-hardening behaviour, which limits their application [35]. The deformation of metallic glasses is extremely dependent on the temperature, the applied stress and the strain rate. The influence of these parameters can be visualized in deformation maps as given in Figure 2.4. It shows that at high temperatures, low stresses or strain rates, metallic glasses deform homogeneously with stable Newtonian flow conditions [10]. The capability to flow homogeneously is exploited during thermoplastic forming of BMGs [95, 96]. In contrast, at low temperatures, high stresses or strain rates, the deformation is inhomogeneous and
concentrated in narrow shear bands. The focus here is on the low-temperature deformation of metallic glasses, with description of the structural origin of shear localization and the evolution of shear bands. For more details about homogeneous flow the reader is referred to the reviews of Schuh et al. [10] and Greer et al. [97].

Deformation mechanisms during inhomogeneous flow and shear band formation in metallic glasses

There is a general consensus that the fundamental process behind the inhomogeneous deformation of metallic glasses is connected with local rearrangements of atoms in order to accommodate the imposed shear strain [10]. Upon loading, the strain is first accommodated elastically until a critical stress is reached after which flow starts to occur in locally perturbed regions. The nature of this atomic flow is explained in two different models [10]: the shear transformation zone (STZ) model proposed by Argon and Kuo [98] and the free-volume model of Turnbull and co-workers [99, 100] and Spaepen [101]. In the former model, a group of atoms is sheared from one, relatively low-energy configuration to a second configuration, overcoming an energetic barrier (Figure 2.5(a)). The STZ can be defined only after an external stimuli [10] considering that the deformation in this local region is much larger than the surround matrix. The average size of a shear
transformation zone is around 1 nm and it contains a few tens to a few hundred atoms depending on external loading and the material state [97].

The free-volume model depicts the deformation as a series of discrete atomic jumps, as shown in Figure 2.5(b), which are favoured in local regions with a large amount of free volume [10]. This model allows the development of constitutive laws based on the competition between creation and annihilation of free volume, which can explain for example the homogeneous deformation of metallic glasses (for details, see reference [10]). Nevertheless, this model does not make clear why these local atomic jumps are biased by shear stress [10].

As the loading continues to increase during deformation of a metallic glass, more rearrangements of atoms occur. The next step is to explain how shear bands (SBs) initiate from these transformed regions (STZs or local atomic jump regions). Three different scenarios have been proposed [97]: homogeneous or heterogeneous nucleation of SBs or a two stage process. During homogeneous nucleation, a percolation of transformed regions occurs along the plane of maximum shear stress forming a deformation band [102], which then softens as a result of the activation of more transformed regions inside the band [97, 103]. It is well known that during shearing of an amorphous alloy, the atoms do not find a perfectly dense fitting and must create holes [10, 103]. This increases the volume inside the band and consequently decreases the viscosity. On the other hand, if the deformation is concentrated into a few narrow bands, a substantial increase in temperature is expected to

![Figure 2.5 – (a) Two-dimensional schematics of a shear transformation zone and (b) of a local atomic jump based in the free volume theory. Figure taken from reference [10].](image-url)
occur with a subsequent drop in viscosity inside these bands, although it appears to be just a secondary effect and cannot be responsible for the shear localization [103, 104].

The heterogeneous nucleation of shear bands occurs at defects as (micro- or nanoscale) voids and surface notches formed during casting [97]. These defects will promote stress concentrations, which induce the formation of an embryonic shear band. This SB will then propagate and develop into a mature shear band [97].

In the two-stages scenario, a process similar to heterogeneous nucleation happens in the first step but with a smaller shear strain throughout the band [97]. This deformation band propagates in the plane of maximum shear stress in order to create a softened path with the activation of STZs along the band, with insignificant local heating. In the second step, a synchronized sliding and shear-off occurs along this deformation plane and the material experiences a larger shear strain with possible local heating [97]. The second step immediately follows the first in such way that just a single stress drop (serration) is observed in the stress-strain curve [97].

Factors affecting inhomogeneous plastic deformation of metallic glasses

Broadly speaking, composition, crystallization during deformation, sample shape and size (aspect ratio), temperature, testing method (compression, tensile, bending, etc.), machine stiffness and loading rate are known to affect the mechanical behaviour [10, 97]. Some of these factors are briefly discussed here. More information can be obtained from the recent review of A.L. Greer et al. [97].

i) Crystallization during deformation

Precipitation of nanocrystals within or outside shear bands has been observed by many researchers and it depends on the composition and the loading conditions [105-108]. The reasons are connected with the increased free volume inside the shear band during its generation and, to some minor extent, to the effect of temperature during the movement of a “hot” shear band [97]. Because of the fast propagation of shear bands, only a limited time is available for diffusion and as a result mainly the deformation-induced crystallization of polymorphic phases is expected [97] as is indeed observed for some CuZr-based alloys
Bulk metallic glasses showing deformation-induced crystallization usually show larger fracture strains [106]. Lee et al. [106] showed an inverse relation between the activation energy for crystallization in CuZr-based BMGs and their plastic strain before failure. Chen et al. [105] have observed that a shear band becomes thicker when it approached a nanocrystal, which showed defects as dislocations, stacking faults and deformation twins in contrast to defect-free nanocrystals generally formed during annealing. This proves that the nanocrystals participate in the deformation process and hamper the fast movement of shear bands [105]. The polymorphic nanocrystallization during deformation followed by deformation twinning in the nanocrystals were used to explain the distinct work-hardening capability of CuZr-based BMGs [107]. Pauly et al. [107] have shown that the shear modulus scales with the total energetic barrier for structural rearrangements. They proposed that under stress, local softening of the shear modulus occurs, which promotes a decrease in the energy barrier, facilitating polymorphic precipitation of a nanocrystalline cubic B2-CuZr phase. Both nanocrystallization and twinning of the B2 phase will consume energy and retard the fracture.

**ii) Effect of composition**

The plasticity of BMGs is very sensitive to composition [97, 109]. As one example, the fracture toughnesses of different glasses, which corresponds to the maximum energy that can be absorbed before fracture [110], range over four decades of magnitude depending on their composition [28]. This compositional dependence has been commonly explained based on the difference in their Poisson’s ratio (ν) or the ratio between the shear (μ) and bulk (G) modulus [110]. Either a higher ν or equivalently a lower μ/G ratio gives rise to a larger plasticity [97, 110]. The shear modulus is proportional to the resistance to plastic shear and the bulk modulus is proportional to the resistance to dilatation and cracking [97]. Both ν and μ/G have been used to understand the mechanical behaviour of TiCu-based alloys. Zheng et al. [109] have shown that minor additions of large metallic atoms to a TiCu-based BMG increases its plasticity as a result of the more metallic bonding character, with a decrease in the shear resistance proved by a decreasing in the μ/G ratio. In contrast, a slight
decrease of toughness after minor additions of 1 at.% Si to a TiCu-based bulk metallic glass was observed by Garret et al. [111], also explained based on an increasing \( \mu/G \) ratio.

The fictive temperature \( (T_f) \) has been used by Kumar et al. [112] to predict the effects not only of composition but also cooling rate and annealing on the room-temperature ductility of metallic glasses. The fictive temperature of a metallic glass represents the actual temperature of the same material in the equilibrium liquid state [113]. It has been shown that BMGs exhibit room-temperature plasticity in bending when annealed at temperatures higher than a critical fictive temperature \( (T_{fc}) \). Above \( T_{fc} \), structural relaxation processes change to crystallization and the time to cause thermally-induced embrittlement increases (Figure 2.6). It has been suggested that metallic glasses with critical cooling rates for embrittlement (estimated from time-temperature-transformation diagrams for embrittlement as shown in Figure 2.6) lower than the critical cooling rate for glass formation are always ductile in the as-cast state.

**Figure 2.6 – Time-temperature-transformation (TTT) diagram for embrittlement of a Pd-based BMG. The origin of embrittlement changes above \( T_{fc} \) from structural relaxation to crystallization. The time \( t_e \) at temperature \( T_{fc} \) represents the nose of the TTT diagram.**

**iii) Sample size, aspect ratio and test method**

The shear bands spacing and consequently the shear displacement at the surface are affected by the sample size [114]. If the same amount of strain is accommodated by samples with different sizes, it is expected that the smaller samples exhibit more shear
bands and consequently, a smaller characteristic shear band spacing [10]. The crack formation and extension depends on the shear displacement, as a critical shear displacement is required to form a crack of critical length, which then leads to fracture. It follows that samples with smaller sizes form smaller shear displacements than the critical value, which in turn results in a larger macroscopic fracture strain [114] as depicted in Figure 2.7.

The aspect ratio, H/D, (where H is height and D is the diameter) of samples is also important as discussed by Zhang et al. [115]. They showed that rods with an aspect ratio of 0.67 show more than 10 times larger fracture strain than samples with an aspect ratio of 2 in compression. In samples with low aspect ratios, shear bands terminate at the contact between the sample and the machine crosshead in such way that they are confined and cannot generate a critical shear offset. The larger friction between the sample and the loading plate observed for smaller aspect ratio samples also generates a greater lateral confining stress, which favours formation of multiple shear bands [97]. Both friction and geometrical confinement may also explain the differences in the fracture strain obtained during tensile and compression tests. Cu-Zr-Al BMGs are ductile in compression [106] but fracture in a brittle manner in tension [107].

![Figure 2.7 – Correlation between bending fracture strain and sample dimension for several bulk metallic glasses. Plastic strain is observed in bending only for samples with thickness/diameter below 1 mm. Taken from Conner et al. [114].](image-url)
The shear band formation is also very sensitive to the stress field, which depends on the method used. For multiaxial stress fields, as they appear for example during indentation and small-punch testing, metallic glasses usually exhibit a higher strength and plasticity since a heterogeneous stress distribution occurs with the formation of multiple shear bands [97].

2.3 Formation and properties of bulk metallic glass composites

Apart from the factors listed above, which influence the deformability of metallic glasses, there are also additional methods in order to increase their ductility [97]. Among them, the formation of glass matrix composites is one of the most promising [3, 4] with a good compromise between strength and ductility [3, 4, 116]. There are several ways to obtain these composites, which can be divided into two groups [2, 11]: in-situ and ex-situ composites. The former group includes composites formed during partial solidification of the undercooled liquid and the latter group corresponds to composites formed by addition of insoluble particles (fiber, wires, spherical particles, carbon-nanotubes etc.) to the melt. Alternatively, composites can be obtained by mixing crystalline particles with a glassy powder prior to consolidation or by the partial devitrification during thermal treatments or severe deformation [2, 11]. A good combination of ductility and strength was observed for both groups of composites [4, 11, 13, 116, 117] but so far, considerable deformation under unconstrained conditions (tensile or bending) has been obtained only for in-situ formed composites [4, 13, 117], which is probably connected to the good load transfer between matrix and secondary phase [118] as will be discussed later on. The focus here is on in-situ formed composites; for more information the reader is referred to the review of Eckert et al. [11].

In-situ formed bulk metallic glass composites (BMGCs)

The incorporation of a crystalline phase into the glass matrix is desirable in order to disrupt the propagation of shear bands and suppress their proliferation, which promotes a more homogeneous deformation. Several different phases can be formed during solidification, including quasicrystalline precipitates, nano- or micrometric-sized crystalline
phases or even another amorphous phase formed during spinodal decomposition [11]. An enhanced plasticity was obtained in practically all these different types of composites [11].

The phase formation of in-situ composites is dependent on the cooling rate applied during solidification: High cooling rates allow for the formation of bulk glassy samples whereas intermediate or lower cooling rates (below the critical cooling rate) yield a partially or completely crystalline sample, respectively. Apart from glass formation, to obtain a composite with good ductility the composition should be carefully selected in order to form a ductile crystalline phase during solidification. When both conditions of an appropriate cooling rate and composition are satisfied, a ductile primary phase precipitates in the glassy matrix forming dual phase composites [119, 120]. Such composites can be formed in TiZrBe-based systems where the soft β-(Ti,Zr) phase precipitates in the glassy matrix [3, 12, 117] and they exhibit high yield strength around 1600 MPa and large tensile ductility up to 10% [3]. Nevertheless, these composites incorporate Be, which is a toxic element [121] and show a “work-softening” behaviour [13], which is unwanted in structural applications.

A common characteristic of in-situ BMGCs with large ductility is that the crystalline precipitates usually have a cubic structure, i.e. they satisfy the von Mises (or Taylor) criterion, which states that at least five independent slip systems are necessary to deform a polycrystalline metal [122]. Nevertheless, although having a cubic structure some B2-type intermetallics exhibit a brittle behaviour at room temperature [123], which suggests that their composition is also important. The different compositions result in different electronic structures. Gschneidner et al. [123] have shown that ductile B2 intermetallics show an absence of d-band electrons near the Fermi Level [124]. Such favourable electronic structure also reduces the stacking fault energy, which enhances the twinning propensity and facilitates the martensitic transformation in shape memory bulk metallic glass composites [125] as will be discussed in the next section.

Next to the nature of the secondary phase, its size, distribution, shape, volume fraction and interface characteristics also control the mechanical behaviour of the composites [11]. It is difficult to observe the influence of each of these parameters in experiments independently. This drawback can be circumvented when simulations are
employed [118, 126-129]. Abdeljawad et al. [126, 127] simulated the mechanical behaviour of composites consisting of glass and spherical precipitates of a crystalline phase. They used a phase-field model to show that increasing the volume fraction of the crystalline phase decreases the ultimate strength as commonly observed in experiments [11, 13, 14] and increases the strain to fracture, whereas keeping the volume fraction fixed and increasing the diameter of the spherical crystalline phase gives rise to a lower ultimate strength and fracture strain.

The bonding between the matrix and the second phase was studied by Biener [118]. He simulated the effect of partial de-bonding of a spherical ductile crystalline phase inserted in a glass matrix and observed that deformation localizes around this region. Sharp shear bands are formed in the de-bonded region in contrast with a perfect interface glass/crystalline phase. In the case of the in-situ bulk metallic glass composites, a strong metallurgical bond occurs between the reinforcement and the matrix in contrast with ex-situ composites, where de-bonding can occur and may limit their ductility.

H. Zhou et al. [129] performed large-scale molecular dynamics simulations to investigate the effect of shape, volume fraction and orientation of nano-sized crystalline phase on the mechanical behaviour of different BMGCs. They found that elongated crystalline phases are more effective to suppress the shear band propagation than spherical particles and that elongated nanocrystals with their orientation parallel or perpendicular to the load direction are better to hinder the propagation of shear bands. They also showed that a cooperative lattice sliding and local shear transformation zones occur near the glass-crystal interface due to strain mismatch and stress concentration and the crystalline phase is an effective barrier for the shear band propagation.

A bulk metallic glass composite can also be formed by a combination of pores and the glassy phase. Such composites were studied by Sarac and Schroers [130] concerning the correlation between the size of the pore ($d$) and its spacing ($s$). They produced metallic glass heterostructures with pores equally spaced through the material (Figure 2.8) by a combination of Si lithography and thermoplastic forming. Their fabrication method has a dimensional precision better than 1 µm and the second phase (in their case pores) can be
carefully controlled in terms of size and distribution. A maximum toughness and plastic strain in tensile was achieved for \( d/s = 1 \). They showed that a critical parameter is the difference between the spacing of the second phase and the critical crack length of the glassy matrix \( (a_c) \) [131, 132]:

\[
a_c = \frac{1}{\pi} \left( \frac{K_c}{\sigma} \right)^2, \tag{2.9}
\]

where \( K_c \) and \( \sigma \) are the fracture toughness and yield strength, respectively. If \( s - a_c > 0 \), the shear bands develop into a crack before the strain energy is released into the second phase, which leads to the formation of a small number of shear bands and earlier fracture. They also suggest that the width of the sample \( (w) \) should be much larger than the spacing \( s \) in order to avoid excessive stress concentrations between the pores during shear band formation [130].

**Figure 2.8** – (a,b) Shear bands formation around the pores (the scale bar in the figures correspond to 50 and 100 µm, respectively) caused by stress concentrations as shown by...
finite element simulation in (c). (d) The fracture of the samples occurs perpendicular to the loading direction.

2.4 Shape memory bulk metallic glass composites

These composites are formed by the combination of a glassy and a shape memory phase [14], which is responsible for their strong work-hardening behavior [4] (Figure 2.9) as will be discussed later on. Crystalline samples of this phase have the ability to recover their original shape after plastic deformation of the low-temperature phase by a structural transformation upon heating to a critical temperature [133]. This “shape memory effect” is seen in some Cu-based, Fe-based and TiNi-based alloys [133]. They also have another unique property called ‘superelasticity’ (SE), which is associated with a large nonlinear recoverable strain upon loading and unloading.

Figure 2.9 – Comparison between the mechanical behaviour during tensile loading of a CuZr-based shape memory BMGC and a conventional TiZrBe-based dendritic BMGC [3]. A strong work-hardening behaviour is observed for the shape memory BMGC. Figure adapted from [16].

As discussed by Pauly et al. [14], the strength of CuZr-based shape memory BMG composites is extremely dependent on the fraction of the shape memory phase (cubic B2-type CuZr phase, Figure 2.10(a)). For volume fractions of B2 phase lower than 30%, the strength of the composites follows the rule of mixtures given by equation [14]:
\[ \sigma_{\text{Composite}} = f_{\text{Crystalline}} \sigma_{\text{Crystalline}} + f_{\text{Glass}} \sigma_{\text{Glass}} \] (2.10),

where \( f_{\text{crystalline}} \) and \( f_{\text{glass}} \) and \( \sigma_{\text{Crystalline}} \) and \( \sigma_{\text{Glass}} \) are the volume fraction and yield strength of the crystalline and glassy phases, respectively. For higher B2 volume fractions, the strength is given by the load-bearing model, which depends basically on the strength of the B2 phase [14]:

\[ \sigma_{\text{Composite}} = \sigma_{\text{Crystalline}} (1 + 0.5 f_{\text{Glass}}) \] (2.11).

**Figure 2.10** – Correlation of the (a) yield strength and (b) fracture strain with the crystalline volume fraction in a Cu\(_{47.5}\)Zr\(_{47.5}\)Al\(_5\) shape memory bulk metallic glass composites. Figures from reference [14].

The correlation between the fracture strain and the amount of cubic phase in Cu\(_{47.5}\)Zr\(_{47.5}\)Al\(_5\) shape memory bulk metallic glass composites [14] is shown in Figure 2.10(b). The fracture strain follows a model originally proposed by Fan and Miodownik [134], which considers the composite as a three microstructural element body (Figure 2.11). The element \( \alpha \) represents the cubic phase and the element \( \beta \) the amorphous phase. The third element \( \alpha + \beta \) is a mixture between \( \alpha \) and \( \beta \) in equal parts, homogeneously partitioned between each other and forming an ideal interdispersed structure. For such composites, the fracture strain can be modeled by equation [14]:
\[ \varepsilon_{\text{Composites}}^f = f_{\alpha c} \varepsilon_{\alpha}^f + f_{\beta c} \varepsilon_{\beta}^f + K f_{\alpha \beta c} \varepsilon_{\alpha \beta}^f \quad (2.12), \]

where \( f_{\alpha c}, f_{\beta c} \) and \( f_{\alpha \beta} \) and \( \varepsilon_{\alpha}^f, \varepsilon_{\beta}^f, \) and \( \varepsilon_{\alpha \beta}^f \) are the volume fractions and fracture strains of the elements \( \alpha, \beta \) and \( \alpha + \beta \), respectively. \( K \) is a dimensionless constant which considers the constraint effect of the elements \( \alpha \) and/or \( \beta \) on the element \( \alpha + \beta \) [14].

**Figure 2.11** – Representation of a composite microstructure into a three microstructural element body. \( \alpha \) denotes the shape memory crystalline phase, \( \beta \) the BMG matrix and \( \alpha + \beta \) is the mixture between these two elements. Taken from reference [14].

The ductility of the cubic shape memory phase is also strongly dependent on its composition. Wang [135] has shown that the deformability of cubic B2-TiX (X = Fe, Co, Ni) intermetallics increases by increasing the number of valence electrons per atom of the compound \( (e_v/a) \) [136]:

\[ \frac{e_v}{a} = \sum_{i=0}^{n} f_i e_v^i \quad (2.13), \]

where \( f_i \) and \( e_v^i \) are the atomic fraction and number of valence electrons in each element \( i \) of the alloy, respectively. A high \( e_v/a \) value results in a larger amount of free electrons in the alloy. Gschneidner et al. [124] have shown that a larger ductility is observed for alloys with a large amount of bonding electrons s-like (“free electrons”) instead of directional d-like [124]. A large amount of free electrons will allow the atoms to move past one another with little difficulty [124]. Additionally, a recent work [125] has demonstrated that the stacking fault energy of the cubic B2-CuZr shape memory phase is decreased by adding elements with small difference in size and electronegativity (Figure 2.12), which enhances the twinning propensity during the martensitic transformation of the cubic phase and
consequently, improves its ductility. As will be shown, the use of chemical elements with similar size and electronegativity (Ti/Zr and Cu/Ni/Co) was made by considering this compositional effect.

**Deformation behaviour of shape memory bulk metallic glasses composites**

The deformation behaviour of shape memory bulk metallic glass composites reflects the mechanical response of the crystalline shape memory phase. This phase exhibits the so-called “double-yielding” behaviour during deformation [7, 137] as schematically shown in Figure 2.13. After yielding (onset of martensite detwinning in Figure 2.13), the cubic shape memory phase starts to undergo a martensitic transformation. A plateau is seen in the stress-strain curve until the end of transformation and then another inflection point (fully detwinned martensite in Figure 2.13) occurs when the martensitic phase starts to deform elastically. Another inflection point, commonly named “second yielding”, is observed when the martensite starts to deform plastically until the fracture of the material. A very similar behaviour can be seen when a fully martensitic sample is deformed [7] but instead of an austenite-to-martensite transformation at the plateau region, the martensitic crystals start to re-orientate (undergo detwinning) in the first step of deformation, with the remaining steps being the same as described before.
The strong work-hardening behaviour observed in CuZr-based shape memory BMGC (Figure 2.9) is related to the martensitic transformation of the crystalline phase. Song et al. [138] showed that different inflection points (named yielding points) are also seen in the stress-strain curve of CuZr-based shape memory bulk metallic glass composites (Figure 2.14), which are composed of spherical B2-CuZr precipitates in an amorphous matrix [138]. Careful microscopy and X-ray diffraction analyses were conducted at the different stages of deformation and they concluded that the appearance of these different inflections points is dependent on the volume fraction of the shape memory phase and is strictly related with its deformation. The “first” yield point (Figure 2.14) marks the start of the martensitic transformation of the cubic B2 phase. The “second” yielding corresponds to the generation of multiple shear bands in the amorphous phase with continuation of the martensitic transformation and occurrence of martensite re-orientation (detwinning). The “third” yielding marks the start of the plastic deformation of the martensitic phase, which occurs until fracture.

Figure 2.13 – Schematic stress-strain curve during compression of the B2 phase. Reproduced from [137].
2.5 Shape memory alloys and bulk metallic glass formation in TiCu-based systems

In order to develop a new family of shape memory bulk metallic glass composites, the alloys should be selected in a compositional region of a system, which forms both bulk metallic glasses and a shape memory phase. The TiNi-TiCu pseudo-binary system is well known for the formation of several shape memory alloys [7], with the presence of the cubic shape memory B2-TiNi phase (space group Pm3m) which undergoes a martensitic transformation around 75 °C to the monoclinic B19’ phase (space group P2_1/m) during cooling. The transformation characteristics change with increasing Cu content in the B2-Ti(Ni,Cu) [6] and the cubic phase transforms to the monoclinic through the orthorhombic B19 phase (space group Pmma) as an intermediate state, which is stable at room temperature (Figure 2.15). Beside these phases, the tetragonal TiCu (space group P4/nmm) also forms, which has a very limited solubility of Ni (less than 2 at.%, Figure 2.15).

The glass-forming ability (GFA) of the Ti-Cu [139, 140], Ti-Ni [78, 141] and Ti-Ni-Cu [5, 9, 142] systems has been extensively studied and just recently bulk metallic glasses have been found near the pseudo-binary eutectic (L → TiCu + TiNi) [9] (Figure 2.15). Rods with diameters ranging from 1 to 1.5 mm were obtained with a fully amorphous structure. In general, the glass-forming ability (GFA) of TiNi alloys is very low [78, 141] and the addition
of certain elements such as Cu and Zr increases their tendency to vitrify [5, 9], caused mainly by the increased stability of the liquid [143]. These new bulk metallic glasses were found in an extended compositional region (Figure 2.15) as reported by Wang and Xu [9], most of them falling into the TiNi-TiCu pseudo-binary diagram. The Ti_{50}Cu_{43}Ni_{7} alloy exhibits the largest GFA observed in the ternary system so far (critical casting thickness of 1.5 mm). Figure 2.15 shows that a combination between glassy and the shape memory TiNi phase can be obtained in the NiTi-CuTi pseudo-binary system, in the range 40 < Cu at.% < 44.

Additions of other elements is needed to further improve the GFA of the Ti-Cu-Ni alloys. Zr and Co are good candidates because they have similar size and electronegativity with Ti and Cu/Ni [144], respectively, and consequently, their addition may not significantly decrease the ductility of the B2-TiNi phase as was discussed in section 2.4. Literature data suggest a higher GFA with the addition of Zr to the ternary Ti-Cu-Ni alloys. Figure 2.16 summarizes literature data of glassy alloys obtained in the pseudo-ternary TiCu-TiNi-CuZr system. This diagram is plotted as a ternary equilibrium phase diagram with X = TiNi, Y = CuZr and Z = TiCu. Several bulk metallic glasses (BMGs) have been obtained to date, particularly in the TiCu-rich region where BMGs with critical casting thickness up to 3 mm are found [5, 142, 145-147]. The compositions with the highest glass-forming ability are

**Figure 2.15** – Pseudo-binary TiCu-TiNi equilibrium phase diagram [6]. The compositional region where bulk metallic glasses (BMGs) are formed [5] is indicated in the figure.
generally located around the eutectic points in the pseudo-binary TiCu-TiNi and TiCu-CuZr systems [6, 148] (indicated by black arrows in Figure 2.16).

Figure 2.16 – Literature data of amorphous alloys obtained in the TiCu-TiNi-CuZr pseudo-ternary system [5, 142, 145-147]. There are limited data on the GFA especially when moving away from pseudo-binary compositions. CCT-rods denotes the critical casting thickness for amorphization. The black arrows indicate the eutectic compositions in the pseudo-binaries TiNi-TiCu and TiCu-CuZr systems [6, 148].

The addition of Co to the pseudo-binary TiCu-TiNi (Figure 2.15) does not alter the phase formation [149] (Figure 2.17). The pseudo-ternary TiNi-TiCu-TiCo system is formed by the cubic B2-Ti(Ni,Co,Cu) and the tetragonal γ-TiCu phases (Figure 2.17). A full solubility of Co in the B2-TiNi phase is observed in the TiNi-TiCo pseudo-binary system. This phase has a large compositional field in the TiCu-TiCo-TiNi system (Figure 2.17) and it extends up to 32 and 30 at.% Cu in the pseudo-binary TiNi-TiCu and TiCo-TiCu [149], respectively. Besides, a eutectic region occurs between the Ti_{50}Cu_{45}Ni_{5} and Ti_{50}Cu_{40}Co_{10} compositions (indicated by points e2 and e1 in Figure 2.17, respectively).
Figure 2.17 – Schematic of the (TiCu)-(TiCo)-(TiNi) pseudo-ternary phase diagram [149].
3 Experimental Procedure

3.1 Sample preparation

The starting materials were Ti, Cu, Ni, Si and Zr with purity higher than 99.99%. Their surface was cleaned with acid solutions (with exception of Si) in order to remove oxide layers and other impurities at the surface. The solutions used are given in Table 3.1. The Si element used in this work was cleaned only in an ultrasonic bath.

Table 3.1 – Acid solutions used during cleaning of the chemical elements.

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Acid solution (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>80 % HNO₃ + 20 % HF</td>
</tr>
<tr>
<td>Cu</td>
<td>70 % H₂O + 30 % HCl</td>
</tr>
<tr>
<td>Ni</td>
<td>36 % CH₃COOH + 60 % HNO₃ + 4 % HF</td>
</tr>
<tr>
<td>Zr</td>
<td>47.6 % H₂O + 47.6 % HNO₃ + 4.8 % HF</td>
</tr>
</tbody>
</table>

Ingots were re-melted in a Ti-gettered Ar atmosphere using an Edmund Bühler GmbH arc-melter. They were re-melted at least five times in order to ensure complete homogeneity. More specific information about the compositions investigated and their casting methods will be given together with their results.

Suction casting

All bulk samples prepared in this work were produced by a suction casting device attached to the arc-melter (Edmund Bühler GmbH), as schematically shown in Figure 3.1. In the beginning, valves V1 and V2 (Figure 3.1) are opened and tubes connect the melting and suction chambers. These chambers are then evacuated to 10⁻⁵ mbar and then valves V1 and V2 are closed and the melting chamber is filled with Argon in order to obtain a protective atmosphere, enable the formation of the plasma-arc and create the difference in pressure, which is responsible for the suction force. A Ti-getter is first melted in order to remove residual oxygen in the melting chamber. The alloy is then melted and by opening valve V2, the difference in pressure between the two chambers sucks the liquid alloy into the water-cooled Cu-mould (Figure 3.1). The currents used to melt the alloys ranged from 224 to 290
A (level 7 to 9) and the time during melting varied from 15 to 25 s. The difference in pressure applied during suction was around 700 mbar. The mass of ingot used to cast the samples ranged from 4 g for a 1 mm diameter and 40 mm long rod up to 10 g for a 3 mm diameter and 70 mm long rod. More details of the dimensions of rods and plates produced by suction casting will be given together with the results.

![Figure 3.1– Schematic of the arc-melter with in-situ suction casting device attached. Figure taken from reference [150].](image)

**Melt-spinning**

Five to six grams of the alloy were melted by induction inside a quartz crucible with a hole of 1 mm in diameter at the tip. Considering that both Ti and Zr can react with oxygen of the quartz tube, the internal surface of the crucibles was coated with a solution of BN and alcohol. After the evaporation of the alcohol, the BN sticks to the crucible and avoids the reaction between the melt and the crucible. The liquid metal is then ejected through the nozzle onto a rotating Cu wheel, forming ribbons solidified under high cooling rates up to $10^6$ K/s [45]. The device used was a melt-spinner from the Edmund Bühler GmbH. The melt chamber is first evacuated up to $10^{-5}$ mbar and then Ar is injected up to a pressure of around 700 mbar. The distance between the crucible and the Cu wheel was 0.5 mm and the difference in pressure responsible for the final melt ejection was around 300 mbar. The rotational frequency of the wheel was 65 Hz, which corresponds to a surface speed of 42
m/s. The ejection temperature was varied from 1150 to 1250 °C and the ribbons produced have 2 – 3 mm in width and 30 – 40 µm in thickness. The ejection temperature is chosen to be at least 100 °C higher than the liquidus temperature of the alloy.

3.2 Microstructural and thermal characterization

Metallography

The samples were first embedded using epoxy resin (Specifix Resin Struers) and then ground with grinding paper in the sequence 600, 1200, 2500 and 4000 grit, followed by polishing around 15 min with a solution of silica colloidal and 10 vol.% of H$_2$O$_2$ (OP-S, particle size 0.04 µm) and applied force of around 10 N.

Optical microscopy and phase analyses

The rods’ microstructures were observed by a Nikon EPIPHOT 300 optical microscope. The images were obtained either from the embedded samples or from each parallel face of the compression test samples after polishing, and the amount of crystalline phases was estimated by the manual point account method (ASTM E 562-08).

X-ray diffraction (XRD)

The XRD experiments were carried out using three different devices. A STOE STADI P diffractometer, which operates in a transmission mode and with Mo-Kα$_1$ radiation (λ= 0.07093187 nm) was used. The samples were scanned with a step size and time per step of 0.1 and 30 to 100 s, respectively. At least two parts of each sample were analyzed. The thickness of the samples was reduced by gridding (600, 1200, 2500 and 4000 grit) up to a thickness of around 150 µm. The surface of Ti-Cu-Ni-Zr-(Si) ingots were also checked by a Philips PW 1050 diffractometer in reflection mode, with a graphite monochromator and Co-Kα radiation (λ = 0.17902 nm) using a step size and time per step of 0.001 and 0.053 s. In-situ XRD experiments were conducted in order to check the martensitic transformation of Ti-Cu-Ni alloys. A Philips X’Pert diffractometer equipped with a Par Physics TCU 750 temperature control unit and Cu-Kα radiation (λ = 0.15418 nm) was used. The step size and
time per step used were 0.017° and 10 s, respectively, and measurements were conducted at every temperature increment of 10 °C in a temperature range of 25 to 80 °C.

**High-energy synchrotron X-ray diffraction**

In-situ crystallization experiments of Ti-Cu-Ni ribbons were performed at the beam line ID11 (European Synchrotron Radiation Facility (ESRF) in Grenoble, France) with a high-energy synchrotron radiation of 99.15 keV (λ = 0.01249 nm, selected using a Si(111) monochromator). Slices of a melt-spun ribbon were put inside a 1 mm diameter quartz capillary and then heated at 30 K.min\(^{-1}\) using a computer-controlled Linkam THMS 600 furnace. XRD patterns were collected in transmission mode every 13 °C during heating (acquisition time of 25 s) using a two-dimensional charge-coupled detector (CCD) FRELON 2k16 (2048 pixels x 2049 pixels) and a beam size of 50 µm\(^2\). A continuous Ar flow was supplied to the sample during the experiments and the distance between the samples and detector was 272 mm.

In-situ XRD experiments in a transmission mode were also conducted during compression of a TiCuNiZr 1 mm diameter rod using a crosshead speed of 2 µ/s (\(\sim 10^{-3}\) s\(^{-1}\)) in order to check the occurrence of the martensitic transformation during deformation. The experiment was conducted in the same beam line. The photon energy was 99.04 keV, which corresponds to a wavelength, λ = 0.01252 nm, the distance to the detector was 178 mm and the beam size was 50 µm\(^2\). The two-dimensional XRD patterns obtained were integrated using the FIT2D software package [151].

**Scanning electron microscopy (SEM) and chemical analysis**

The microstructure of the samples was observed using a LEO 1530 SEM and the chemical composition of the different alloys and phases were measured by means of a BRUKER EDX detector attached to the SEM. The fracture surface of some samples was analyzed by means of a Hitachi TM 1000. The structure of phases was further checked by electron backscatter diffraction (EBSD), which is attached to the LEO 1530 SEM. A NORDLYS II digital EBSD camera and the EBSD software system CHANNEL5 (HKL Technology, Denmark) were used. The amount of oxygen and silicon in the Ti-Cu-Ni-Zr-(Si) rods was
measured by inductively-coupled plasma optical emission spectroscopy (ICP OES) using a TC-436 DR (LECO) and a iCAP 6500 Duo View (Thermo Fisher Scientific GmbH), respectively.

**Transmission electron microscopy (TEM)**

Three different microscopes were used: a Philips CM 20, a FEI Tecnai F30 and a TECNAI G2 F20. The thickness of the samples was reduced to around 100 µm by manual grinding and then a spherical cavity with a thickness at the centre smaller than 5 µm was made in the samples by grinding and polishing using a dimple grinder Gatan 656. The samples were then made electron-transparent at the centre of the cavity region by ion-milling using a Gatan 691 Precision Ion Polishing System (PIPS) with a liquid-nitrogen cooling system. The voltage of the ion beam was 2.7 KV, the angle was 5 – 6 ° and the ion milling time duration was around 70 hours. The software ELDISCA version C1.2 [152] was used to evaluate the electron diffraction patterns obtained by TEM.

**Differential scanning calorimetry (DSC) and dilatometry**

The glass transition and crystallization behaviour were studied with a Perkin-Elmer Diamond DSC using a heating rate of 30 K.min$^{-1}$ in a temperature range of 298 to 923 K, and the martensitic transformation was analyzed in a Pyris DSC Perkin-Elmer at heating and cooling rates of 10 K.min$^{-1}$ from 223 to 623 K. All measurements were carried out in an argon atmosphere. The thermal behaviour at higher temperatures was studied with a Netzsch DSC 404C at a heating rate of 30 K.min$^{-1}$ and under different cooling rates of 10, 30, 40 and 50 K.min$^{-1}$. Annealing experiments were also performed at temperature between the glass transition and crystallization temperature in Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{55}$Cu$_{35}$Ni$_{10}$ glassy ribbons at 693 and 700 K for 2 and 1 minute, respectively.

Ti-Ni-Cu and Ti-Ni-Cu-Co alloys were also investigated by a Netzsch CC 200 LT dilatometer in the temperature range 148 to 423 K. Rods with 2 mm diameter and ~25 mm length were used and the cooling and heating rate used were 10 K/min. The top and bottom surfaces were ground and polished before the experiments and their coplanarity was confirmed with a caliper.
3.3 Mechanical characterization

Compression and tensile tests

Compression and tensile tests were carried out using an Instron 5869 testing device at a constant strain rate of $0.001 \text{ s}^{-1}$ and the strain was measured by a laser extensometer (Fiedler Optoelektronik). For the compression tests, at least three cylindrical samples of each rod with a 2:1 aspect ratio were tested to ensure reproducibility. The top and bottom surfaces were ground and polished before the experiments and their coplanarity was checked carefully with a caliper to avoid deviation from orthogonality. For the tensile test samples, a flat “dog-bone” sample was used with dimensions shown in Figure 3.2. At least 3 samples of each alloy were tested. The surface of the samples were polished prior the tests in order to remove superficial imperfections.

![Figure 3.2 – Geometry of the tensile test samples.](image)

In order to simulate the mechanical response under compression of the Ti$_{50}$Cu$_{43}$Ni$_7$ alloy, finite-element simulation was carried out by means of the software ABACUS. Uniaxial compression of a 1 mm diameter and 2 mm long rod composed of a glass matrix and two martensitic crystals with a diameter of 200 µm in the center of the rod, equally spaced from bottom to top, was mimicked in the simulation. Additional data about the deformation behaviour of the amorphous and martensitic phase were taken from literature [5, 7].
Three-point bending and hardness measurements

Three-point bending tests were conducted using a Bose Electroforce 3230 device with crosshead displacement speed of $0.0083 \text{ mm.s}^{-1}$. Two geometries were used in the tests. For the Ti-Cu-Ni alloys, rods 1 mm in diameter and 4 mm long were tested with lower distance of the mountings of 3 mm. For the Ti-Cu-Ni-Zr and Ti-Cu-Ni-Zr-Si samples, rectangular specimens with the dimensions 1 x 1 x 16 mm were tested using a lower distance of the mountings of 10 mm. These samples were cut from the top and bottom regions of the as-cast plates. The displacement at the surface of the specimen on the convex or the tensile side is measured together with the applied force. The bending stress ($\sigma$) and strain ($\varepsilon$) can be then calculated as [153]:

$$\sigma = \frac{3lF}{2wt^2} \quad (3.1),$$

$$\varepsilon = \frac{6tx}{l^2} \quad (3.2),$$

where, $l$ is the lower distance of the mountings, $F$ is the force, $w$ and $t$ are the width and thickness of the sample, respectively, and $x$ is the vertical displacement of the sample, as shown in Figure 3.3.

**Figure 3.3 – Schematic of the three-point bending test system.** $F$ is the force applied during the test, $t$ and $w$ are the thickness and the width of the sample, respectively, and $l$ is the lower distance of the mountings.

Additional microhardness measurements were carried out using a HMV-2000 Microhardness tester SHIMADZU. Load of 50 and 200 g were used for the Ti-Cu-Ni and Ti-Cu-Ni-Zr-(Si) alloys, respectively.
4 Glass-forming ability and phase formation of Ti-Cu alloys

Although several TiCu-based bulk metallic glasses (BMGs) were discovered in the past years [9, 18-23], a systematic approach is needed to reveal the full potential of the binary Ti-Cu system by understanding its glass-forming ability (GFA) before expanding the search to multi-component systems. Therefore, the binary system was thoroughly characterized in this work. In the following chapters, this binary system is extended by adding different alloying elements and the according compositions are discussed in the chapters 5 – 9. The GFA of the binary Ti-Cu system is revisited here with the help of the $\gamma^*$ and $\lambda+(\Delta h)^{1/2}$ criteria, also attempt to study the influence of the Cu$_3$Ti metastable phase [154] in the criteria calculation. The predictions are linked with experiments to thusly assess the validity of the criteria and their predictability. Additionally, the phase formation during crystallization and its activation energy are also investigated.

The results of the $\gamma^*$ and $\lambda+(\Delta h)^{1/2}$ criteria calculation are shown in Figure 4.1, superimposed to the binary equilibrium phase diagram [154]. Two maxima are observed for the $\gamma^*$ criterion at Cu$_{54}$Ti$_{46}$ and Cu$_{47}$Ti$_{53}$ (indicated by numbers 4 and 5, respectively). In contrast, the $\lambda+(\Delta h)^{1/2}$ criterion shows seven maxima, with the three largest values at Cu$_{63.5}$Ti$_{33.5}$, Cu$_{54}$Ti$_{46}$ and Cu$_{41}$Ti$_{59}$ (numbers 3, 4 and 6, respectively). The maximum at Cu$_{54}$Ti$_{46}$ coincides for both criteria and the best glass former appointed by the $\gamma^*$ and $\lambda+(\Delta h)^{1/2}$ criteria are the alloys Cu$_{54}$Ti$_{46}$ and Cu$_{63.5}$Ti$_{33.5}$, respectively. Four alloys were selected to be studied (indicated by the numbers 3, 4, 5 and 6) at the maxima of $\gamma^*$ and $\lambda+(\Delta h)^{1/2}$.

The GFA is expected to be higher around deep eutectic points [35, 52, 155] because of the higher stability of the liquid, which tends to be undercooled more readily to form an amorphous phase. Surprisingly, no maxima appear in the vicinity of the deepest eutectic composition at Cu$_{75}$Ti$_{25}$. In order to evaluate the GFA around this composition, two more alloys were selected to be investigated (Cu$_{76}$Ti$_{24}$ and Cu$_{70}$Ti$_{30}$, number 1 and 2, respectively). These six selected alloys together with the $\gamma^*$ and $\lambda+(\Delta h)^{1/2}$ values are given in Table 4.1.

The Ti-Cu system had first been studied by Buschow [139, 140]. Amorphous ribbons of alloys in the range 24 to 72 at.% Ti were prepared by melt-spinning and their composition
is indicated in Figure 4.1 by olive crosses. One can see that all compositions in this range with maxima of \( \lambda + (\Delta h)^{1/2} \) formed amorphous ribbons (Figure 4.1) and considering the two compositions with maxima of \( \gamma^* \) (number 4 and 5), only alloy number 4 formed an amorphous ribbon. None of these ribbons exhibited glass transition during continuous heating, which already indicates a low GFA.

**Figure 4.1** – Results of the \( \gamma^* \) and \( \lambda + (\Delta h)^{1/2} \) criteria (indicated by blue and red lines, respectively) superimposed to the binary equilibrium phase diagram [154]. The compositions investigated are shown with numbers from 1 to 6. The composition of amorphous ribbons obtained by Buschow [139, 140] are indicated in the figure by olive crosses.
Table 4.1 – Selected compositions and their $\gamma^*$ and $\lambda + \Delta h^{1/2}$ values, without and with consideration of the Cu$_3$Ti metastable phase (recalculated values) and their onset crystallization temperature ($T_x$) obtained at a heating rate of 20 K/min.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\gamma^*$ values</th>
<th>$\lambda + (\Delta h)^{1/2}$ values</th>
<th>$\gamma^*$ recalculated values</th>
<th>$\lambda + (\Delta h)^{1/2}$ recalculated values</th>
<th>$T_x$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Cu$<em>{76}$Ti$</em>{24}$</td>
<td>0.425</td>
<td>0.221</td>
<td>0.416</td>
<td>0.216</td>
<td>-</td>
</tr>
<tr>
<td>2-Cu$<em>{70}$Ti$</em>{30}$</td>
<td>0.637</td>
<td>0.299</td>
<td>0.630</td>
<td>0.253</td>
<td>682±2</td>
</tr>
<tr>
<td>3-Cu$<em>{66.5}$Ti$</em>{33.5}$</td>
<td>0.709</td>
<td>0.341</td>
<td>0.709</td>
<td>0.294</td>
<td>688±2</td>
</tr>
<tr>
<td>4-Cu$<em>{54}$Ti$</em>{46}$</td>
<td>0.859</td>
<td>0.281</td>
<td>0.859</td>
<td>0.281</td>
<td>690±2</td>
</tr>
<tr>
<td>5-Cu$<em>{47}$Ti$</em>{53}$</td>
<td>0.856</td>
<td>0.256</td>
<td>0.856</td>
<td>0.256</td>
<td>662±2</td>
</tr>
<tr>
<td>6-Cu$<em>{41}$Ti$</em>{59}$</td>
<td>0.796</td>
<td>0.293</td>
<td>0.796</td>
<td>0.293</td>
<td>657±2</td>
</tr>
</tbody>
</table>

Ribbons of the six selected composition (Table 4.1) were then prepared by melt-spinning. The rapidly solidified ribbons of the Cu$_{63.5}$Ti$_{33.5}$, Cu$_{54}$Ti$_{46}$ and Cu$_{41}$Ti$_{59}$ alloys (number 3, 4 and 6, respectively) show a fully amorphous structure according to the XRD measurements (Figure 4.2). Two broad peaks can be seen around $2\theta = 19$ ° and 33 °, which is in contrast to the ribbons of the other compositions. For the as-cast Cu$_{47}$Ti$_{53}$ ribbon (number 5), sharp Bragg peaks of the phases, TiCu (tetragonal, space group P4nmm) and Ti$_2$Cu (tetragonal, space group I4mmm), are observed and for the Cu$_{76}$Ti$_{24}$ (number 1), only peaks of the metastable Cu$_3$Ti (orthorhombic, space group Pmmn) were identified. This phase was also detected for the Cu$_{70}$Ti$_{30}$ alloy (number 2), together with the Cu$_4$Ti (orthorhombic, space group Pnma) and Cu$_3$Ti$_2$ (tetragonal, space group P4/nmm) phases. With exception of the Cu$_3$Ti, the other crystalline phases are expected to be formed considering the equilibrium Ti-Cu phase diagram [154]. The crystalline peaks observed in the diffraction pattern of the Cu$_{70}$Ti$_{30}$ alloy are superimposed on a broad amorphous peak around $2\theta = 19$ °, which already indicates the presence of amorphous phase in this ribbon.
The presence of the amorphous phase in the as-cast ribbons was furthermore verified by DSC and the results are shown in Figure 4.3 and summarized in Table 4.1. Exothermic crystallization peaks are observed for almost all samples with exception of the Cu$_{76}$Ti$_{24}$ alloy but no clear glass transition ($T_g$) was detected at heating rate of 20 K/min for any of the samples, which indicates their low GFA. Since Cu$_{76}$Ti$_{24}$ does not show crystallization peaks, which could be observed for Cu$_{70}$Ti$_{30}$ and Cu$_{66.5}$Ti$_{33.5}$ (Figure 4.3) and considering that for these two compositions, a fully amorphous structure was observed only for the latter by XRD (Figure 4.2), one can conclude that the GFA increases in the sequence Cu$_{76}$Ti$_{24}$ < Cu$_{70}$Ti$_{30}$ < Cu$_{66.5}$Ti$_{33.5}$, following the trend predicted by the $\lambda$+$(\Delta h)^{1/2}$ criterion. The ribbons were further analysed at a higher heating rate of 40 K/min in order to detect $T_g$ and only the Cu$_{54}$Ti$_{46}$ (alloy number 4) exhibited a clear $T_g$ around 649 K (Figure 4.4) and $T_x$ around 701 K. The detection of a glass transition only for the Cu$_{54}$Ti$_{46}$ proves its higher GFA when compared with the other alloys as suggested by thermal parameters [48, 53]. It is interesting to point out that the Cu$_{54}$Ti$_{46}$ composition is the only common maxima of the $\gamma^*$ and $\lambda$+$(\Delta h)^{1/2}$ criteria (Figure 4.1), which suggests that the most reliable prediction could be obtained by the combination of the two criteria in order to identify common maxima.
Both DSC and XRD results prove that the best glass formers are Cu$_{63.5}$Ti$_{33.5}$, Cu$_{54}$Ti$_{46}$ and Cu$_{41}$Ti$_{59}$ (alloys number 3, 4 and 6), which have the largest values of the $\lambda+(\Delta h)^{1/2}$ criterion. All these alloys show a fully amorphous structure by XRD. The results also indicate
that the GFA increases from alloy 1 to 3 (Figure 4.1), following the trend of $\lambda + (\Delta h)^{1/2}$. This suggests a good correlation between prediction given by the $\lambda + (\Delta h)^{1/2}$ criterion and the GFA observed.

From the two alloys selected with highest $\gamma^*$ value, only Cu$_{54}$Ti$_{46}$ (alloy 4) showed a fully amorphous structure in contrast to the Cu$_{47}$Ti$_{53}$ (alloy 5) even though they have almost similar $\gamma^*$ values (table 4.1). The reason may be related to the similar values of the interface enthalpy between Ti-Cu and Cu-Ti and shear and bulk modulus of Ti and Cu (-40 and -33 KJ/mol, 44 and 48 GPa, 110 and 140 GPa, respectively), which reduces the sensitivity of the prediction.

The criteria were also calculated considering the presence of the metastable Cu$_3$Ti phase. No significant difference is observed in the calculation of the $\gamma^*$ criterion in contrast with the $\lambda + (\Delta h)^{1/2}$ for which two maxima appear at 24 and 35.5 at.% Ti, instead of just one at 33.5 at.% Ti (Figure 4.5). With the consideration of the metastable phase, the three peaks at 33.5, 46 and 59 at.% Ti (alloys number 3, 4 and 6 in Figure 4.1) appears with similar $\lambda + (\Delta h)^{1/2}$ value (see Table 4.1). This indicates an almost similar GFA for these compositions, which is more coherent with the experimental results obtained.

The structure of the ribbons after complete crystallization was checked by XRD and the phases formed are summarized in Table 4.2. The ribbons precipitate the phases predicted by the equilibrium phase diagram [154]. The metastable Cu$_3$Ti phase formed in the as-cast Cu$_{76}$Ti$_{24}$ and Cu$_{70}$Ti$_{30}$ ribbons decomposes irreversibly upon heating, transforming

---

**Figure 4.5** - The green and red lines indicate the $\lambda + (\Delta h)^{1/2}$ values calculated with and without consideration of the metastable Cu$_3$Ti phase. Alloys 1 to 3 are indicated.

The structure of the ribbons after complete crystallization was checked by XRD and the phases formed are summarized in Table 4.2. The ribbons precipitate the phases predicted by the equilibrium phase diagram [154]. The metastable Cu$_3$Ti phase formed in the as-cast Cu$_{76}$Ti$_{24}$ and Cu$_{70}$Ti$_{30}$ ribbons decomposes irreversibly upon heating, transforming
to the equilibrium phases, Cu₄Ti and Ti₂Cu₃. Figure 4.6 shows the XRD pattern of the Cu₇₀Ti₃₀ as-cast ribbon and after heating up to two different temperatures: 723 and 1073 K. One can see that the Bragg peaks related to the Cu₃Ti phase progressively disappear with increasing annealing temperature and totally decomposes into the equilibrium phases after heating to 1073 K. The formation of this metastable phase during rapid solidification can be explained by the large compositional difference between the equilibrium phases (Cu₄Ti and Ti₂Cu₃), which is also reflected in the large $\lambda + (\Delta h)^{1/2}$ values calculated for this region.

**Table 4.2 – Phases formed in the as-cast ribbons and after complete crystallization.**

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Phases formed in the as-cast sample</th>
<th>Phases after complete crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Cu₇₀Ti₂₄</td>
<td>Cu₃Ti</td>
<td>Cu₄Ti+Ti₂Cu₃</td>
</tr>
<tr>
<td>2-Cu₇₀Ti₃₀</td>
<td>Cu₃Ti+Cu₄Ti+Ti₂Cu₃+amorphous</td>
<td>Cu₄Ti+Ti₂Cu₃</td>
</tr>
<tr>
<td>3-Cu₆₆.₅Ti₃₃.₅</td>
<td>amorphous</td>
<td>Cu₄Ti+Ti₂Cu₃</td>
</tr>
<tr>
<td>4-Cu₅₄Ti₄₆</td>
<td>amorphous</td>
<td>TiCu +Cu₄Ti</td>
</tr>
<tr>
<td>5-Cu₄₇Ti₅₃</td>
<td>TiCu+Ti₂Cu+amorphous</td>
<td>TiCu+Ti₂Cu</td>
</tr>
<tr>
<td>6-Cu₄₁Ti₅₉</td>
<td>amorphous</td>
<td>TiCu+Ti₂Cu</td>
</tr>
</tbody>
</table>

**Figure 4.6 –** XRD results for the Cu₇₀Ti₃₀ alloy in the as-cast state and after heating up to 773 and 1073 K. The metastable TiCu₃ phase decomposes to the Ti₂Cu₃ and TiCu₄ during heating.
The activation energy for crystallization ($E_c$) of the three amorphous ribbons obtained in this work (Cu$_{63.5}$Ti$_{33.5}$, Cu$_{54}$Ti$_{46}$ and Cu$_{41}$Ti$_{59}$) were calculated according to the method proposed by Khonik et al. [156]. After investigation of a large amount of experimental and literature data, they showed that the application of the Kissinger method [157] leads to false values of $E_c$. They proposed a different method, based on the linear relation between the activation energy $E_c$ and the temperature for crystallization $T_c$ [156]:

$$E_c = A(\nu, \beta) T_c,$$  \hspace{1cm} (4.1)

where $A(\nu, \beta)$ is a function of the apparent attempt frequency, $\nu$, and the heating rate, $\beta$. Within an accuracy of 18% the value of $A$ is independent of the apparent attempt frequency if taken in the range reported for metallic glasses ($10^{10} \leq \nu \leq 10^{16} \text{s}^{-1}$) and the dependence of $A$ on the heating rate is $A(\beta) = 2.92 \times 10^{-3} - 1.92 \times 10^{-4} \log \beta$ [156]. The calculated activation energy for different heating rates is given in Figure 4.7. One can see that the $E_c$ values increase in the sequence Cu$_{41}$Ti$_{59}$, Cu$_{63.5}$Ti$_{33.5}$ and Cu$_{54}$Ti$_{46}$. The values obtained vary from 1.97 to 2.12 eV, which is in the range usually observed for metallic glasses [156].

![Figure 4.7 - Activation energy for crystallization ($E_c$) versus heating rate.](image)

To conclude, a good correlation was obtained between experiments and the $\lambda + (\Delta h)^{1/2}$ criterion and the results showed that the Cu$_{54}$Ti$_{46}$ is the best glass former in the binary Ti-Cu system. Despite the formation of a full amorphous structure in the micrometer-
thick ribbon, this composition does not form amorphous phase in a 1 mm diameter rod as will be shown in subsection 8.1.1, which proves a low GFA for the binary Ti-Cu system.
5 Ti-Cu-Ni bulk metallic glass composites

Although the glass-forming ability (GFA) in the Ti-Cu system is quite low as discussed in the last chapter, it was observed that the best glass-forming composition is located around Ti$_{50}$Cu$_{50}$. As shown by Wang et al. [9], the GFA of these alloys can be further improved by adding Ni. Ni additions up to 10 at.% in the pseudo-binary TiCu-TiNi can already promote the formation of bulk metallic glasses with critical diameters up to 1.5 mm [9]. These bulk metallic glasses are formed in the primary solidification field of the shape memory phase B2-Ti(Cu,Ni), as shown in section 2.5, and for an appropriate combination of cooling rate and composition [119, 120], a bulk metallic glass composite consisting of this shape memory phase and a glassy matrix could be obtained.

Several shape memory alloys are formed in the TiCu-TiNi system because the shape memory B2-Ti(Cu,Ni) phase has a large compositional field up to around 32 at.% Cu as predicted in the equilibrium phase diagram [6]. This phase is not stable at room temperature and undergoes a martensitic transformation to the orthorhombic B19 phase during cooling [7]. The Cu-rich shape memory alloys formed in the pseudo-ternary TiCu-TiNi system exhibit a smaller temperature hysteresis during transformation than TiNi-based alloys, which renders them more suitable for actuator applications [158] and the substitution of Ni by Cu also decreases the cost of such SMAs [159].

Nevertheless, these Cu-rich bulk crystalline samples exhibit a low ductility and poor workability which restricts their applicability [160]. The reasons for this poor ductility are still not clear but it may be associated with the precipitation of the tetragonal TiCu phase at the grain boundaries or inside the B2 phase [161]. Yet, rapid solidification may extend the compositional field of the primary B2 phase and limit or even suppress the formation of these Cu-rich phases (TiCu and Ti$_2$Cu), as observed in the work of Nam et al. [160]. They produced ribbons of Ti$_{50}$Ni$_{15}$Cu$_{35}$ with a metastable microstructure consisting of B19 and B2 phase by means of the melt overflow technique. Ti$_{50}$Ni$_{15}$Cu$_{35}$ is the Ti-Cu-Ni shape memory alloy with the highest amount of Cu found so far [161]. The influence of the cooling rate on the microstructure and the phase formation of these TiCu-rich shape memory alloys were not systematically studied yet. Both characteristics define the shape memory behaviour of
TiCu-based BMGs composites, which can be very useful in applications such as actuators and sensors [162].

The effect of rapid solidification on the phase formation, mechanical properties and thermal stability of glass formers in the pseudo-binary TiCu-TiNi system [9], Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$, are studied here. They were prepared under different cooling rates in order to obtain shape memory BMG composites. Ribbons and rods of 1 mm - 2 mm in diameter and with a length of 40 mm - 70 mm were prepared by melt-spinning and suction casting, respectively. Subsequently, their microstructure, their thermal and mechanical properties were systematically investigated.

5.1 Microstructure and phase formation of Ti-Cu-Ni alloys

The XRD results for the rods and ribbons of the alloys Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ are shown in Figure 5.1(a) and 5.1(b), respectively. For the ribbons, two broad diffuse diffraction maxima appear, which are characteristic of an amorphous structure. In case of the rods, the same phases precipitate in both compositions, i.e. the B11-TiCu and B19-Ti(Ni,Cu) equilibrium phases as expected from the phase diagram [6], along with B2-Ti(Ni,Cu) and Ti$_2$(Cu,Ni). The relative peak intensities indicate a larger amount of B11-TiCu phase and B2-Ti(Ni,Cu) phase for the Cu-richer alloy, Ti$_{50}$Cu$_{43}$Ni$_7$ (see reflection of the (200) B2 plane at 2θ = 26.7 ° for the 1 and 2 mm rods, Figure 5.1(a)). The cooling rate of the rods is inversely proportional to the square of the radius [19] and is estimated to be around 2000 K/s and 500 K/s for the 1 mm and 2 mm rods, respectively [163]. For the ribbons, the estimated cooling rate is $10^4$ - $10^6$ K/s [45]. According to the phase diagram [6], the B2 phase should transform into the B19 phase at room temperature. However, the small grain size and constraints imposed by the TiCu phase can hamper the transformation and hence can shift it to lower temperatures [164, 165].
Figure 5.1 – XRD results for ribbons and rods of the (a) Ti<sub>50</sub>Cu<sub>43</sub>Ni<sub>7</sub> and (b) Ti<sub>50</sub>Cu<sub>41</sub>Ni<sub>9</sub> alloys. Similar results are observed for the different parts (top, middle and bottom) of the rods.

The microstructures of the 1 mm diameter rods of Ti<sub>50</sub>Cu<sub>43</sub>Ni<sub>7</sub> and Ti<sub>50</sub>Cu<sub>41</sub>Ni<sub>9</sub> show similar features. Both samples exhibit spherical darker precipitates embedded in a homogeneous, featureless matrix (Figure 5.2(a)). EBSD measurements were conducted in the matrix and no crystalline signal was found, confirming that this region is fully glassy. The size of the spherical regions varies significantly from 20 to 250 µm and the smaller precipitates are mainly located near the bottom part of the specimen. They form in the centre of the rod as well as in the outer region and in some parts of the sample the crystals impinge, leaving larger agglomerates, especially in the top part.

In the case of precipitates smaller than 200 µm a fully martensitic structure is observed (Figure 5.2(b)). In contrast, a heterogeneous structure is found for most of the larger precipitates, in which smaller B2-Ti(Ni,Cu) dendrites are found in the centre region together with an inter-dendritic TiCu phase and small black inclusions of the tetragonal Ti<sub>2</sub>(Cu,Ni) phase (Figure 5.2(c)). Moving from the centre to the outer part of these precipitates, the TiCu and Ti<sub>2</sub>(Cu,Ni) phases do not grow and just martensite grains can be observed (Figure 5.2(c)). The arm length of the B2 dendrites is around 500 nm for the Ti<sub>50</sub>Cu<sub>43</sub>Ni<sub>7</sub> and 2 µm for the Ti<sub>50</sub>Cu<sub>41</sub>Ni<sub>9</sub>.

The presence of the Cu-rich phases along the grain boundaries can change the composition of the B2/B19 Ti(Ni,Cu) phase. By means of EDX analysis for the 1 mm Ti<sub>50</sub>Cu<sub>41</sub>Ni<sub>9</sub> rod, it is verified that the B2-Ti(Ni,Cu) dendrites in the centre of the precipitates are richer in Ni than the B19-Ti(Ni,Cu) martensitic grains in the outer surface (11.0±0.4 and 8.0±0.3 at.% Ni in B2 and B19, respectively). This influences the transformation temperature and may also explain why B19-Ti(Ni,Cu) can be just found in the outer surface, since the increased Ni content in the B2-Ti(Ni,Cu) phase can decrease the martensite transformation temperature tremendously [7]. This enrichment of Ni in the B2-Ti(Ni,Cu) dendrites formed at the centre of the relatively larger crystalline precipitates occurs as a result of the Cu rejection into the interdendritic space and subsequent formation of the TiCu and Ti<sub>2</sub>(Cu,Ni) phases as will be discussed in the next paragraph.
The presence of these precipitates can also generate stress fields, which aggravate the martensitic transformation [164, 166]. Since no precipitates were observed in the grain boundaries or inside the martensitic grains at the outer surface, the martensitic transformation is expected to proceed more easily. Both the composition of the Ti(Ni,Cu) phase and constraints created by the Cu-rich phases, can influence the martensitic transformation and are believed to be the origins of the present microstructure [7, 164, 166].

Figure 5.2 – (a) Optical microscopy image of the longitudinal section of the 1 mm diameter Ti$_{50}$Cu$_{43}$Ni$_{7}$ rod/bottom region. The crystalline and amorphous regions are indicated. Figure (b) shows details of the spherical precipitates formed by B19 Ti(Cu,Ni) martensite. (c) SEM image showing the microstructural evolution of a large spherical precipitate.

The transition from a dendritic structure in the centre to the martensitic grains at the outer surface of the larger spherical precipitates can be understood as follows: Spherical precipitates are formed both in the centre and close to the surface of the rods (depending on the nucleation process and the local cooling rate), while the former grow radially the
latter follow the solidification front and solidify towards the centre of the rod. The primary B2 dendrites start to crystallise together with the Cu-rich (TiCu and Ti$_2$(Cu,Ni)) phases along the grain boundaries.

The diffusion in B2 compounds is mediated by vacancy-type defects [167] whose concentration decreases exponentially with decreasing temperature. As a consequence, the diffusion rate slows down during solidification, hampering the formation of Cu-rich precipitates that become smaller until they finally disappear in the outer regions where just B19-Ti(Ni,Cu) grains are observed. The cooling rate is high enough to prevent excessive growth of the spherical precipitates and to vitrify the remaining liquid. As a result, the spherical crystalline “islands” with a metastable microstructure near the outer surface are embedded in the glassy matrix. The spherical morphology seems to be connected with a polymorphic crystallisation of these grains at the outer surface, since they virtually have the same composition as the amorphous phase without constitutional undercooling. For instance, the composition measured for the precipitates and glassy matrix in the Ti$_{50}$Cu$_{43}$Ni$_7$ 1 mm diameter rod was Ti$_{49.0±0.4}^{49.0±0.4}$Cu$_{44.9±0.4}^{44.9±0.4}$Ni$_{6.1±0.1}^{6.1±0.1}$ and Ti$_{49.37±0.01}^{49.37±0.01}$Cu$_{44.61±0.02}^{44.61±0.02}$Ni$_{6.02±0.01}^{6.02±0.01}$, respectively. The spherical morphology is the response of the material in order to minimise the free energy of the system by adopting a state of minimum interface [86]. Moreover, a similar polymorphic crystallisation was observed in Cu-Zr-based bulk metallic glass composites [14], in which B2-CuZr crystals with spherical morphology precipitate in the glassy matrix.

Figure 5.3 shows the cross-section of the 2 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod. Glassy and crystalline regions are indicated in the figure by the letters A and C, respectively. In some regions near the edge of the 2 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod, a homogeneous amorphous phase without any contrast was observed, whereas in other regions the amorphous phase coexists with spherical martensitic precipitates. The presence of the amorphous phase was confirmed by EBSD and XRD taken from the outer surface. B2-Ti(Ni,Cu) dendrites with a typical size of around 2 µm develop in the centre of the rod surrounded by B11-TiCu and Ti$_2$(Cu,Ni) crystals at the grain boundaries. Towards the outer surface the amount of precipitates around the dendrites becomes lower, as shown in the inset of Figure 5.3. These dendrites
are smaller than 1 µm and have thin Cu-rich particles at the interdendritic region, in a similar way as observed in the larger precipitates of the 1 mm rod samples. Near the interface, between the amorphous and crystalline phases, martensitic plates are observed (Figure 5.3). A similar microstructure was found for the 2 mm Ti$_{50}$Cu$_{43}$Ni$_{7}$ rod.

Figure 5.3 – OM image of the 2 mm diameter Ti$_{50}$Cu$_{43}$Ni$_{7}$ rod. The letters A and C refer to regions with presence of amorphous and crystalline phases, respectively. The insets depict features of the different regions in the rod cross-section.

To gain more insights, TEM investigations were performed in the 2 mm diameter rods. The TEM analyses prove that the martensitic phase consists of plates with different sizes on a nanometer scale (Figure 5.4(a)). For some of them twins are observed. A diffraction pattern taken from this region is shown Figure 5.4(b) and reveals reflections of the orthorhombic B19-Ti(Ni,Cu) phase together with double reflections (indicated by the
red arrows in Figure 5.4(b) resulting from the different twin variants. Nishida et al. [168] have demonstrated that two twin variants coexist in the B19 phase: \{111\} Type I and \{121\} Type II, which also agrees with observations by Santamarta et al. [169].

Figure 5.4 – (a) Bright field TEM of the 2 mm diameter Ti$_{50}$Cu$_{41}$Ni$_{9}$ rod showing B19 martensite plates with different sizes and (b) selected area diffraction pattern taken from this region on a zone axis [1 0 0]. The red arrows show double reflections which are formed from the different twin variants.

5.2 Phase transformations during continuous heating of Ti-Cu-Ni alloys

Ribbons and rods of Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ were analysed in a calorimeter in the temperature range 223 to 923 K in order to explore the martensitic transformation, the glass transition and the crystallization behaviour. Figures 5.5(a) and 5.5(b) show the DSC curves for these samples in the higher temperature range and the results are summarized in Table 5.1.
The Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ ribbons crystallise in two steps preceded by a clear glass transition at 688±2 and 667±2 K, respectively. The 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods exhibit a similar behaviour as the ribbons. A two-step crystallization follows the glass transition, as can be seen in Figures 5.5(a) and 5.5(b), respectively. The glass transition occurs at 688±2 and 680±2 K and the crystallization starts at 707±2 and 714±2 K for the 1 mm diameter Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods, respectively. The different glass transition and crystallization temperatures for the ribbon and the 1 mm rod of the same composition are attributed to the partial crystallization of the rod, which changes the composition of the amorphous phase (the composition of the amorphous phase in the 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ rod is Ti$_{49.4±0.1}$Cu$_{44.6±0.1}$Ni$_{6.0±0.1}$ in contrast to the ribbon, where the amorphous phase has the nominal composition). In contrast to the rods with a diameter of 1 mm, the 2 mm rods contain only a small amount of amorphous phase, as can be seen comparing the area of the crystallization peaks. These samples not only exhibit the two crystallization peaks observed for the ribbons but also a third peak (as shown in the respective insets of Figures 5.5(a) and 5.5(b)).

The values of the supercooled liquid region $\Delta T_x$ and the $\gamma_m$ parameter were calculated (Table 5.1) considering the glass transition and crystallization temperatures measured for the ribbons and the liquidus temperature available in the equilibrium phase diagram [6]. The $\Delta T_x$ increases from Ti$_{50}$Cu$_{43}$Ni$_7$ to Ti$_{50}$Cu$_{41}$Ni$_9$ (Table 5.1), which shows that the supercooled liquid is more stable with increasing the amount of Ni. On the other hand, the $\gamma_m$ value increases with decreasing Ni (Table 5.1), suggesting that the Ti$_{50}$Cu$_{43}$Ni$_7$ alloy has a higher GFA than the Ti$_{50}$Cu$_{41}$Ni$_9$, in agreement with experiments [5].
Figure 5.5 – DSC results for ribbons and rods of the (a) Ti$_{50}$Cu$_{43}$Ni$_{7}$ and (b) Ti$_{50}$Cu$_{41}$Ni$_{9}$ alloys. The arrows indicate the onset glass transition ($T_g$) and crystallization temperatures ($T_x$). The insets show details of the crystallization peaks observed in the 2 mm diameter rods. These samples did not show glass transition.

Table 5.1 – DSC data obtained at a heating rate of 30 K/min. $T_g$ and $T_x$ are defined as the onset glass transition and crystallization temperatures, respectively, $T_l$ is the liquidus temperature obtained from [6], $\Delta T_x = T_x - T_g$ and $\gamma_m = (2T_x - T_g) / T_l$. $\Delta H_c$ is the enthalpy of crystallization, $f_a$ is the fraction of amorphous phase and $A_s$ is the onset austenite start transformation temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$T_l$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$\gamma_m$</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$f_a$%</th>
<th>$A_s$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{50}$Cu$</em>{43}$Ni$_{7}$</td>
<td>ribbon</td>
<td>688±2</td>
<td>1233±5</td>
<td>23±2</td>
<td>0.595±0.004</td>
<td>-154±5</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
<td>688±2</td>
<td>1233±5</td>
<td>19±2</td>
<td>-63±5</td>
<td>41±3</td>
<td>328±2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rod 2mm</td>
<td>-</td>
<td>1233±5</td>
<td>-</td>
<td>-16±5</td>
<td>10±3</td>
<td>340±2</td>
<td></td>
</tr>
<tr>
<td>Ti$<em>{50}$Cu$</em>{41}$Ni$_{9}$</td>
<td>ribbon</td>
<td>667±2</td>
<td>1273±5</td>
<td>41±2</td>
<td>0.588±0.004</td>
<td>-146±5</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
<td>680±2</td>
<td>1273±5</td>
<td>34±2</td>
<td>-76±5</td>
<td>52±3</td>
<td>324±2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rod 2mm</td>
<td>-</td>
<td>1273±5</td>
<td>-</td>
<td>-15±5</td>
<td>10±3</td>
<td>333±2</td>
<td></td>
</tr>
</tbody>
</table>

The volume fraction of crystalline phases in each rod can be estimated using the crystallization enthalpy of a fully amorphous ribbon:

$$f_c = \left( \frac{\Delta H_{ribbon} - \Delta H_{rod}}{\Delta H_{ribbon}} \right) \times 100$$  \hspace{1cm} (5.1)

where $\Delta H_{ribbon}$ and $\Delta H_{rod}$ are the crystallization enthalpies of ribbon and rod, respectively.

Table 5.1 shows the average values of the crystallization enthalpy for the different samples. Based in these values, the volume fractions of amorphous phase estimated using equation 5.1 for the Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ rods with a diameter of 1 mm are 41±3 and 52±3 vol.%, respectively, and for the 2 mm rods, the amount of amorphous phase is estimated to be 10±3 vol.% for both Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$. All these results are summarized in Table 5.1, together with the corresponding glass transition and crystallization temperatures.

In order to investigate the martensitic transformation, the samples were analysed in a DSC in the temperature regime between 223 and 423 K during two heating-cooling cycles.
Figure 5.6(a) shows the results of the first heating run. Endothermic martensitic transformation peaks were observed for both the rods with a diameter of 1 and 2 mm and the austenitic start temperatures ($A_s$) are summarised in Table 5.1. For the 1 mm rods, two overlapping peaks were measured around 338 K and for both 2 mm rods, only one small and broad peak was discerned. The measured transformation temperatures fall in the range usually observed for Ti-Ni-Cu crystalline alloys [7].

The two transformation peaks observed for the 1 mm rods suggest a different kind of transformation. As discussed above, some spherical B19-Ti(Ni,Cu) crystals precipitate at the surface of the rods with different sizes (most of them are smaller compared to the precipitates formed in the centre) and the martensitic phase of these precipitates has a similar chemical composition as those of the centre region. An amorphous/martensite interface reduces the reverse transformation temperature $B19 \rightarrow B2$ [169], in which the parent B2 phase is stabilised when being in contact with the amorphous matrix. This means that the spherical precipitates at the surface (denoted as $m_2$ in the schematic rod cross section shown in the inset of Figure 5.6(b)) should exhibit a higher reverse transformation temperature ($A_s$) than the precipitates in the centre ($m_1$ in the inset of Figure 5.6(b)) since they are mostly not surrounded by the glass and hence not constrained (see inset Figure 5.6(b)). In order to study the effect of the martensitic phase at the surface of these samples, this outer part of the rods was removed, and a parallelepiped (0.65 x 0.65 x 10 mm) obtained. Then the DSC analysis was repeated. The results for the 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod are displayed in Figure 5.6(b). As can be seen, the peak located at higher temperature (340 K) disappears completely, which confirms that the splitting is most likely related to the presence of the B19-Ti(Ni,Cu) precipitates at the outer surface.
Figure 5.6 – (a) Low-temperature DSC curves for the Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ rods obtained during the first heating run. The endothermic martensitic transformation peaks are displayed. The arrows indicate the onset ($A_s$) and the final ($A_f$) temperature of the reverse transformation. Figure (b) compares the low-temperature DSC results for the 1 mm
diameter $Ti_{50}Cu_{41}Ni_{9}$ rod before and after removing the outer surface region. The scheme in the inset compares the $A_s$ temperature for martensitic grains totally ($m_1$) and partially ($m_2$) embedded in the amorphous phase.

The 2 mm rods were further analysed by means of in-situ XRD experiments (Figure 5.7). No measurements were possible for the 1 mm rods because the size of the XRD beam was too big. The results confirm the reverse transformation of $B19 \rightarrow B2$ predicted by the TiCu-TiNi phase diagram [6]. Besides, the reversibility of these transformations is corroborated by in-situ XRD and DSC during two heating and cooling cycles. Figure 5.8 shows the DSC results for the 1 mm diameter $Ti_{50}Cu_{41}Ni_{9}$ rod obtained during two thermal cycles. One can see that the martensitic transformation peak areas as well as transformation temperatures are similar: the austenitic start temperatures and the enthalpies of transformation in the first and second heating cycles are $324\pm2$ and $323\pm2$ K and $5.6\pm0.5$ and $6.0\pm0.5$ J/g, respectively.

![In-situ XRD results obtained during heating of the 2 mm diameter $Ti_{50}Cu_{41}Ni_{9}$ rod.](Figure 5.7)
A more distinct martensitic transformation was observed for the 1 mm rods than for the 2 mm rods, and for the 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod when compared with the 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ rod (Figure 5.6(a)). This is connected with the formation of TiCu and Ti$_2$(Cu,Ni) phases, which is controlled by the cooling rate and the composition. The higher cooling rate in the 1 mm samples and the lower amount of Cu in the Ti$_{50}$Cu$_{41}$Ni$_9$ samples limit the formation of TiCu and Ti$_2$(Cu,Ni) crystals, which are observed mainly in the centre region of the 2 mm rods (Figure 5.3). These precipitates create elastic strain fields [164], which hamper or even completely suppress the martensitic transformation as observed in some Ti-Cu-Ni alloys [170].

5.3 Mechanical properties of Ti-Cu-Ni alloys

The focus of the following paragraphs is on the mechanical behaviour of the rods with a diameter of 1 mm since they formed the larger amount of amorphous phase (around

Figure 5.8 – DSC results for the 1 mm diameter Ti$_{50}$Cu$_{41}$Ni$_9$ rod. The black and red lines correspond to the first and second heating and cooling cycles, respectively. No significant differences are observed in the transformation peak areas as well as transformation temperatures comparing these two cycles.
50 vol.%; cf. Table 5.1) when compared with the 2 mm diameter samples (Table 5.1). The mechanical behaviour of these samples will be shown in the last chapter.

For the compression tests, the 1 mm diameter rods were divided into two sections (bottom (B) and top (T) part) and three samples were tested for each part. The consideration of bottom and top part is important since a heterogeneous microstructure can be produced due to differences in the cooling rate from bottom to top upon Cu-mould suction casting [171]. Figure 5.9 shows two representative results for each sample and the results are summarized in Table 5.2. The 1 mm diameter Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods exhibit large fracture strains of 14.2±0.5 and 27.9±0.5 % together with a high yield strength of 1170±50 and 1150±50 MPa, respectively, when compared with other Ti-based alloys [172]. Zhang et al. [173] observed similar yield strength during compressive deformation of a 1 mm Ti$_{58}$Cu$_{32}$Ni$_{10}$ bulk metallic glass matrix composite rod but with a lower fracture strain of around 9.3 %. The Young’s modulus determined from the compression test curves for the Ti$_{50}$Cu$_{43}$Ni$_7$ alloy (61±10 – 73±10 GPa, Table 5.2) is also similar as reported by Zhang et al. [173] but lower for the Ti$_{50}$Cu$_{41}$Ni$_9$ rod (41±10 – 55±10 GPa). This value is comparable with the Young’s moduli known for low-modulus biomedical Ti-based alloys (ranging from 45 to 55 GPa [174]).

The good mechanical behaviour observed for the Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods is supposed to be due to the combination of the high-strength amorphous phase with the crystalline agglomerates, which mainly consist of ductile B19-Ti(Ni,Cu) phase. The mechanisms responsible for this increase in compressive strain will be shown in the end of this chapter. A very strong work hardening was observed for both compositions, with fracture strength almost two times higher than the yielding strength, around 2000 MPa. No significant differences were observed in the mechanical behaviour of the top and bottom part of the rods (Figure 5.9).
Table 5.2 – Mechanical properties of the different samples under compressive loading. $E$ denotes the Young’s modulus.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield Strength (MPa)</th>
<th>Fracture Strain (%)</th>
<th>Maximum Stress (MPa)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{50}$Cu$</em>{43}$Ni$_{7}$ - rod 1mm</td>
<td>1150 - 1170</td>
<td>12.1 - 14.2</td>
<td>1870 - 2000</td>
<td>61 - 73</td>
</tr>
<tr>
<td>Ti$<em>{50}$Cu$</em>{41}$Ni$_{9}$ - rod 1mm</td>
<td>1000 - 1150</td>
<td>24.1 - 27.9</td>
<td>1960 - 2010</td>
<td>41 - 55</td>
</tr>
</tbody>
</table>

Figure 5.9 – True stress-strain curves upon compressive loading for the 1 mm rods of the Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ alloys. Results for the top and bottom part of each rod are shown (there is no significant difference between the top and the bottom part of the rods). The inset shows an indentation region of a B19-Ti(Cu,Ni) spherical precipitate in the 1 mm
$\text{Ti}_{50}\text{Cu}_{41}\text{Ni}_9$ rod around which a pronounced formation of twins is observed due to the deformation of the martensitic phase.

The hardness of the spherical martensitic precipitates (see inset Figure 5.9) was measured to be $282\pm21$ and $264\pm13$ HV 0.05 for the B19-Ti(Cu,Ni) precipitates formed in the 1 mm $\text{Ti}_{50}\text{Cu}_{43}\text{Ni}_7$ and $\text{Ti}_{50}\text{Cu}_{41}\text{Ni}_9$ rods, respectively, with a value of $536\pm10$ HV 0.05 for the amorphous phase of both compositions. The lower hardness value suggests that the B19-Ti(Cu,Ni) phase formed in the 1 mm $\text{Ti}_{50}\text{Cu}_{41}\text{Ni}_9$ rod is softer compared to the one formed in the Cu-rich alloy. This could partially explain the different fracture strains observed (Figure 5.9), together with the fact that a larger amount of brittle TiCu and Ti$_2$(Cu,Ni) phases is formed in the Cu-rich alloy (see X-ray patterns, Figure 5.1). The hardness measured for the martensitic B19-Ti(Cu,Ni) phase is comparable to the values measured for the ductile B2-CuZr phase formed in a $\text{Cu}_{50}\text{Zr}_{42.5}\text{Ti}_{7.5}$ bulk metallic glass composite (266 HV 0.1) [175]. Several studies have been conducted for TiNiCu alloys, showing that the martensitic phase deforms plastically with a yield strength lower than 100 MPa followed by extensive elongation at room temperature with work-hardening behaviour [7]. This good deformability is attributed to the low twinning shear of the {011}$_o$ compound or {111}$_o$ type-I twinning. The inset of Figure 5.9 shows an indentation region of a B19-Ti(Cu,Ni) spherical precipitate in the 1 mm $\text{Ti}_{50}\text{Cu}_{41}\text{Ni}_9$ rod. A pronounced amount of twins is formed around the indentation mark as a result of the martensite re-orientation during deformation.

The B2 phase retained after quenching observed in some larger spherical precipitates (Figure 5.1 and Figure 5.2(c)) may undergo a stress-induced martensitic transformation, as generally observed in CuZr-based [176] and TiNi-based shape memory alloys [177] and be responsible for the work hardening. In order to verify possible phase transformations during deformation, XRD measurements were also performed after fracture. Although the peaks became broader after deformation as a result of the increased amount of defects (dislocations, twins and shear bands) introduced during deformation [178], no clear difference was observed when comparing XRD patterns before and after deformation. This indicates that the small amount of B2 phase does not undergo martensitic transformation.
The polished longitudinal section of the deformed 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod (bottom part), which exhibited the largest plastic strain of 27.9 % (Figure 5.9) is shown in Figure 5.10(a). A barrel shape is observed after deformation, which also confirms that this sample experienced a large plastic deformation. As can be observed, the spherical crystals are smaller (< 250 µm) and exhibit a more homogeneous distribution compared with the bottom part of the 1 mm diameter Ti$_{50}$Cu$_{43}$Ni$_7$ rod (Figure 5.2(a)). Recent simulation studies have shown that a larger strain and a higher strength can be obtained when the crystals are small and homogeneously distributed in the glassy matrix [126, 127].

A completely deformed structure with a high density of twins and deformation bands is found in the smaller crystalline precipitates of the 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod. In the case of larger precipitates (Figure 5.10(b)), the dendrites in the centre apparently do not contain any twins in contrast with the severely deformed martensitic phase in the outer region. These results also indicate that the B2 dendrites in the coarsened region may not undergo a martensitic transformation.

The lateral surfaces of the samples after deformation were analysed carefully in order to obtain information about the fracture mechanisms. The images for the 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods are shown in Figures 5.10(c) and 5.10(d), respectively. Figure 5.10(c) displays the surface of the 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ rod, where the spherical precipitates are dispersed in the amorphous matrix. Shear bands were observed around these crystals at almost 90 ° to the loading direction (SB1). Long and well-spaced shear bands (SB2) were also observed in the glassy matrix in the maximum shear stress plane around 45 ° to the loading direction. The intersection between these two kinds of shear bands is shown by the dashed circle in Figure 5.10(c). Steps in the SBs 1 are observed as a result of the SB2 motion, which indicates that the SBs 1 appear first. Figure 5.10(d) also shows SBs 1 and SBs 2 on the surface of the 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod: The SBs 1 are marked by a full arrow in the direction almost perpendicular to the loading direction and SBs 2 are marked by dashed arrows and they are inclined by 45 ° to the loading direction. The SB1 shear bands have a characteristic wavy edge, as shown in the inset of Figure 5.10(d), which is different compared with SBs 2 where a sharp/straight edge is observed.
Figure 5.10 – (a) Longitudinal section of the deformed 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod (bottom part), which exhibits the largest fracture strain among the compressed samples (Figure 5.8). The details of the larger precipitates observed in these deformed samples are shown in (b). The surface of the 1 mm Ti$_{50}$Cu$_{43}$Ni$_7$ rod (bottom part) after compression is shown in (c). The two kinds of shear bands observed, SB1 and SB2, and the load direction are indicated in the figure. The dashed region shows the intersection between these two different shear bands. The surface of the 1 mm Ti$_{50}$Cu$_{41}$Ni$_9$ rod (bottom part) is shown in (d). The full and dashed arrows indicate SB1 and SB2 shear bands, formed under 90 ° and 45 ° to the loading direction, respectively. The inset shows the characteristics of the SB1 shear bands, which display a wave-shape morphology.

Out of all 12 tested 1 mm diameter Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods, just one of them broke in two parts and its fracture surface could be analysed. The fracture surface of the samples exhibits a vein pattern, as it is typically observed for bulk metallic glasses as a result of local melting caused by shear band propagation [10]. For the other samples, usually a
crack was observed around 45 ° but it did not propagate through the entire sample, which also proves their large toughness.

As an attempt to confirm the deformability of these new shape memory bulk metallic glass composites not just in compression, three-point bending tests were performed and the results are shown in Figure 5.11. The displacement at the surface of the specimen on the convex or tension side starts to be measured after an initial pre-load of around 20 N. Significant plasticity is observed together with strong work-hardening behaviour. The 1 mm Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ rods exhibit 0.27 and 0.45 mm of displacement, respectively, which confirms the larger deformability of Ti$_{50}$Cu$_{41}$Ni$_{9}$ compared to the Ti$_{50}$Cu$_{43}$Ni$_{7}$ alloy also witnessed by the compression tests. One of the samples (bottom part, alloy Ti$_{50}$Cu$_{41}$Ni$_{9}$) did not break but even reached the maximum load available and a large elastic recovery was observed upon unloading (Figure 5.11), as it is usually observed for TiNi-based shape memory alloys [7].
Figure 5.11 – Force-displacement curves obtained in three-point bending tests of the 1 mm diameter \( \text{Ti}_{50}\text{Cu}_{43}\text{Ni}_{7} \) and \( \text{Ti}_{50}\text{Cu}_{41}\text{Ni}_{9} \) rods. Results for the top and bottom part of each rod are shown.

In order to better understand the deformation mechanisms of these new BMG composites during compression, a finite element simulation of the deformability was carried out. In doing so, a rod with 1 mm diameter and 2 mm length composed of a glassy matrix and two martensitic crystals, 200 µm across, disposed in the centre of the rod and equally spaced from the bottom and the top was generated. The microstructural heterogeneity observed in some of the large precipitates in the 1 mm rods (Figure 5.2(c) and 5.10(b)) was not considered for reason of simplicity.

The following assumptions also had to be made for the finite element model: an ideal stress–strain curve was constructed with the corresponding yield strength and elastic modulus of the \( \text{Ti}_{50}\text{Cu}_{43}\text{Ni}_{7} \) metallic glass [5], 1914 MPa and 107 GPa, respectively. The Mohr-Coulomb criterion, as often used for metallic glasses [179], was chosen to describe the yielding of the amorphous phase with a friction coefficient of 0.11 [180]. The Poisson’s
ratio used for the calculations was 0.35, as observed for other TiCuNi-based BMGs [181, 182]. It was considered that the formation of shear bands occurs in regions were the equivalent stress has reached the yield strength of the glassy phase (1914 MPa [5]). For the B19 martensitic phase, data were taken from reference [7] for a polycrystalline B19 sample with a nominal composition of Ti$_{50}$Ni$_{40}$Cu$_{10}$ that exhibits an elastic modulus and a yield strength of 23.3 GPa and 30 MPa, respectively. The yielding of the B19 phase was simulated considering the stress-strain curve of the Ti$_{50}$Ni$_{40}$Cu$_{10}$ alloy at 303 K [7]. Considering the lack of information about the B19 martensite, the Poisson’s ratio of the monoclinic B19’-TiNi martensite (0.3) was used [172]. Small differences in the Poisson’s ratio did not significantly affect the results.

The distribution of the von Mises stress and the equivalent strain were analysed during compressive loading applied to both ends of the cylindrical sample and the results are summarised in Figure 5.12 for 1.5 % strain, which corresponds to the beginning of the plastic regime. Figures 5.12(a) and 5.12(b) show the von Mises stress and the equivalent strain distribution, respectively. A stress concentration is observed at the interface precipitate/matrix in a direction perpendicular to the loading axis. This can explain the appearance of the SB1 shear bands (Figure 5.10(c)) in the first step of deformation, since the stress reaches the yield strength of the amorphous phase first at these points.
Figure 5.12 – Finite element simulation of a rod with 1 mm diameter and 2 mm length consisting of a glass matrix and two martensitic crystals with 200 µm in diameter disposed in the centre of the rod, equally spaced from bottom to top at a strain of 1.5 %. The von Mises stress (S) and the equivalent strain distributions (PEEQ) analysed under uniaxial compressive loading are shown in figures (a) and (b), respectively. The units of S and PEEQ are MPa and mm/mm.

The SB2 shear bands should form later when the entire matrix experiences yielding. In this way, the propagation of SB2 competes with the previously formed SB1. The formation of multiple shear bands will then promote a more homogeneous deformation, thus increasing the macroscopic plasticity. The presence of the precipitates generates a heterogeneous stress field in the matrix (Figure 5.12(a)), which may influence the formation of the shear transformation zones (see section 2.2). Figure 5.12(b) shows that the equivalent strain inside the crystals has a heterogeneous distribution with a maximum at their surface, and at some points, a strain of 3.5% can be obtained already before the yield
point of the amorphous matrix is reached. This also indicates that these crystals start to deform before the appearance of the main shear bands (SB2) that will be responsible for the fracture.

Based on these simulation results and the experimental observations we propose a deformation mechanism as sketched in Figure 5.13. The low yield strength of the martensitic phase makes these crystals start to deform first and to work-harden, by means of twinning and detwinning of the martensitic phase formed in the smaller precipitates and in the outer regions of the larger ones [7]. This can explain the strong work hardening observed for these composites. Heterogeneous stress concentrations occur around the particles, which are responsible for the formation of the SB1 shear bands shown in Figure 5.10(c). After the matrix uniformly reaches the yield strength, the main shear bands (SB2) start to appear. The stress-induced martensitic transformation of the B2 phase in the centre of the larger precipitates is not considered in the mechanism sketched in Figure 5.13, since no clear evidence was found for the 1 mm rods, as discussed before. The formation of multiple shear bands promote shear band interactions, and the presence of SB1 as well as the heterogeneous stress distribution caused by the spherical precipitates can hamper the movement of the main shear bands (SB2) formed in the maximum shear stress plane around 45 ° [183]. The precipitates also have the important function to impede the movement of the main shear bands (“blocking effect”), and thus to avoid premature fracture (Figure 5.10(c)) [184].

Some studies also suggested that the heat released during crack propagation could promote the B19 → B2 transformation of crystals in front of the crack tip [185]. A similar mechanism could also apply during the shear band propagation. The temperature may increase within a shear band during its operation [104], which could reach values higher than the austenitic start temperature. In this case, the martensitic transformation of B19 precipitates is promoted and part of the deformation energy is consumed. This could be another mechanism for the increased toughness of these alloys.
Figure 5.13 – Proposed deformation mechanism for the Ti-Cu-Ni bulk metallic glass matrix composites with a diameter of 1 mm during compression. **(1)** Microstructure prior to deformation, where the orange circles represent the crystalline precipitates in the amorphous (grey) matrix. **(2)** During uniaxial compression, the precipitates start to deform first by means of martensite reorientation (indicated by white regions). The stress-induced martensitic transformation of the B2 phase in the centre of larger precipitates (Figure 5.9(b)) was not considered because no clear evidence of their transformation was found. **(3)** Stress concentrations promote the formation of the first shear bands (SB1) in the vicinity of these crystals in a direction almost perpendicular to the loading direction. **(4)** After the entire glass
matrix reaches its yield strength, the main shear bands (SB2) form around 45 ° to the loading direction. Before fracture, SB1 and SB2 intersect and develop, and the precipitates block the fast movement of SB2. All these processes hamper the formation of a detrimental shear band and thus retard fracture and lead to significant plastic deformation.

To summarize, the use of proper cooling rates allows for the formation of a metastable microstructure in the 1 mm Ti-Cu-Ni rods consisting mainly of spherical ductile martensitic precipitates in an amorphous matrix and with a small volume fraction of TiCu and Ti$_2$(Cu,Ni) precipitates. As a result, a large compressive strain and a high strength can be obtained combined with a strong work-hardening behaviour.

This good mechanical behaviour can be understood considering a deformation mechanism proposed with the help of experimental observations and finite element simulations. The simulations demonstrate that stress concentrations occur around the precipitates, which generates a heterogeneous stress distribution and the formation of multiple shear bands.

The interaction between shear bands, the heterogeneous stress distribution during loading, the “blocking effect” of the precipitates and the work-hardening effect of the martensitic phase that is responsible for the high fracture stress of these samples are revealed as the main reasons for the enhanced mechanical properties of these alloys. The results also show that different transformation temperatures occur for those martensitic crystals that are completely or partially embedded in the amorphous matrix.
6 Structural evolution in Ti-Cu-Ni metallic glasses during heating

Although several bulk metallic glasses were recently found in the Cu-rich region of the pseudo-binary TiCu-TiNi system [5, 9, 186], no work was carried out to identify their phase formation during crystallization [187]. These alloys could form new Cu-rich Ti-Cu-Ni shape memory alloys with lower cost and smaller thermal and stress hysteresis during transformation than traditional TiNi-based alloys [7].

Considering that these Cu-rich compositions are also expected to precipitate other phases than the shape memory TiNi phase, it is important to understand how the characteristics of the martensitic transformation (MT) are affected by the level of precipitation around or inside the shape memory phase [164, 166]. As also discussed in the last chapter, these precipitates generate elastic strain fields, which interfere with the MT of the shape memory phase, changing the start transformation temperature [164] or the transformation steps [166]. The size of the shape memory crystals also influences the MT [165] since grain boundaries hinder the growth of the martensite and hamper its autocatalytic nucleation, which is triggered by stresses that arise during its growth [188]. The transformation can be even suppressed for small grain sizes (around 50 nm for TiNi-based alloys [165]) because the stresses required increase with decreasing crystal size [165].

To reveal how these phases are formed during crystallization and to understand their influence on the MT a systematic and extensive study was conducted and the results are presented in the following subsections. This investigation makes use of in-situ high-energy synchrotron radiation (section 3.2), electron microscopy (section 3.2) and differential scanning calorimetry (DSC, section 3.2) to identify the structural evolution and phase formation during the crystallization of glassy Ti₅₀Cu₄₃Ni₇ and Ti₅₅Cu₃₅Ni₁₀ ribbons. These insights are moreover linked with their shape memory behaviour. These two compositions were selected because they form different phases besides the shape memory TiNi. The equilibrium phase diagram [6] also predicts the formation of the tetragonal TiCu phase for the former, whereas for the latter the TiCu and the tetragonal Ti₂Cu precipitate.
Three transformations can be clearly seen during continuous heating of the Ti$_{50}$Cu$_{43}$Ni$_{7}$ glassy ribbon (Figure 6.1(a)). A broad and shallow exothermic peak is observed preceding the glass transition at 681 K ($T_g$) (inset Figure 6.1(a)). As a result of the relatively high cooling rate during melt-spinning (around $10^6$ K/s [45]), the glass structure exhibits local heterogeneities with regions of shorter atomic bonds, i.e. higher density, named “anti-free-volume” sites [189] and regions with longer atomic bonds, i.e. regions with lower density or equivalently larger free volume [189].

This structure relaxes during heating which releases heat and causes the observed exothermic peak. This structural relaxation starts at 476 K ($T_r$) and it is followed by a glass transition after which the metallic glass transforms in a supercooled liquid with high viscosity, which further crystallizes in two exothermic crystallization events at 711 and 734 K. The glassy Ti$_{55}$Cu$_{35}$Ni$_{10}$ ribbon shows a similar thermal behaviour like Ti$_{50}$Cu$_{43}$Ni$_{7}$ (Figure 6.1(b)). A broad exothermic relaxation peak is observed starting at 498 K and is followed by a glass transition at 691 K (inset Figure 6.1(b)). Two exothermic crystallization peaks are seen at 710 and $\approx$ 766 K, with the second peak seeming to be an overlap of two peaks (Figure 6.1(b)).
Figure 6.1 – DSC results for the (a) Ti<sub>50</sub>Cu<sub>43</sub>Ni<sub>7</sub> and (b) Ti<sub>55</sub>Cu<sub>35</sub>Ni<sub>10</sub> at heating rate of 30 K/min. The insets show details of the exothermic relaxation peak. \( T_r \), \( T_g \) and \( T_x \) refer to the onset relaxation, glass transition and crystallization temperatures, respectively.

6.1 Relaxation behaviour and glass transition of Ti-Cu-Ni glasses

The relaxation behaviour seen in the DSC traces was investigated in more detail by high-energy synchrotron radiation. This technique has proven to be suitable to determine the local atomic structure of metallic glasses [190]. Small changes in the amorphous structure during heating can be detected using high-brilliance synchrotron radiation sources [190, 191]. Figure 6.2(a) shows the high-energy X-ray diffraction pattern of the Ti<sub>50</sub>Cu<sub>43</sub>Ni<sub>7</sub> ribbon at room temperature. Four diffuse peaks are observed around \( q_0 = 15 \), \( q_1 = 29 \), \( q_2 = 49 \) and \( q_3 = 57 \) nm\(^{-1}\) (Figure 6.2(a)). The first peak at \( q_0 = 15 \) nm\(^{-1}\) (pre-peak) is related to the Linkam hot stage used in the experiment to heat the samples (the peak position and intensity do not change with increasing temperature). The second, third and fourth diffuse peaks stem from the actual sample and they are characteristic of a fully amorphous structure. A similar pattern was obtained for the Ti<sub>55</sub>Cu<sub>35</sub>Ni<sub>10</sub> ribbon with three broad peaks around \( q_1 = 29 \), \( q_2 = 49 \) and \( q_3 = 57 \) nm\(^{-1}\) (Figure 6.2(b)). The pre-peak still occurs for this
sample (not indicated in Figure 6.2(b)) but with a much lower intensity. The position, intensity and full width at half maximum (FWHM) of each diffuse peak were obtained by fitting the experimental curves with the analytical function:

\[
F(x) = A e^{(-\log(2)((x-Q)/W)^2)} + b_0 + b_1 x, \quad (6.1)
\]

where \( A \) is the amplitude, \( 2W \) is the FWHM, \( Q \) is the position of the peak maximum and \( b_0 \) and \( b_1 \) are the constants describing the background. Equation 6.1 is a combination of a Gaussian and a linear function (assuming a linear background). The profile parameters were determined by a nonlinear least-squares fitting of the function to a set of experimental data points corresponding to each diffuse peak of the sample. A good fitting was obtained using this function as shown in Figure 6.2.
Figure 6.2 – High-energy XRD results for the (a) Ti$_{50}$Cu$_{43}$Ni$_7$ and (b) Ti$_{55}$Cu$_{35}$Ni$_{10}$ ribbon at room temperature. A fitting (denoted fit1, fit2, fit23 and fit34) was carried out in order to determine the position and the FWHM value of the broad peaks observed around $q = 15, 29, 49$ and 57.5 nm$^{-1}$ (labeled in the sequence $q_0$, $q_1$, $q_2$ and $q_3$).

XRD patterns were recorded every 13 K during in-situ heating of the samples (section 3.2). An example of the results obtained is given in Figure 6.3 for the Ti$_{50}$Cu$_{43}$Ni$_7$ ribbon.
The position, intensity and FWHM of each diffuse peak observed for these samples were recorded as a function of temperature and the results are summarized in Figure 6.4 and 6.5. The position of the most intense peak (at $q_1 = 29 \text{ nm}^{-1}$, Figure 6.2) decreases linearly with increasing temperature up to the glass transition for both compositions (Figure 6.4(a) and 6.5(a), respectively). In the reciprocal space, a decrease in the peak position results from the increase in the interatomic distance (thermal expansion). A similar behaviour was observed for other BMGs [190, 191]. No changes are observed in this linear fashion after the beginning of the structural relaxation at $T_r$. In contrast, the peak width first increases and then becomes smaller after structural relaxation (FWHM, Figure 6.4(a) and 6.5(a)), which reflects a higher structural ordering after beginning of the relaxation process.

The intensity (or height) of the respective peaks shows a completely different trend for the two samples with increasing temperature. For the Ti$_{50}$Cu$_{43}$Ni$_7$ ribbon (Figure 6.4(b)), it first decreases and then jumps to a plateau after structural relaxation. For the Ti$_{55}$Cu$_{35}$Ni$_{10}$ (Figure 6.5(b)), the intensity also decreases in the beginning but it shows a “peak” after the
relaxation starts and then continues to decrease with increasing temperature. Although the position and width of the most intense peak at \( q_1 = 29 \, \text{nm}^{-1} \) shows a similar trend with increasing temperature as observed for other BMGs [190, 191], the intensity exhibits a different and unexpected variation, which might be caused by an increase in the probed sample volume during the experiments. For these measurements pieces of ribbons were placed in a capillary and exposed to the beam and probably the filling density changed during the heating. It should not affect the position or width of the peaks since the structure of the material does not change but could change the intensity of the peak because the amount of material analyzed by the X-ray beam would change. The fact that the \( q_2/q_1 \) ratio is not affected by the sudden change of intensity of \( q_1 \) (Figure 6.4(b)) seems to corroborate this assumption.

(a)
Figure 6.4 – (a) Position, full width at half maximum (FWHM) and (b) intensity of the most intense peak ($q_1$) of the glassy Ti$_{50}$Cu$_{43}$Ni$_7$ ribbon measured at different temperatures. The ratio between the position of this peak and the second most intense ($q_2/q_1$) is also shown in (b).
Figure 6.5 – (a) Position, FWHM and (b) intensity of the most intense XRD peak ($q_1$) of the glassy $\text{Ti}_{55}\text{Cu}_{35}\text{Ni}_{10}$ ribbon as a function of temperature. The ratio between the position of this peak and the second most intense ($q_2/q_1$) is shown in (b).
A similar trend as described above was found for the position, the width and the intensity for the second most intense peak at \( q_2 = 49 \text{ nm}^{-1} \) (Figure 6.2). The ratio between the position of the first and the second most intense peaks at \( q \approx 29 \text{ nm}^{-1} \) and \( 49 \text{ nm}^{-1} \) \((q_2/q_1)\) are shown in Figures 6.4(b) and 6.5(b) for Ti\(_{50}\)Cu\(_{43}\)Ni\(_7\) and Ti\(_{55}\)Cu\(_{35}\)Ni\(_{10}\), respectively. One can see that the ratio is constant below the glass transition temperature and changes abruptly for higher temperatures, which is a clear indication of ongoing structural changes in the material after glass transition [190]. A linear ratio means that the Ehrenfest equation is satisfied [190, 192] and an approximated value of the volumetric thermal expansion coefficient, \( \alpha \), can be obtained by the relation [192]:

\[
\left( \frac{Q(T_0)}{Q(T)} \right)^3 = \frac{V(T)}{V(T_0)} = 1 + \alpha(T - T_0)
\]

where \( Q \) is the peak position, \( V \) is the reduced mean atomic volume, \( T \) is the temperature and \( T_0 \) is the reference temperature (311 K in this study). Figure 6.6 correlates the \((Q(T_0)/Q(T))^3\) values with temperature. A volumetric thermal expansion coefficient \( \alpha_v \) of \((3.66 \pm 0.05) \times 10^{-5}\) and \((4.08 \pm 0.06) \times 10^{-5}\) K\(^{-1}\) were obtained for Ti\(_{50}\)Cu\(_{43}\)Ni\(_7\) and the Ti\(_{55}\)Cu\(_{35}\)Ni\(_{10}\), respectively, by means of a linear fitting of the curves shown in Figure 6.6. These values correspond to a linear thermal expansion coefficient, \( \alpha_l \) \((\alpha_v = 3\alpha_l)\) of \((1.22 \pm 0.02) \times 10^{-5}\) and \((1.36 \pm 0.02) \times 10^{-5}\) K\(^{-1}\), which are very close to the value measured for a Ti\(_{50}\)Cu\(_{43}\)Ni\(_7\) alloy \((1.20 \times 10^{-5}\) K\(^{-1}\)) by dilatometry as will be shown in the last chapter.
6.2 Crystallization behaviour of the Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{55}$Cu$_{35}$Ni$_{10}$ glasses

Selected diffraction patterns collected during heating of the Ti$_{50}$Cu$_{43}$Ni$_{7}$ glassy ribbon are shown in Figure 6.7. Crystallization starts at 711 K ($T_{x1}$) (Figure 6.1(a)) with the precipitation of the cubic B2-Ti(Cu,Ni), followed by crystallization of the tetragonal γ-TiCu phase at 721 K ($T_{x2}$). The lattice parameters of these phases after complete crystallization ($T = 988$ K) were determined by means of Rietveld refinement (Figure 6.8) to be $a = 3.07 \pm 0.01$ Å for the cubic B2-Ti(Cu,Ni) and $a = 3.14 \pm 0.01$ and $b = 5.97 \pm 0.01$ Å for the tetragonal γ-TiCu at 988 K.
Figure 6.7 – XRD results obtained during heating of a glassy Ti$_{50}$Cu$_{43}$Ni$_7$ ribbon. The values of $T_{x1}$ and $T_{x2}$ are 711 and 721 K, respectively.

![Diagram of XRD results](image)
Figure 6.8 – (a) Rietveld refinement of a Ti$_{50}$Cu$_{43}$Ni$_{7}$ XRD pattern taken at 988 K and (b) difference between the calculated and experimental curves (blue and red lines in (a), respectively). The peaks corresponding to the γ-TiCu and B2-TiNi phases are also indicated.

The Ti$_{50}$Cu$_{43}$Ni$_{7}$ glass was annealed between $T_g$ and $T_x$ (693 K for 2 minutes) in order to precipitate the B2-Ti(Cu,Ni) phase. The microstructure of this sample as seen in the TEM is shown in Figure 6.9(a). It consists of small crystals with sizes < 10 nm and with irregular morphology, inserted in an amorphous matrix. The selected area electron diffraction pattern (SAED) of this region is shown in Figure 6.9(b). Diffuse diffraction rings of the amorphous phase are seen together with thin and weak rings, which can be indexed to the B2-Ti(Cu,Ni) phase (Figure 6.9(b)). The microstructure of this sample after complete crystallization is shown in Figure 6.9(c). A very fine microstructure is seen with equiaxial grains of the γ-TiCu phase surrounded by a very small amount of B2-Ti(Cu,Ni) in the grain boundary with average grain sizes around 200 and < 50 nm, respectively. The γ-TiCu phase has a contrast ranging from white gray to black as a result of small variations in the local chemical composition (around 0.5 at.%) as measured by EDX in the SEM.
Figure 6.9 – (a) High-resolution TEM image of the Ti$_{50}$Cu$_{43}$Ni$_7$ ribbon annealed at 693 K (between $T_g$ and $T_x$) for 2 minutes. Crystals with size < 10 nm can be seen in the glassy matrix as indicated in the figure. The selected area electron diffraction pattern (SAED) of this region is shown in (b). (c) SEM micrograph of the same alloy heated up to 923 K until complete crystallization.

Figure 6.10 shows selected XRD patterns of the Ti$_{55}$Cu$_{35}$Ni$_{10}$ glassy ribbon taken at different temperatures. The first phase precipitates at 711 K and it is a metastable nanocrystalline phase with broad peaks at 15, 28.5 and 47.5 nm$^{-1}$ (the peaks of this phase are highlighted by dashed blue circles in Figure 6.10). These reflections could not be indexed as the equilibrium phases TiCu, TiNi or Ti$_2$Cu, which are expected to be formed [6]. Subsequently, the tetragonal $\gamma$-TiCu phase precipitates at 756 K followed by the decomposition of the metastable nanocrystalline phase into B2-Ti(Cu,Ni) and tetragonal CuTi$_2$ at 766 K (Figure 6.10). Only peaks related to the $\gamma$-TiCu, B2-Ti(Cu,Ni) and CuTi$_2$ phases are observed at 969 K. These results suggest that the second crystallization peak observed in Figure 6.1(b) is actually the superposition of two exothermic events related to the precipitation of the $\gamma$-TiCu and the decomposition of the metastable nanocrystalline phase (formed in the first crystallization step at $T = 711$ K) into the B2-Ti(Cu,Ni) and CuTi$_2$ phases.
Figure 6.10 – In-situ XRD results obtained during heating of the Ti$_{55}$Cu$_{35}$Ni$_{10}$ glassy ribbon. The blue dashed circles show peaks of an unknown metastable nanocrystalline phase.

Also a glassy Ti$_{55}$Cu$_{35}$Ni$_{10}$ ribbon was annealed between the onset glass transition and the first crystallization event, at $T = 700$ K for one minute. Figure 6.11(a) shows a TEM image of the resulting microstructure and a spherical nanocrystalline phase with size ~ 5 nm can be seen homogeneously dispersed in the matrix. It is supposed to be the metastable nanocrystalline phase observed by the in-situ XRD experiments (Figure 6.10). The SAED pattern of this region (Figure 6.11(b)) shows broad diffraction rings typical of an amorphous structure together with weak but sharp rings, which are probably related to the metastable phase.

The bright field TEM images 6.11(c) and 6.11(d) show the microstructure of a fully crystalline sample after being heated to 973 K. Crystals with sizes smaller than 50 nm are observed surrounded by a black phase (Figure 6.11(c)). More details of these crystals can be
seen in Figure 6.11(d). EDX analyses prove that the black phase is CuTi₂, whereas the crystals may correspond to the B2-Ti(Cu,Ni) and TiCu as detected by XRD.

![Figure 6.11 - (a) High-magnification TEM image of the Ti₅₅Cu₃₅Ni₁₀ ribbon annealed at 700 K (between T₉ and Tₓ₁) for 1 minute. The SAED of this region is shown in (b). (c) and (d) Bright field TEM image of the ribbon heated up to 973 K until complete crystallization.]

Interestingly, no martensitic transformation was observed by DSC for the annealed ribbons of Ti₅₀Cu₄₃Ni₇ and Ti₅₅Cu₃₅Ni₁₀ in the temperature range between 223 and 473 K. As
shown in the last chapter, this transformation occurs at temperatures below 373 K. The B2 crystals presented in the annealed samples exhibit typical sizes below 50 nm (Figures 6.9 and 6.11(c)). As discussed by Waitz et al. [165, 188], a transformation barrier of strain and interface energy arises, which suppresses the transformation in crystals with sizes smaller than 50 nm. The large amount of grain boundaries act as obstacles that hinder the growth of the martensite and its autocatalytic nucleation potency [188].

To conclude, the structural changes during heating of two metallic glasses, Ti_{50}Cu_{43}Ni_{7} and Ti_{55}Cu_{35}Ni_{10}, were monitored by in-situ high-energy XRD. During relaxation, the elimination of structural defects (free volume) is observed by a slight decrease in the full width at half maximum (FWHM) of the most intense diffraction peak of the amorphous phase. Significant structural changes start to occur only after the glass transition temperature, after which the ratio between the position of the first and second most intense peaks of the amorphous phase starts to change significantly.

The crystallization of the Ti_{50}Cu_{43}Ni_{7} glassy ribbon occurs with the formation of the B2-TiNi and γ-TiCu phase, respectively, and the crystallization of the Ti_{55}Cu_{35}Ni_{10} alloy occurs in three steps with the formation of a nanometric metastable phase in the first step of crystallization followed by the precipitation of the γ-TiCu phase and the decomposition of the metastable nanocrystalline phase into B2-Ti(Cu,Ni) and CuTi_{2}, respectively. None of the partially or fully crystalline ribbons exhibit a martensitic transformation of the B2-Ti(Cu,Ni), which is attributed to the small size of this phase (< 50 nm).
7 Phase formation and mechanical behavior of Ti-Cu-Ni-Zr bulk metallic glass composites

Although new composites with advanced mechanical properties have already been obtained in the Ti-Cu-Ni system, their formation is generally limited to 1 mm diameter rods because of the relatively low GFA of these alloys (see Chapter 5). Therefore, this work also focuses on improving the critical casting thickness (i.e. the glass forming-ability) through the development of new TiCu-rich composites in the pseudo-ternary TiCu-TiNi-CuZr system. Alloys with a higher GFA and with advanced mechanical properties are obtained as discussed below. As shown in the following subsections their phase formation, microstructures and mechanical behaviour were systematically investigated and correlated.

7.1 Assessment of the glass-forming ability in the Ti-Cu-Ni-Zr system

The GFA of this quaternary system was first investigated by the \( \lambda + (\Delta h)^{1/2} \) criterion (section 2.1). The calculations were carried out following the equations (2.2) to (2.6), considering all equilibrium phases in the Ti-Cu, Ti-Ni, Cu-Zr, Ni-Zr, Cu-Ni-Ti, Cu-Ni-Zr, Cu-Ti-Zr and Ni-Ti-Zr equilibrium phase diagrams [6, 148, 193-196] and in the ICDD PDF+4/2011 Database [197]. Table 7.1 summarizes the phases considered in the calculations. The B2-(Ti,Zr)(Cu,Ni) phase forms in an extended compositional field up to 38 at.% of Cu in the pseudo-binary TiCu-TiNi system [6] and up to 30 at.% of Zr in the TiNi-TiZr system [195]. Such phases with a large compositional field were considered in their entire solubility range (Table 7.1), since they compete with the formation of the amorphous phase. All other required data such as atomic radii [30], work function [198] and electron density of the elements [199] were taken from literature as indicated.
Table 7.1 – Phases considered in the calculations and their references.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>[200]</td>
</tr>
<tr>
<td>Zr</td>
<td>[195]</td>
</tr>
<tr>
<td>Ti</td>
<td>[200]</td>
</tr>
<tr>
<td>Ni</td>
<td>[202]</td>
</tr>
<tr>
<td>NiTi₂</td>
<td>[202]</td>
</tr>
<tr>
<td>Ni₃Ti</td>
<td>[202]</td>
</tr>
<tr>
<td>Ni₂Zr</td>
<td>[195]</td>
</tr>
<tr>
<td>Ni₃Zr</td>
<td>[195]</td>
</tr>
<tr>
<td>Ni₂Zr₈</td>
<td>[195]</td>
</tr>
<tr>
<td>NiZr</td>
<td>[195]</td>
</tr>
<tr>
<td>NiZr₂</td>
<td>[195]</td>
</tr>
<tr>
<td>Cu₃Ti₂</td>
<td>[200]</td>
</tr>
<tr>
<td>Cu₄Ti₃</td>
<td>[200]</td>
</tr>
<tr>
<td>CuTi</td>
<td>[200]</td>
</tr>
<tr>
<td>CuTi₂</td>
<td>[200]</td>
</tr>
<tr>
<td>CuTi₃</td>
<td>[200]</td>
</tr>
<tr>
<td>Cu₄Ti</td>
<td>[200]</td>
</tr>
<tr>
<td>Zr₂Cu</td>
<td>[201]</td>
</tr>
<tr>
<td>(Ti_{1-x}Zr_{x})Ni</td>
<td>x = 0 - 0.6</td>
</tr>
<tr>
<td>Ni(Ti_{2-x}Zr_{x})</td>
<td>x = 0.66 - 1</td>
</tr>
<tr>
<td>Ti₁₀Zr₇Ni₃</td>
<td>[194]</td>
</tr>
<tr>
<td>Ti₄₀Zr₃₈Ni₁₇</td>
<td>[194]</td>
</tr>
<tr>
<td>(Ni_{2,85}Cu_{0,15})Ti₂</td>
<td>[6]</td>
</tr>
<tr>
<td>(Ni_{1-x}Cu_{x})Ti</td>
<td>x = 0 - 0.76</td>
</tr>
<tr>
<td>Ti(Cu₁₈₅Ni₀₁₅)</td>
<td>[6]</td>
</tr>
<tr>
<td>Ti(Ni_{2-x}Cu_{x})</td>
<td>x = 0.35 - 1.73</td>
</tr>
<tr>
<td>Zr₇(Ni_{10-x}Cu_{x})</td>
<td>x = 0 - 10</td>
</tr>
<tr>
<td>Zr(Cu_{5-x}Ni_{x})</td>
<td>x = 0 - 1.8</td>
</tr>
<tr>
<td>Zr(Cu_{1-x}Ni_{x})</td>
<td>x = 0.1 - 0.5</td>
</tr>
<tr>
<td>(Cu_{2-x}Ni_{2+x})Zr</td>
<td>x = 0 - 1</td>
</tr>
<tr>
<td>(Cu_{4+x}Ni_{13-x})Zr₃</td>
<td>x = 0 - 1</td>
</tr>
<tr>
<td>Cu₂TiZr</td>
<td>[148]</td>
</tr>
<tr>
<td>Cu(Ti_{2-x}Zr_{x})</td>
<td>x = 0 - 2</td>
</tr>
<tr>
<td>(Cu_{51-x}Ni_{x})Zr₁₄</td>
<td>x = 0 - 26</td>
</tr>
</tbody>
</table>

The calculation results are shown in Figure 7.1(a), where the brighter regions correspond to higher $\lambda + (\Delta h)^{1/2}$ values, i.e. higher GFA. This diagram is plotted as a pseudoternary equilibrium phase diagram with X = TiNi, Y = CuZr and Z = TiCu. The GFA increases with increasing the amount of (CuZr) added to the ternary Ti-Cu-Ni alloys (Figure 7.1(a)) and a region with a larger GFA is observed in the compositional field between the TiCu and B2-TiNi phases (around 19 at.% of TiNi and 10 at.% of CuZr, Figure 7.1(a)). The composition and critical casting thicknesses (abbreviated “CCT rods”) of BMGs reported in literature [5, 145, 146] are given in Figure 7.1(b) for comparison. One can see that several BMGs are formed in the TiCu-TiNi pseudo-binary system (Figure 7.1(b)) in the compositional range with
The maximum GFA predicted by the $\lambda+\sqrt{\Delta h}$ criterion (Figure 7.1(a)). The literature data also suggest a maximum in GFA in the TiCu-CuZr pseudo-binary system (Figure 7.1(b)), although the exact composition appears to be controversial. Men et al. [14] have showed that a maximum occurs at (TiCu)$_{80}$(CuZr)$_{20}$ with the formation of a 3 mm diameter amorphous rod (Figure 7.1(b)) but Kovneristy et al. [203] have observed a maximum at the eutectic composition (TiCu)$_{70}$(CuZr)$_{30}$ with only 1 mm of critical casting thickness (results not shown in Figure 7.1(b)).

The maximum suggested by the $\lambda+\sqrt{\Delta h}$ criterion, however, is around (TiCu)$_{60}$(CuZr)$_{30}$. The deviation between the calculated and measured maximum in GFA is probably due to the formation of the Cu$_2$TiZr phase. It was considered in the calculations that this compound has a fixed composition (Cu$_2$TiZr) although some results show that this phase can actually dissolve a large amount of Ti, Zr and Ni [148]. Taking into account the similar size and electronegativity between Cu and Ni and Ti and Zr, a considerable solubility of these elements during fast cooling is expected. The consideration of a larger compositional range for this phase changes the prediction for the CuZr-rich compositions in this TiCu-rich region of the TiCu-TiNi-CuZr system and it could explain the deviation between the predicted and the experimental maximum GFA at the CuTi-CuZr side (Figure 7.1(b)). Further phase formation studies are required in order to determine the solubility limits of the primary Cu$_2$TiZr phase and improve the results of the $\lambda+\sqrt{\Delta h}$ criterion in this compositional region.
Figure 7.1 – (a) \( \lambda+\Delta h^{1/2} \) values calculated for TiCu-rich compositions in the TiCu-TiNi-CuZr pseudo-ternary system. The brighter regions represent compositions with higher values of \( \lambda+\Delta h^{1/2} \), i.e. with higher GFA. The compositions selected to be investigated are shown by numbers from 1 to 9 and are given in Table 7.2. (b) Bulk metallic glasses obtained in this compositional region [5, 145, 146]. CCT rods means critical casting thickness for amorphization and the red arrows in the figure indicate eutectic compositions [6, 148].
Table 7.2 – Compositions of the studied alloys and the DSC data obtained at heating rate of 30 K/min. $T_g$, $T_x$ and $T_l$ are defined as the onset glass transition, crystallization and liquidus temperatures, respectively. $\Delta T_x = T_g - T_x$, $\gamma = T_x / (T_g + T_l)$ and $\gamma_m = (2T_x - T_g) / T_l$.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>$\lambda + \Delta h^{1/2}$</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$T_l$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$\gamma$</th>
<th>$\gamma_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti$<em>{47.5}$Cu$</em>{44}$Ni$<em>6$Zr$</em>{2.5}$</td>
<td>0.326±0.001</td>
<td>661±2</td>
<td>691±2</td>
<td>1220±2</td>
<td>30±3</td>
<td>0.367±0.001</td>
<td>0.591±0.004</td>
</tr>
<tr>
<td>2</td>
<td>Ti$<em>{45}$Cu$</em>{46.5}$Ni$_{3.3}$Zr$_5$</td>
<td>0.317±0.001</td>
<td>651±2</td>
<td>688±2</td>
<td>1208±2</td>
<td>37±3</td>
<td>0.370±0.001</td>
<td>0.600±0.004</td>
</tr>
<tr>
<td>3</td>
<td>Ti$<em>{45}$Cu$</em>{44.75}$Ni$_{5.25}$Zr$_5$</td>
<td>0.325±0.001</td>
<td>662±2</td>
<td>696±2</td>
<td>1197±2</td>
<td>34±3</td>
<td>0.374±0.001</td>
<td>0.610±0.004</td>
</tr>
<tr>
<td>4</td>
<td>Ti$<em>{45}$Cu$</em>{43}$Ni$_2$Zr$_5$</td>
<td>0.347±0.001</td>
<td>669±2</td>
<td>697±2</td>
<td>1189±2</td>
<td>28±3</td>
<td>0.375±0.001</td>
<td>0.610±0.004</td>
</tr>
<tr>
<td>5</td>
<td>Ti$<em>{45}$Cu$</em>{42}$Ni$_2$Zr$_5$</td>
<td>0.372±0.001</td>
<td>666±2</td>
<td>716±2</td>
<td>1211±2</td>
<td>50±3</td>
<td>0.381±0.001</td>
<td>0.633±0.004</td>
</tr>
<tr>
<td>6</td>
<td>Ti$<em>{45}$Cu$</em>{39}$Ni$_{1.5}$Zr$_5$</td>
<td>0.337±0.001</td>
<td>669±2</td>
<td>721±2</td>
<td>1241±2</td>
<td>52±3</td>
<td>0.377±0.001</td>
<td>0.623±0.004</td>
</tr>
<tr>
<td>7</td>
<td>Ti$<em>{41.75}$Cu$</em>{47.75}$Ni$<em>{12.5}$Zr$</em>{8.25}$</td>
<td>0.356±0.001</td>
<td>653±2</td>
<td>690±2</td>
<td>1197±2</td>
<td>37±3</td>
<td>0.373±0.001</td>
<td>0.607±0.004</td>
</tr>
<tr>
<td>8</td>
<td>Ti$<em>{42.5}$Cu$</em>{42.5}$Ni$_{2.5}$Zr$_7$</td>
<td>0.361±0.001</td>
<td>651±2</td>
<td>707±2</td>
<td>1172±2</td>
<td>56±3</td>
<td>0.388±0.001</td>
<td>0.651±0.004</td>
</tr>
<tr>
<td>9</td>
<td>Ti$<em>{42.5}$Cu$</em>{41}$Ni$_2$Zr$_7$</td>
<td>0.379±0.001</td>
<td>674±2</td>
<td>716±2</td>
<td>1180±2</td>
<td>42±3</td>
<td>0.386±0.001</td>
<td>0.642±0.004</td>
</tr>
</tbody>
</table>

Nine TiCu-rich compositions in the vicinity of the best quaternary glass formers (Figure 7.1(b)) were selected to be studied and they are shown in Figure 7.1(a) and Table 7.2. Ribbons of these nine composites were prepared by melt spinning to determine their thermal behaviour and then rods of selected compositions were cast with 1 mm diameter and 40 mm length and 2 and 3 mm diameter and 70 mm length to form bulk metallic glass composites as will be shown in section 7.2.

The rapidly solidified ribbons of all compositions exhibit a fully amorphous structure as confirmed by the XRD results (Figure 7.2) for which only two broad peaks are seen around $2\theta = 18.5 ^\circ$ and $32 ^\circ$. The thermal stability and crystallization behaviour of these samples were investigated by DSC and the results are summarized in Table 7.2 and shown in Figure 7.3. All ribbons exhibit a glass transition, followed by two or more exothermic crystallization peaks (Figure 7.3(a)). The crystallization temperature increases with addition of TiNi, as can be seen by comparing alloys number 2 to 6 (Figure 7.3(a), Table 7.2), which have the same CuZr content. No clear trend, however, was observed for the glass transition temperature since it apparently increases with TiNi additions (from alloy 2 to 4) but decreases again from alloy 8 to 9, which also have same CuZr amount.
Figure 7.2 – XRD results for the rapid solidified ribbons. The compositions are named A1 to A9, which refers to the alloys 1 to 9 given in Table 7.2.

Figure 7.3 – (a) Low- and (b) high temperature DSC results recorded at a heating rate of 30 K.min\(^{-1}\) for the nine studied compositions. The arrows in (a) indicate the glass transition and crystallization temperatures, respectively, and in (b) they indicate the liquidus temperature. The compositions are named A1 to A9, which refers to the alloys 1 to 9 given in Table 7.2.

The changes in the melting behaviour of these alloys are shown in the high-temperature DSC traces of Figure 7.3(b). Three or four endothermic melting peaks occur for
these alloys and an obvious trend in the liquidus temperature (indicated by the arrows in Figure 7.3(b), Table 7.2) is observed when alloys number 2 to 6 and alloys number 7 to 9 are compared, with local minima around alloys 4 and 8. These results are combined with available literature data [5, 6, 145, 146] in Figure 7.4(a), which shows isolines of the liquidus temperature. The addition of CuZr decreases the liquidus temperature of these TiCu-rich alloys (Figure 7.4(a)) and when alloys with the same CuZr content are considered (for instance, compositions on the dashed blue line of Figure 7.4(a)), a region with lower local liquidus temperature occurs around the green line shown in Figure 7.4(a). This finding suggests an extension of the eutectic region of the TiCu-TiNi pseudo-binary system (Figure 7.4(b)) towards the TiCu-TiNi-CuZr system as shown by the green line, which represents a possible connection between the eutectics in the TiCu-TiNi and CuTi-CuZr systems. To the right of the green line in Figure 7.4(a), the liquidus temperature increases relatively quickly towards the pseudo-binary TiCu-TiNi diagram (Figure 7.4(a)), which seems to be caused by the extension of the B2-Ti(Ni,Cu) phase field seen in the TiCu-TiNi diagram (Figure 7.4(b)) into the region of quaternary compositions.

**Figure 7.4 – (a)** Isolines of the liquidus temperature in the TiCu-rich region of the TiCu-TiNi-CuZr system, obtained combining the experimental results and some literature data [5, 6, 145, 146]. The blue dashed line indicates compositions with same CuZr content and the
green line suggests possible eutectic compositions (see text). (b) Equilibrium phase diagram of the pseudo-binary TiCu-TiNi system [6].

In order to quantify the GFA of these alloys, GFA parameters based on the characteristic temperatures \( T_g, T_x \) and \( T_l \) were calculated [48, 49, 52] and the results are shown in Table 7.2. All parameters demonstrate that the GFA increases with CuZr additions and the highest GFA of the studied compositions is expected for alloys 5, 6, 8 and 9 (Table 7.2). This is more clearly seen in Figure 7.5(a), which shows isolines of the GFA parameter \( \gamma_m \) \( (= (2 T_x - T_g) / T_l) \) [52], built by combining present experiments and literature data [5, 6, 145, 146]. As can be seen comparing Figure 7.5(a) and Figure 7.1(a), the same fashion is observed for \( \gamma_m \) and \( \lambda + (\Delta h)^{1/2} \) with an increasing in GFA with further additions of CuZr to Ti-Cu-Ni alloys. Figure 7.5(b) shows the correlation between the \( \gamma_m \) and the \( \lambda + (\Delta h)^{1/2} \) criterion. A satisfactory agreement between both was observed (linear correlation coefficient \( R = 0.78 \)), although further refinement in the calculation of the \( \lambda + (\Delta h)^{1/2} \) criterion should be carried out as was discussed before.
Figure 7.5 - (a) Isolines of the $\gamma_m$ values obtained by combining experimental and literature data [5, 145, 146]. (b) Correlation between the $\gamma_m$ and $\lambda + (\Delta h)^{1/2}$ values. A linear correlation coefficient $R$ of 0.78 was obtained, which indicates that there is a correlation between both parameters.

As discussed by Ma et al. [120] and Lu et al. [119], in irregular eutectic systems as TiCu-TiNi [6], which consists of a non-faceted phase (cubic, B2-Ti(Cu,Ni)) and a faceted phase (tetragonal, TiCu) [9], the region with larger GFA is observed off-eutectic as a result of kinetic constraints during growth of the faceted phase [119]. In the case of the TiCu-TiNi system, the best glass formers are located in the region, in which B2-Ti(Cu,Ni) solidifies primarily, viz. in the range between $\text{Ti}_{50}\text{Cu}_{44}\text{Ni}_6$ and $\text{Ti}_{50}\text{Cu}_{40}\text{Ni}_{10}$ [5] while the eutectic composition is found at $\text{Ti}_{50}\text{Cu}_{45}\text{Ni}_5$ [6] (Figure 2.15).

A similar trend seems to occur in the TiCu-rich region of the TiCu-TiNi-CuZr system with the best GFA region being located in the primary crystallization field of the B2-Ti(Cu,Ni) phase, around the compositions 5, 6, 8 and 9, which exhibit the highest $\gamma_m$ values among the studied alloys (Table 7.2). For such an irregular eutectic system, composites consisting only of the primary phase solidifying and the glassy phase can be obtained by carefully adjusting the cooling rate during solidification [119, 120]. The B2-TiNi phase is well known for its large
deformability of up to more than 30% during tensile loading [7]. In order to confirm our assumptions and to produce composites, which combine the soft B2 phase with a glassy matrix, alloys number 5, 6, 8 and 9 were selected to be investigated further.

7.2 Phase formation in the Ti-Cu-Ni-Zr bulk metallic glass composites

The XRD results for the 2 and 3 mm diameter rods of alloys 5, 6, 8 and 9 are shown in Figure 7.6. Bragg peaks of the cubic B2-(Ti,Zr)(Cu,Ni) phase can be observed in all samples. For the 2 mm rods, a broad diffraction maximum around $2\theta = 18.5^\circ$ can be clearly seen next to the B2 peaks which corresponds to the presence of the amorphous phase. The intensity of the B2 peaks is much higher for the 3 mm rods than for the 2 mm, which suggests a higher volume fraction of crystals in the larger samples.

![Figure 7.6 - XRD results for the 2 and 3 mm diameter rods of alloys 5, 6, 8 and 9 (Table 7.2). A5, A6, A8 and A9 denote alloys 5, 6, 8 and 9, respectively, and the numbers 2 and 3 indicate 2 and 3 mm diameter rods. Peaks of the B2-(Ti,Zr)(Cu,Ni) phase can be seen in all samples.](image)
Figures 7.7(a) and 7.7(b) exemplify the microstructure of selected rods with a diameter of 2 mm. Spherical precipitates of the B2 phase are formed in the glassy matrix as additionally confirmed by EBSD analyses. The precipitates have a heterogeneous distribution and are isolated for low crystalline volume fractions and become agglomerated for higher volume fractions. Their size ranges from 10 to 500 µm and their chemical composition is very close to that of the glassy matrix, which suggests a polymorphic crystallization from the liquid and explains the spherical morphology as a result of the absence of constitutional undercooling [86]. For instance, the composition measured by EDX of a B2 precipitate in the rod with a diameter of 2 mm of alloy 6 is Ti\text{45.05±0.01}Ni\text{9.90±0.09}Cu\text{39.6±0.2}Zr\text{5.38±0.09} and the composition of the amorphous phase is Ti\text{45.3±0.2}Ni\text{9.8±0.2}Cu\text{39.7±0.2}Zr\text{5.1±0.2}.

Apart from the amorphous phase and the spherical precipitates of the B2 phase, higher magnification images also show the presence of black (Ti,Zr)_2(Cu,Ni) dendrites with an average size around 1 µm (Figure 7.7(c)). This phase has a cubic structure (Fd-3m) with a composition of Ti\text{60±2}Zr\text{5±1}Ni\text{14±1}Cu\text{21±2} (at.%) in the 2 mm diameter rod of alloy 8. However, (Ti,Zr)_2(Cu,Ni) could not be detected by XRD (Figure 7.6) as a consequence of its low volume fraction estimated to be below 1 vol.%. Yet, its presence is confirmed by EBSD measurements (Figure 7.7(d)). Although EDX analyses cannot precisely measure the amount of oxygen in the different phases, they show the trend that (Ti,Zr)_2(Cu,Ni) contains more oxygen than the other phases (about three times more) and may act as “internal getter”, dragging oxygen from the liquid during solidification. Previous work shows that a large amount of oxygen can be dissolved in this phase [205].
Figure 7.7 – OM image of the cross section of (a) 2 mm diameter rod of Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (alloy 5, top part) and (b) Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (alloy 9, bottom part). The amorphous phase and the B2 precipitates are indicated in the figures. The inset depicts the microstructure of the 3 mm diameter rod (bottom region) of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6). Dendrites of the B2 phase are seen together with a small amount of black unidentified phase at their grain boundary. (c) The region marked by the dashed circle in (b) at a higher magnification. It shows black dendrites surrounded by grey contrast regions in the glassy matrix. (d) EBSD pattern obtained from the black dendrites, which can be indexed as the cubic (Ti,Zr)$_2$(Cu,Ni) phase with space group Fd-3m.

A grey contrast region with a similar composition like the glassy matrix is also seen around the dark (Ti,Zr)$_2$(Cu,Ni) dendrites (Figure 7.7(c)) for alloys 8 and 9. A TEM image of the interface between the matrix and the grey region is shown in Figure 7.8(a) together
with its selected area electron diffraction pattern (SAED) (Figure 7.8(b)). The reflections correspond to the hexagonal Cu$_2$TiZr phase (P63/mmc). The SAED pattern of the matrix is shown in Figure 7.8(c), which exhibits the diffuse rings typical of an amorphous structure. The Cu$_2$TiZr phase is expected to form in the present compositional region rather than the cubic (Ti,Zr)$_2$(Cu,Ni) phase [6, 148], which is probably stabilised by oxygen as commonly observed in CuZr-based alloys [15]. The SEM images of alloys 8 and 9 also show that (Ti,Zr)$_2$(Cu,Ni) crystals act as heterogeneous nuclei for the formation of Cu$_2$TiZr (Figure 7.7(c)). A similar nucleation effect was not observed for the B2 (Ti,Zr)(Cu,Ni) phase.

![Figure 7.8](image_url)

**Figure 7.8** – *(a)* TEM micrograph of the grey phase around the (Ti,Zr)$_2$(Cu,Ni) dendrites displayed in Figure 7.7(c) (alloy Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$, number 8). Next to the glassy phase, crystals are found. *(b)* Selected area electron diffraction (SAED) reveals that they are Cu$_2$TiZr crystals (zone axis: [1 0 0]). *(c)* SAED pattern of the amorphous matrix.

Apart from the glass, the B2 phase and (Ti,Zr)$_2$(Cu,Ni) (below 1 vol.%) formed in alloys 5 and 6. Alloys 9 and 8 also show the presence of Cu$_2$TiZr, which suggests that the increase in the amount of CuZr favours its formation. It is interesting that the B2 phase formed in the latter alloys exhibits sharp corners (Figure 7.7(b)), probably related to the
presence of the Cu₂TiZr phase, which could concentrate stress and induce crack formation during loading. Aside from the B2 morphology, the presence of the hexagonal Cu₂TiZr phase is expected to also have pronounced effects on the mechanical behaviour as will be discussed later.

The 3 mm rods form a smaller volume fraction of amorphous phase than the rods with a diameter of 2 mm judged from the micrographs (Figure 7.9). For the alloys 5, 6 and 9, amorphous phase was observed only in a very small region at the outer surface of some samples (Figure 7.9) as a result of the higher cooling rate in this region. These rods consist mainly of B2-(Ti,Zr)(Cu,Ni) dendrites with a small amount of an unidentified second phase in the interdendritic region (inset in Figure 7.7(a)). This unidentified phase may be responsible for the small reflections observed around 2θ = 18 ° and 19.5 ° in the XRD patterns of the 3 mm rods of alloys 9 and 6 (Figure 7.6). Rietveld refinement [206] was performed for the 3 mm diameter rod of alloy 6 to obtain further information about the B2 phase. A lattice parameter of 3.082 Å was obtained, which is very close to the lattice parameter of the pure B2-TiNi (3.007 Å [6]). Nonetheless, the present EDX measurements (see above) prove that significant amounts of both Zr and Cu are dissolved in the B2 phase (Ti₄₅.₀₅±0.₀₁Ni₉.₉₀±0.₀₁Cu₃₉.₆₂±0.₀₂Zr₅.₃₈±0.₀₁), which has been also observed before [6, 195]. This might be a result of the very small difference in size and electronegativity between Ti and Zr and Cu and Ni [144].
Figure 7.9 – Microstructure of the 3 mm diameter rod (cross section) of the Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (alloy 9). Amorphous phase can be seen only in a small part at the outer surface.

In contrast, the 3 mm diameter rod of Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (alloy 8) exhibits a larger amount of amorphous phase, mixed with spherical B2 precipitates, small (Ti,Zr)$_2$(Cu,Ni) dendrites and the hexagonal Cu$_2$TiZr phase. The volume fraction of crystalline phases in each rod was estimated based in the crystallization enthalpies (equation 5.1, section 5.2). Table 7.3 lists the crystallization enthalpies measured by DSC for the bottom and top part of each rod and the estimated amorphous volume fractions. One can see that the volume fraction of the amorphous phase in the 3 mm rods increases for the different alloys in the sequence 6, 5, 9 and 8, which corroborates the GFA estimated by the $\gamma_m$ parameter (Table 7.2).
Table 7.3 – Crystallization enthalpies ($\Delta H_c$) and volume fractions of the amorphous phase for the different samples (ribbons, 2 and 3 mm diameter rods) taken from various regions (top and bottom part).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Geometry/Region</th>
<th>$\Delta H_c$ (J/g)</th>
<th>Amorphous (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>ribbon</td>
<td>-106±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Top</td>
<td>-65±10</td>
<td>61±11</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Bottom</td>
<td>-58±10</td>
<td>55±11</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-9±5</td>
<td>9±5</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-9±5</td>
<td>9±5</td>
</tr>
<tr>
<td>6</td>
<td>ribbon</td>
<td>-105±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Top</td>
<td>-87±10</td>
<td>83±12</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Bottom</td>
<td>-20±5</td>
<td>19±5</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-6±5</td>
<td>6±5</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>ribbon</td>
<td>-96±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Top</td>
<td>-96±10</td>
<td>100±15</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Bottom</td>
<td>-81±10</td>
<td>84±14</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-81±10</td>
<td>84±14</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-64±10</td>
<td>67±12</td>
</tr>
<tr>
<td>9</td>
<td>ribbon</td>
<td>-88±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Top</td>
<td>-90±10</td>
<td>100±16</td>
</tr>
<tr>
<td></td>
<td>2 mm dia. rod/Bottom</td>
<td>-79±10</td>
<td>90±15</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-17±5</td>
<td>20±6</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-14±5</td>
<td>16±6</td>
</tr>
</tbody>
</table>

In order to compare the phase formation in the rapid solidified rods of the Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (alloy 5), Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6), Ti$_{42.5}$Cu$_{42.5}$Ni$_7$Zr$_{7.5}$ (alloy 8) and Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (alloy 9, Figure 7.6) with samples formed in conditions more close to the equilibrium, the amorphous ribbons of these compositions were heated up to 973 K until complete crystallization. The XRD results for these samples are depicted in Figure 7.10. It shows that the ribbons form mainly the tetragonal $\gamma$-TiCu phase with lower amount of the B2-(Ti,Zr)(Cu,Ni), Ti$_2$Cu and Ti$_2$Ni. It can be also seen that the amount of the Ti$_2$Cu and Ti$_2$Ni increases with increasing the Zr content from alloys 5 and 6 to alloys 8 and 9. It is interesting to point that the phases formed during crystallization are completely different from the phases formed during rapid solidification (amorphous and B2 phase, Figure 7.6). Under rapid solidification conditions, the compositional field of the B2-(Ti,Zr)(Cu,Ni) phase
may be extended [207] and a larger amount of this phase is obtained in a non-equilibrium condition within the amorphous matrix.

Figure 7.10 – XRD results for the fully crystalline ribbons of Ti₄₅Cu₄¹Ni₉Zr₅ (A5), Ti₄₅Cu₃₉Ni₁₁Zr₅ (A6), Ti₄₂₅Cu₄₂₅Ni₇₅Zr₇₅ (A8) and Ti₄₂₅Cu₄₁Ni₇₅Zr₇₅ (A9). These results appoint that the ribbons are formed mainly by the tetragonal γ-TiCu together with low amount of the B2-(Ti,Zr)(Cu,Ni), Ti₂Cu and Ti₂Ni. The amount of these two latter phases increases with increasing the Zr content in alloys A8 and A9.

The results show that the rods have only slightly varying amorphous volume fractions at the top and bottom part (Table 7.3) with exception of the 2 mm rod of the Ti₄₅Cu₃₉Ni₁₁Zr₅ (alloy 6), which exhibits a large difference of 83±12 and 19±10 vol.%, respectively. Considering that the same parameters were used during casting of the rods, this large difference is attributed to the lower GFA of this alloy (Table 7.2). This large
difference along the length of the rod allows the study of the influence of volume fraction of crystalline phase in the mechanical behaviour as will be discussed in section 7.3.1.

7.3 Correlation between phase formation and mechanical behaviour of the Ti-Cu-Ni-Zr alloys

The mechanical behaviour of the 2 and 3 mm diameter rods of alloys Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (alloy 5), Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6), Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (alloy 8) and Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_7.5$ (alloy 9) during compression is shown in Figure 7.11(a) and 7.11(b), respectively. All rods with a diameter of 2 mm exhibit high strength when compared to other Ti-based alloys [172] with yield strengths up to 1690±50 MPa (Figure 7.11(a), Table 7.4). The fracture strain is greatly affected by the composition and changes from alloys 5 and 6 to alloys 8 and 9. The former two alloys show large fracture strains of 19.5±0.5 and 23.7±0.5 % whereas the latter two exhibit values of only 1.9±0.5 and 2.8±0.5 %, respectively. The mechanical properties of the bigger rods, with 3 mm diameter, are also dependent on the composition. Alloys 5, 6 and 9 exhibit a relatively large fracture strain up to 15.5±0.5 % (Figure 7.11(b), Table 7.4) but combined with significantly lower yield strengths than the more rapidly quenched rods with a diameter of 2 mm (Table 7.4). These samples mainly consist of the softer B2 phase (more than 90 vol.%, see Table 7.3 and Figure 7.6), which explains this behaviour. In contrast, the 3 mm diameter rod of alloy 8 with an amorphous volume fraction between 84-67 vol.% (Table 7.3) has a high yield strength of 1380±50 MPa but a limited fracture strain of 1.2±0.5 %.

Not only the characteristic values like yield strength, yield strain and fracture strain are dictated by the respective volume fractions but also the shape of the stress-strain curve. While the material cooled at higher rates (2 mm in diameter) shows an extended elastic regime followed by a single yielding, the rods with a diameter of 3 mm apparently undergo several yielding phenomena, which has been observed for shape memory alloys and BMG matrix composites containing shape memory crystals [138, 208]. These differences in the mechanical behaviour are associated with the different crystalline volume fractions as well as with the phase evolution and both will be addressed in more depth in the following paragraphs.
Figure 7.11 – (a) True compressive stress-strain curves for the 2 mm and (b) 3 mm diameter rods of alloys 5, 6, 8 and 9, denoted by A5, A6, A8 and A9.
Table 7.4 – Mechanical properties under compressive loading and estimated crystalline volume fraction for each tested sample. A5, A6, A8 and A9 denote alloys 5, 6, 8 and 9. The crystalline volume fractions were obtained from image analyses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rod region</th>
<th>Yield strength (MPa)</th>
<th>Fracture strain (%)</th>
<th>Young's modulus (GPa)</th>
<th>Estimated cryst. vol. fract. (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mm rod Ti$<em>{45}$Cu$</em>{41}$Ni$_9$Zr$_5$ (A5)</td>
<td>top</td>
<td>1300±50</td>
<td>19.5±0.5</td>
<td>94±5</td>
<td>38±5</td>
</tr>
<tr>
<td>2 mm rod Ti$<em>{45}$Cu$</em>{41}$Ni$_9$Zr$_5$ (A5)</td>
<td>top</td>
<td>360±50</td>
<td>15.5±0.5</td>
<td>72±5</td>
<td>100±5</td>
</tr>
<tr>
<td>2 mm rod Ti$<em>{45}$Cu$</em>{39}$Ni$_{12}$Zr$_5$ (A6)</td>
<td>top</td>
<td>1490±50</td>
<td>23.7±0.5</td>
<td>78±5</td>
<td>28±5</td>
</tr>
<tr>
<td>3 mm rod Ti$<em>{45}$Cu$</em>{39}$Ni$_{12}$Zr$_5$ (A6)</td>
<td>middle</td>
<td>430±50</td>
<td>15.5±0.5</td>
<td>46±5</td>
<td>100±5</td>
</tr>
<tr>
<td>2 mm rod Ti$<em>{42.5}$Cu$</em>{42.5}$Ni$<em>{7.5}$Zr$</em>{7.5}$ (A8)</td>
<td>middle</td>
<td>1690±50</td>
<td>1.9±0.5</td>
<td>124±5</td>
<td>2±5</td>
</tr>
<tr>
<td>3 mm rod Ti$<em>{42.5}$Cu$</em>{42.5}$Ni$<em>{7.5}$Zr$</em>{7.5}$ (A8)</td>
<td>middle</td>
<td>1380±50</td>
<td>1.2±0.5</td>
<td>106±5</td>
<td>9±5</td>
</tr>
<tr>
<td>2 mm rod Ti$<em>{42.5}$Cu$</em>{41}$Ni$<em>9$Zr$</em>{7.5}$ (A9)</td>
<td>middle</td>
<td>1320±50</td>
<td>2.8±0.5</td>
<td>108±5</td>
<td>10±5</td>
</tr>
<tr>
<td>3 mm rod Ti$<em>{42.5}$Cu$</em>{41}$Ni$<em>9$Zr$</em>{7.5}$ (A9)</td>
<td>middle</td>
<td>260±50</td>
<td>12.9±0.5</td>
<td>72±5</td>
<td>100±5</td>
</tr>
</tbody>
</table>

The B2-TiNi phase undergoes a martensitic transformation to the monoclinic B19’ phase during deformation [7] similarly as the B2-CuZr phase in bulk metallic glass composites, which transforms to the B19’ and B33 phases [138, 208]. This transformation explains the work hardening observed in these composites [4, 138, 208]. Most likely the pronounced work hardening seen in the present stress-strain curves (Figure 7.11) is also related to a phase transformation in the B2-(Ti,Zr)(Cu,Ni) phase. To reveal this, XRD experiments were conducted on the as-cast rods (BC) and selected rods (alloys 5 and 6) after deformation (AC) (Figure 7.12). The peaks of the orthorhombic B19 phase become more prominent after deformation at the expense of the B2 reflections (2θ = 18.7 °), indicating that the martensitic transformation indeed takes place but is not completed after deformation to fracture. Moreover, the addition of Cu to B2-TiNi changes the transformation from cubic B2 → monoclinic B19’ to cubic B2 → orthorhombic B19 [6], which is in agreement with our results.
Figure 7.12 – XRD results for the 2 mm diameter rods of alloys 5 and 6 (Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ and Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$, respectively), before (BC) and after (AC) compression. The lower peak intensities and peak broadening occur as a result of the phase transformation and accumulation of defects in the phases such as dislocation, stacking faults and cracks [178].

The martensitic transformation during deformation of the B2 phase was also confirmed by in-situ XRD experiments. A 1 mm diameter rod of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6) was selected to be investigated and the results are shown in Figure 7.13. The first pattern taken at 130 MPa shows that this sample consists of an amorphous phase with a small amount of B2 crystals (Figure 7.13), which was estimated by image analyses to be about 20±5 vol.%. It can be seen that with increasing the load, the B2 phase transforms to B19. The yield strength observed during compression for this sample was 1500±50 MPa. Figure 7.13 shows that the transformation of the B2 phase starts around 620±50 MPa, which is much lower than the yield strength observed for the composite. This proves that the soft second phase starts to deform earlier than the glass matrix as was suggested in chapter 5 (section 5.3) but this deformation cannot be macroscopically detected because it is confined by the elastically-deforming glassy matrix. The macroscopic yield strength is only observed after the beginning of the plastic deformation of the amorphous phase. These results are in agreement with recent experimental results obtained for a TiZrBe-based alloy [209].
Figure 7.13 – \textit{In-situ} high-energy XRD results obtained during compression of a 1 mm diameter Ti_{45}Cu_{39}Ni_{11}Zr_{5} rod. The transformation of the cubic B2-(Ti,Zr)(Cu,Ni) phase to the orthorhombic B19-(Ti,Zr)(Cu,Ni) starts at around 620±50 MPa, which is below the observed yield strength (1500±50 MPa). The arrows up indicate Bragg peaks of the B2 phase whereas the arrows down indicate peaks of the B19 phase.

The amount of the amorphous and crystalline phase is one of the most important quantities in order to understand the mechanical behaviour of these alloys [14]. All rods mainly consist of the B2 phase and glass but with different volume fractions (Figure 7.6 and Table 7.3), although alloys 8 and 9 also show a small amount of the Cu_{2}TiZr phase (Figures 7.7(b), 7.7(c) and 7.8(a)), which also influences in the mechanical behaviour as will be discussed later. In order to determine the volume fractions of crystalline phases in each compression test sample, optical micrographs as shown in Figures 7.7(a) and 7.7(b) were obtained from both parallel end faces and the crystalline volume fractions were estimated by the manual point account method (ASTM E 562-08) prior to the compression tests. The average crystalline volume fraction for each sample is given in Table 7.4. One can see that these values are in good agreement with the results of the DSC analyses (Table 7.3).
As elaborated above for the volume fractions of the crystalline phases obtained from the micrographs of the compression test samples (Table 7.4), one can infer that the lower fracture strain of the 2 mm rod samples of alloys 8 and 9 and 3 mm rod sample of alloy 9 is primarily caused by a lower content of the crystalline phases as discussed above. In addition, differences in the composition of the B2 phase may also affect the fracture strain as suggested in a recent work [125]. In order to determine possible differences in the deformability of the B2 and the amorphous phase caused by slightly different compositions, Vickers hardness measurements were carried out for the different alloys. The values obtained were 336±19 HV0.2, 316±13 HV0.2, 348±13 HV0.2 and 344±7 HV0.2 for the B2 phase and 530±35 HV0.2, 536±19 HV0.2, 516±16 HV0.2 and 551±6 HV0.2 for the glassy matrix of alloys 5, 6, 8 and 9 (2 mm diameter rods), respectively. In the light of such similar hardness values, the influence of the different composition of the B2 phase and the amorphous phase on the mechanical behaviour of these alloys (comparing the results for alloys 5, 6, 8 and 9, Figure 7.11) should be marginal. The martensitic transformation of the B2 crystals during deformation is evident after indentation as shown in Figure 7.14, where several twins are seen around the indent.

Figure 7.14 – Formation of twins during indentation of a B2-(Ti,Zr)(Cu,Ni) precipitate in the Ti₄₅Cu₃₉Ni₁₁Zr₅ 2 mm diameter rod. The B2 phase transforms to the B19-(Ti,Zr)(Cu,Ni) during deformation by means of twinning.

As discussed in section 7.2, a relatively large amount of the Cu₂TiZr phase precipitates in alloys 8 and 9 (Figure 7.7(b) and 7.7(c)), which have a higher CuZr amount
than alloys 5 and 6. The hardness of this phase is 654±25 HV0.2 and 669±18 HV0.2 for the 2 mm diameter rods of alloys 8 and 9, respectively, which gives a strength (using the relation $\rho = \frac{HV}{3}$ [122], where $\rho$ and HV are the yield strength (kgf/mm$^2$) and Vickers hardness, respectively) around 20 % higher than the amorphous matrix. This high-strength intermetallic phase seems to influence the deformation behaviour significantly (Figure 7.11). The fracture surface of the 3 mm diameter rod of alloy 8 after polishing is shown in Figures 7.15(a) and 7.15(b). Multiple cracks develop inside the Cu$_2$TiZr phase (Figure 7.15(a)) and they seem to percolate through the material following the network of Cu$_2$TiZr crystals (Figure 7.15(b)). The cracks stop at the interface with the matrix, which suggests that Cu$_2$TiZr has a lower toughness than the glassy matrix. The plastic zone with size $a_c$ at the tip of a sharp crack is given by equation 2.9 [131, 132]. Since Cu$_2$TiZr shows a lower toughness than the glassy matrix and also a higher yield strength, its $a_c$ value is expected to be much smaller, i.e. this phase is more brittle than the glassy matrix, which explains the cracks formed during deformation. The Cu$_2$TiZr phase [210] has a hexagonal structure with only 3 slip systems available (<1120> directions at the (0001) basal plane [122]), which limits the ductility and toughness, similarly as observed for other Laves Phases [211]. Consequently, the lower plasticity observed for alloys 8 and 9 seems to be also related to the presence of the Cu$_2$TiZr phase, whose volume fraction increases as the CuZr content becomes higher.

![Figure 7.15](image)

**Figure 7.15** – (a) SEM image of the polished fracture surface of the 3 mm diameter rod of alloy 8. Cracks are seen inside the Cu$_2$TiZr phase, confirming its brittleness. (b) These cracks seem to follow the network of the Cu$_2$TiZr crystals.
7.3.1 Work hardening, yield strength, fracture strain and crystalline volume fraction of B2 phase in the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ alloy

Several compression test samples of the 2 mm diameter rod of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ (alloy 6) were prepared in order to study the influence of different volume fractions of B2 phase on the mechanical behaviour. As shown in section 7.2, the crystalline volume fraction in the rod with a diameter of 2 mm varies strongly from bottom to the top, which makes it a suitable candidate for this investigation. In addition, the B2 phase precipitates almost exclusively in the 3 mm diameter rod (Figure 7.6 and inset Figure 7.7(a)) and the deformation behaviour is not influenced by additional phases (such as Cu$_2$TiZr for alloys 8 and 9, see above).

Figure 7.16(a) compares the mechanical behaviour of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ (alloy 6) with different volume fractions of B2 phase (the values are given in the figure). One can see that the work-hardening ability of this alloy is extremely dependent on the volume fraction of the B2 phase. Up to three different inflection points can be identified in the curves (dashed rectangles in Figure 7.16(a)), which might be connected with the plastic deformation of the B2 phase, the amorphous phase and the martensite, respectively [138]. A deformation behaviour typical of shape memory alloys is observed for the fully crystalline sample with the occurrence of a “double” yielding behaviour [7] and very strong work hardening. This results in a fracture strength of 1890±50 MPa, which is about four times higher than the yield strength (Figure 7.16(a)). In contrast, the sample with the lowest volume fraction of B2 phase (about 28 vol.%) only work-hardens in the beginning of deformation before its hardenability is exhausted.

To quantify the different work-hardening behaviour the work-hardening rate (derivative of plastic part of the true stress-strain curve of Figure 7.16(a) [122]) versus true strain for the different samples of alloy 6 was calculated and is shown in Figure 7.16(b). Two distinct regions can be seen in Figure 7.16(b): below 3 % of true strain, the samples with a lower amount of B2 phase exhibit larger work-hardening rates whereas for larger strains the reverse occurs.
Figure 7.16 – (a) True compressive stress-strain curves for the 2 mm diameter rods of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6). The volume fractions of the B2 phase estimated by images analyses are shown in the figure. The dashed rectangles denote different inflection points observed in the curves. (b) Work-hardening rate (derivative of the true stress-strain curve after the yield strength) versus true strain for the same samples.
As discussed in chapter 5, plastic deformation in these particular types of composites starts in the crystalline precipitates, which promotes local stress concentrations and a heterogeneous stress distribution in the glassy matrix. The results of Figure 7.16(b) demonstrate that a small amount of B2 precipitates dispersed in the glassy matrix is more effective to enhance the work hardening of the composites in the beginning of deformation (below 3 % of true strain). Yet, because their volume fraction is relatively low, the overall hardenability in these composites saturates earlier than for the other samples. This might be responsible for the opposite situation after 3 % of true strain, when higher work-hardening rates occur for composites with larger volume fractions of B2 phase. It might as well explain the almost similar and constant work-hardening rate at the end of deformation at strains exceeding about 12 %, when the hardening rates reach a plateau for all samples. A characteristic “hump” is observed for the 55 vol.% and 100 vol.% samples at intermediate strains (2.5 to 5 % of strain), which is probably connected with the plateau of the martensitic transformation usually observed during deformation of the cubic B2 phase [7].

By casting the same alloy (Ti<sub>45</sub>Cu<sub>39</sub>Ni<sub>11</sub>Zr<sub>5</sub>, alloy 6) into rods with different diameters, one can produce samples with different crystalline volume fractions since the cooling rate scales with the radius [19]. In order to have a larger spectrum of samples with different volume fractions of the B2 phase, a 1 mm diameter rod of alloy 6 was prepared in addition. Again a composite microstructure mainly consisting of the amorphous phase and a very small amount of B2 phase is formed for these rods as determined by image analyses (Figure 7.17).
Figure 7.17 – Cross-section of the 1 mm diameter rod of alloy 6 (Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$). Only a small amount of B2 phase (around 3 vol.%) is seen in the amorphous matrix.

Figure 7.18(a) shows the correlation between the yield strength and the estimated volume fraction of the B2 phase for the 1, 2 and 3 mm diameter rod samples of alloy 6. The mechanical test data and estimated volume fractions of the B2 phase are moreover summarized in Table 7.5. It is interesting to point out here that although the samples have different diameters, this does not considerably affect the yield strength [115]. Instead, the strength of these composites strongly depends on the fraction of the B2 phase. For B2 fractions less than 30 vol.%, the strength of the composites follows a rule of mixtures (ROM, Figure 7.18(a)) given by equation (2.10) [14]. For higher B2 volume fractions, the strength is given by the load-bearing model [14] (Figure 7.18(a), equation (2.11)) and in this case the strength of the composite is mainly governed by the strength of the B2 phase.
**Figure 7.18** – Correlation between the crystalline volume fraction and (a) yield strength (Table 7.5) and (b) fracture strain for Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6, only rods with diameters of 2 mm are considered in this case, see Table 7.5). The fracture strain for a full amorphous sample was assumed to be 3 % (see text) and it is indicated with a red star in (b). The full and dashed curves in (b) refer to the calculation of the fracture strain based in the three microstructural element body model (equation 2.12, section 2.4) using different $K(\varepsilon_f^\beta/\varepsilon_j^a)$ values.

**Table 7.5** – Compression test data of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ rods (alloy 6) with 1 and 2 mm diameter. The crystalline volume fractions are estimated from image analyses. The diameter
of the 3 mm diameter rod was reduced to 2 mm for sake of comparison (these samples are indicated with the word “machined”).

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Estimated cryst. vol. frac. (vol.%%)</th>
<th>Yield strength (MPa)</th>
<th>Fracture strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5±5</td>
<td>1780±50</td>
<td>25.2±0.5</td>
</tr>
<tr>
<td>1</td>
<td>3±5</td>
<td>2010±50</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>28±5</td>
<td>1490±50</td>
<td>23.7±0.5</td>
</tr>
<tr>
<td>2</td>
<td>31±5</td>
<td>570±50</td>
<td>20.4±0.5</td>
</tr>
<tr>
<td>2</td>
<td>38±5</td>
<td>490±50</td>
<td>13.0±0.5</td>
</tr>
<tr>
<td>2</td>
<td>55±5</td>
<td>510±50</td>
<td>20.1±0.5</td>
</tr>
<tr>
<td>2</td>
<td>65±5</td>
<td>500±50</td>
<td>13.7±0.5</td>
</tr>
<tr>
<td>2</td>
<td>69±5</td>
<td>390±50</td>
<td>16.3±0.5</td>
</tr>
<tr>
<td>2</td>
<td>89±5</td>
<td>370±50</td>
<td>17.8±0.5</td>
</tr>
<tr>
<td>3</td>
<td>100±5</td>
<td>400±50</td>
<td>15.9±0.5</td>
</tr>
<tr>
<td>2 (machined)</td>
<td>100±5</td>
<td>410±50</td>
<td>15.8±0.5</td>
</tr>
<tr>
<td>2 (machined)</td>
<td>100±5</td>
<td>430±50</td>
<td>11.1±0.5</td>
</tr>
</tbody>
</table>

Figure 7.18(b) shows the correlation between the fracture strains found in the 2 mm diameter rod samples of alloy 6 and the according crystalline volume fraction. In this case, only 2 mm diameter samples were considered since the fracture strain is size-dependent [115]. Hence, the rod with a diameter of 3 mm of alloy 6, which contains almost entirely the B2 phase (Figure 7.6 and inset of Figure 7.7(a)) was machined in order to reduce the diameter to 2 mm. As can be seen in Figure 7.18(b), a maximum fracture strain occurs around 28 vol.% of the B2 phase. All samples exhibit fracture strains equal or larger than 11%, which proves the large deformability of these alloys compared to CuZr-based composites [13].

The fracture strain of the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ (alloy 6) was calculated considering the three microstructural element body model (equation (2.12), section 2.4) [14, 134]. One needs to have the fracture strain of both a fully amorphous and a fully crystalline (B2 phase) sample. Since it is impossible to obtain a 2 mm diameter rod of alloy 6 with a fully amorphous structure, the fracture strain was assumed to be 3% as measured for a BMG with an almost similar composition [146]. Moreover, this value agrees with the fracture strains observed for the 2 mm diameter rods of alloys 8 and 9 with the lowest amounts of
crystalline phase (Table 7.4). The sample machined to a diameter of 2 mm is considered to contain 100 vol.% of the B2 phase. All B2 precipitates isolated or agglomerated, with sizes larger than 500 µm were ranked as element α, and the remaining B2 phase as element α + β, which implies that $f_\alpha = f_{\alpha c} + \frac{1}{2} f_{\alpha \beta}$ and $f_\beta = f_{\beta c} + \frac{1}{2} f_{\alpha \beta}$. The measured volume fraction of the α + β element versus the overall crystalline volume fraction is given in Figure 7.19.

![Figure 7.19 – Volume fraction of the element (α + β) (α < 500 µm) for 2 mm diameter rods of alloy 6 as a function of their overall crystalline volume fraction.](image)

In order to apply the three microstructural element body model (equation (2.12), section 2.4), one needs to know the fracture strain of the element α + β or define a value for $K(\epsilon_f^{\alpha \beta}/\epsilon_f^{\alpha})$ (equation (2.12)). Figure 7.18(b) shows the results of the calculation using different $K(\epsilon_f^{\alpha \beta}/\epsilon_f^{\alpha})$ values. The best fitting considering the experimental data was obtained for $K(\epsilon_f^{\alpha \beta}/\epsilon_f^{\alpha}) = 10.5$ as shown in Figure 7.18(b). The calculated values of the fracture strain show a reasonable agreement with the experimental ones. Three samples (38, 65 and 100 vol.% crystalline phase) exhibit a lower fracture strain than the predicted value, which may result from the presence of defects such as pores or imperfections at the surface. A maximum is also suggested by the model around 20 - 40 vol.% of crystals, which can be explained by a maximum in the amount of the α + β element around this crystalline volume fraction (Figure 7.19). The mixture α + β (with α < 500 µm) shows larger fracture strains than the pure α or β element, which could explain the maximum observed around 28 vol.%
of the B2 phase. The $\alpha + \beta$ element reflects the influence of the stress concentrations at the glass/crystal interface as described in chapter 5, which is responsible for the generation of multiple shear bands, with a more homogeneous and stable deformation of the composite. Additionally, this element also reflects the positive effect on the mechanical behaviour that especially relatively small and homogeneously distributed second phase(s) have, as also observed in simulations [126, 127]. Very similar correlations between yield strength, fracture strain and crystalline volume fractions were observed for Cu$_{47.5}$Zr$_{47.5}$Al$_5$ shape memory bulk metallic glass composites, which exhibit a similar microstructure and phase formation but a lower deformability [14].

### 7.4 Tensile tests of Ti-Cu-Ni-Zr bulk metallic glass composites

The mechanical properties of some Ti-Cu-Ni-Zr alloys were also investigated by tensile tests. The Ti$_{45}$Cu$_{43}$Ni$_7$Zr$_5$ (alloy 4), Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (alloy 5), Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6), Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (alloy 8) and Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (alloy 9) were selected for this study since they exhibit the highest GFA between the studied compositions as suggested by the $\gamma_m$ parameter (Table 7.2). Plates with thicknesses of 1 and 1.5 mm, with 10 mm in width and with 50 mm in length were fabricated by suction casting and were cut into a flat dog bone shape (Figure 3.2). At least three plates of each geometry (1 and 1.5 mm thick) and alloy (4, 5, 6, 8 and 9) were prepared for the tensile tests and samples for XRD, SEM and DSC were taken around the centre region/border part of the plates.

Similar XRD results like for the rod shape samples (Figure 7.6) were obtained for the 1 mm thick plates, with the formation of peaks of the B2 phase overlapping the amorphous phase broad peaks (Figure 7.20(a)). For the 1.5 mm thick plates (Figure 7.20(b)), apart from the B2 peaks and the broad peak of the amorphous phase at $2\theta = 18.3^\circ$ (alloys 8 and 9), reflections of the $\gamma$-TiCu phase were also detected for alloys 4 and 5 (Figure 7.20(b)). It proves that the $\gamma$-TiCu tends to precipitate with increasing the Cu amount in the sequence Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$, Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ and Ti$_{45}$Cu$_{43}$Ni$_7$Zr$_5$ (alloy 6, 5 and 4, respectively, Figure 7.20(b)), considering that they have the same Ti and Zr amount. Alloy 8 formed the largest amount of amorphous phase as could be inferred from the XRD results of Figure 7.20 (A8),
where broad peaks are observed with a sharp tip (see peak at $2\theta = 18.5^\circ$), which reveals also the presence of a small amount of crystalline phases.
Figure 7.20 – XRD results obtained for the (a) 1 and (b) 1.5 mm thick plates of Ti$_{45}$Cu$_{43}$Ni$_7$Zr$_5$ (A4), Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (A5), Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (A6), Ti$_{42.5}$Cu$_{42.5}$Ni$_7$Zr$_{7.5}$ (A8) and Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (A9).

The microstructure of the 1 and 1.5 mm plates is also similar to the one observed for the rods (Figure 7.7(a)). Spherical B2 precipitates form in the glassy matrix in an inhomogeneous way. Many of these B2 precipitates coalesce and form elongated crystalline regions as exemplified in Figure 7.21(a) for Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6), which are aligned along the flow direction during casting. The presence of a small amount of crystalline phases in alloy 8 is evident in Figure 7.21(b), which shows small crystalline precipitates of the B2 and Cu$_2$TiZr phases as judged by the micrographs. For the 1.5 mm thick plates of alloys 4 and 5, the γ-TiCu was observed inside large crystalline precipitates as shown in Figure 7.21(c) and 7.21(d). This phase has the morphology of black needles [9] as can be seen in Figure 7.21(c) and 7.21(d), taken from the 1.5 mm thick plates of Ti$_{45}$Cu$_{43}$Ni$_7$Zr$_5$ (alloy 4) and Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (alloy 5), respectively.
Figure 7.21 – (a) Microstructure of the 1 mm thick plate of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6) (image taken in the longitudinal direction). The precipitates are elongated along the casting direction. (b) Although no clear crystalline peaks were observed in the XRD results of Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (alloy 8, Figure 7.20(b)), small crystalline precipitates are seen in the optical micrograph of a 1.5 mm thick plate. (c) and (d) Microstructure of the 1.5 mm thick plates of alloys Ti$_{45}$Cu$_{43}$Ni$_{7}$Zr$_5$ (alloy 4) and Ti$_{45}$Cu$_{41}$Ni$_{9}$Zr$_5$ (alloy 5), respectively. Black needles of the γ-TiCu can be seen in the centre of large crystalline precipitates.

The martensitic transformation in the 1.5 mm thick plates of the five alloys was investigated by DSC and the results are shown in Figure 7.22 and Table 7.6. No transformation was observed for the Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (alloy 8) and Ti$_{42.5}$Cu$_{41}$Ni$_{9}$Zr$_{7.5}$ (alloy 9). The results for the other compositions (Ti$_{45}$Cu$_{43}$Ni$_{7}$Zr$_5$ (alloy 4), Ti$_{45}$Cu$_{41}$Ni$_{9}$Zr$_5$ (alloy 5) and Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6)) are shown in Figure 7.22. A clear endothermic martensitic transformation peak is observed for Ti$_{45}$Cu$_{43}$Ni$_{7}$Zr$_5$ and Ti$_{45}$Cu$_{41}$Ni$_{9}$Zr$_5$ (Figure 7.22) but the transformation is not completed for the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (alloy 6) (the martensite-cubic start transformation temperature ($A_s$) occurs below 223 K, Figure 7.22).

$A_s$ increases by increasing the amount of Cu in the alloys, from Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ to Ti$_{45}$Cu$_{41}$Ni$_{9}$Zr$_5$ to Ti$_{45}$Cu$_{43}$Ni$_{7}$Zr$_5$ (Figure 7.22). A similar trend was observed for Ti-Cu-Ni alloys (Figure 5.6). The addition of CuZr also seems to decrease the transformation temperatures as can be seen comparing alloys 8 and 9 with alloys 4, 5 and 6 (Table 7.6) since no transformation was observed for the former, which has higher CuZr amount (Table 7.6).
This compositional dependence of the transformation temperatures is related to the electronic structure of the B2 phase as will be discussed in more detail in chapter 9.

**Figure 7.22** – DSC results of the 1.5 mm thick plates of \( \text{Ti}_{45}\text{Cu}_{43}\text{Ni}_7\text{Zr}_5 \) (alloy 4), \( \text{Ti}_{45}\text{Cu}_{41}\text{Ni}_9\text{Zr}_5 \) (alloy 5) and \( \text{Ti}_{45}\text{Cu}_{39}\text{Ni}_{11}\text{Zr}_5 \) (alloy 6) obtained during heating at 10 K/min. The endothermic martensitic transformation peaks are displayed. The arrows indicate the onset start (\( A_s \)) and final (\( A_f \)) temperatures of the transformation from martensite to cubic structure. The martensitic transformation of the \( \text{Ti}_{45}\text{Cu}_{39}\text{Ni}_{11}\text{Zr}_5 \) alloy is not completed because the minimum temperature available was 223 K. The other two alloys (\( \text{Ti}_{42.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{7.5} \) (alloy 8) and \( \text{Ti}_{42.5}\text{Cu}_{41}\text{Ni}_{9}\text{Zr}_{7.5} \) (alloy 9)) did not show any martensitic transformation.
Table 7.6 – Martensite-to-cubic start ($A_s$) and finish ($A_f$) transformation temperatures for the 1.5 mm thick plates of the different compositions measured by DSC at heating rate of 10 K/min.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$A_s$ (K)</th>
<th>$A_f$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{45}$Cu$</em>{43}$Ni$_7$Zr$_5$ (A4)</td>
<td>239±2</td>
<td>262±2</td>
</tr>
<tr>
<td>Ti$<em>{45}$Cu$</em>{41}$Ni$_9$Zr$_5$ (A5)</td>
<td>237±2</td>
<td>270±2</td>
</tr>
<tr>
<td>Ti$<em>{45}$Cu$</em>{39}$Ni$_{11}$Zr$_5$ (A6)</td>
<td>&lt;223</td>
<td>252±2</td>
</tr>
<tr>
<td>Ti$<em>{42.5}$Cu$</em>{42.5}$Ni$<em>{7.5}$Zr$</em>{7.5}$ (A8)</td>
<td>&lt;223</td>
<td>&lt;223</td>
</tr>
<tr>
<td>Ti$<em>{42.5}$Cu$</em>{41}$Ni$<em>9$Zr$</em>{7.5}$ (A9)</td>
<td>&lt;223</td>
<td>&lt;223</td>
</tr>
</tbody>
</table>

The tensile tests results are shown in Figure 7.23 and are additionally summarized in Table 7.7. Alloys 4, 5 and 6 exhibit a low yield strength for both 1 and 1.5 mm thick plates. In contrast, alloys 8 and 9 have a much higher fracture strength but with lower fracture strain. The mechanical behaviour of these samples mainly depends on the different amount of the amorphous phase. Its volume fractions were estimated by DSC (equation (5.1) and the results are also given in Table 7.7. The 1 and 1.5 mm thick plates of alloys 4, 5 and 6 show an amorphous volume fraction lower than 67 vol.% (Table 7.7), which is below the limit (around 72 vol.%, Figure 7.18(a)) needed in order for the composite to inherit the high strength of the amorphous phase as observed in compression (section 7.3.1). In contrast, alloys 8 and 9 show a larger amount of amorphous phase (more than 80 vol.%, Table 7.7), nevertheless the presence of the brittle Cu$_2$TiZr compromises the ductility of these alloys as was discussed before.
A lower yield strength and fracture strain was obtained in tension (Figure 7.23 and Table 7.7) when compared with the results obtained in compression (Figure 7.11 and Table 7.4). The lower yield strength of alloys 4, 5 and 6 (Table 7.7) seems be connected with the lower amount of amorphous phase (< 67 vol.%) as was discussed above. The fracture strain
obtained in tensile is expected to be lower than in compression because in this case, the shear bands terminate at the contact between the sample and the machine crosshead in such way that they are confined and cannot generate a critical shear offset. Additionally, the friction between the sample and the loading plate generates a greater lateral confining stress in compression, which favours formation of multiple shear bands [97].

Apart from these differences, it was observed that in some points of the samples the precipitates agglomerate as shown in Figure 7.21(a). Several simulation results (see section 2.3) appoint that a larger fracture strain is obtained when the precipitates are homogeneously distributed in the glassy matrix and have small size. No pore was found to be responsible for premature failure according to the fractographic analyses.

Almost all tensile samples fracture under an angle of 90 ° to the load direction as usually seen for brittle materials [212]. Their fracture surfaces exhibit features typical of ductile and brittle materials, such as dimples and cleavage surface/steps (Figure 7.24(a) and 7.24(b), respectively). Figure 7.24(a) shows dimples seen on the fracture surface of the 1 mm thick plate of Ti₄₅Cu₄₁Ni₉Zr₅ (A5) and Figure 7.24(b) shows cleavage steps in the fracture surface of the 1 mm thick plate of Ti₄₂.₅Cu₄₁Ni₉Zr₇.₅ (A9). Cracks were also seen on the fracture surface of this sample (Figure 7.24(b)), probably formed because of the presence of the brittle Cu₂TiZr phase as was discussed in section 7.3.

A vein pattern was observed on the fracture surface of the 1 mm thick plate of Ti₄₂.₅Cu₄₂.₅Ni₇.₅Zr₇.₅ (A8, Figure 7.24(c)) as usually seen on the fracture surface of metallic glasses [10]. This pattern results from the local melting caused by shear band propagation (see section 2.2). Figure 7.24(d) shows the longitudinal section of the 1 mm plate of Ti₄₅Cu₃₉Ni₉Zr₅ (A6). The image was taken near the fracture surface of the sample. It shows that cracks are formed ranging from one B2 precipitate to another (Figure 7.24(d)) probably caused by the large stress concentrations generated at the interface (see section 5.3).

Sarac and Schroers [130] showed that the ratio between particle size (d) and particle spacing (s) influences significantly the mechanical properties of BMG composites (see section 2.3). As shown in Figure 7.24(d), some particles are very large (up to 250 µm), which results in large d/s ratio. A large ratio results in a lower fracture strain and yield strength
It is believed that the presence of large particles in some regions of the tensile test samples may also explain the lower fracture strain and yield strength observed (Table 7.7) when compared with the results obtained in compression (Table 7.4).

Figure 7.24 – (a) Fracture surface of the plate 1 mm thick of the alloy Ti$_{45}$Cu$_{41}$Ni$_9$Zr$_5$ (A5). Dimples typical of ductile fracture can be seen. (b) Fracture surface of the 1 mm thick plate of Ti$_{42.5}$Cu$_{41}$Ni$_9$Zr$_{7.5}$ (A9), which shows crack and cleavage steps typical of brittle fracture. (c) Fracture surface of the 1 mm thick plate of Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ (A8). Vein patterns occur as a result of local melting caused by shear band propagation. (d) Longitudinal section of the 1 mm thick plate of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ (A6). The image was obtained near the fracture surface of the sample. B2 precipitates are seen in the glassy matrix. Cracks are formed in between the precipitates.
To summarize, the GFA in the pseudo-ternary TiCu-TiNi-CuZr system increases with the addition of CuZr to Ti-Cu-Ni alloys and composites with diameters ranging from 2 to 3 mm can be formed, which consist mainly of the cubic B2 (Ti,Zr)(Cu,Ni) and the glassy phase (Figure 7.6). An excellent combination of high yield strength and large fracture strain in compression occurs for alloys with a lower CuZr amount (Figure 7.11(a)).

The correlations between the volume fraction of the B2 phase and the yield strength as well as the fracture strain were studied systematically and a maximum in these properties seems to occur in compression for volume fractions of the B2 phase around 20 - 40 vol.% (Figure 7.18), which is in agreement with previous studies [14].

A reduced ductility in compression was found for the CuZr-richer compositions of the present study (Figure 7.7(a)), which is related with the precipitation of the brittle Cu$_2$TiZr phase in the glassy matrix.

Although a good mechanical behaviour was observed for some Ti-Cu-Ni-Zr alloys in compression (Figure 7.7), a low yield strength and fracture strain was observed in tensile (Figure 7.23). The main reason seems to be connected to the heterogeneous microstructure, with agglomeration of B2-(Ti,Zr)(Cu,Ni) precipitates in some parts of the sample forming large crystalline regions (Figure 7.21(a)). A high stress concentration may occur at the interface of these precipitates (section 5.3), which results in the formation of cracks in the glassy matrix (Figure 7.24(d)) and earlier fracture.
8 Effect of Si on the glass-forming ability and mechanical properties of TiCu-based alloys

In the past years there was a significant advance in the understanding of the glass-forming ability (GFA) of metallic systems. Several empirical and theoretical tools have been developed such as the Inoue’s empirical rules [49], topological [8, 70, 82], electronic [67, 83], thermodynamic [17, 68] and structural GFA criteria [30, 38, 68, 75], computer simulation [36, 68, 213], several GFA thermal parameters like \( \gamma \) [48] and reduced glass transition (\( T_{rg} \)) [53]. Nevertheless, none of them can really account for the improvement of GFA induced by minor additions of some elements [214, 215].

In the case of TiCu-based metallic glasses minor additions of Si have been reported to have a beneficial effect on their GFA [18, 216]. Figueroa et al. [216] have shown that 0.5 at.% Si increases the critical casting diameter of a Cu-Ti-Hf alloy by 75% (from 4 mm to 7 mm). Choi-Yim et al. [18] demonstrated that small additions of Si between 0.5 and 1 at.% increase the critical casting thickness from 4 to 7 mm of a Cu-Ti-Ni-Zr alloy. These researchers have suggested that it is caused by a scavenging effect of Si, which could remove oxygen from the liquid metal by the formation of complex oxides [18, 216] but no clear explanation or systematic study has been conducted in order to elucidate the reasons for the role of Si so far.

Therefore, the effect of minor additions of Si on the GFA of two alloys, Ti\(_{46}\)Cu\(_{54}\) and Ti\(_{42.5}\)Cu\(_{42.5}\)Ni\(_{7.5}\)Zr\(_{7.5}\), was determined within this work and is discussed in the first part of this chapter (section 8.1). These alloys exhibit the best GFA among the binary Ti-Cu and quaternary Ti-Cu-Ni-Zr alloys as described above (sections 4 and 7.1, respectively). Si not only affects the GFA but also the mechanical properties as will be discussed in the second part of this chapter (section 8.2). Several ductile Ti-Cu-Ni-Zr-(Si) composites were obtained combining a high yield strength with large plasticity in compression and bending tests. The phase transformations, which occur during deformation of these Ti-Cu-Ni-Zr-(Si) alloys will be discussed in the last part of this chapter (section 8.3).
8.1 Effect of minor additions of Si on the GFA of TiCu-based alloys

Ribbons were produced by melt spinning to investigate the effect of Si additions on the thermal stability of \((\text{Ti}_{0.46}\text{Cu}_{0.54})_{100-x}\text{Si}_x\) and \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{100-x}\text{Si}_x\) with \(x = 0, 0.5, 1\) and 2. The GFA was then investigated by casting rods with 1 mm diameter and 40 mm length of the former alloys and with 3 mm diameter and 70 mm length of the latter. These results will be shown in the next sections. A negligible weight loss (< 0.01 %) was measured after ingot preparation and the nominal amount of Si in the rods was confirmed by EDX analyses.

8.1.1 Si additions to Ti_{46}Cu_{54}

The XRD results for rapidly solidified ribbons of \((\text{Ti}_{0.46}\text{Cu}_{0.54})_{100-x}\text{Si}_x\) with \(x = 0, 0.5, 1\) and 2 is shown in Figure 8.1. Three broad peaks at \(2\theta \approx 19, 32\) and 38 ° are observed and they prove that the structure of the ribbons is fully amorphous. The DSC results are shown in Figure 8.2 and summarized in Table 8.1. One can notice that the addition of Si increases the glass transition and crystallization temperatures and also decreases the liquidus temperature as shown in Figure 8.2(a) and 8.2(b), respectively. The \(\gamma_m\) and \(\Delta T_x\) values also increase with the Si addition (Table 8.1).
Figure 8.1 – XRD results for the melt-spun (Ti<sub>0.46</sub>Cu<sub>0.54</sub>)<sub>100-x</sub>Si<sub>x</sub> with x = 0, 0.5, 1 and 2 ribbons.
Figure 8.2 – (a) Low- and (b) high-temperature DSC results recorded at a heating rate of 20 K.min⁻¹ for the (Ti₀.₄₆Cu₀.₅₄)₁₀₀₋ₓSiₓ x = 0, 0.5, 1 and 2 ribbons. The arrows in (a) indicate the glass transition and crystallization temperature, respectively, and in (b) they indicate the liquidus temperature.
Table 8.1 - DSC data obtained at a heating rate of 20 K/min. $T_g$, $T_x$ and $T_l$ are defined as the onset glass transition, crystallization and liquidus temperatures, respectively. $\Delta T_x = T_x - T_g$. $\gamma_m = (2T_x - T_g) / T_l$, $T_{rg} = T_g / T_l$. $\Delta H_c$ is the crystallization enthalpy and $f_a$ is the fraction of the amorphous phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$T_l$(K)</th>
<th>$\gamma_m$</th>
<th>$T_{rg}$</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$f_a$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{46}$Cu$</em>{54}$</td>
<td>ribbon</td>
<td>-</td>
<td>685±2</td>
<td>-</td>
<td>1255±2</td>
<td>-</td>
<td>-</td>
<td>-120±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1255±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ti$<em>{0.46}$Cu$</em>{0.54}$)$<em>{99.5}$Si$</em>{0.5}$</td>
<td>ribbon</td>
<td>665±2</td>
<td>695±2</td>
<td>30±3</td>
<td>1249±2</td>
<td>0.580±0.001</td>
<td>0.532±0.003</td>
<td>-124±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1249±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ti$<em>{0.46}$Cu$</em>{0.54}$)$<em>{99}$Si$</em>{1}$</td>
<td>ribbon</td>
<td>677±2</td>
<td>707±2</td>
<td>30±3</td>
<td>1245±2</td>
<td>0.590±0.001</td>
<td>0.544±0.003</td>
<td>-131±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1245±2</td>
<td>-</td>
<td>-</td>
<td>-16±5</td>
<td>13±5</td>
</tr>
<tr>
<td>(Ti$<em>{0.46}$Cu$</em>{0.54}$)$<em>{98}$Si$</em>{2}$</td>
<td>ribbon</td>
<td>686±2</td>
<td>719±2</td>
<td>33±3</td>
<td>1241±2</td>
<td>0.600±0.001</td>
<td>0.553±0.003</td>
<td>-127±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>rod 1mm</td>
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<td>-</td>
<td>-</td>
<td>1241±2</td>
<td>-</td>
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</tr>
</tbody>
</table>

In order to confirm the expected larger GFA of (Ti$_{0.46}$Cu$_{0.54}$)$_{98}$Si$_{2}$, rods with 1 mm in diameter were cast and their diffraction patterns are shown in Figure 8.3. Sharp Bragg peaks of the tetragonal TiCu and Cu$_4$Ti$_3$ phases are observed for all samples but it is observed that the intensity of the Cu$_4$Ti$_3$ peaks increases with further Si additions, which suggests that the addition of Si induces the precipitation of this phase during rapid solidification. Both CuTi and Cu$_4$Ti$_3$ have tetragonal structure but with different space groups (P4/nmm and I4/mmm, respectively) and are the phases expected to be formed according to the TiCu equilibrium phase diagram.
Figure 8.3 – XRD results for the 1 mm diameter rods of \((\text{Ti}_{0.46}\text{Cu}_{0.54})_{100-x}\text{Si}_x\) with \(x = 0, 0.5, 1\) and 2.

The DSC results confirm that these samples are fully crystalline with exception of the \((\text{Ti}_{0.46}\text{Cu}_{0.54})_{99}\text{Si}_1\) which formed around 13 vol.% of amorphous phase in its bottom part (Table 8.1) as could be inferred from the enthalpy of crystallization (equation 5.1, section 5.2), which is proportional to the crystallization peak area (Figure 8.4 and Table 8.1).
Although the addition of Si to the Ti$_{46}$Cu$_{54}$ increases the GFA as suggested by the GFA parameters $\Delta T_x$, $T_{rg}$ and $\gamma_m$ (Table 8.1), its GFA is still quite limited and therefore more elements should be added to the system as will be exemplified in the next section. It was observed that a maximum in GFA occurs for the composition (Ti$_{0.46}$Cu$_{0.54}$)$_{99}$Si$_{1}$, which forms amorphous phase (around 10 vol.%, Table 8.1) in the 1 mm diameter rods. The reasons for this optimum in GFA will be discussed in section 8.1.3.

8.1.2 Si additions to Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$

It was shown in chapter 7 that 3 mm diameter rods of the Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ alloy forms between 67 and 84 vol.% of amorphous phase (Table 7.3). In order to further study the effect of Si additions in the thermal stability and GFA of this alloy, ribbons and rods with a diameter of 3 mm and 70 mm length of (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ with $x = 0, 0.5, 1$ and 2 were investigated.

All melt-spun ribbons exhibit a fully amorphous structure as could be inferred by XRD (results not shown here), with the presence of three broad peaks around $2\theta = 18.5$, 32 and 37 °. A glass transition occurs during continuous heating of the ribbons (Figure 8.5(a)) followed by four or five exothermic crystallization peaks. Glassy Ti$_{50}$Cu$_{43}$Ni$_{7}$ and Ti$_{50}$Cu$_{41}$Ni$_{9}$ ribbons exhibit only two or three exothermic crystallization peaks (Figure 5.5). The four or
five crystallization steps observed for \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{100-x}\text{Si}_x\) with \(x = 0, 0.5, 1\) and 2 already indicate that the crystallization process becomes more complex, which may be reflected in the better GFA when compared with the ternary Ti-Cu-Ni alloys. Both glass transition \((T_g)\) and crystallization temperature \((T_x)\) increase with minor additions of Si (Table 8.2), similarly as observed for Cu-Ti, Cu-Hf-Ti [216], and Cu-Ti-Zr-Ni [18] alloys.

The high-temperature DSC traces are shown in Figure 8.5(b). The liquidus temperature \((T_l)\) decreases from 1171±2 to 1163±2 K for additions of 0.5 at.% Si and then increases up to 1177±2 K when 2 at.% Si are added. With these three characteristic temperatures \((T_g, T_x \text{ and } T_l)\), one can calculate thermal parameters in order to quantify the GFA of these compositions.

![Figure 8.5 – (a) Low- and (b) high-temperature DSC results for the ribbons of the Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$$_{100-x}$Si$_x$ with $x = 0.5$, 1 and 2. The amount of Si in each alloy is given in the curves. The arrows in (a) indicate the glass transition and crystallization temperatures, respectively, and in (b) the liquidus temperature.](image-url)
Table 8.2 – \((Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{100-x}Si_x\) alloys and their respective DSC data obtained at heating rate of 30 K/min. \(T_g\), \(T_x\) and \(T_l\) are defined as the onset glass transition, crystallization and liquidus temperatures, respectively, and \(R_c\) is the calculated critical cooling rate for amorphization based on the Colmenero and Barandiaran method.

<table>
<thead>
<tr>
<th>at.% Si</th>
<th>(T_g) (K)</th>
<th>(T_x) (K)</th>
<th>(T_l) (K)</th>
<th>(\Delta T_x) (K)</th>
<th>(T_{rg})</th>
<th>(\gamma_m)</th>
<th>(R_c) (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>656±2</td>
<td>698±2</td>
<td>1171±2</td>
<td>42±3</td>
<td>0.560±0.003</td>
<td>0.632±0.004</td>
<td>2±1</td>
</tr>
<tr>
<td>0.5</td>
<td>659±2</td>
<td>707±2</td>
<td>1163±2</td>
<td>48±3</td>
<td>0.567±0.003</td>
<td>0.649±0.004</td>
<td>6±1</td>
</tr>
<tr>
<td>1</td>
<td>669±2</td>
<td>714±2</td>
<td>1165±2</td>
<td>45±3</td>
<td>0.574±0.003</td>
<td>0.652±0.004</td>
<td>22±1</td>
</tr>
<tr>
<td>2</td>
<td>676±2</td>
<td>730±2</td>
<td>1177±2</td>
<td>54±3</td>
<td>0.574±0.003</td>
<td>0.666±0.004</td>
<td>33±1</td>
</tr>
</tbody>
</table>

Table 8.2 summarizes the characteristic temperatures together with the values of the \(\Delta T_x\) \(= T_g - T_x\) \([49]\), \(T_{rg} \(= T_g / T_l\) \([53]\) and \(\gamma_m \(= (2 T_x - T_g) / T_l\) \([52]\) parameters. All these thermal parameters show an increasing GFA within the experimental errors (Table 8.2). The increase in \(T_g\) and \(T_x\) is much more pronounced than in \(T_l\), which explains the trend of the \(T_{rg}\) and \(\gamma_m\) values (Table 8.2). A similar increase in these GFA parameters by minor additions of Si was observed for Cu-Ti and Cu-Hf-Ti alloys \([216]\). Following the empirical rules proposed by Inoue \([49]\), an increase in the GFA is expected since Si has a negative heat of mixing with Cu, Ti, Ni and Zr (-2, -49, -23 and -67 kJ/mol \([81]\), respectively) and also a large difference in atomic size with Ti and Zr (21% and 28% of difference \([217]\), respectively), which leads to an increase in the atomic packing density \([38]\).

Another parameter considered the most reliable in order to quantify the GFA of alloys is the critical cooling rate for amorphization \((R_c) \([52, 218]\). \(R_c\) is defined as the minimum cooling rate required to avoid crystallization, with lower values corresponding to higher GFA. The experimental determination of \(R_c\) is difficult \([54]\) and several methods have been used for its estimation \([52]\) like the time-transformation-temperature (TTT) curve method \([219]\), linear approximation of the cooling rate by measuring the temperature versus time during solidification \([218]\) and the Colmenero and Barandiaran method \([54, 220]\). The latter method was tested using glass-forming oxides \([221, 222]\) with a good agreement between the calculated and experimentally obtained \(R_c\) values. More than that, it has been constantly used to estimate \(R_c\) values of metallic glasses \([52]\). \(R_c\) is calculated by measuring the solidification peak temperature \((T_s)\) at different cooling rates \(R\) \([220]\):
\[
\ln R = \ln R_c - \frac{B}{(T_l - T_s)^2}, \quad (8.1)
\]

where \(B\) is a constant and \(T_l\) is the onset liquidus temperature. \(R_c\) is obtained from the \(\ln R\) versus \(1/(T_l - T_s)^2\) plot, as shown in Figure 8.6. The calculated \(R_c\) values using this method (Table 8.2) are in the range usually observed for other bulk metallic glasses [213] and they show exactly the opposite trend given by the thermal parameters, suggesting a decrease in GFA since the addition of 0.5, 1 and 2 at.% Si increases around 3, 11 and 16 times \(R_c\), respectively.

![Figure 8.6 – \(\ln R\) versus \(1/(T_l - T_s)^2\) plot, where \(R\) is the cooling rate and \(T_l\) and \(T_s\) are the onset liquidus and the peak solidification temperature of the investigated \((Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{100} - xSi_x\) alloys.](image)

The results obtained for the ribbons show that the crystallization and glass-transition temperatures increase with the Si addition to the \((Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{100} - xSi_x\) alloys (Table 8.2), in a similar fashion as observed for the \((Ti_{0.46}Cu_{0.54})_{100} - xSi_x\) alloys with \(x = 0, 0.5, 1\) and 2 (Table 8.1). The liquidus temperature decreases with Si addition to both binary and quaternary alloys. The \(\Delta T\), \(T_g\) and \(\gamma_m\) parameters suggest that the GFA of these alloys increases with the Si addition.

In order to confirm the enhancement of GFA, 3 mm diameter rods of \((Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{100} - xSi_x\) alloys with \(x = 0, 0.5, 1\) and 2 were investigated. The chemical analyses of the rods confirmed the nominal amount of Si and the amount of
oxygen measured for the four different compositions was similar (around 400 ppm). The XRD results for the rapidly solidified 3 mm diameter rods are shown in Figure 8.7. Sharp Bragg peaks of the cubic B2-(Ti,Zr)(Cu,Ni) phase can be seen in all samples, superimposed on a broad peak at $2\theta = 18.5^\circ$ typical of the amorphous phase.

The intensity of the B2-peaks is smaller in the sample with 0.5 at.% Si when compared with the other compositions, which suggests a larger amount of amorphous phase in this sample. Similar patterns were obtained for the bottom and top parts of the rods.

![Figure 8.7 – XRD results for the 3 mm diameter rods of (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ with $x = 0, 0.5, 1$ and $2$.](image)

Their cross sections are shown in the backscatter-electron images of Figure 8.8. The darker regions correspond to the crystalline phases and the grey matrix to the amorphous phase as could be inferred by TEM and EBSD analyses. More details will be given in the next paragraphs.
Figure 8.8 – Cross sections of the 3 mm diameter rods of \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{100-x}\text{Si}_x\) with \(x = 0, 0.5, 1\) and 2 as observed in the SEM. The darker regions correspond to the crystalline phases whereas the light grey matrix is the amorphous phase. The amount of Si in each alloy is shown in the upper region of the figures.

From a first glance, it appears that the alloy with 0.5 at.% of Si has a larger amount of amorphous phase than the alloys with 0, 1 and 2 at.% of Si, which corroborates the XRD results (Figure 8.7). It can be also seen that these alloys have a heterogeneous distribution of phases, with a larger amount of amorphous phase in their outer surface as a result of the higher cooling rate during solidification in this region. In order to quantify the amorphous phase volume fraction, its amount in the top and bottom part of the rods was estimated by relating the enthalpies of crystallization as described in section 5.2 and the results are shown in Table 8.3. A small difference is observed from top to bottom, with an average volume fraction of amorphous phase around 69±13, 99±16, 78±15 and 38±13 vol.% for the
alloys with 0, 0.5, 1 and 2 at.% of Si, respectively, which is in good agreement with the SEM and XRD results.

**Table 8.3 – Crystallization enthalpy (ΔH\textsubscript{c}) and the estimated volume fraction of amorphous phase in the (Ti\textsubscript{0.425}Cu\textsubscript{0.425}Ni\textsubscript{0.075}Zr\textsubscript{0.075})\textsubscript{100-x}Si\textsubscript{x} alloys with x = 0, 0.5, 1 and 2, considering the different sample geometries (ribbons and 3 mm diameter rods) and regions from which the specimens were taken from (top and bottom part).**

<table>
<thead>
<tr>
<th>at.%Si</th>
<th>Geometry/Region</th>
<th>ΔH\textsubscript{c} (J/g)</th>
<th>Amorphous Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>Ribbon</td>
<td>-96±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-63±10</td>
<td>65±12</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-70±10</td>
<td>73±13</td>
</tr>
<tr>
<td>0.5 %</td>
<td>Ribbon</td>
<td>-87±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-86±10</td>
<td>99±16</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-86±10</td>
<td>99±16</td>
</tr>
<tr>
<td>1 %</td>
<td>Ribbon</td>
<td>-90±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-64±10</td>
<td>71±14</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-77±10</td>
<td>85±15</td>
</tr>
<tr>
<td>2 %</td>
<td>Ribbon</td>
<td>-82±10</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Top</td>
<td>-22±10</td>
<td>27±13</td>
</tr>
<tr>
<td></td>
<td>3 mm dia. rod/Bottom</td>
<td>-33±10</td>
<td>40±13</td>
</tr>
</tbody>
</table>

Although only the B2 phase and the amorphous phase could be detected by XRD, other phases precipitate with minor volume fractions as microscopy at higher magnification reveals (Figure 8.9).
Figure 8.9 – (a) Cross section of the 3 mm diameter rod of the \((Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{99.5}Si_{0.5}\) alloy after etching. Four phases can be clearly seen: the cubic B2 phase, the hexagonal \(Cu_2TiZr\), the cubic \((Ti,Zr)_2(Cu,Ni)\) (indicated as \(Ti_2Ni\)) and the amorphous matrix (denoted by A) as confirmed by TEM and EBSD. The EBSD pattern of the B2 phase is shown in (b). (c) Centre region of the rod with 2 at.% Si. A refined dendritic structure is seen with arm spacing around 1 µm. A black \(Ti_5Si_3\) precipitate can also be seen in the image.

The microstructure of the 3 mm diameter rod with 0.5 at.% Si after etching is shown in the SEM image of Figure 8.9(a). Three different phases are observed embedded in the amorphous matrix (denoted with A in Figure 8.9(a)). Spherical B2-(Ti,Zr)(Cu,Ni) precipitates form (B2 in Figure 8.9(a)) and their cubic CsCl-type structure was confirmed by EBSD analyses (Figure 8.9(b)). Another spherical phase, \(Cu_2TiZr\), was also observed together with small dendrites of the \((Ti,Zr)_2(Cu,Ni)\) phase (\(Ti_2Ni\) in Figure 8.9(a)), usually in the centre of the \(Cu_2TiZr\) crystals. The chemical composition of the \((Ti,Zr)_2(Cu,Ni)\) was measured as \(Ti_{58}Zr_{3}Ni_{12}Cu_{24}Si_1\) (at.%) for rod with 1 at.% Si and its structure was confirmed by EBSD as cubic having the space group Fd3m (similar as \(Ti_2Ni\)). The presence of the \((Ti,Zr)_2(Cu,Ni)\) dendrites in the centre of the \(Cu_2TiZr\) phase suggests that it may nucleate heterogeneously around the dendritic phase. Although EDX cannot precisely measure the amount of oxygen
in the phases, it shows that the (Ti,Zr)$_2$(Cu,Ni) phase has three times more oxygen than the other phases which may help to stabilize the Cu$_2$TiZr (section 7.2).

These four different phases (glass, B2-(Ti,Zr)(Cu,Ni), Cu$_2$TiZr and (Ti,Zr)$_2$(Cu,Ni)) were observed in the alloys with up to 1 at.% Si, although their distribution is different as can be seen in Figure 8.8. In addition, the amount of Cu$_2$TiZr seems to decrease with further additions of Si. The sample with 2 at.% of Si has a large amount of amorphous phase in its outer surface region (Figure 8.8) whereas the centre is composed of a refined dendritic structure (Figure 8.9(c)) formed by B2 grains with typical sizes around 1 µm and an unidentified phase at its grain boundaries. For this sample instead of the cubic (Ti,Zr)$_2$(Cu,Ni) phase, black Ti$_5$Si$_3$ inclusions (hexagonal structure with space group P63/mcm) are seen (Figure 8.9(c)) with micrometre size and a chemical composition of Ti$_{54}$Zr$_9$Ni$_2$Cu$_8$Si$_{27}$ (at.%). As predicted by the Ti-Cu-Si phase diagram [223], additions of Si induce the formation of Ti$_5$Si$_3$ as a result of the large heat of mixing between Ti and Si (-49 kJ/mol).

In order to gain more insights, TEM investigations were carried out. High-resolution TEM images of the amorphous phase in the rod with 0.5 at.% Si are shown in Figure 8.10(a) and 8.10(b). Although the selected area electron diffraction pattern (SAED) of the amorphous matrix exhibits only diffuse rings typical of an amorphous structure (inset of Figure 8.10(a)), the TEM images show the presence of spherical nanocrystals (Figure 8.10(a)) with diameters around 5 to 10 nm. They were not detected by electron diffraction because of their low volume fraction and small size. Figure 8.10(b) exhibits more details of these nanocrystals. Lattice fringes can be seen with an interplanar spacing around 2.2 Å, similar to the (110) interplanar distance of the B2-TiNi phase (Reference code 00-050-1148 of the International Centre for Diffraction Data (ICDD) database).
Figure 8.10 – (a) Bright field TEM image of the amorphous matrix of the rod with 0.5 at.% Si. Nanocrystals with sizes around 5 to 10 nm can be seen. The selected area electron diffraction pattern (SAED) of this region is shown in the inset. Only diffuse diffraction rings typical of a full amorphous structure are seen. More details of a nanocrystal are given in (b). Lattice fringes are seen and the interplanar distance was determined to be around 2.2 Å, which correspond to the (110) interplanar distance of the B2-TiNi phase.

The interface between the glass and a Cu$_2$TiZr crystal is shown in Figure 8.11(a) and details of the (Ti,Zr)$_2$(Cu,Ni) phase can be seen in Figure 8.11(b) taken from different regions of the rod with 0.5 at.% Si. The SAED pattern obtained from the Cu$_2$TiZr phase along a [100] zone axis is shown in Figure 8.11(c), which proves its hexagonal structure with P63/mmc space group. The composition of the glass, B2-(Ti,Zr)(Cu,Ni) and Cu$_2$TiZr measured by SEM are very similar and close to the nominal composition.

Figure 8.11(a) shows that the Cu$_2$TiZr phase is mottled, with striations and regions of disorder, which may result from the large deviation from the nominal Cu$_2$TiZr composition. The formation of the B2 phase and Cu$_2$TiZr is expected from the TiCu-TiNi and TiCu-CuZr equilibrium phase diagram [6, 148], respectively. The dendritic morphology of the cubic (Ti,Zr)$_2$(Cu,Ni) phase can be clearly seen in Figure 8.11(b) and its cubic structure with space group Fd3m was confirmed by its SAED pattern shown in Figure 8.11(d).
Figure 8.11 – (a) Dark Field TEM image of the interface between amorphous and Cu$_2$TiZr phase and (b) bright field TEM image of the (Ti,Zr)$_2$(Cu,Ni) phase, taken from different regions of the rod with 0.5 at.% Si. The SAED pattern of the Cu$_2$TiZr in a [100] zone axis and of the (Ti,Zr)$_2$(Cu,Ni) phase in a [311] zone axis are given in (c) and (d), respectively. A slightly deviation is observed between the calculated Cu$_2$TiNi pattern (yellow dots) when compared with the experimental pattern (white dots). It may be caused by the large deviation from the nominal chemical composition of this phase.

The rods of the (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ alloys with x = 0, 0.5, 1 and 2 formed the B2-(Ti,Zr)(Cu,Ni) phase, which may undergo martensitic transformation during cooling (subsection 5.2). In order to check this, low temperature DSC measurements were carried
out in the temperature range 223 to 473 K. No martensitic transformation was observed in this range, which suggests that the martensitic transformation may occur below 223 K. As will be discussed in chapter 9, the martensitic transformation is dependent on the composition, which affects the electronic structure of the B2 phase. The larger amount of Zr and Si in these alloys when compared with the ternary Ti-Cu-Ni alloys (subsection 5.2) may shift the transformation to temperatures lower than 223 K.

The experimental results show that the amount of amorphous phase in the rods increases up to 0.5 at.% Si and then decreases with further Si additions (Table 8.3). Both the thermal parameters ($\Delta T_x$, $T_{rg}$ and $\gamma_m$) and the critical cooling rate calculated by the Colmenero and Barandiaran method [54, 220] fail to predicted this maximum in GFA (Table 8.2), although the latter correctly indicates the decreasing in GFA with further addition of Si. These results suggest that these parameters are not sensitive enough to capture small variations in GFA caused by the minor additions.

### 8.1.3 Optimum GFA with the Si additions to TiCu-based alloys

As shown before, an optimum GFA occurs after the addition of 0.5 and 1 at.% Si to Ti$_{42.5}$Cu$_{42.5}$Ni$_{7.5}$Zr$_{7.5}$ and Ti$_{46}$Cu$_{54}$, respectively. None of the GFA parameters ($\Delta T_x$, $T_{rg}$, $\gamma_m$ or $R_c$) could predict this maximum in GFA. As discussed before, similar improvements in the GFA after minor additions of Si have been also found in other systems [18, 216]. It has been suggested that the enhanced GFA results from a scavenging effect of Si because of the formation of very stable oxides [216], although their presence has not been observed so far [216]. This explanation is debatable because the amount of oxygen measured in such alloys is extremely small (on the order of 200-400 ppm [216]), which should most probably be dissolved in other phases instead of forming oxides [224]. If such stable oxides really form, they could trigger the crystallization of other phases by forming nucleation sites.

Hence, ingots and rods of the ($\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{100-x}\text{Si}_x$ alloys ($x = 0, 0.5, 1$ and $2$) were carefully checked by SEM and XRD but no oxides were observed, even at the surface of the ingots. The oxygen amount measured for the four different rods was similar, around 400 ppm, which is quite low and should be completely dissolved in other phases as was discussed in the last chapter.
As discussed before, Si has a large negative heating of mixing with the other elements and a large difference in size when compared with Ti and Zr. As first discussed by Inoue [49], this results in an enhanced short-range order and an efficient packing in the liquid which should lead to a higher stability of the melt, i.e. promote the GFA. For both Ti_{42.5}Cu_{42.5}Ni_{7.5}Zr_{7.5} and Ti_{46}Cu_{54}, the addition of Si decreases the liquidus temperature (Table 8.1 and 8.2), which demonstrates the higher thermodynamic stability of the liquid phase. The stability of the supercooled liquid also increases as shown by the increasing in ΔT_s with further Si additions (Table 8.1 and 8.2).

Nevertheless, as pointed out by Lu and Liu [225], the GFA is not only dependent on the stability of the liquid or supercooled liquid phase but also on the kinetics of the phase formation during solidification. The addition of Si induces the formation of highly stable Ti_5Si_3 precipitates, with a liquidus temperature around 2400 K [226] and they should form first during solidification. Indeed, the presence of Ti_5Si_3 was observed in the rods of (Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{98}Si_2 and (Ti_{0.46}Cu_{0.54})_{98}Si_2 alloys (Figure 8.9(c)). Figure 8.12 moreover shows the presence of this silicide also in the ingot of the (Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{98}Si_2. One can see a black Ti_5Si_3 particle completely surrounded by the B2 phase, which proves that this silicide can heterogeneously nucleate the cubic B2 phase. The nucleation of the B2 phase by Ti_5Si_3 might be favoured as the differences in the interplanar distances for the four main planes of the B2-TiNi and Ti_5Si_3 only differ by less than 5% (PDF-4+ 2011 database of the International Centre for Diffraction Data (ICDD)). Small differences in the interplanar distances and a certain chemical affinity are prerequisites for the effectiveness of nucleants [227].
Considering this, the addition of Si improves the GFA by increasing the stability of the liquid or the supercooled liquid but it is counterbalanced by the increasing amount of Ti<sub>5</sub>Si<sub>3</sub>, which acts as heterogeneous nucleation site for the formation of other crystalline phases (e.g. B2 phase) and thus decreases the GFA. In this way, a maximum in the tendency of the melt to vitrify could occur at a composition with a high thermodynamic stability of the liquid/supercooled liquid and a low amount of Ti<sub>5</sub>Si<sub>3</sub> precipitates. A similar optimum in the GFA occurs in Cu<sub>55</sub>Hf<sub>25</sub>Ti<sub>20</sub> [216] and Cu<sub>47</sub>Ti<sub>34</sub>Zr<sub>11</sub>Ni<sub>8</sub> [18] after minor additions of 0.5 and 1 at.% Si, respectively. All these alloys contain Ti and Hf or Zr, which have a quite large negative heating of mixing with Si and form highly stable silicides [228, 229]. There is also a consensus that the addition of Si increases the stability of the supercooled liquid of these alloys [18, 216] whereas the liquidus temperature almost does not change with Si addition to the Cu<sub>55</sub>Hf<sub>25</sub>Ti<sub>20</sub> [216] and Cu<sub>47</sub>Ti<sub>34</sub>Zr<sub>11</sub>Ni<sub>8</sub> [18]. These literature results seem to be coherent with the explanations given above.

### 8.2 Effect of Si on the mechanical properties of TiCu-based alloys

In the following paragraphs, the mechanical behaviour of Ti-Cu-Ni-Zr-(Si) alloys in compression (subsection 8.2.1), bending and tensile tests (subsection 8.2.2) is shown. The effect of the Si additions on the strength and ductility of these alloys will be discussed.

**Figure 8.12** – SEM image of the ingot of alloy (Ti<sub>0.425</sub>Cu<sub>0.425</sub>Ni<sub>0.075</sub>Zr<sub>0.075</sub>)<sub>98</sub>Si<sub>2</sub>. B2 grains (dark grey contrast phase) heterogeneously nucleate at the interface of the black Ti<sub>5</sub>Si<sub>3</sub>.
8.2.1 Compression tests

Mechanical behaviour of 2 mm diameter rods

Additions of silicon were also carried out in other quaternary Ti-Cu-Ni-Zr alloys and their compositions are given in Table 8.4. Rods with 2 mm in diameter and a length of 70 mm were fabricated by suction casting. The XRD patterns of these samples are shown in Figure 8.13. All rods (indicated by letters from A to E, see Table 8.4) show Bragg peaks of the B2-(Ti,Zr)(Cu,Ni) phase together with a broad peak of the amorphous phase around 2θ = 18.7°.

Table 8.4 – Compositions of the rods with diameters of 2 mm, their mechanical properties obtained during compression tests, the estimated volume fraction of the B2 phase by image analysis and the hardness of the B2 phase and the glass for the according samples. The calculated yield strength of the composites using equation 2.10 (see text for more details) is also shown.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Yield Strength (MPa)</th>
<th>Fract. Strain (%)</th>
<th>E (GPa)</th>
<th>B2 Vol. Fract. (%)</th>
<th>Hardness (HV 0.2) B2 Amor.</th>
<th>Calc. Yield Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ti0.45Cu0.41Ni0.09Zr0.05)99.5Si0.5 (A)</td>
<td>1650 ±50</td>
<td>14.1 ±0.1</td>
<td>86 ±5</td>
<td>21 ±5</td>
<td>331 ±17 559 ±7</td>
<td>1671 ±175</td>
</tr>
<tr>
<td>(Ti0.45Cu0.41Ni0.09Zr0.05)99Si1 (B)</td>
<td>1830 ±50</td>
<td>13.8 ±0.1</td>
<td>102 ±5</td>
<td>28 ±5</td>
<td>349 ±14 555 ±17</td>
<td>1626 ±201</td>
</tr>
<tr>
<td>(Ti0.44Cu0.40Zr0.055Si0.5 (C)</td>
<td>1890 ±50</td>
<td>12.5 ±0.1</td>
<td>101 ±5</td>
<td>6 ±5</td>
<td>342 ±20 531 ±17</td>
<td>1699 ±199</td>
</tr>
<tr>
<td>(Ti0.45Cu0.39Ni0.11Zr0.05)99.5Si0.5 (D)</td>
<td>1700 ±50</td>
<td>19.7 ±0.1</td>
<td>92 ±5</td>
<td>15 ±5</td>
<td>329 ±14 550 ±7</td>
<td>1689 ±170</td>
</tr>
<tr>
<td>(Ti0.45Cu0.39Ni0.11Zr0.05)99Si1 (E)</td>
<td>1750 ±50</td>
<td>20.0 ±0.1</td>
<td>105 ±5</td>
<td>39 ±5</td>
<td>350 ±12 586 ±16</td>
<td>1615 ±200</td>
</tr>
</tbody>
</table>
Figure 8.13 – XRD results for the 2 mm diameter rods of Ti-Cu-Ni-Zr-(Si) alloys (A to E, compositions given in Table 8.4). Only the amorphous and the cubic B2 phase are formed in the samples.

The microstructure of these samples is very similar to the rapidly solidified Ti-Cu-Ni-Zr alloys discussed in the previous chapter (Figure 8.14 and 7.7(a)). Spherical precipitates of the cubic B2 phase form in the glassy matrix with a heterogeneous distribution. These are isolated in the amorphous matrix for higher glassy volume fraction (Figure 8.14) or agglomerated when the volume fraction of crystals increases. The composition of the B2 precipitates at their outer region is similar to the amorphous matrix as measured by EDX.
Considering that a desired microstructure to obtain ductile shape memory bulk metallic was formed with the presence of the ductile shape memory B2 phase and glass, the mechanical properties of these composites were further investigated. Figure 8.15 shows the mechanical behavior during compression for the 2 mm diameter rods of the five compositions investigated and the data are summarized in Table 8.4. For all investigated alloys, a high yield strength above 1650 MPa is observed combined with a large fracture strain exceeding 12.5% (Table 8.4).

**Figure 8.14** – Optical micrograph of a 2 mm diameter rod of (Ti$_{0.45}$Cu$_{0.39}$Ni$_{0.11}$Zr$_{0.05}$)$_{99.5}$Si$_{0.5}$ (D, cross section). Amorphous and B2 phase are formed as indicated in the figure.

**Figure 8.15** – Stress-strain curves for 2 mm diameter rods of the five compositions given in Table 8.4 (indicated from A to E).
Figure 8.16(a) compares the yield strength and the fracture strain obtained upon compressive loading of this new family of TiCu-based alloys with other as-cast Ti-based and CuZr-based high-strength alloys from literature [38-50]. The new TiCu-based alloys exhibit an excellent combination of strength and ductility, extending limits previously observed. Although Ti-based metallic glasses and TiFe-based alloys exhibit a high yield strength, they show a smaller fracture strain (Figure 8.16(a)). In contrast, the Ti-based glass-dendrites, TiZrBe-based nanostructure-dendrites and Ti6Al4V alloy show a larger ductility than the other alloys but a lower yield strength. The fracture strain of these new TiCu-based alloys is also higher than the usually observed for CuZr-based BMG composites [14, 175] (Figure 8.16(a)).

The density of the alloys is considered in Figure 8.16(b), which correlates their specific strength (= yield strength/density) and fracture strain. An average density was calculated based in the density and atomic fraction of the chemical elements. It is observed that the specific strength of the new TiCu-based alloys (calculated density around 6.8 g.cm$^{-3}$) is comparable with the observed for the Ti-based glass-dendrites, TiZrBe-based nanostructure-dendrites and Ti6Al4V alloy. The relative lower strength of these three families of alloys when compared with the other alloys is counterbalanced by their low density, which ranges between 4.5 to 5.7 g.cm$^{-3}$. 
Figure 8.16 – (a) Ashby-like map of yield strength and fracture strain obtained for the new TiCu-based composites developed in this work (denoted TiCu-based BMGCs) in comparison with as-cast: Ti-based bulk metallic glasses (BMGs) [146, 181, 230, 231], TiFe-based [232], Ti-based nanostructure-dendrite [233, 234], TiZrBe-based glass-dendrite composites [12, 235, 236], CuZr-based BMG composites [14, 175] and commercial Ti6Al4V [237]. Only results
for samples with diameters of 1.5, 2 and 3 mm obtained during compression tests were considered. (b) Ashby-like map of the specific strength (= yield strength/density) and fracture strain (the same data set was used). An average density was calculated considering the atomic fraction and density of the chemical elements (with exception of TiFe-based alloys. Their density was measured experimentally by Louzguine-Luzgin et al. [232] using the Archimedes’ Principle).

The hardness of the B2 phase and the glass measured in each 2 mm diameter rod is shown in Table 8.4. The B2 phase is much softer than the glassy matrix, which is one of the prerequisites to produce ductile in-situ bulk metallic glass composites [16]. The addition of Si seems to promote a slight increase in the hardness of the B2 and the amorphous phase, which could be related to the effect of solid solution hardening [122]. As an example, the hardness of the B2 and amorphous phase measured for the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$ is 316±13 and 536±19 HV 0.2. The addition of 0.5 and 1 at.% Si to this alloy increases the hardness for 329±14 and 550±7 and 350±12 and 586±16 HV 0.2, respectively. Considering the correlation between hardness and strength ($\rho \approx HV/3$ [122], where $\rho$ and HV are the yield strength (kgf/mm$^2$) and Vickers hardness, respectively), it is expected that the addition of Si also increases the yield strength slightly, although this effect should be only marginal given the small differences in hardness (Table 8.4).

Optical micrographs were obtained from each parallel face of the compression test samples and the amount of B2 phase was estimated by image analysis (results also given in Table 8.4). All samples exhibit a high yield strength because their low volume fraction of B2 phase (< 40 vol.%, Table 8.4). As discussed in subsection 7.3.1, composites with low volume fraction of B2 phase inherit the high strength of the glassy phase and their strength can be calculated by the rule of mixture (equation 2.10). The hardness of the B2 and glass in each sample were used to calculated the yield strength of the composites, which are given in Table 8.4. A good agreement between calculated and experimental yield strength is observed considering the experimental errors (Table 8.4).

**Mechanical behaviour of 3 mm diameter rods**
The mechanical behaviour in compression of the 3 mm diameter rods of (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ (x = 0, 0.5, 1 and 2) are described in this subsection. The phase formation and microstructure of these alloys were shown in subsection 8.1.2. These rods formed mainly B2-(Ti,Zr)(Cu,Ni) and amorphous phase, together with small fraction of the hexagonal Cu$_2$TiZr. This phase will have implications in the mechanical behaviour of these rods as will be shown in the end of this subsection.

Figure 8.17 shows the mechanical behaviour of the (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ (x = 0, 0.5, 1 and 2) rods during compression and the results are summarized in Table 8.5. All alloys exhibit a high strength up to 1830±50 MPa and the fracture strain increases with Si additions. Two curves are shown for each composition (Figure 8.17) to demonstrate that some differences in the fracture strain are observed for the samples taken from different regions of the rod (Table 8.5). These differences in the fracture strain are expected to occur because the samples have different amounts of pores or superficial imperfections, apart from the similar microstructure and phase formation observed in their different parts (subsection 3.2.1).

As discussed before, the fracture strain in these composites is dependent on the volume fraction of the crystalline phase and also on its size and distribution (subsection 7.3.1). Both rods with 0 and 0.5 at.% Si exhibit a lower fracture strain than the alloy with 1 at.% Si. This difference is partially attributed to the presence of a larger amount of B2 phase in the latter alloy in contrast with the 0.5 at.% Si sample (Figure 8.8) and the more homogeneous distribution and small size (10 to 100 µm) of B2 phase when compared with the 0 at.% Si alloy (Figure 8.8). Nevertheless, just the amount and distribution of the B2 phase cannot explain the large difference in fracture strain between these alloys.
Figure 8.17 – True compressive stress-strain curves for 3 mm diameter rods of the (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ alloys (the amount of Si is indicated in the curves).

Table 8.5 Mechanical properties under compressive loading of the rods with 3 mm in diameter of the (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{100-x}$Si$_x$ ($x = 0, 0.5, 1$ and $2$) alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rod region</th>
<th>Yield strength (MPa)</th>
<th>Fracture Strain (%)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{42.5}$Cu$</em>{42.5}$Ni$<em>{17.5}$Zr$</em>{7.5}$</td>
<td>bottom</td>
<td>1240±50</td>
<td>1.2±0.5</td>
<td>106±5</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>1590±50</td>
<td>1.7±0.5</td>
<td>95±5</td>
</tr>
<tr>
<td>(Ti$<em>{0.425}$Cu$</em>{0.425}$Ni$<em>{0.075}$Zr$</em>{0.075}$)$<em>{99.5}$Si$</em>{0.5}$</td>
<td>top</td>
<td>1830±50</td>
<td>1.8±0.5</td>
<td>101±5</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>1560±50</td>
<td>1.5±0.5</td>
<td>101±5</td>
</tr>
<tr>
<td>(Ti$<em>{0.425}$Cu$</em>{0.425}$Ni$<em>{0.075}$Zr$</em>{0.075}$)$<em>{99}$Si$</em>{1}$</td>
<td>middle</td>
<td>1720±50</td>
<td>3.5±0.5</td>
<td>93±5</td>
</tr>
<tr>
<td></td>
<td>top</td>
<td>1600±50</td>
<td>7.9±0.5</td>
<td>92±5</td>
</tr>
<tr>
<td>(Ti$<em>{0.425}$Cu$</em>{0.425}$Ni$<em>{0.075}$Zr$</em>{0.075}$)$<em>{98}$Si$</em>{2}$</td>
<td>middle</td>
<td>1510±50</td>
<td>7.2</td>
<td>91±5</td>
</tr>
<tr>
<td></td>
<td>middle</td>
<td>1500±50</td>
<td>10.3</td>
<td>91±5</td>
</tr>
</tbody>
</table>

The analysis of the polished fracture surface of the (Ti$_{0.425}$Cu$_{0.425}$Ni$_{0.075}$Zr$_{0.075}$)$_{99.5}$Si$_{0.5}$ rod reveals that the hexagonal Cu$_2$TiZr phase has a brittle behaviour (this phase can be seen with a dark grey contrast in Figure 8.18(a) and 8.18(b)). Cracks are seen inside this phase (Figure 8.18(a)) and they seem to percolate the material (Figure 8.18(b)). Figure 8.18(a) clearly shows that the glassy matrix is tougher than the hexagonal Cu$_2$TiZr phase since the cracks stop exactly at the frontier with the matrix. Interestingly, the cracks even cut through the (Ti,Zr)$_2$(Cu,Ni) dendrites (Figure 8.18(a)).
Figure 8.18 – SEM images of the polished fracture surface of the 3 mm diameter \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{99.5}\text{Si}_{0.5}\) rod. (a) Cracks were formed inside the brittle \(\text{Cu}_2\text{TiZr}\) (dark grey) and (b) percolate the rod following this phase.

Larger \(\text{Cu}_2\text{TiZr}\) precipitates were only observed in the samples with a larger amount of amorphous phase (0, 0.5 and 1 at.% Si), particularly in the alloy with 0.5 at.% Si (Figure 8.9(a)). The lower volume fraction of the \(\text{Cu}_2\text{TiZr}\) phase with increasing the Si amount is probably related with the reduction of both Cu and Zr \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{100-x}\text{Si}_x\)). The presence of the spherical precipitates of the hexagonal phase is one of the reasons for the lower plasticity of the alloys with 0, 0.5 and 1 at.% Si when compared with the 2 at.% Si composition. This alloy exhibits a larger fracture strain up to 10.3 % combined with a high strength of 1500±50 MPa. These values are comparable to the ones of high-strength nanocrystalline Ti-based alloys [234, 238]. Many of the compression samples did not break in two parts although the amorphous phase at the surface was completely cracked, which proves the large deformability of the refined dendritic core (Figure 8.9(c)).

As was shown in Figure 8.8, the rod with 2 at.% Si has a “core-shell” microstructure, where a crystalline core composed by a refined eutectic structure (Figure 8.9(c)) is surrounded by a glassy ring (Figure 8.8). This type of microstructure is expected to result in a good mechanical behaviour when compared with a full crystalline sample as will be shown in the next paragraphs.

Recently, Yavari et al. [239] have reported the effect of a chill surface zone on the mechanical behaviour of Cu-based alloys. They demonstrated that a more refined microstructure at the surface (chill zone) with higher strength than the inner core increases
the strength of the material without decreasing the ductility. The yield strength can be estimated by the Vickers hardness \( (H_v) \) using the relation \([122]\):

\[
\rho = \frac{H_v}{3} (0.1)^{n' - 2} \approx \frac{H_v}{3}
\]

(8.2),

where \( \rho \) is the yielding strength (kgf/mm\(^2\)) and \( n' \) is a constant related with the strain hardening of the alloy \( (n' \approx 2) \). The Vickers hardness measured for the crystalline inner core and the amorphous outer surface was 563±12 and 395±23 HV0.2, respectively, which renders yield strengths of 1840±40 and 1290±70 MPa, respectively. The strength of the composite can be calculated by the following equation \([239]\):

\[
\rho \approx \left( \frac{r^2_c}{r^2} \right) \rho_{\text{core}} + \left( 1 - \frac{r^2_c}{r^2} \right) \rho_{\text{surf}}
\]

(8.3),

where \( r_c \) is the radius of the crystalline inner core, \( r \) is the rod radius, \( \rho_{\text{core}} \) and \( \rho_{\text{surf}} \) are the yield strength estimated for the crystalline inner core and amorphous outer surface region, respectively. The average measured value of \( r_c \) was 1.16±0.02 mm, which gives an estimated yield strength of 1500±100 MPa, which indeed is in good agreement with the observed value of 1510±50 MPa (Table 8.5). The strengthening effect of the amorphous outer surface as given by the second term in equation (8.3) leads to an increase of strength of about 17% compared to the crystalline core alone.

### 8.2.2 Bending and tensile tests of the \((\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}\) alloy

The mechanical behaviour of the \((\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}\) alloy, which shows a yield strength of 1830±50 MPa and a fracture strain of 13.8±0.5 % in compression (Table 8.4), was further investigated by three point bending and tensile tests. The samples were taken from plates (1 mm thick, 10 mm wide and 50 mm long), which were fabricated by suction casting.

The XRD patterns of the bottom and top part of a plate are shown in Figure 8.19. The sample consists of glass and B2-(Ti,Zr)(Cu,Ni) phase (B2 peaks are seen superimposed on broad peaks of the amorphous phase at 2\( \theta \) = 18.6 and 32.2 °). It can be also seen that the sample exhibits different amount of B2 phase when its top and bottom part are compared. The top part experiences a lower cooling rate because the mold gets warmer around this
region during the processing, which results in a larger amount of crystalline phase at the top [171].

Figure 8.19 – XRD patterns of a 1 mm thick $(\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$ plate taken from the bottom and top region. The sample consists of glass and the $\text{B2-}(\text{Ti,Zr})(\text{Cu,Ni})$ phase. Different amount of B2 phase is observed comparing top and bottom region, which results from differences in the local cooling rate.

The microstructure of the $(\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$ plate is shown in Figure 8.20(a) and 8.20(b). Only small amount of spherical precipitates of the B2 phase are seen in the amorphous matrix at the longitudinal section of the centre region of the plate. Nevertheless, more to the top part of the plate, a much larger amount of B2 phase is formed (Figure 8.20(b)). These results corroborate with the XRD results shown in Figure 8.19.
A 1 mm thick ($\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$) plate was then cut into several parallelepipeds of size 1 x 1 x 16 mm for the bending tests. The plastic strain at the surface of the specimen on the convex or the tensile side is plotted in Figure 8.21 with the bending stress. The bending stress and plastic strain were calculated using equations (3.1) and (3.2), respectively. A considerable plastic deformation of around 8.0±0.5 % was observed for this sample combined with a large yield strength of around 2670±50 MPa.
Figure 8.21 – Bending test results for \((\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_1\). The plastic strain at the surface of the specimen on the convex or the tensile side is plotted with the bending stress. The inset shows an image of a sample after the bending test. The sample did not break in two parts and a large inflection of around 1.4 mm was observed.

The yield strength observed during bending tests is usually higher than in compression or tensile tests [240], which is attributed to the lower amount of defects in the thin layer subjected to the maximum tensile stress and to the negative stress gradient in the bending samples [240]. A typical serrated flow caused by instantaneous drops in stress is seen in the curves as it often occurs during compression test of ductile metallic glasses [97]. The plasticity obtained for the \((\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_1\) composite (Figure 8.21) is larger than the observed for bulk metallic glasses [114] since they usually do not show any plastic strain during bending tests of samples with thickness equal or larger than 1 mm at room temperature [114].

The longitudinal section of the samples (side view) after the bending tests are shown in Figure 8.22. The shear bands formed on the tensile and compressive sides of the sample exhibit different morphologies (Figure 22(a)). On the tensile side, they are straight (around
45 ° to the loading direction) and well-spaced whereas on the compressive side the shear bands have a wavy morphology and have a much closer spacing. Figure 22(b) shows a B2-(Ti,Zr)(Cu,Ni) precipitate located closer to the tensile side of a sample. It seems to block the shear bands coming from the tensile side. Several shear bands are formed at the interface precipitates/glassy matrix and lines can be seen inside the precipitates, which indicates that the B2 phase probably transforms to the orthorhombic B19 martensite.
**Figure 8.22** – Longitudinal section of two samples of the 1 mm thick $(Ti_{0.45}Cu_{0.41}Ni_{0.09}Zr_{0.05})_{99}Si_1$ plate after the bending tests. The shear band formation in the tensile and compressive side is shown in figure (a). (b) Interaction between shear bands and a B2 precipitate, indicated in the figure by a dashed circle. Several shear bands emanate from the precipitate. It also blocks the shear bands movement on the tensile side.

The fracture surface of a bending sample of the alloy $(Ti_{0.45}Cu_{0.41}Ni_{0.09}Zr_{0.05})_{99}Si_1$ is shown in Figure 23(a). Two different regions can be seen and are indicated by A and B. The smooth region A is magnified in Figure 23(b) whereas region B is shown in more details in Figure 23(c). A vein pattern is observed in the region A (Figure 23(b)), which indicates local melting caused by shear band propagation. This side corresponds to the tensile side, where straight shear bands are formed (Figure 8.22(a)). Region B, which is much rougher and rugged than region A, shows the presence of dimples (Figure 23(c)), typically observed for ductile fracture.
Figure 8.23 – (a) Fracture surface of a bending sample of the $(\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$ alloy. Two different regions are seen indicated by A and B. (b) Vein patterns are seen in the magnification of the region A and (c) dimples are seen in the region B. The region A corresponds to the tensile side whereas B corresponds to the compressive side.

The mechanical behaviour of the 1 mm thick $(\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$ plates was also investigated by tensile tests. Although a high strength and a considerable plastic strain was observed in bending, a small fracture strain and a low yield strength was observed during tensile tests (Figure 8.24). The average yield strength, fracture strain and Young’s modulus obtained were 500±110 MPa, 1.9±0.2 and 79±5 GPa, respectively.

Figure 8.24 – Tensile test results for 1 mm thick $(\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99}\text{Si}_{1}$ plates.
The possible reasons for the lower yield strength and fracture strain obtained in tensile when compared with the bending (Figure 8.21) and compression tests (Table 8.4) are the same explained in section 7.4 for the Ti-Cu-Ni-Zr plates and they are listed below:

i) It can be associated with the heterogeneous microstructure of the samples (Figure 8.20). Some parts of the plates exhibit an almost fully amorphous structure as shown in Figure 8.20(a), although other regions exhibit the presence of larger B2 precipitates with vol. fractions around 50 vol.% (Figure 8.20(b)), below the limit for the composite inherits the high strength of the amorphous phase (subsection 7.3.1);

ii) Sarac and Schroers [130] argued that large ratio between particle size (d) and particle spacing (s) results in lower fracture strain and yield strength (section 2.3). Figure 8.20(b) shows that large precipitates occur in some parts of the samples, which results in large \( \frac{d}{s} \) ratio. Several simulation results also suggest that a larger fracture strain is obtained when the precipitates are homogeneously distributed in the glassy matrix and have small sizes (see section 2.3).

iii) The fracture strain obtained in compression is usually larger than in tensile or bending because of the confinement of shear bands and the friction between sample and loading plate, which generates a lateral confining stress [97]. Both factors favour the formation of multiple shear bands.

Similar features were observed in the fracture surface of the tensile samples of alloy \( \left( \text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05}\right)_{99}\text{Si}_{1} \) when compared with the Ti-Cu-Ni-Zr plates (section 7.4). For this reason, the fractography results will be not shown here.

8.3 Deformation-induced phase transformations in Ti-Cu-Ni-Zr-(Si) composites

Some bulk metallic glasses can precipitate nanocrystals during deformation [105-108] as was discussed in section 2.2. These nanocrystals are particularly important for the deformation behaviour of CuZr-based bulk metallic glasses, in which B2-CuZr nanocrystals form during deformation. These nanocrystals can further participate in the deformation process [107] and contribute to enhance the plasticity of these glassy alloys [106, 107]. In
order to investigate if a similar mechanism occurs in TiCu-based bulk metallic glass composites, 2 mm diameter rods of the alloys Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ and (Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$)$_{99.5}$Si$_{0.5}$ were investigated by transmission electron microscopy (TEM) before and after deformation. As shown in subsection 7.2 and 8.2.1 (Figure 7.7(a) and Figure 8.14), the microstructure of these rods consists of spherical precipitates of the B2-(Ti,Zr)(Cu,Ni) phase embedded in a glassy matrix.

Figure 8.25(a) illustrates the microstructure of the matrix in the as-cast Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ rod. No indication of crystals formation (e.g., fringes of crystalline lattices) was observed. The selected area electron diffraction pattern (SAED) taken from this region only shows a characteristic amorphous pattern with diffuse rings (Figure 8.25(b)). Nevertheless, the dark field TEM image of Fig. 8.25(a) exhibits white spots (speckles) of a few nanometers in size which are probably related to chemical fluctuations as observed in amorphous Ti-Cu-Ni ribbons [241].

Figures 8.25(c) illustrate the microstructure of the matrix after deformation. Nanocrystals with sizes ranging from 20 to 50 nm are observed in the amorphous matrix and their presence was confirmed by the slender diffraction rings in the SAED pattern of this region (Figure 8.25(d)), which could be indexed according to the cubic B2-(Ti,Zr)(Cu,Ni) phase. Similar nanocrystals were observed in the deformed (Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$)$_{99.5}$Si$_{0.5}$ rod (Figure 8.26(a)). The interplanar distances measured in the high-resolution TEM images of the nanocrystals in Figure 8.26(b) also correspond to the cubic B2-TiNi phase. These results suggest that they precipitate during deformation and the presence of twins and lattice defects (Figure 8.26(b)) suggests that they participate in the deformation process.

The nanocrystals observed here are different when compared with the ones formed during solidification (Figure 8.10(a)) or during crystallization (Figure 6.11(a)). They are not homogeneously dispersed in the glass matrix and have large size up to 50 nm (Figure 8.25(c)).
Figure 8.25 – (a) Dark field TEM image of the glassy matrix in the as-cast rod of Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$. Speckles can be seen which could be related with chemical fluctuations. (b) Selected area electron diffraction pattern (SAED) of the region shown in (a). Only diffuse rings typical of a full amorphous sample are seen. (c) Bright field TEM image of the glassy matrix after compression (13% of strain), showing the presence nanocrystals with sizes around 25 to 40 nm. (d) SAED pattern of the region shown in (c). Slender diffraction rings can be seen, which confirm the presence of nanocrystals in the glass.
Figure 8.26 – (a) Bright field TEM image of the (Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_5$)$_{99.5}$Si$_{0.5}$ rod after 5% of plastic deformation. Similarly, nanocrystals can be seen in the glassy matrix. Figure (b) exhibits more details of one nanocrystal, where twins and dislocations are observed, which seem to form during deformation.

The formation of nanocrystals during deformation of metallic glasses is commonly observed [97] and recent results show that they may participate during the deformation process [105, 107]. In the case of CuZr-based bulk metallic glasses this process appears to play a critical role in the enhancement of the mechanical properties [106, 107]. The formation of nanocrystals and their further deformation consumes energy and alleviates stresses during deformation, which retards the fracture [107].

According to the potential energy landscape theory [242], the energy barrier associated with structural rearrangements in the glassy matrix is proportional to the local shear modulus and to the size of the rearranging zone [107, 243]. The shear stress applied during deformation lowers the shear modulus and consequently lowers the energy barrier for structural rearrangements [107]. This in turn facilitates flow and promotes crystallization. The decrease in the energy barrier for crystallization under compressive loading can also be understood based on the thermodynamic approach proposed by Lee et
al. [106], which shows that a hydrostatic compressive stress lowers the free energy barrier to form a nucleus of critical size and enhances the nucleation rate [106].

Despite the changes in the glassy matrix during deformation, the B2 precipitates can also undergo a martensitic transformation during deformation, as was discussed in subchapter 7.3. This accounts for the strong work-hardening behaviour of these composites (subchapter 7.3). In order to investigate the occurrence of structural changes in the precipitates during deformation of the Ti-Cu-Ni-Zr-(Si) alloys, the 2 mm diameter rod of \((\text{Ti}_{0.45}\text{Cu}_{0.41}\text{Ni}_{0.09}\text{Zr}_{0.05})_{99.5}\text{Si}_{0.5}\) and 3 mm rod of \((\text{Ti}_{0.425}\text{Cu}_{0.425}\text{Ni}_{0.075}\text{Zr}_{0.075})_{98}\text{Si}_{2}\) were selected to be studied. Their XRD patterns before and after deformation are shown in Figure 8.27. It can be seen that the cubic B2-(Ti,Zr)(Cu,Ni) phase transforms during deformation to the B19-(Ti,Zr)(Cu,Ni) but B2 peaks are still seen for both samples after deformation (see peak \(2\theta = 18.7^\circ\)), which shows that the transformation was not completed. The peaks became broader and with lower intensity because the occurrence of martensitic transformation and accumulation of defects as dislocations, stacking faults and cracks inside the material [178].
Figure 8.27 - XRD results for the 3 mm rod of $(Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_{0.075})_{98}Si_{2}$ and 2 mm rod of $(Ti_{0.45}Cu_{0.41}Ni_{0.09}Zr_{0.05})_{99.5}Si_{0.5}$ before (BC) and after (AC) compression. The cubic B2 phase partially transforms to the orthorhombic B19 after deformation.

To conclude, two different mechanisms have an important influence on the mechanical behaviour of the Ti-Cu-Ni-Zr-(Si) alloys: the precipitation of B2 nanocrystals in the glassy matrix during deformation with subsequent participation in the deformation process and the martensitic transformation of the ductile B2 precipitates already present in the as-cast state. Both mechanisms consume energy during deformation and counterbalance the strain softening of the glassy matrix, which results in composites with a combination of high strength, large fracture strain and work-hardening behaviour (Figure 8.15).
9 Phase formation and mechanical behaviour of Ti-Cu-Ni-Co alloys

Co additions to CuZr-based alloys are associated with a decreasing in GFA [244], which is connected with an increasing thermal stability of the B2-CuZr phase and a lower stability of the liquid [245, 246]. The substitution of Co for Cu in B2-CuZr has been also reported to decrease the stacking fault energy and consequently to promote the twinning propensity, which improves the ductility of CuZr-based shape memory bulk metallic glass composites [125].

The CuZr- and TiCu-based systems are very similar in some aspects as phase formation and microstructure (both of them form shape memory bulk metallic glass composites consisting of spherical B2 precipitates and glass [14], Figure 7.7(a)) and have similar chemical elements (Ti and/or Zr and Cu and/or Ni). It is worth investigating if similar effects of the addition of Co, e.g. increased stability of the B2 phase, decreasing in GFA and improved deformability, can also be observed for TiCu-based alloys.

The pseudo-binary TiCu-TiNi phase diagram (Figure 2.15) shows that the B2-Ti(Ni,Cu) phase undergoes martensitic transformation to the orthorhombic B19-Ti(Ni,Cu) during cooling at a temperature slightly above the ambient (around 50 °C). It was also shown in chapter 7 and 8 that this transformation can also occur during deformation. Yet, the effect of Co on the martensitic transformation of TiCu-based alloys was not investigated so far.

The influence of Co on the phase formation, thermal stability and mechanical properties of TiCu-based alloys is described here. Rods of 2 mm in diameter and with a length of 70 mm of 4 different alloys (indicated by F3, F4, F5 and F6 in Figure 9.1) were prepared for these experiments. These compositions were selected near the eutectic region of the TiCu-TiCo-TiNi pseudo-ternary phase diagram because TiCu-rich systems follow strictly the empirical rule proposed by Inoue [49] which states that the best GFA occurs around eutectic regions [5, 9, 145]. Two other Ti-Cu-Ni rods (indicated by F1 and F2 in Figure 9.1) with similar size and previously investigated (chapter 5) were also considered in this study for comparative purposes. The six compositions selected for this investigation
(Ti$_{50}$Cu$_{43}$Ni$_{7}$ (F1), Ti$_{50}$Cu$_{41}$Ni$_{9}$ (F2), Ti$_{50}$Cu$_{39}$Co$_{11}$ (F3), Ti$_{50}$Cu$_{42.5}$Ni$_{5}$Co$_{2.5}$ (F4), Ti$_{50}$Cu$_{40.5}$Ni$_{2.5}$Co$_{7}$ (F5) and Ti$_{50}$Cu$_{43.5}$Ni$_{2.5}$Co$_{4}$ (F6)) are given in Figure 9.1.

Figure 9.1 – The following compositions were selected for this study: F1 (Ti$_{50}$Cu$_{43}$Ni$_{7}$), F2 (Ti$_{50}$Cu$_{41}$Ni$_{9}$), F3 (Ti$_{50}$Cu$_{39}$Co$_{11}$), F4 (Ti$_{50}$Cu$_{42.5}$Ni$_{5}$Co$_{2.5}$), F5 (Ti$_{50}$Cu$_{40.5}$Ni$_{2.5}$Co$_{7}$) and F6 (Ti$_{50}$Cu$_{43.5}$Ni$_{2.5}$Co$_{4}$). The phase formation and microstructure of F1 and F2 were previously investigated (chapter 5). The triangles indicate composites consisting of glass and crystals and the squares indicate fully crystalline samples (A: amorphous, C: crystalline). The eutectic compositions [149] are also indicated in the figure by a straight blue line.

9.1 Phase formation and thermal stability of Ti-Cu-Ni-Co alloys

DSC analyses showed that crystallization peaks occur only for the alloys F1 (Ti$_{50}$Cu$_{43}$Ni$_{7}$) and F2 (Ti$_{50}$Cu$_{41}$Ni$_{9}$) as previously shown in chapter 5 (Figure 5.5), with an amount of amorphous phase around 10 vol.% (Table 5.1). The rods of the other compositions are fully crystalline as indicated in Figure 9.1. These results already suggest that the addition of Co decreases the GFA as observed for CuZr-based alloys [244].
To investigate the microstructure and phase formation, these samples were further checked by XRD and SEM. The XRD results are depicted in Figure 9.2. The cubic B2-Ti(Ni,Cu,Co) and the tetragonal γ-TiCu phases are detected in all samples. For the samples without Co (F1 and F2), the orthorhombic B19-Ti(Cu,Ni,Co) also forms in contrast with the Co-added alloys (F3 to F6), where only B2 and γ-TiCu phases occur but with different volume fractions and sizes as can be inferred by the different peak intensities and peak shapes.

![Figure 9.2 – XRD results of the alloys indicated in Figure 9.1: F1 (Ti$_{50}$Cu$_{43}$Ni$_7$), F2 (Ti$_{50}$Cu$_{41}$Ni$_9$), F3 (Ti$_{50}$Cu$_{39}$Co$_{11}$), F4 (Ti$_{50}$Cu$_{42.5}$Ni$_3$Co$_{2.5}$), F5 (Ti$_{50}$Cu$_{40.5}$Ni$_2.5$Co$_{7}$) and F6 (Ti$_{50}$Cu$_{43.5}$Ni$_2.5$Co$_4$). No martensite (B19) was detected for the alloys with Co (F3 to F6). This suggests that the B2-Ti(Cu,Ni,Co) is stabilized by the Co additions.](image_url)

The microstructures of the Ti$_{50}$Cu$_{43}$Ni$_7$ and Ti$_{50}$Cu$_{41}$Ni$_9$ rods were already described in chapter 5: Dendrites of the B2-Ti(Cu,Ni) are formed in a γ-TiCu matrix around the centre region of the rods whereas martensite was formed in the outer surface region together with the glass (Figure 5.3). The microstructure of the other samples are shown in Figure 9.3. A
similar phase formation is seen in the case of the F3, F4, F5 and F6 samples. Dendrites of the B2 phase were formed in a γ-TiCu matrix. Black precipitates of the Ti$_2$Ni phase are also seen (Figure 9.3(b), 9.3(c) and 9.3(d)) and their composition was measured to be Ti$_{62}$Cu$_{26}$Co$_9$Ni$_7$ in the Ti$_{50}$Cu$_{42.5}$Ni$_5$Co$_{2.5}$ alloy (F4). The B2 and γ-TiCu phases are expected to form as predicted by the equilibrium phase diagram (Figure 2.17) in contrast to the “Big Cube” phase, Ti$_2$Ni (space group Fd3m). This phase can dissolve a large amount of oxygen [205] and is stabilized by the presence of oxygen [15] as is commonly seen in rapid solidified TiCu-based alloys (subsections 7.2 and 8.1.2).

Figure 9.3 – Microstructure of the (a) F3 (Ti$_{50}$Cu$_{39}$Co$_{11}$), (b) F4 (Ti$_{50}$Cu$_{42.5}$Ni$_5$Co$_{2.5}$), (c) F5 (Ti$_{50}$Cu$_{40.5}$Ni$_2$Co$_{7}$) and (d) F6 (Ti$_{50}$Cu$_{43.5}$Ni$_{2.5}$Co$_4$). Dendrites of the B2 phase are observed in a γ-TiCu matrix, together with black precipitates of the Ti$_2$Ni phase.

Dilatometry studies were also carried out in a temperature range of 148 to 423 K (Figure 9.4) in order to measured the martensitic transformation temperature of these alloys. A clear martensitic transformation was observed only for the F2, F4 and F6 alloys.
with an martensite-to-austenite transformation temperature ($A_s$) around 321, 258 and 171 K, respectively. The transformation observed in two heating-cooling cycles shows a perfect reversibility, without changes in the transformation characteristics. Although no martensitic transformation was observed for F1 by dilatometry, a small transformation peak can be seen by DSC (Figure 5.6) at 340 K ($A_s$). A small difference was observed comparing $A_s$ measured by DSC and dilatometry for F2 ($\text{Ti}_{50}\text{Cu}_{41}\text{Ni}_9$), which is probably caused by the different nature of these tests. $A_s$ was measured as 333±2 K by DSC (Figure 5.6) and as 321±2 K by dilatometry (Table 9.1).

The linear thermal expansion coefficient, $\alpha_l$, ranges between 1.17 and 1.23 x $10^{-5}$ K$^{-1}$ (in the case of alloys, which show a martensitic transformation, $\alpha_l$ was measured at the higher temperatures) in the range usually observed for TiCu-based alloys [172, 247].

It has been demonstrated that the martensitic transformation temperatures of TiNi-based shape memory alloys are dependent on the number ($e_v/a$) and concentration ($c_v$) of valence electrons of the alloys [136]. Since this transformation occurs only in the B2 phase, it should be investigated if $e_v/a$ and $c_v$ calculated based on the composition of this phase instead of the composition of the alloy scales with the transformation temperatures. Table
9.1 shows the compositions of the B2 phase in the different alloys measured by EDX together with the values of $A_s$, $e_v/a$ and $c_v$. One can see that increasing $c_v$ and $e_v/a$, the transformation temperature also increases (Table 9.1 and Figure 9.5) as observed for other TiNi-based alloys [136].

**Table 9.1 – Composition of the B2 phase in the different alloys measured by EDX, the austenite start transformation temperature ($A_s$) measured by dilatometer and by DSC, the valence electron concentration $c_v$ and number of valence electrons per atom $e_v/a$ of the B2 phase. The typical error for the EDX measurements is ±0.5 at.%.**

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Nominal composition</th>
<th>B2 composition</th>
<th>$A_s$ dilatom. (K)</th>
<th>$A_s$ DSC (K)</th>
<th>$c_v$</th>
<th>$e_v/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Ti$<em>{50}$Cu$</em>{43}$Ni$_7$</td>
<td>Ti$<em>{50}$Cu$</em>{43}$Ni$_7$</td>
<td>-</td>
<td>340±2</td>
<td>0.293±0.001</td>
<td>7.45±0.01</td>
</tr>
<tr>
<td>F2</td>
<td>Ti$<em>{50}$Cu$</em>{42}$Ni$_9$</td>
<td>Ti$<em>{49}$Cu$</em>{42}$Ni$_9$</td>
<td>321±2</td>
<td>333±2</td>
<td>0.294±0.001</td>
<td>7.48±0.01</td>
</tr>
<tr>
<td>F3</td>
<td>Ti$<em>{50}$Cu$</em>{39}$Co$_{11}$</td>
<td>Ti$<em>{50}$Cu$</em>{32}$Co$_{18}$</td>
<td>-</td>
<td>-</td>
<td>0.284±0.001</td>
<td>7.14±0.01</td>
</tr>
<tr>
<td>F4</td>
<td>Ti$<em>{50}$Cu$</em>{42.5}$Ni$<em>{5}$Co$</em>{2.5}$</td>
<td>Ti$<em>{50}$Cu$</em>{41}$Ni$<em>{5}$Co$</em>{4}$</td>
<td>258±2</td>
<td>-</td>
<td>0.291±0.001</td>
<td>7.40±0.01</td>
</tr>
<tr>
<td>F5</td>
<td>Ti$<em>{50}$Cu$</em>{40.5}$Ni$<em>{2.5}$Co$</em>{7}$</td>
<td>Ti$<em>{50}$Cu$</em>{35}$Ni$<em>{4}$Co$</em>{11}$</td>
<td>-</td>
<td>-</td>
<td>0.287±0.001</td>
<td>7.25±0.01</td>
</tr>
<tr>
<td>F6</td>
<td>Ti$<em>{50}$Cu$</em>{43.5}$Ni$<em>{2.5}$Co$</em>{4}$</td>
<td>Ti$<em>{50}$Cu$</em>{42}$Ni$<em>{3}$Co$</em>{5}$</td>
<td>171±2</td>
<td>-</td>
<td>0.291±0.001</td>
<td>7.37±0.01</td>
</tr>
</tbody>
</table>

**Figure 9.5 – Concentration of valence electrons of the B2 phase ($c_v$) and the martensite-to-austenite transformation temperature ($A_s$, Table 9.1). $A_s$ increases with increasing $c_v$.**
9.2 Mechanical properties of Ti-Cu-Ni-Co alloys

The compression test results for the 2 mm diameter rods are displayed in Figure 9.6. The substitution of Ni by Co increases the yield strength (Table 9.2). Ti$_{50}$Cu$_{41}$Ni$_9$ (F2) exhibits a very low yield strength around 110±50 MPa in contrast to the Ti$_{50}$Cu$_{39}$Co$_{11}$ (F3), which shows a significantly higher yield strength of 970±50 MPa combined with a high fracture strain of 23 % (Table 9.2). A “double yielding” can be observed for some samples (indicated by a second arrow in the stress-strain curves of Figure 9.6) as usually seen for shape memory alloys [7] and it is connected with the presence of B2 or B19-Ti(Ni,Cu,Co) phase. Both phases may undergo a transformation during deformation, which is responsible for the characteristic “double yielding” behaviour [7]. The cubic B2 phase transforms to the B19 phase during deformation and the orthorhombic B19 undergoes martensite reorientation [7].

![Figure 9.6](image)

*Figure 9.6 – Compression test results of alloys F1 – F6 (compositions given in Table 9.1). The yield strength increases with increasing the amount of Co from F1 = F2 < F4 < F6 < F5 < F3.*
The yield strength is indicated by an arrow, whereas the second arrow in the curve of F4 and F6 indicates the “second” yielding.

Table 9.2 – Summary of the phases present in each sample, volume fraction of B2 phase estimated by image analysis and mechanical properties of the 2 mm diameter rods under compressive loading. B2 and B19 refers to the cubic B2-Ti(Cu,Ni,Co) and orthorhombic B19-Ti(Cu,Ni,Co), respectively. The Ti₂Ni was not considered because its low volume fraction (<2%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases</th>
<th>Amount B2 phase (vol.%)</th>
<th>Yield strength (MPa)</th>
<th>Fracture Strain (%)</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>B19, B2, γ-TiCu and amorphous</td>
<td>-</td>
<td>&lt;50</td>
<td>7.8±0.5</td>
<td>-</td>
</tr>
<tr>
<td>F2</td>
<td>B19, B2, γ-TiCu and amorphous</td>
<td>-</td>
<td>110±50</td>
<td>18.5±0.5</td>
<td>-</td>
</tr>
<tr>
<td>F3</td>
<td>B2 and γ-TiCu</td>
<td>75±4</td>
<td>970±50</td>
<td>23.4±0.5</td>
<td>119±5</td>
</tr>
<tr>
<td>F4</td>
<td>B2 and γ-TiCu</td>
<td>78±3</td>
<td>510±50</td>
<td>12.8±0.5</td>
<td>102±5</td>
</tr>
<tr>
<td>F5</td>
<td>B2 and γ-TiCu</td>
<td>70±8</td>
<td>860±50</td>
<td>19.1±0.5</td>
<td>99±5</td>
</tr>
<tr>
<td>F6</td>
<td>B2 and γ-TiCu</td>
<td>70±10</td>
<td>630±50</td>
<td>13.2±0.5</td>
<td>77±5</td>
</tr>
</tbody>
</table>

The XRD patterns taken before and after deformation of alloys F4 and F5 are shown in Figure 9.7 (the F4 and F5 samples were deformed 12% and 20%, respectively). These results show that the B2 phase transforms to B19 during deformation in the case of F4 but no clear evidence is seen for F5. This difference should be also connected with the effect of the addition of Co since these two alloys have similar microstructure and phase formation (Figure 9.3(b), 9.3(c) and Table 9.2). The addition of Co decreases eₐ/a and cᵥ of the B2 phase as was discussed in section 9.1, which shifts the martensitic transformation (MT) to lower temperatures (Table 9.1, Figure 9.5). The fact that alloy F5 (Ti₅₀Cu₄₀.₅Ni₂.₅Co₇) does not exhibit a MT during deformation like alloy F4 (Ti₅₀Cu₄₂.₅Ni₅Co₂.₅) shows that the larger amount of Co in the former alloy may also impede the MT during deformation because larger stresses are required.
Figure 9.7 – XRD results for the alloys F4 (Ti_{50}Cu_{42.5}Ni_{5}Co_{2.5}) and F5 (Ti_{50}Cu_{40.5}Ni_{2.5}Co_{7}) before (BC) and after compression (AC). The B2 phase in alloy F4 partially transforms to the B19 phase during deformation, which is not observed for alloy F5.

The low strength of F1 and F2 (Figure 9.6) seems to be also connected with the presence of the martensite B19 phase. The shear stress needed to start the reorientation of the martensite by means of twinning/detwinning is very low (0.11 and 0.17 for the \{011\}_o compound or \{111\}_o Type-I-twinning, respectively [7]) and this explains the low yield strength observed. Stress drops are also seen in the stress-strain curve of alloy F1 (Figure 9.6) and they are connected with the brittleness of the amorphous phase at the outer surface. During deformation, the outer part of the rod cracks, which causes a drop in stress as registered in the stress-strain curve (Figure 9.6).

As discussed in chapters 5, 7 and 8, the mechanical behaviour depends on certain factors such as the presence of macroscopic defects (e.g. pores), the phases formed, their
amount, size and morphology and also their composition. For instance, the alloys F3 to F6 show an almost identical phase formation (Figure 9.3, Table 9.2), with a similar volume fraction (the amount of B2 phase ranges between 70 and 78 vol.% as estimated by image analyses (Table 9.2)) and size (Figure 9.3) but their mechanical behaviour is completely different nonetheless, which may be connected with the different composition especially of the B2 phase.

This compositional effect is depicted in Figure 9.8, which correlates the yield strength of the present Ti-Cu-Ni-Co alloys with the number and concentration of valence electrons of the B2 phase [136]. Figure 9.8 shows that the yield strength of the alloys decreases with increasing the concentration of valence electrons ($c_v$) in the B2 phase (a similar fashion was observed considering the number of valence electrons ($e_v/a$)). A high $c_v$ or $e_v/a$ means a larger amount of free electrons in the B2 atomic structure which allows the atoms to move past one another with little difficulty [124]. This may facilitate the dislocations movement and could explain the decreasing in the yield strength with increasing $c_v$ as observed in Figure 9.8.

**Figure 9.8** – Correlation between the true yield strength in compression and the valence electrons concentration ($c_v$) for the 6 alloys investigated (Table 9.1). The dashed line is a guide for the eyes.
To summarize, the results showed that the addition of Co decreases the GFA of Ti-Cu-Ni alloys and stabilizes the B2-Ti(Cu,Ni,Co) at room temperature. The martensitic transformation temperature was observed to be directly proportional to the number \((e_v/a)\) or concentration \((c_v)\) of valence electrons of the B2 phase (Figure 9.5), which decreases with the addition of Co. Additionally, it was observed an inverse correlation between the yield strength of the Ti-Cu-Ni-Co alloys with \(e_v/a\) or \(c_v\) (Figure 9.8).
10 Conclusions

A new family of TiCu-based shape memory bulk metallic glass composites was developed in this work. These alloys were selected with the help of the recently proposed $\lambda + \Delta h^{1/2}$ amorphization criterion and composites were produced using rapid solidification methods such as melt spinning and Cu-mould suction casting. Appropriate microstructures consisting mainly of a glassy matrix with spherical and ductile precipitates of the Ti(Cu,Ni) shape memory phase were obtained, which results in a relatively high strength, large ductility and work-hardening behaviour.

Composites with a diameter of 1 mm were obtained in the ternary Ti-Cu-Ni system. They formed mainly the orthorhombic B19-Ti(Cu,Ni) and glass and exhibited a high yield strength and fracture strain during compression (up to 1170±50 MPa and 27.9±0.5 %, respectively) combined with strong work-hardening behaviour.

Finite element simulations and experimental studies showed that stress concentrations occur around the B19-Ti(Cu,Ni) precipitates during deformation, which induce the formation of shear bands (SB) at the interface with the glassy matrix. These SBs together with the main SBs formed around 45° in the glass matrix (direction with maximum shear stress) promote a more homogeneous deformation of the composites and consequently, lead to an enhanced ductility.

Precipitates completely embedded in the glassy matrix differ from the ones formed at the surface of samples when concerning the martensitic transformation temperatures since precipitates at the surface have a free surface not in contact with the glassy matrix, which stabilizes the cubic B2-Ti(Cu,Ni) phase. This stabilization effect is related to the surface energy of the interface glass/precipitates, which may lower the Gibbs energy of the precipitates or rise the non-chemical terms in the energy balance equation of the martensitic transformation, which oppose the transformation.

The glass-forming ability (GFA) of these Ti-Cu-Ni alloys is improved after the addition of CuZr. Bulk metallic glass composites consisting mainly of the cubic B2 and glassy phase can be obtained in the pseudo-ternary TiCu-TiNi-CuZr system with diameter ranging from 2 to 3 mm. The study of these Ti-Cu-Ni-Zr composites shows that the volume fraction of the
constituent phases is one of the most important parameters in order to control their mechanical behaviour. The yield strength of the composites scales with the volume fraction of the B2 phase and follows a rule of mixtures for values lower than 30 vol.\% and the load-bearing model for higher values. The fracture strain reaches a maximum of 23.7±0.5\% at around 30 vol.\% of B2 phase, in agreement with the “three-body element” model.

It was observed that the cubic B2 phase undergoes a martensitic transformation during deformation, which is responsible for the strong work hardening and the high fracture stress of these alloys. The work-hardening behaviour is also dependent on the volume fraction of phases. A small amount of B2 precipitates dispersed in the glassy matrix is more effective to enhance the work hardening of the composites in the beginning of deformation (below 3\% of true strain) but because their volume fraction is relatively low, the overall hardenability in these composites saturates earlier than for samples with high volume fraction of B2 phase and an inverse situation is seen after 3\% of true strain.

The addition of Si to binary Ti-Cu or quaternary Ti-Cu-Ni-Zr alloys enhances the GFA, with a maximum observed for minor additions of 1 and 0.5 at.\% Si, respectively. This optimum amount results from a balance between the increased stability of the liquid and the supercooled liquid as well as the formation of a relatively low amount of highly stable Ti$_5$Si$_3$ precipitates, which act as nuclei for other crystalline phases.

In contrast, the addition of Co drastically decreases the GFA of these TiCu-rich alloys and both the martensitic transformation temperature and their mechanical behaviour seem to correlate with the number and concentration of valence electrons of the B2 phase. The transformation temperature decreases with increasing the concentration of valence electrons of the B2 phase, which is attributed to the increased amount of free electrons in the structure of this phase.

An excellent combination of a relatively high yield strength and large fracture strain (ranging from 1400±50 to 1891±50 MPa and 12.5±0.5 to 23.7±0.5 \%, respectively) was observed in compression for Ti-Cu-Ni-Zr and Ti-Cu-Ni-Zr-(Si) alloys with a lower amount of CuZr, which exhibit a fracture strain almost two times larger than that for CuZr-based composites [14]. For instance, a yield strength of 1490±50 MPa combined with 23.7±0.5 \%
plastic strain was obtained for the Ti$_{45}$Cu$_{39}$Ni$_{11}$Zr$_{5}$ alloy. Nevertheless, a reduced ductility was found for the CuZr-richer compositions, which is related with the precipitation of the brittle Cu$_2$TiZr phase in the glassy matrix. Because the lower toughness of the Cu$_2$TiZr, cracks are formed inside this phase and percolate through the material.

The current systematic investigations deliver important insights into the correlation between phase formation, microstructure, mechanical properties and thermal stability of this new family of TiCu-based composites. Additionally, they prove the universality of the concept of shape memory BMG composites and upon further optimization, might be promising candidates for high-performance applications as flow meters [248], sensors [248] and micro- or millimeter-sized gears [1].
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**12 Outlook**

Some aspects of these new TiCu-based composites could be further investigated, including:

1. how to promote a more homogeneous distribution of the shape memory B2 phase in the glassy matrix. It was observed that small amount of the Ti$_2$Si$_3$ phase forms in these composites with the addition of Si and they may nuclei the B2 phase. It is worth investigating if additions of Si beside improve the GFA, could also promote a more homogeneous precipitation of the B2 phase;

2. continue to improve the GFA of these alloys. This could be done by extending the search from quaternary alloys in the TiCu-TiNi-CuZr to quintenary alloys in the pseudo-quaternary TiCu-TiNi-CuZr-CuHf system. The addition of Hf promotes an improvement in the GFA of Ti-Cu-Ni-Zr alloys [249];

3. study the superelastic behaviour (pseudoelasticity) of these alloys. The TiNi alloy in the austenitic state exhibits a superelasticity up to 4.5 % [7]. Such behaviour was never observed in a shape memory BMG composite so far. The B2-phase in the TiCu-based composites may also show such superelastic behaviour despite the stabilization effect of the glassy matrix;

4. investigate the influence of minor additions of Si in the viscosity of Ti-Cu-Ni-Zr metallic glasses and its role in the enhancement of the GFA. Another interesting point is how these additions change the short and medium range order of the glass;

5. understanding how to avoid the formation of the Cu$_2$TiZr phase in the CuZr-rich Ti-Cu-Ni-Zr alloys in order to improve their ductility.
13 References

Hiermit bestätige ich, dass ich die von mir am heutigen Tag eingereichte Doktorarbeit zum Thema:

“Phase Formation, Thermal Stability and Mechanical Behaviour of TiCu-based Alloys”

vollkommen selbständig und nur unter Verwendung der in der Arbeit angegebenen Literatur und Abstimmungspartner angefertigt habe.

Unterschrift mit Vor- und Zunamen

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