

Design and fabrication of ductile in situ bulk metallic glass composites

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School of Materials Science and Engineering
Faculty of Science

Design and Fabrication of Ductile In Situ Bulk Metallic Glass Composites

A thesis submitted in complete fulfilment of the
requirements for the award of the degree of

Doctor of Philosophy

in

Materials Science and Engineering

Olga Biletska

March, 2014

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LIST OF PUBLICATIONS

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2. M. Ferry, K.J. Laws, C. White, D.M. Miskovic, K.F. Shamlaye, W. Xu, O. Biletska: *Recent developments in ductile bulk metallic glass composites*, **MRS Communications**, v.3 (2013), 1-12

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3. O. Biletska, K.J. Laws, M. Gibson, M. Ferry: *Production of Mg-based bulk metallic glass composites with high magnesium content*, **Materials Science Forum**, v. 773-774 (2013), 263-267
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6. *Application of lightweight bulk metallic glass composites*, 2011 AMCRC PhD Symposium, June 2011, Melbourne, Australia

ABSTRACT

Bulk metallic glasses (BMGs) possessing high strength and elasticity are excellent candidates for the high-demanding market of advanced materials. Inherent brittleness of the amorphous structure, however, inhibits wide use of the metallic glasses as structural materials. The problem of low plasticity and toughness can be alleviated through formation of a composite structure containing crystalline phase(s) in the high-strength amorphous matrix.

In this thesis, bulk metallic glass composites have been produced in different glass-forming systems. By utilising a copper mold casting method, a series of BMG composites with high Mg concentration (>80 at. %) was fabricated in the Mg-Ni-Gd and Mg-Ni-Gd-Y systems. Zr-rich BMG composites were produced in Zr-Cu-Ni-Al alloy system by arc-melting. To promote formation of crystalline phases in Zr-based glasses, Y_2O_3 particles were introduced to the melt as possible inoculants.

The conditions for formation of amorphous, amorphous-crystalline and completely crystalline structures were found to be dependent on alloy chemistry and sample thickness in both the Mg and Zr-based systems. Stability of the amorphous matrix and devitrification processes during heating were investigated in the Mg-based system. The precipitation of a soft primary Mg-rich phase in the monolithic glass was observed in the compositions with Mg content ≥ 84 at. %. Soft crystallites homogeneously dispersed throughout the Mg-rich glassy matrix enhanced the plasticity of the resulting composite structure with a compressive plastic strain to failure of ~ 9.5 %. For the Zr-Cu-Ni-Al system, the formation of a monolithic amorphous structure and composite structure was observed for a maximum Zr content of 76 and 72 at. %, respectively. The initiation or suppression of crystalline phase growth on the surface of inoculating Y_2O_3 particles in the Zr-based glass was dependent on the cooling rate during casting. The glass-forming ability and thermal stability of the Zr-rich composite alloys was affected by these inoculating particles.

The relatively high glass transition temperatures of the Mg-based composites, their low density ($2.4 - 2.6 \text{ g/cm}^3$) and improved plastic strain to failure may prove useful for future lightweight engineering applications. Heterogeneous nucleation of crystalline phases on the surface of oxide particles introduced into amorphous high Zr-bearing matrix shows possibilities for generating new types of the composite structures.

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CHAPTER 1 - INTRODUCTION

The search for new and advanced materials has always been a subject of high interest for scientists and engineers. A novel class of material was realised with the initial discovery of the first Au-Si metallic glass in 1960. Since this initial discovery, the unique combination of mechanical, chemical and physical properties of glassy alloys has spawned much attention and research activities. This has resulted in the development of wide range of metallic glasses based on, for instance, Zr, Ti, Cu, Fe, Pd and Mg. Some high-performance metallic glasses are on the market already and adopted for applications in industrial coatings, electronics, sporting goods and medical devices.

Due to the disordered (amorphous) atomic structure and, hence, lack of crystallinity and dislocations, metallic glasses generally possess high elasticity, strength and hardness. For example, typical values of compressive yield strength and elasticity for the well-researched Zr-based glasses are ~ 2 GPa and ~ 2 %, respectively. Of relevance for this thesis, lightweight Mg-based glasses exceed the strength of conventional crystalline Mg alloys by 2-4 $\times$, thereby indicating that the former may be potentially used in structural applications. Other useful properties of metallic glasses, as discovered in a large number of researches, include high corrosion resistance, near-net-shape (thermoplastic) processing above the glass transition temperature, reduced sliding friction, improved wear resistance and low magnetic energy losses etc.

One of the major challenges of metallic glasses restricting their use in wider applications is, for most alloy systems, their inherent brittleness. These materials fail by the formation of highly localized shear bands, leading to a catastrophic failure without much macroscopic plasticity. An effective way to alleviate brittleness is to alter the structural features by generating amorphous-crystalline composites. Metallic glass/composite structures containing a wide variety of second (reinforcing) phases can be produced by a range of processing methods. These phases are incorporated in the monolithic amorphous matrix for controlling both the formation and growth of shear bands. For example, if the second phase can promote multiple shear band events in the amorphous matrix, substantial improvement in ductility is possible.

The motivation for this thesis is to design and fabricate new amorphous-crystalline composite structures with various types of reinforcing phase, focusing on Mg- and Zr-based glass-forming alloys. Mg-based glasses discovered in late 1980's exhibit good glass-forming ability and high specific strength due to their low density. These alloys are also relatively cheap since they do not contain expensive alloying elements. Zr-based amorphous alloys developed in early 1990's are one of the best glass-formers that have large critical thickness (i.e. they can be cast into large components), good thermal stability, high values of strength and toughness.

A number of ex situ and in situ bulk metallic glass (BMG) matrix composites have been fabricated in both the Zr- and Mg-base systems, whereby a large increase in plastic strain has been reported for some compositions. In situ precipitation of a soft primary crystalline phase in glassy matrix during casting appears to be a promising route for generating better plasticity in glassy alloys. However, optimization of alloy chemistry and adjustment of casting conditions are necessary to attain improved mechanical characteristics in new BMG composites. Therefore, the aim of this thesis is to design and fabricate new low-density BMGCs exhibiting high strength as well as reasonable plasticity.

CHAPTER 2 - LITERATURE REVIEW

2.1. OVERVIEW

The first metallic glass¹ discovered in the Au-Si system more than a half century ago [1] has triggering extensive research on glass formation and properties of these materials. The knowledge acquired from the early studies on glassy alloys exhibiting extremely limited glass-forming ability (GFA) and, hence, a very small sample thickness/diameter, was used as a platform for producing amorphous alloys in bulk form. The advent of bulk metallic glasses (BMGs) in 1980s has stimulated numerous fundamental studies into their amorphous nature for understanding structure-property relationships in these materials.

Some representative properties attained so far in BMGs are shown in Fig. 2.1. While BMGs with thickness/diameter ranging from millimetres to a few centimetres have been regularly obtained, the maximum diameter of 80 mm was achieved in Pd-based glass [2]. Pt-based BMGs are on the best performers in terms of mechanical properties with maximum tensile elongations up to 20 % achievable [3]. Excellent hard and soft magnetic properties have been achieved in Nd-based [4] and Fe-based [5] metallic glasses. Extremely high strength has been observed in Co-rich BMGs [6, 7].

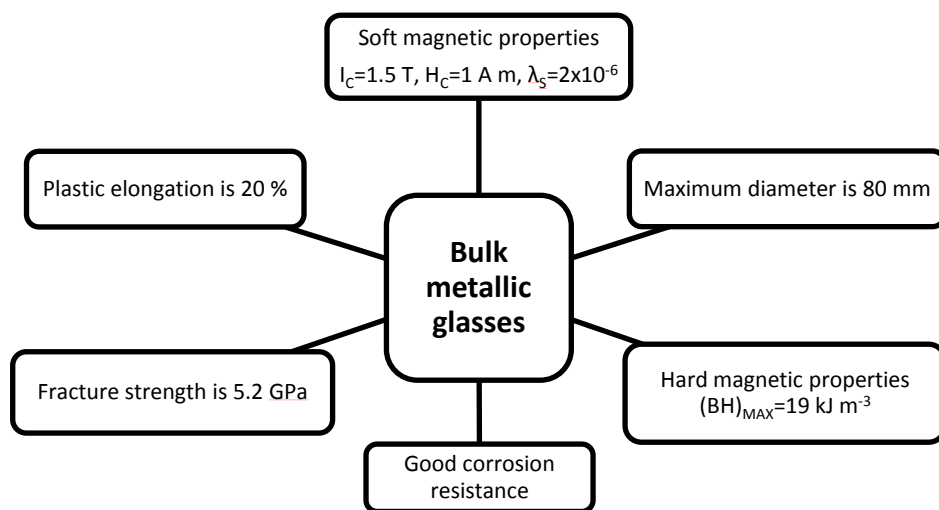


Figure 2.1. Current achievements in some properties of BMGs. Adopted from [8].

¹ A metallic glass is also called a glassy alloy, amorphous alloy etc. In this thesis, ‘metallic glass’ will be used.

Over the past few decades a large variety of metallic glasses have been developed, and various classification schemes currently exist; they can broadly be categorized into metal-metal and metal-metalloid types [9]. Typical metal-metalloid glasses contain roughly 80% of metallic elements and 20% of metalloid atoms (C, B, Si, P). Glasses of metal-metal type have no such compositional restrictions.

In terms of classification by dimension, metallic glasses can be represented as films, ribbons or in bulk form. Generally, metallic glasses with a section thickness or diameter of at least 1 mm are termed bulk metallic glasses (BMGs). These alloys are spawning much interest nowadays due to their practical real and potential applications. A range of typical BMGs reported to date in conjunction with year of production is listed in Table 2.1.

Table 2.1. Typical BMG systems and their year of development.

Alloy type	Year	Ref.
Nonferrous metal based (M=Cu, Zn; TM=Fe, Co, Ni)		
Pd-Cu-Si	1974	[10]
Pt-Ni-P, Au-Si-Ge	1975	[11]
Mg-Ln-M	1988	[12]
Zr-Al-TM	1990	[13]
Zr-Ti-Al-TM	1990	[14]
Ti-Zr-TM-Be	1993	[15]
Pd-Cu-Ni-P	1996	[16]
Ti-Ni-Cu-Sn	1998	[17]
Ca-Mg-(Cu,Ag)	2002	[18]
Mg-Zn-Ca	2005	[19]
Ferrous metal based		
Fe-(Al,Ga)-(P,C,B,Si,Ge)	1995	[20]
Fe-(Zr,Hf,Nb)-B	1996	[21]
Ni-(Nb,Cr,Mo)-(P,B)	1996	[22]

2.2. THEORETICAL PRINCIPLES OF GLASS FORMATION

Metallic glasses are defined as non-crystalline solids with a “frozen-in” liquid structure and produced by the continuous cooling from the liquid state. Upon cooling the atomic mobility in the glass-forming liquid is heavily restrained and, as a consequence, crystallisation is impeded. At the certain temperature, the undercooled melt becomes so viscous that flow of the liquid ceases and its structural configuration “freezes” in a glassy state. The lack of long-range order is the common structural feature of metallic glasses.

Glass-forming ability (GFA) of metallic glasses is a long-standing problem which is not completely resolved in many systems. Understanding the nature of glass formation and GFA is the key for development of new BMGs with improved properties and economic manufacturability for different applications.

The main factors affecting GFA in multicomponent alloy systems are the driving force (thermodynamic factor), diffusivity or viscosity (kinetic factor) and configuration (structure) factor [23].

2.2.1. Thermodynamic aspects of glass formation

From a thermodynamic viewpoint, the glassy state is unstable in regards to the crystalline state. On the other hand, glass is in a condition of internal equilibrium that is attainable when the system has the lowest possible Gibbs free energy compared to those of competing crystalline phases. In other words, in the course of solidification, glass formation will be favoured if the undercooled liquid has a lower free energy than crystalline solid. Therefore, the change of free energy, ΔG , defined by the following expression becomes negative:

$$\Delta G = \Delta H_f - T\Delta S_f \quad (2.1)$$

where ΔH_f and ΔS_f are the enthalpy of fusion and the entropy of fusion, respectively.

Negative difference of Gibbs free energy can be achieved by lowering the enthalpy of fusion or increasing the entropy of fusion. Entropy of fusion is proportional to the number of macroscopic states which, in turn, depends on the number of components in the system [24]. Consequently, an increase in the number of constituent elements in the

alloy promotes larger ΔS_f and higher degree of dense random packing in the liquid state which is favourable for reducing ΔH_f and the solid/liquid interfacial energy. This stands to reason why multicomponent metallic glasses are thermodynamically more stable than their counterparts with less number of components.

The difference in Gibbs free energy between the undercooled melt and competing crystalline phases for various glass-forming alloys is exemplified in Fig. 2.2. The alloys with lower critical cooling rates have smaller values of this free energy difference. This indicates their weak driving force for crystallisation in contrast to the glass-formers produced at higher cooling rates.

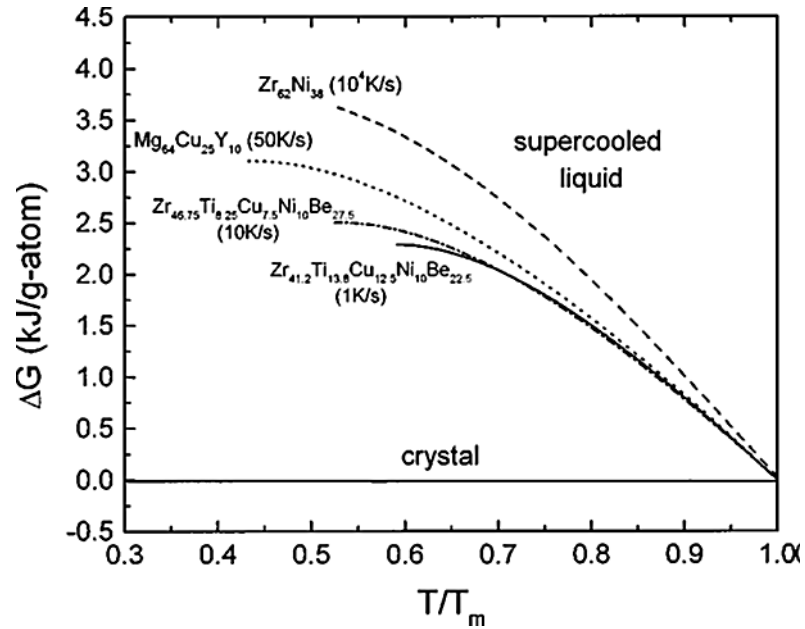


Figure 2.2. Difference of Gibbs free energy between supercooled liquid and crystalline solid for various metallic glass-formers [25].

2.2.2. Kinetic factors affecting GFA

From a kinetics perspective, glass formation can be treated as a process of supercooling from the melt at a rate rapid enough to avoid the nucleation of detectable amount of crystalline phase/s. An important role in this process is the change in viscosity of the cooling liquid. When the liquid is cooled below the melting point, two competing processes occur. On one hand, the change in free energy between the undercooled melt and any competing crystalline phases provides a driving force for crystal nucleation. On the other hand, nucleation is retarded due to the positive interfacial energy associated

with the formation of liquid-crystal interfaces. This creates an energy barrier for nucleation. The resulting nucleation rate of crystals in the undercooled liquid consists of two terms: (i) a thermodynamic factor that depends on the probability of composition fluctuation to surmount a nucleation barrier, and (ii) a kinetic factor that is a function of atomic mobility defined by the viscosity η or diffusivity of the liquid [26]. The rate of nucleation can be expressed as:

$$I = \frac{A}{\eta(T)} \exp\left(\frac{-\Delta G}{k_B T}\right) \quad (2.2)$$

where A is a constant, k_B the Boltzmann constant, ΔG the nucleation barrier defined by $\Delta G = (16/3)\pi\sigma^3/(\Delta g(T))^2$, Δg the Gibbs free energy difference, and σ is the liquid-nuclei interfacial energy.

Depending on the liquid, its viscosity can be described by several different relations [27, 28], including the well-known Vogel-Fulcher-Tamman (VFT) relation [29]:

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T-T_0}\right) \quad (2.3)$$

where η_0 is the high temperature limit of viscosity, D the fragility parameter which identifies stability of the liquid, and T_0 is the VFT temperature at which liquid flow is ceased.

The change in liquid viscosity as a function of temperature reflects the change in atomic mobility upon cooling and can be used to classify glass-forming liquids [29]. “Strong” liquids exhibit Arrhenius-like temperature dependence of viscosity and have large fragility indices D (>20). A liquid is referred as “fragile” if it has low viscosity at the melting point that changes abruptly when approaching the glass transition temperature. Good glass-forming liquids exhibit strong liquid behaviour which is manifested in high viscosity and sluggish kinetics of the supercooled state. Low mobility of the constituent elements inhibits the formation of stable nuclei in the melt and their consequent growth and results in high GFA and thermal stability of the supercooled liquid [23]. Figure 2.3 is the classic figure demonstrating the temperature dependence of viscosity for various glass-forming liquids. Metallic glasses usually fall in the zone between strong liquids such as SiO_2 and the fragile liquids such as o-terphenyl.

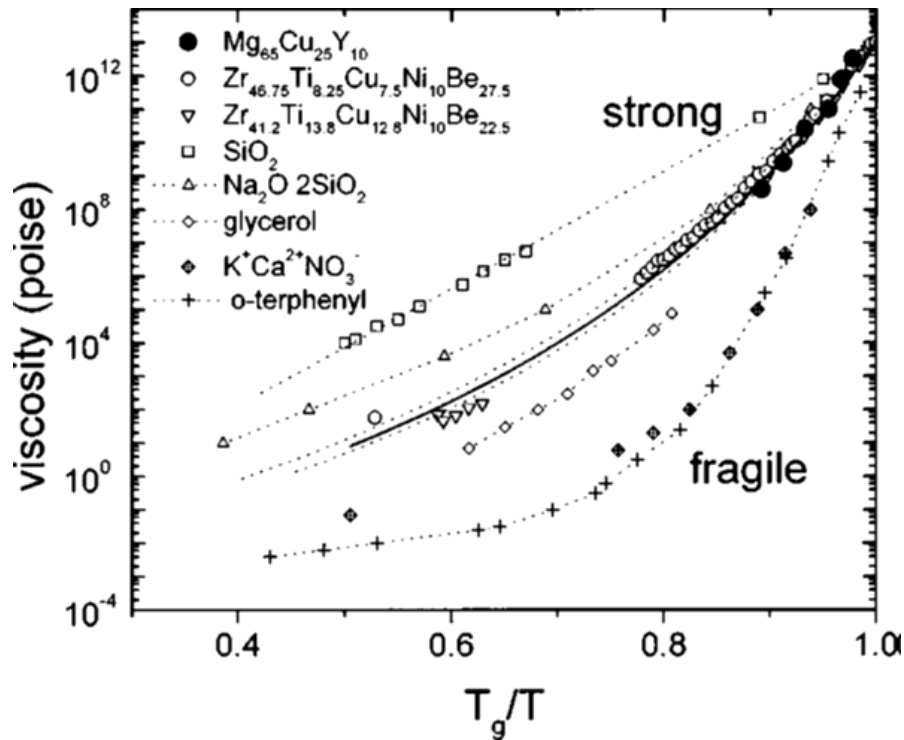


Figure 2.3. Temperature dependence of viscosity for different glass-formers [25].

2.2.3. Synthesis of bulk metallic glasses

The early metallic glasses were produced by rapid solidification techniques such as melt spinning or vapour deposition at extremely high cooling rates of 10^5 - 10^6 K/s. In contrast, production of BMGs does not require such high cooling rates. The two main approaches to produce BMGs include simply cooling the melt to below the glass transition temperature and consolidation of amorphous powders.

One of the simplest techniques is pouring the molten alloy in a metallic (i.e. copper) mould where the average achievable cooling rates are 10-100 K/s; this method is commonly used to fabricate alloys with high GFA [16, 30, 31]. Due to the slow rate of cooling from the melt, the resulting BMG casting usually has a low level of residual stresses.

High pressure die-casting offers higher cooling rates and allows the production of castings with more complex shapes. The concept of this method is to push molten alloy using hydraulic pressure into copper mould. High pressure results in a good contact

between melt and mould, efficient heat transfer between them and excellent surface finish. A range of BMGs have been generated by this method [32, 33].

Suction casting is also used whereby the molten alloy is sucked into a copper mould using pressure difference between melting and casting chambers [34, 35]. The pressure is applied in order to draw the molten alloy into a small die cavity.

Finally, mechanical alloying techniques for the production of BMGs involve application of pressure and/or temperature (hot pressing and warm extrusion) to consolidate amorphous powders in the supercooled liquid region.

2.3. BASIC PARAMETERS DEFINING GLASS-FORMING ABILITY

2.3.1. Cooling rate

To generate the glassy state in a metallic system, the melt must be cooled below the glass transition temperature at a rate higher than the ‘critical’ rate required to suppress crystal nucleation. The critical cooling rate, R_C , in turn, strongly depends on the type of alloy system and chemical composition. The concept of this parameter is elucidated by the time-temperature-transformation (TTT) diagram shown in Fig. 2.4. The classic C-shaped curve represents the time needed to start formation of stable crystalline phase/s at any given temperature. If the melt is cooled at the rate that corresponds to curve 1, then solidification begins at the temperature T_1 and time t_1 with a crystalline solid being the resultant product. However, if the same liquid is cooled at the rate greater than curve 2, it will be in the undercooled state accompanied by the subsequent glass formation. Therefore, curve 2 denotes the critical cooling rate. The critical cooling rate can be determined theoretically within the bounds of theory of isothermal crystallisation kinetics [36, 37].

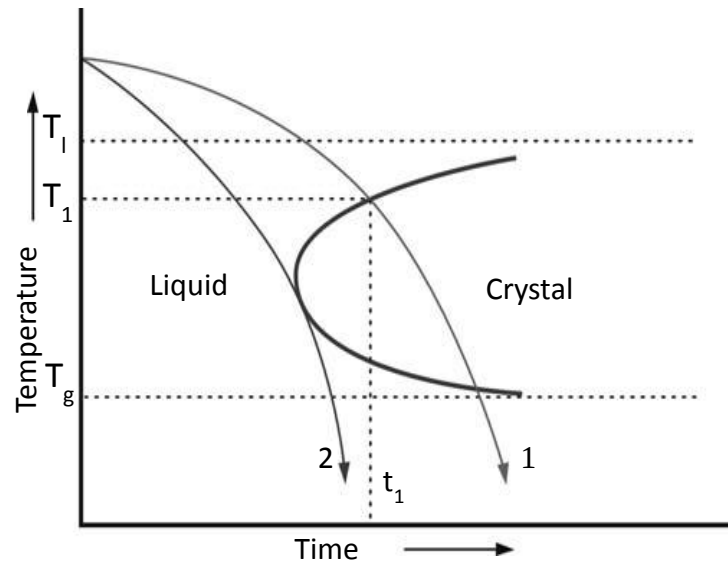


Figure 2.4. Schematic time-temperature-transformation (TTT) diagram.

2.3.2. Reduced glass transition temperature

The concept of reduced glass transition temperature T_{rg} was introduced by Turnbull [26, 38] to substantiate the kinetic reasons of bypassing crystallisation. The viscosity of the undercooled liquid is a fixed parameter at the glass transition temperature. Thus, the high ratio of glass transition temperature T_g to the liquidus temperature T_l indicates high viscosity of the melt and easiness to form glass at the lower cooling rate:

$$T_{rg} = \frac{T_g}{T_l} \quad (2.4)$$

Applying standard nucleation theory, Turnbull suggested that homogeneous nucleation of the crystalline phase is suppressed at $T_{rg} \geq 2/3$.

The principle of reduced glass transition temperature is clearly manifested in the alloy systems with deep eutectic reactions where T_{rg} strongly depends on the composition and has the highest value at the eutectic point. Furthermore, thermodynamically the driving force for the nucleation and growth of crystalline phases is smaller at the eutectic composition relative to the off-eutectic alloys. In eutectic liquids, especially multicomponent systems, several crystalline phases compete for nucleation and growth that, in turn, necessitates significant rearrangement of atoms to form new phases. Thus, the glass formation in eutectic compositions is considered as favourable.

The relationship between the critical cooling rate, reduced glass transition temperature and maximum sample thickness for various metallic glasses is represented in Fig. 2.5. Maximum section thickness is another parameter to estimate GFA. It has been shown to increase with descending critical cooling rate required for the glass formation.

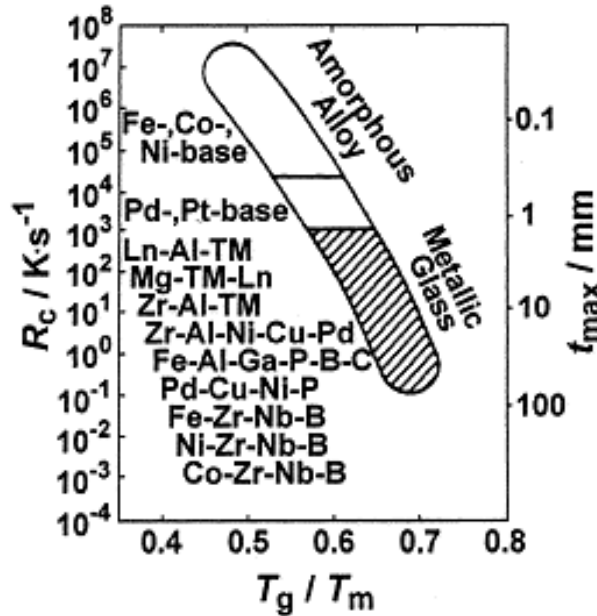


Figure 2.5. Relationship between the critical cooling rate R_c , reduced glass transition temperature T_g/T_m and maximum sample thickness t_{max} [9].

2.3.3. Glass formation criteria for bulk metallic glasses

Based on the vast experimental data on BMGs, Inoue summarized the main empirical criteria [9] responsible for the glass formation in multicomponent BMG systems: (i) alloys must consist of three or more elements; (ii) the difference in atomic size of constituents should be equal or above 12%; (iii) enthalpy of mixing between main components has to be negative. The first rule corroborates Greer's "confusion principle" [39] whereby the larger number of added components destabilizes formation of competing crystalline phases making the undercooled melt more stable. The second principle concerns topological aspect of glass formation. The combination of atoms with significant size mismatch initiates more dense and efficient packing of atoms in the supercooled liquid that is additionally facilitated by the negative enthalpy of mixing between atomic pairs. All these factors stimulate the multicomponent interactions on a short-range scale with creation of new atomic configurations. As such, the surface

energy at the liquid-solid interface increases whereas atomic mobility gets hampered. Ultimately, both these phenomena contribute to enhanced GFA.

2.4. MECHANICAL PROPERTIES OF MONOLITHIC BMGS

The mechanical behaviour of BMGs such as strength, hardness, wear and corrosion resistance are often superior to their crystalline counterparts [7, 40-43] and closely related to the physical and chemical characteristics of constituent elements in conjunction with history of thermal treatment [44]. Figure 2.6 shows the correlation between tensile strength/Vickers hardness and Young's modulus for conventional crystalline alloys and BMGs. Tensile strength and hardness for BMGs clearly outperform those for crystalline alloys and exhibit an almost linear relation with Young's modulus. The substantial difference in mechanical performance between BMGs and crystalline alloys is attributed to their different deformation and fracture mechanisms. However, in contrast to crystalline materials, the correlation between mechanical behaviour of metallic glasses and their atomic and electronic structures is not well understood [45].

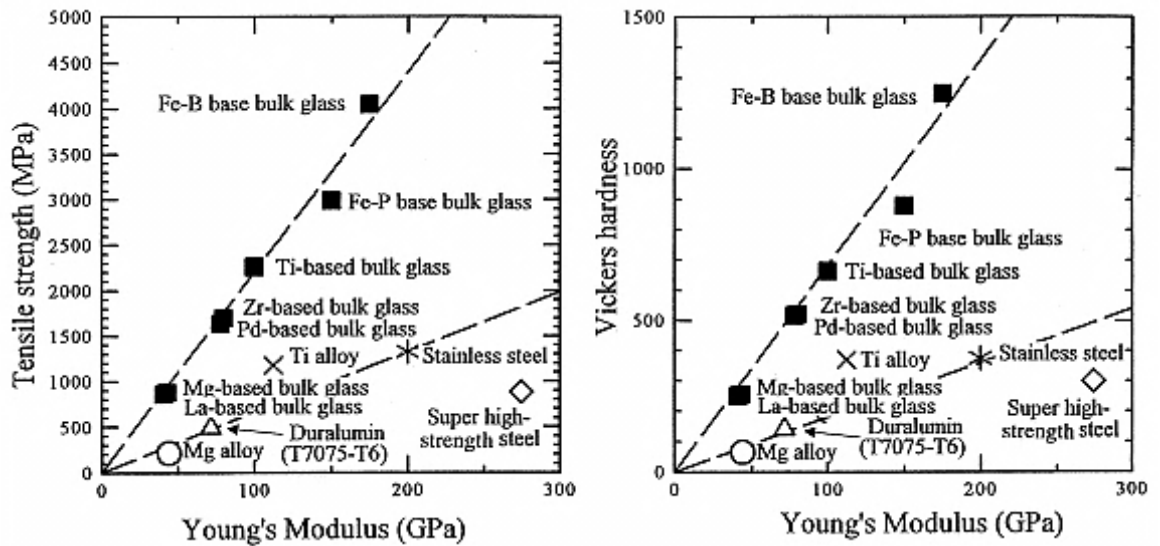


Figure 2.6. Correlation between tensile strength and Vickers hardness versus Young's modulus for crystalline alloys and BMGs [46].

2.4.1. Deformation mechanism in BMGs

It is well-known that deformation of a metallic glass below T_g occurs in an inhomogeneous manner through the formation of highly localized shear bands. Though the exact mechanism of local atomic motion in deforming non-crystalline alloys is not firmly established, a fundamental concept considers deformation as the accommodation of shear strain by the local rearrangement of atoms. A number of theories describing the deformation behaviour of metallic glasses have been elaborated [47-50], including two most popular models of Argon [51] and Spaepen [52].

In Argon's model, the accommodation of local strains occurs through operation of shear transformation zones (STZ) which were introduced as fundamental units of plasticity during deformation [51]. The STZ is defined as a cluster of randomly dense-packed atoms that can be inelastically distorted and rearranged in order to accommodate strain [42]. This is schematically illustrated in Fig. 2.7(a) where the upper layer of atoms moves with respect to the lower layer creating shear displacement and accommodating the applied shear stress. It has also been noted that STZ in the glass is not a structural feature or defect similar to the lattice dislocation in crystals, but rather a transient event confined in a local volume [42].

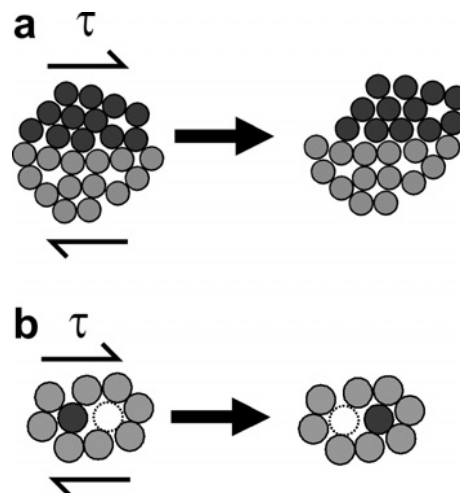


Figure 2.7. Schematic illustration of deformation mechanisms according to different models based on: (a) shear transformation zones; (b) “free-volume” concept. (Reproduced from [42]).

Alternatively, the deformation response of a metallic glass in Spaepen's model [52] is based on the “free volume” concept [53]. Free volume can be defined as empty space between the sites occupied by dense atomic clusters [54]. This model describes the

deformation event in the glassy structure as a series of local atomic jumps that are apparently favoured near the regions of large free volume. The process of atomic jumps to a vacancy in the structure is schematically depicted in Fig. 2.7(b).

It has been mentioned earlier that shear banding in the volume of metallic glasses is a distinctive characteristic of their inhomogeneous deformation. Shear bands were shown to originate from phenomena of strain softening when the increment of applied strain makes material softer allowing it to be further deformed. A number of different reasons were suggested to explain the occurrence of strain softening. These include formation of free volume due to flow dilatation, local change in structural order associated with STZ operation, redistribution of internal stresses and local adiabatic heating [42]. While the exact cause of strain softening can vary in different types of metallic glasses and depend on loading conditions, it is generally believed that the main contributor to shear band localization is a local increment of free volume or local evolution of structural order.

2.4.2. Strength and ductility of monolithic bulk metallic glasses

High strength, which in some cases approach theoretical limits, is a distinctive feature of BMGs (see Fig. 2.6). Earlier it was suggested that shear strength in metallic glasses should be close to the strength of ideal dislocation-free crystals with the order of $\sim 0.1 G$, where G is the shear modulus [44, 55]. However, experimentally determined strength values in metallic glasses are few times smaller than theoretically predicted values [9]. For instance, fracture strength of 5.5 GPa for Co-based, 4 GPa for Fe-based, 3 GPa for Ni-based and 2 GPa for Zr- and Cu-based BMGs has been reported [56, 57].

The fracture strength of a BMG is associated with the strength of its atomic bonds [44]. Therefore, it is reasonable to deduce that the strength of metallic glasses is related to the physical characteristics controlled by cohesive atomic energy such as glass transition temperature, elastic moduli and coefficient of thermal expansion. The correlation between strength and glass transition temperature determined experimentally for a variety of BMG systems was established in Yang's work [58] and represented in Fig. 2.8. The overall trend shows that increment of T_g and reduction of molar volume results in stronger BMGs.

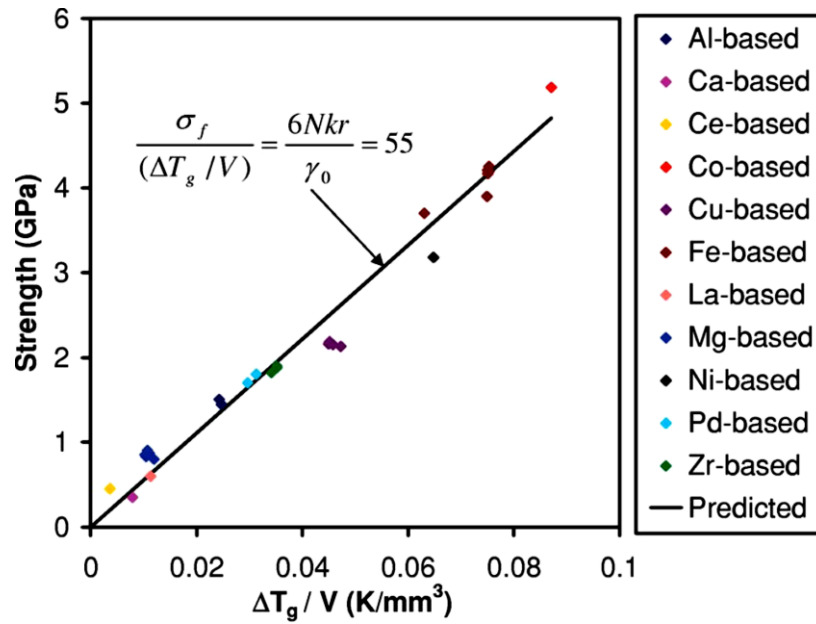


Figure 2.8. Relationship between fracture strength, glass transition temperature and molar volume (reproduced from [58]).

Despite monolithic BMGs possessing high strength, most have a significant drawback – brittleness and subsequent catastrophic failure under loading in tension or compression. BMGs therefore do not usually exhibit much macroscopic plasticity. However, pronounced global plasticity in bending and compression has been observed in Pt-based BMGs [3]. Compressive strain to failure of 20 % (Fig. 2.9(a)) and strain to failure of 3 % during bending has been reached which is not typical of metallic glasses.

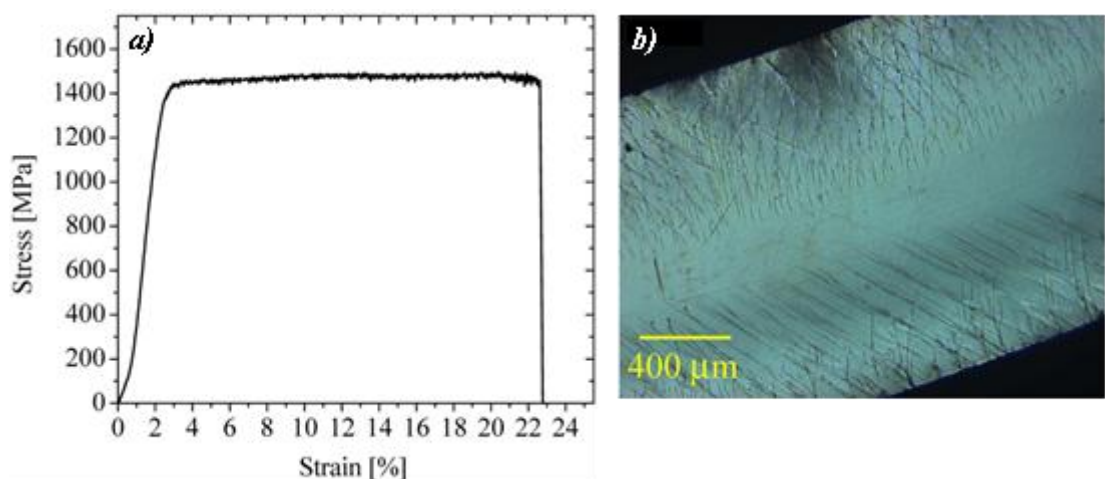


Figure 2.9. Behaviour of monolithic glass Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} in compression and bending: (a) compressive stress-strain curve; (b) formation of shear bands in BMG bent over a mandrel of 9.5 mm radius that corresponds to ~9 % of strain. Reproduced from [3].

Large plasticity was attributed to the formation of multiple shear bands shown in Fig. 2.9(b). The low ratio of shear modulus to bulk modulus (or high Poisson's ratio) in conjunction with a low glass transition temperature is argued to be an indicator of ductile nature of Pt-based metallic glass.

Minor additions of certain elements into the glass-forming alloy may significantly alter the mechanical properties of material [59]. For example, “work-hardenable” metallic glasses have been produced in the Cu-Zr-based system [60, 61]. Introduction of small amount of Al into the binary $\text{Cu}_{50}\text{Zr}_{50}$ glassy alloy resulted in a strength of up to 2.26 GPa and large ductility of 18% under compressive load. Recent Pauly's research [62] has revealed the transformation-mediated mechanism of high ductility in the Cu-Zr-based BMG. Tensile deformation of Cu-Zr-based glassy structure induces the polymorphic precipitation of nanocrystals that undergo subsequent twinning and therefore absorb stresses of surrounding glassy matrix. Such structural inhomogeneities impede shear bands formation thereby promoting the macroscopic plastic strain.

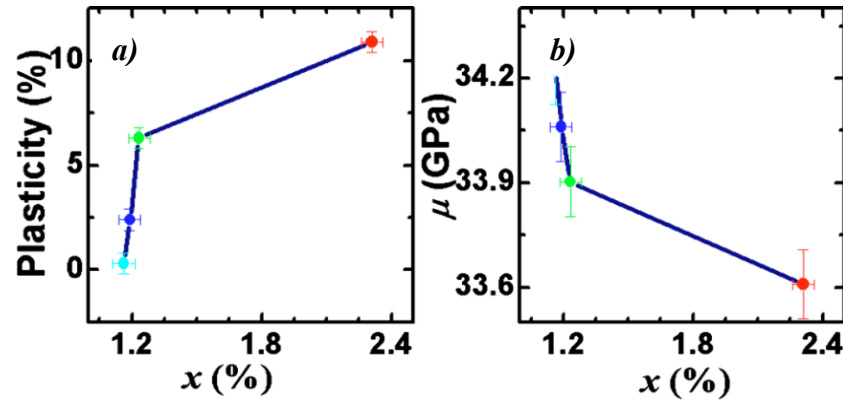


Figure 2.10. Plasticity (a) and shear modulus (b) of monolithic $\text{Zr}_{56}\text{Co}_{28}\text{Al}_{16}$ BMG as a function of free volume content. Reproduced from [63].

The correlation between large plasticity in monolithic metallic glasses and free volume in the glass structure has been investigated by Tan *et al.* [63]. By altering cooling rates in the course of melt solidification, samples with different density were produced.

Estimation of quenched-in free volume was made by comparison with the density of crystallized alloys. As seen in Fig. 2.10(a), the higher plasticity in compression is associated with the larger value of free volume. Greater amount of free volume causes softening of elastic modulus due to increasing atomic spacing and weakening atomic bonding forces. This is confirmed by the decrease in shear modulus with the increment of free volume represented in Fig. 2.10(b). The fact that cooling rate can improve plasticity of a metallic glass has been confirmed in many studies (e.g. [64]) although in bulk samples the use of this strategy is quite limited.

Based on the free volume concept, the modelling of shear banding behaviour in metallic glasses has been undertaken by Chen *et al.* [65]. Results of simulations have confirmed, as anticipated, that larger free volume decreases stresses required to initiate shear band formation. Furthermore, it has been noted that not only overall amount of free volume plays a role in ductility change but, also, its spatial distribution in the glass structure. Non-uniform distribution of free volume promotes multiplication of shear bands. It has been concluded that yield strength is affected by the amount of free volume whereas plasticity depends on the distribution.

It is worth noting that an important parameter affecting measurements of ductility in metallic glasses is sample size. In a major study [66], it was shown that specimen size can alter deformation behaviour: large samples failed catastrophically through one shear band while smaller specimens had stable shear band propagation and exhibited significant plastic deformation. Size-dependence of plastic deformation was also confirmed by Wu *et al.* [67] where samples with completely identical chemistry and structure exhibited brittle or ductile behaviour depending on their size. Transition from ductile to brittle mode was explained by the concept of critical shear offset [68] and energy density of shear fracture surface [67].

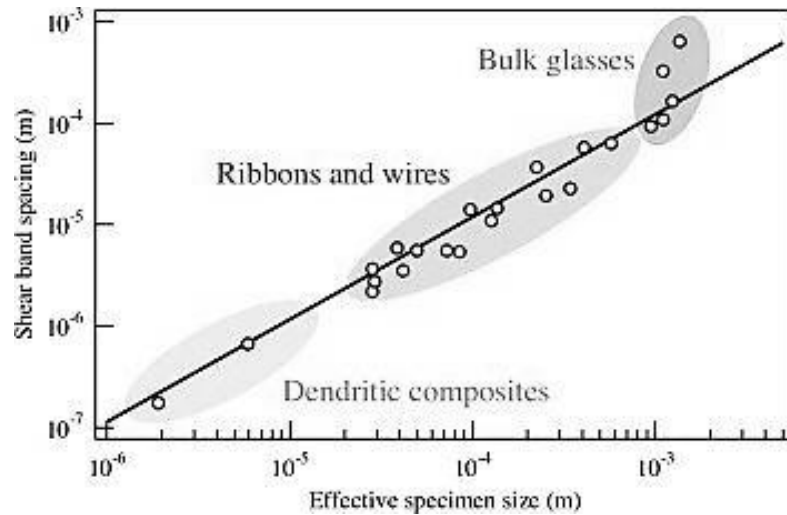


Figure 2.11. Size of shear band spacing as a function of sample dimensions for various metallic glasses deformed under constrained loading. Reproduced from [69].

The direct relation between size of shear band spacing and characteristic sample size (represented in Fig. 2.11) has been noted by Conner [69]. This geometrical size effect results in a scale-dependant fracture strain for glassy alloys during bending when thinner samples can be bent to the higher plastic strains and thicker specimens fail in brittle mode.

2.4.3. Toughness and fracture characteristics of BMGs

Most metallic glasses are considered to be brittle materials for several reasons. They do not have a strain hardening mechanism as well as any barriers to restrict crack propagation (such as grain boundaries). Furthermore, the mechanism to alleviate high stress concentrations at a crack tip is absent. These facts show the low level of toughness in metallic glasses (though some have toughness comparable with the crystalline alloys). In general, reported strength-toughness experimental data for metallic glasses lie between those for marginally tough alloys and brittle ceramics [40, 70]. Toughness is associated with the ability of material to control energy concentrated at the crack tip by dissipating it through different nonlinear processes [42]. Concentration of all elastic strain energy in small deforming area at the crack tip results in the catastrophic brittle fracture. Broadly speaking, bluntness or sharpness of the crack tip is defined by two competing processes of dilatational fracture and shear flow [71].

A rough indicator of toughness in metallic glasses is a scale of fracture pattern on the fracture surface. Deep vein morphology corresponds to the “tough” glassy structure (Fig. 2.12(a)) whereas shallow vein patterns are related to the “brittle” glasses (Fig. 2.12(b)).

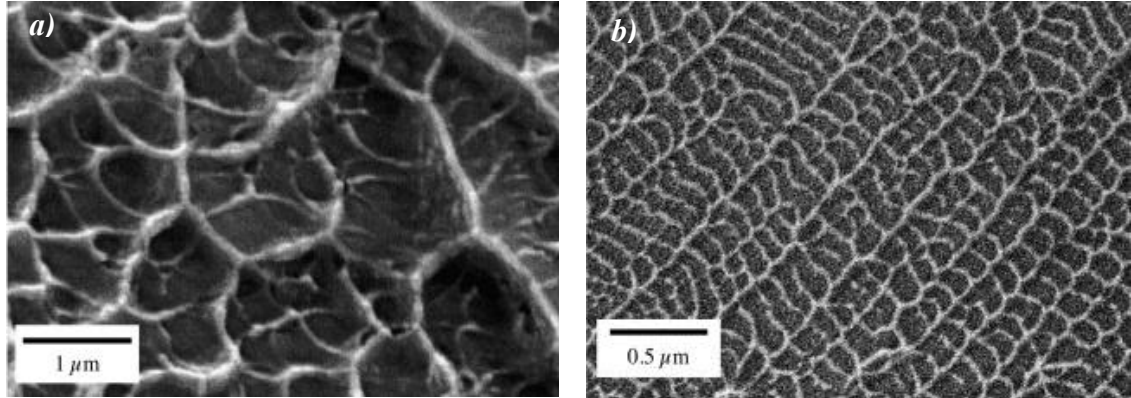


Figure 2.12. Fracture surface of $\text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Ni}_5\text{Co}_5$ metallic glass: (a) fracture from “ductile” sample; (b) smooth fracture from nominally “brittle” sample. Reproduced from [72].

A relationship between fracture toughness K_C , yield strength σ_y and size of plastic zone r_p determined from the fracture pattern of metallic glass have been shown by Xi [73]:

$$r_p = \frac{1}{6\pi} \left(\frac{K_C}{\sigma_y} \right)^2 \quad (2.5)$$

Xi *et al.* noted that toughness of metallic glasses depends on the scale of plastic zone and it is not sensitive to the fracture mechanism [73].

An impressive toughness-strength ratio beyond the typical limits for metallic glasses was originally reported in monolithic Pd-rich BMGs [74], with recent work on Zr-based BMGs showing similar behaviour [75]. In situ fracture toughness tests revealed that, at the opening crack tip, the process of plastic flow is stabilized by formation of distributed damage zone with significant plastic shielding, as shown in Fig.2.13.

The value of toughness of $\sim 200 \text{ MPa m}^{1/2}$ attained in the $\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_6\text{Si}_{9.5}\text{Ge}_2$ metallic glass is comparable to the values for ultra-tough steels [74].

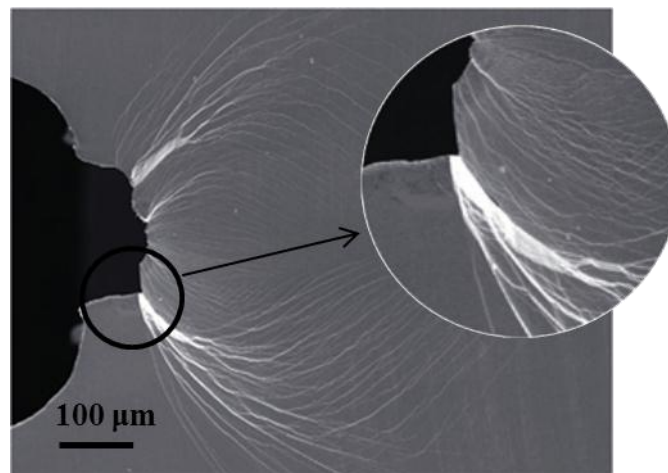


Figure 2.13. Deformed notch in a $\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_6\text{Si}_{9.5}\text{Ge}_2$ glassy sample with extensive plastic shielding of initially sharp crack; inset shows a $50\ \mu\text{m}$ shear offset formed during plastic sliding before the onset of crack opening. Reproduced from [74].

Deformation and fracture mechanisms of BMGs are quite different to those observed in crystalline metals. As noted earlier, deformation in metallic glasses occurs inhomogeneously through formation and propagation of shear bands and fracture surfaces typically show vein patterns. During fracture, a significant amount of shear is concentrated in the shear bands and release of energy is accompanied by the temperature rise that could result in local softening or melting. As a consequence, viscosity of metallic glass in the shear band decreases and the vein pattern on the fractured surface can be represented as a structure created when pulling apart two glass slides with a viscous fluid between them. Typical morphology of BMG fracture surface can include “veins”-like and “river”-like patterns, periodic corrugations, dimples, or featureless smooth zones [76].

Commonly, fracture surfaces of metallic glasses formed during compressive and tensile loading are different from each other since they reflect different fracture mechanisms [77]. As shown in Fig. 2.14(a), the typical compressive fracture surface is characterized by the smooth surface with the uniform vein-like structures arranged in the direction of shear band propagation thereby representing pure shear fracture process. The tensile fracture surface features a mixture of veins-patterned and radiating core structures (Fig. 2.14(b)). Radiating cores are created by normal tensile stress at the initial stage of fracture whereas veins are formed during the process of shear band propagation [77].

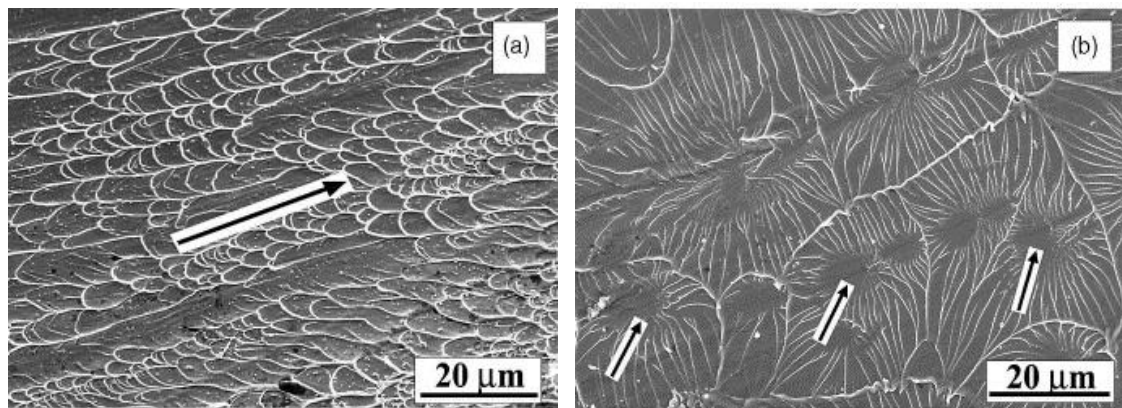


Figure 2.14. Fracture surfaces in $\text{Zr}_{59}\text{Cu}_{20}\text{Al}_{10}\text{Ni}_8\text{Ti}_3$ metallic glass formed during: a) compressive load; b) tensile load. Reproduced from [77].

2.5. FEATURES OF COMPOSITES BASED ON BULK METALLIC GLASSES

The problem of limited plasticity in monolithic BMGs has stimulated the development of the BMG composites (BMGCs). Glass-crystal composite structure is anticipated to have two main functions. The first one is to initiate formation of larger number of shear bands in order to distribute plastic strain macroscopically over the volume of material. The second function is to inhibit rapid shear band propagation, thereby delaying the fracture of material.

2.5.1. Classification of BMG composites

There are several ways to produce BMGCs with a heterogeneous microstructure consisting of a glassy phase and crystalline precipitates: (i) introduction of crystalline particulates to the melt prior to the casting process [78-82]; (ii) formation of crystalline phase/s directly during casting while the remaining melt forms a glass [83-85]; (iii) partial devitrification of the metallic glass during heat treatment [86-88].

Composite materials produced by the first approach are termed *ex situ* BMGCs. Crystalline phase is added separately to the glass-forming melt which is subsequently cast into the composite. Sometimes the melt can be infiltrated into a preform of fibres and particles [89] or one could make a glass-crystalline laminates [90, 91]. Wide selection of reinforcement has been used in *ex situ* techniques such as particulates of W,

WC, Ni, Ta, Mo, Nb, SiC, steel wires, oxide particles, continuous and discontinuous fibres [92-94].

To produce the second type of composites, namely intrinsic or *in situ* BMGCs, a special adjustment of alloy chemistry is required. Deviation of the composition from the actual glass-forming range and solidification conditions predetermine formation of the crystalline phase and its volume fraction. In situ composites are commonly produced in a single processing step. Crystalline phases coexisting with glassy matrix can be represented as dendrites, nano- or micro-sized globules. Figure 2.15 schematically illustrates a range of microstructures that can be formed in the in situ composites.

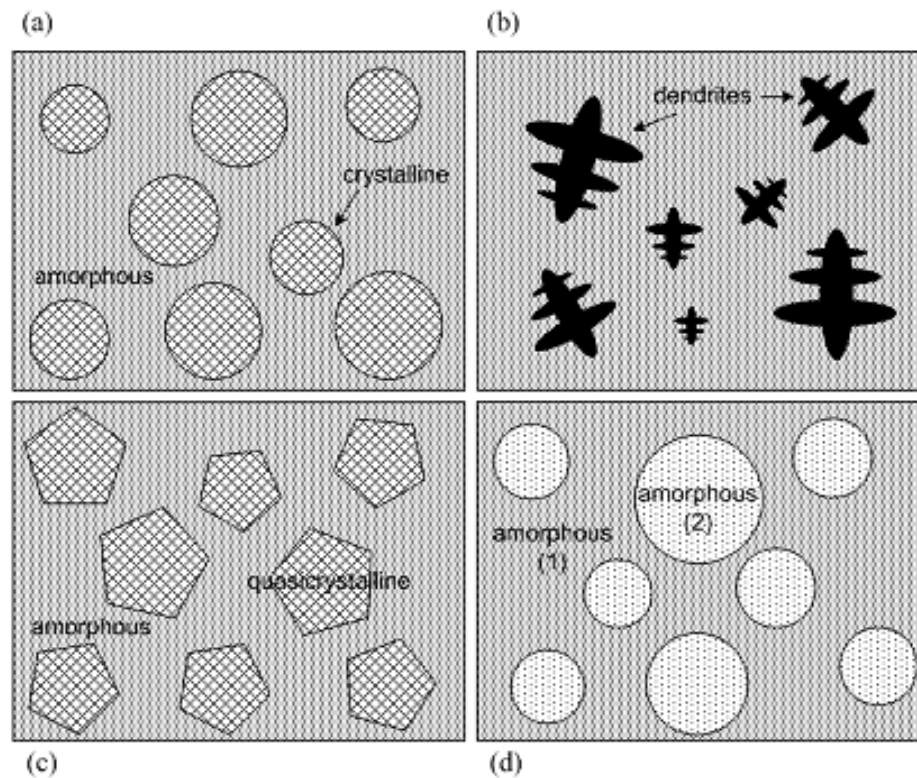


Figure 2.15. Typical microstructure observed in the in situ BMG composites: (a) spherical nano- or micro-scaled crystallites; (b) dendritic phase; (c) quasicrystalline phase; (d) two amorphous phases. Reproduced from [95].

Composites from the third group produced by partial crystallisation can be categorized either as in situ or ex situ types depending on the classification criteria. A precursory glassy alloy is required to be partially devitrified by subsequent processing. This

treatment can include annealing or hot working above the glass transition temperature thereby promoting crystallisation of nano- or micro-scaled phases. Crystallisation does not offer a large variety of dispersed phases in contrast to ex situ methods and usually causes embrittlement of the structure. Instead, it gives even distribution of crystalline phases, control over their size and well-bonded glass-crystal interfaces.

A generalized classification of BMGCs developed by Eckert *et al.* [95] is represented in Fig. 2.16.

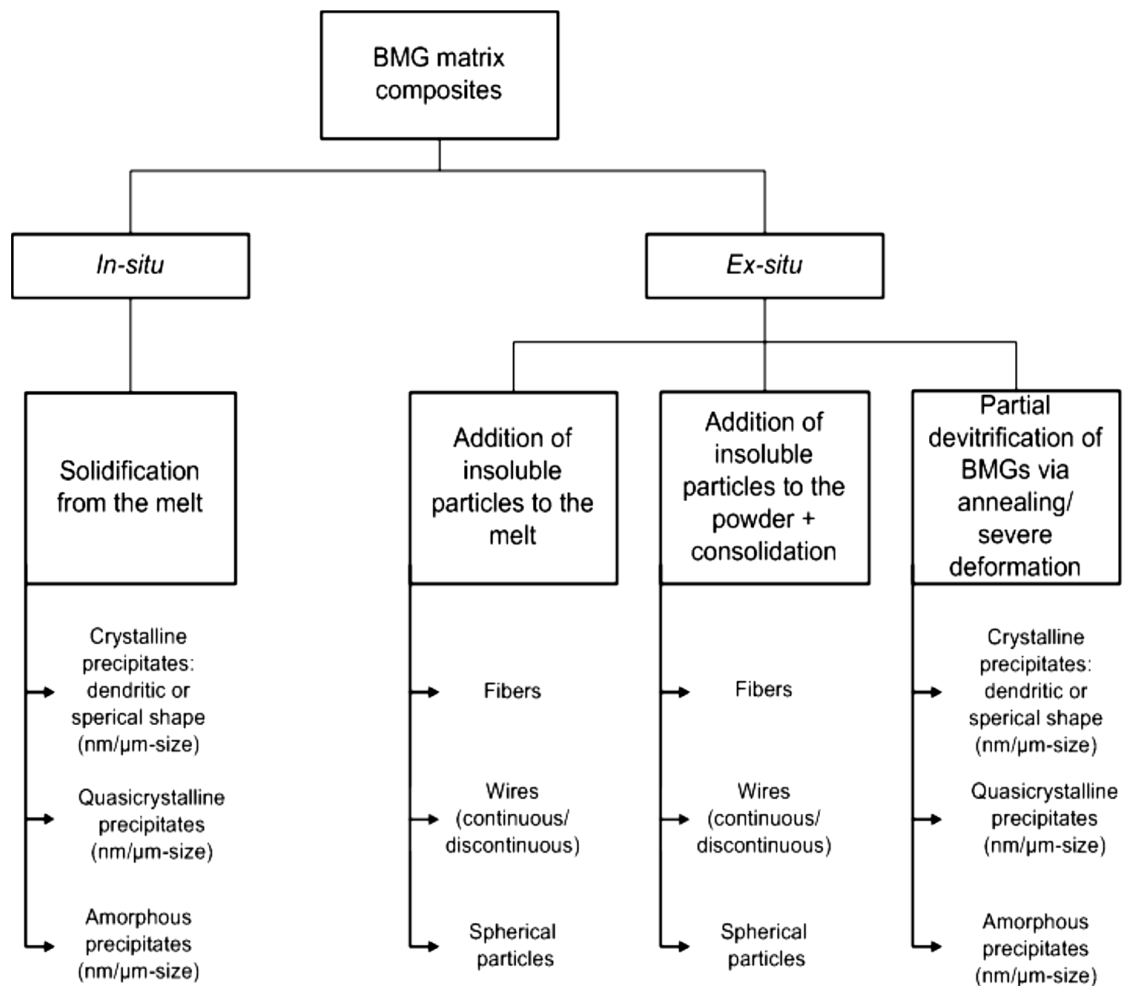


Figure 2.16. Classification of bulk metallic glass composites based on their processing routes. Reproduced from [95].

Bearing in mind that different types of the composites have particulates of diverse nature, it is reasonable to acknowledge their different impact on the mechanical characteristics of the resultant composite structure. Based on the broad analysis of experimental data, Schuh *et al.* [42] have shown how various reinforcing dispersions and their volume fraction can affect strength in BMGCs. This is illustrated in Fig. 2.17 where normalized values of yield stress and flow stress are represented as a function of volume fraction of crystalline phase. The mechanical response of BMGCs remains practically unchanged for the low volume fraction of reinforcing phase when the resultant strength follows a rule of mixtures for constituent phases:

$$\sigma_c = V_{cr}\sigma_{cr} + (1 - V_{cr})\sigma_{am} \quad (2.6)$$

where σ_c , σ_{cr} and σ_{am} are the values of strength for the composite, crystalline reinforcement and amorphous matrix, respectively, and V_{cr} is the volume fraction of crystals.

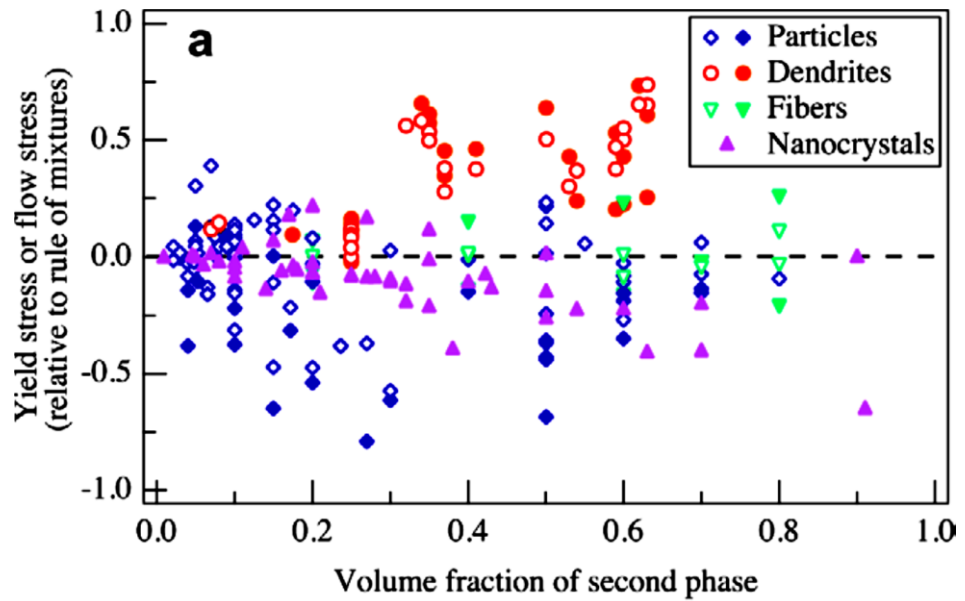


Figure 2.17. Correlation between normalized yield stress, type and volume fraction of reinforcing phase in BMG composites. Reproduced from [42].

At larger volume fractions, the mechanical behaviour depends on the type of crystalline inclusions. Data for dendritic composites are mostly distributed above the rule-of-mixture line indicating that dendrites are more effective in blocking macroscopic plastic deformation.

Thus, mechanical properties of BMGCs are related to the elastic properties of the reinforcing phase (rule of mixtures) [95]. Furthermore, their deformation and fracture behaviour is controlled by the shape, size and the volume fraction of precipitates in conjunction with the characteristics of interface between the amorphous and reinforcing phases [96-98]. Good wettability between the glassy matrix and precipitates yields strong bonding at the interface and promotes optimized stress transfer between two phases [89]. BMG composites produced by ex situ routes commonly have weaker bonding between the matrix and crystalline phase relative to the in situ formed composites [82, 99, 100].

2.5.2. Ex situ BMG composites

Extrinsic BMG composites were first produced by Choi-Yim *et al.* [79] who demonstrated that Zr- and Cu-based BMGs could be processed with external reinforcements. In most cases reinforcing dispersions do not react or react negligibly with the glass-former. Interaction between glassy matrix and particulates can be easier restricted if glass-forming systems have low melting temperatures. However, occasionally, reaction products can be found at the matrix-particle interface. For instance, as seen in Fig. 2.18(a), formation of intermetallic W_5Zr_3 occurs on the surface of W fibre dispersed in $Zr_{55}Al_{10}Ni_5Cu_{30}$ matrix. Alteration of composition by addition of Nb, Ta and Be yields cohesive interface without any matrix reaction products with the same reinforcing fibres (Fig. 2.18(b)).

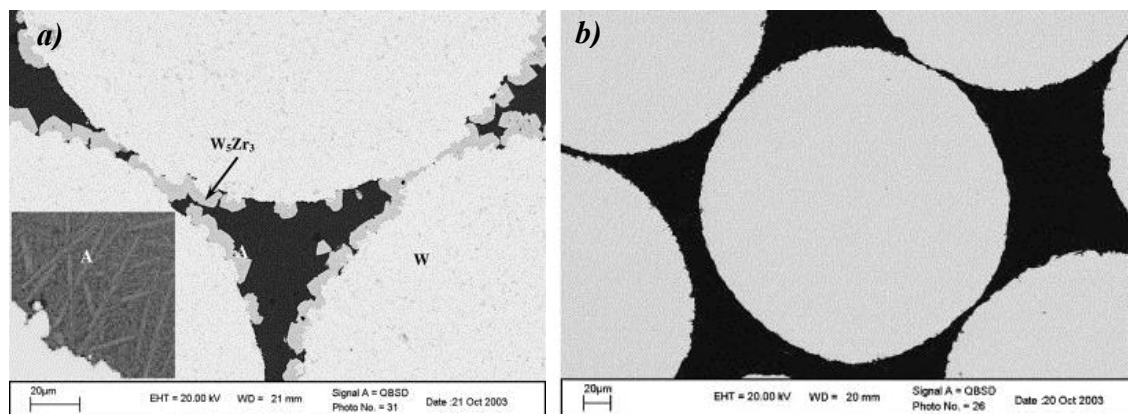


Figure 2.18. Interface between reinforcing W fibre and Zr-based glassy matrix: (a) $Zr_{55}Al_{10}Ni_5Cu_{30}$ matrix; (b) $Zr_{47}Ti_{13}Cu_{11}Ni_{10}Be_{16}Nb_3$ matrix [101].

Zr-based glass-formers have been studied extensively as matrices for extrinsic composites. Alloys of Vitreloy group (Zr-Nb-Cu-Ni-Al) that exhibit good resistance to heterogeneous nucleation were reinforced by SiC, WC, Ta and Mo particles [82]. It was shown that addition of particulates caused significant increment in plastic strain to failure from 0.5 % to 7 % in conjunction with noticeable toughening effect. Likewise, results were observed in Zr-Ti-Cu-Ni-Be alloys with introduced W and steel wires [89]. The reinforcement was found to impede shear band propagation and simultaneously promote creation of multiple shear bands. The blocking of shear band propagation by a W particle in Vitreloy106 matrix is illustrated in Fig. 2.19. The size of the vein-like pattern in front of the particle is reduced indicating a slowdown of material flow [82].

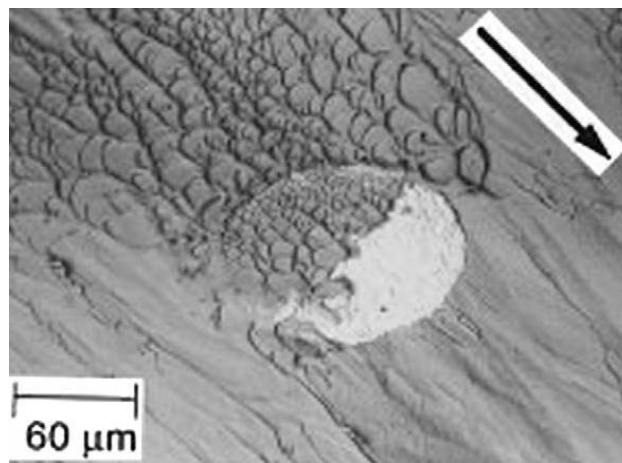


Figure 2.19. Compressive fracture surface of Vitreloy106 glass reinforced by W particles [82].

The large difference in the coefficient of thermal expansion between glass and particles may cause significant thermal mismatch strains during cooling and solidification of the composite [82]. For instance, the residual stress of ~480 MPa was estimated in Zr-based matrix due to mismatch of thermal expansion coefficients between W fibres and glassy matrix [102].

Another factor that may affect mechanical performance of extrinsic composites is the elastic modulus of constituent phases. Using in situ synchrotron X-ray irradiation, Balch *et al.* studied strains and load transfer between Zr-based glassy matrix and W/Ta particles [103]. It was found that, at low level of applied external load, both phases deform elastically while reinforcing particles unload elastic matrix. When particles enter

plastic deformation mode, the efficiency of load transfer is significantly reduced. At high applied stresses plastically deformed particles increase load on the matrix thereby localizing stresses near matrix-particle interface and initiating shear banding in the matrix and subsequent failure. Therefore, the enhanced strength and ductility of ex situ BMG composites is likely due to efficient load transfer to the reinforcing particles that have higher stiffness than the matrix or blocking shear bands by ductile particles [100, 104, 105]. Example of using hard particles in the matrix with relatively low strength has been shown recently [98] where TiB_2 particles were introduced into Mg-based monolithic glass. Substantial difference between the elastic modulus of TiB_2 (529 GPa) and the Mg-glassy matrix (50–70 GPa) resulted in a large elastic strain mismatch during loading, thereby generating stress concentrations favourable for shear band initiation at the interface between matrix and reinforcement particles. As a consequence, plastic strain to failure and compressive fracture strength of the composite increased almost twice compared with the monolithic glass (Table 2.2).

However, significant improvement in plastic properties of ex situ BMG composites is usually accompanied by a reduction in the yield strength compared to the monolithic BMGs. Given that the fabrication of ex situ BMG composites is generally a multi-step processing route, unwanted interfacial reactions between the melt and reinforcing particulates may occur, thereby resulting in a composite with inferior properties.

Overall, the improvements in mechanical properties of ex situ BMG composites, especially in the ductility and toughness have been quite significant. Typical examples of ex situ BMG composites and the corresponding initial monolithic glasses used as matrix materials are represented in Table 2.2.

Table 2.2. Improvement in fracture strength σ_f and plastic strain to failure ε_p achieved in ex situ BMG composites.

Alloy	Reinforcement	σ_f , MPa	ε_p , %	Ref.
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₁₀	Monolithic glass	750	~3	[81]
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₁₀	Ta	1200	40	[81]
Mg ₆₅ Cu ₂₀ Ag ₅ Gd ₁₀	Monolithic glass	830	0	[92]
Mg ₆₅ Cu ₂₀ Ag ₅ Gd ₁₀ +Nb	Nb	900	12.1	[92]
Zr ₅₇ Nb ₅ Al ₁₀ Cu _{15.4} Ni _{12.6}	Mo wires	1200	20	[93]
Zr ₅₇ Nb ₅ Al ₁₀ Cu _{15.4} Ni _{12.6}	Ta wires	550	27	[93]
Zr _{52.5} Cu _{17.9} Ni _{14.6} Al ₁₀ Ti ₅	Monolithic glass	1900	3	[94]
Zr _{52.5} Cu _{17.9} Ni _{14.6} Al ₁₀ Ti ₅	Graphite	1700	15	[94]
Zr _{41.25} Ti _{13.75} Cu _{12.5} Ni ₁₀ Be _{22.5}	Monolithic glass	2000	<0.5	[89]
Zr _{41.25} Ti _{13.75} Cu _{12.5} Ni ₁₀ Be _{22.5}	W	2100	16	[89]
Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₁₀	Monolithic glass	570	1.7	[98]
Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₁₀	TiB ₂	1200	3.2	[98]
Mg ₆₅ Cu ₂₅ Gd ₁₀	Monolithic glass	850	0	[78]
Mg ₆₅ Cu ₂₅ Gd ₁₀	Ti powder	900	40	[78]
Mg ₅₈ Cu _{28.5} Gd ₁₁ Ag _{2.5}	Monolithic glass	850	2	[106]
Mg ₅₈ Cu _{28.5} Gd ₁₁ Ag _{2.5}	Porous Mo particles	1200	14	[106]
Mg ₅₈ Cu _{28.5} Gd ₁₁ Ag _{2.5}	Fe	950	8	[107]

2.5.3. In situ BMG composites

Broadly speaking, the main aim of in situ formation of crystalline phases in the glassy matrix is to enhance macroscopic plastic strain. This can be achieved by introducing structural heterogeneities such as nanocrystalline phases or micron-sized crystallites.

The formation of nano-scaled dispersions can be induced by partial crystallisation during solidification [108], heat treatment [86, 109], in situ reactions [110] or deformation [31, 111]. Inoue's group developed and characterized a number of in situ nanostructured composites in Zr-based systems produced both by annealing and directly

during cooling [108]. Structural features and resulting mechanical characteristics of Zr-based composites with a wide range of volume fraction of nano-scaled reinforcement are summarized in Fig. 2.20.

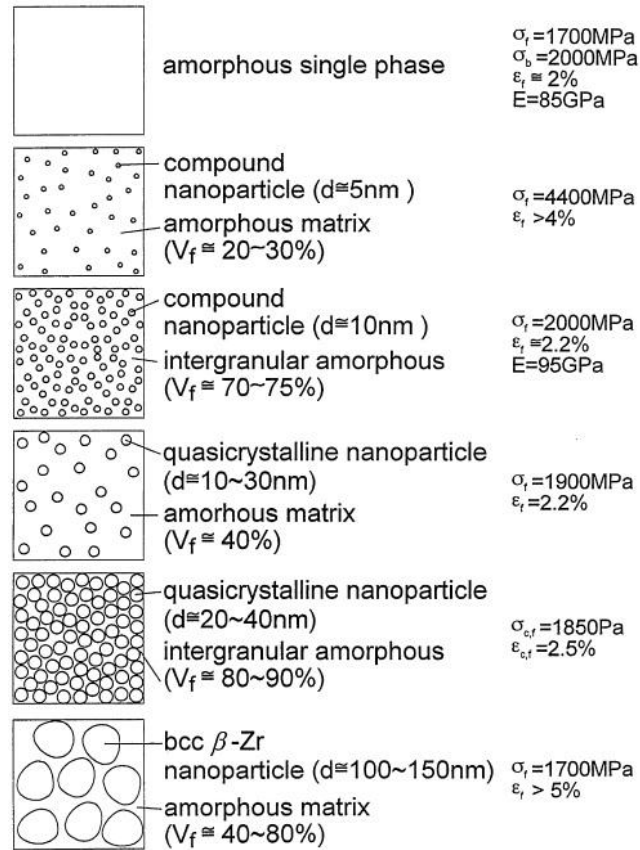


Figure 2.20. Schematic structure and mechanical properties of nano-scaled BMG composites in Zr-Al-Ni-Cu and Zr-Al-Ni-Cu-M systems, M = Ag, Pd, Au, Pt, Nb. Reproduced from [112].

As seen, the composites with nano-sized or quasicrystalline particles exhibit higher values of strength and plastic strain in comparison with the monolithic glassy alloys. However, plastic strain in compression does not seem to be increased more than 3-4% [86].

It has been argued that dispersions on a fine scale act similar to large-scale ex situ particulates blocking and promoting shear bands proliferation in the glassy matrix [109, 113]. In contrast, in the work [114] it is speculated that nanometre-scale crystals are unlikely to behave in such a way due to their sizes which may be smaller than the thickness of shear bands. Some authors suggest that nanodispersions cause the glassy

matrix to flow in a manner similar to the semi-solid slurry [111]. In this case, flow stress can be increased with possible reduction of shear softening in the shear bands thereby decreasing the chance of failure in one or few shear bands.

One of the effective in situ composite structures is a structure consisting of glass with dendritic crystalline phase of larger scale formed during cooling the melt. First dendritic composite was prepared by Hays *et al.* [83] by adjusting the composition of Zr-Ti-Nb-Cu-Ni-Be system such that ductile bcc β -Zr rich phase crystallized from the melt whereas remaining liquid solidified as a glass. Resulting composite showed over 8% of total strain (elastic and plastic) in compression and reduced ultimate stress. However, more impressive results were achieved under uniaxial tension with tensile plastic strain of ~5 %. The origin of such large plasticity was attributed to the soft β -phase dendrites which promoted the initiation of shear bands and restricted their propagation.

The same type of in situ composite with ductile Zr-Ti rich β -phase has been developed by Szuëcs *et al.* [84] in Zr-Ti-Nb-Cu-Ni-Be system with mechanical characteristics similar to [83] (Table 2.3). It was shown that β -phase has lower Young's and shear moduli and higher Poisson's ratio than monolithic glassy matrix. High plasticity of β dendrites could also stem from twinning and martensitic transformations confirmed by TEM analysis [84].

A variation of cooling rate and chemical compositions for Zr-Ti-Nb-Cu-Ni-Al system was found to be important parameters affecting the type and volume fraction of the primary crystalline phase in the glassy matrix [85]. It was shown that mechanical properties of resulting composites were sensitive to the scale of microstructural features and their volume fraction. For instance, dendrites of few μm in length and 0.2-0.3 μm in diameter observed in rapidly quenched sample were too fine to restrict shear bands propagation.

As demonstrated by Sun *et al.* [115], the morphology of in situ precipitated crystallites can also greatly affect mechanical performance of BMG composites. Two differently shaped crystalline phases shown in Fig.2.21 have been obtained from the same glass-former with identical composition. The first sample (a) was quenched directly from the liquid state whereas the second (b) was cast from semi-solid interval between solidus and liquidus temperatures. These two morphologically different structures have

noticeable change in ductility with plastic strain of 8.8 % and 12 % for dendritic and spherical particulates, respectively. Thus, spherical ductile precipitates are more effective in blocking shear band propagation and promoting formation of multiple shear bands.

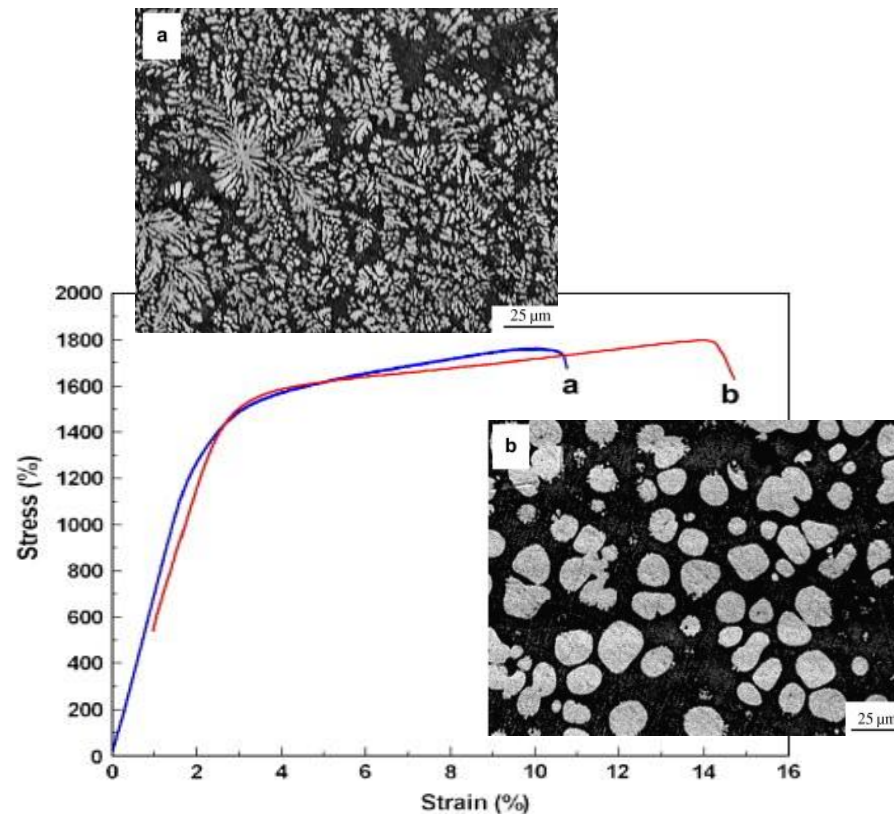


Figure 2.21. Compression stress-strain curves and corresponding microstructures for BMG composites $\text{Zr}_{56.2}\text{Ti}_{13.8}\text{Nb}_{5.0}\text{Cu}_{6.9}\text{Ni}_{5.6}\text{Be}_{12.5}$ with inclusions of different shape: (a) dendritic crystals; (b) spherical particulates. Adopted from [115].

Correlation between plasticity of glass/ductile reinforcement composite and its microstructural scale was established by Hofmann *et al.* [116]. It was suggested that optimal plasticity could be achieved when the domain size in the composite structure (defined as areas in the matrix within which regular patterns of parallel shear bands are formed [83]) is less than the diameter of the plastic zone, but of the same order. Following this concept, Hofmann designed and produced Ti-Zr based composites with impressive improvement in mechanical properties. These composites consist of the glassy matrix and the network of ductile crystalline phase which is bcc solid solution rich in Zr, Ti and Nb. As seen from Fig. 2.22(a), the room-temperature tensile ductility

exceeds 10% accompanied by the yield strength of 1.2-1.5 GPa which were previously unknown in BMG composites. An example of necking in $\text{Zr}_{39.6}\text{Ti}_{33.9}\text{Nb}_{7.6}\text{Cu}_{6.4}\text{Be}_{12.5}$ BMG composite compared with the brittle fracture typical for monolithic glasses is illustrated in Fig.2.22(c-d).

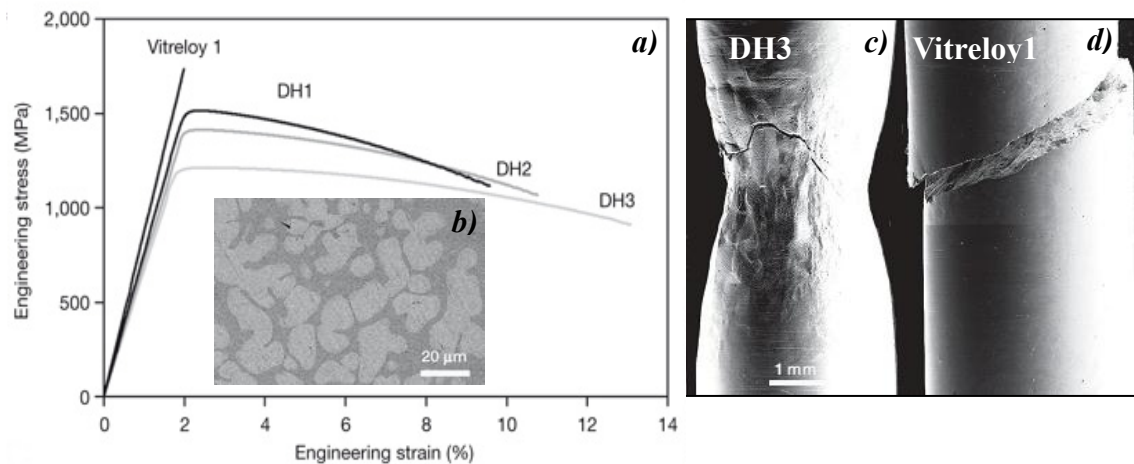


Figure 2.22. (a) Engineering stress-strain curves for Zr-Ti based BMG composites; (b) dendritic phase dispersed in the glassy matrix of $\text{Zr}_{39.6}\text{Ti}_{33.9}\text{Nb}_{7.6}\text{Cu}_{6.4}\text{Be}_{12.5}$ (DH3) composite; (c) SEM images of necking in $\text{Zr}_{39.6}\text{Ti}_{33.9}\text{Nb}_{7.6}\text{Cu}_{6.4}\text{Be}_{12.5}$ (DH3) composite; (d) brittle fracture in monolithic BMG (Vitreloy 1). Adapted from [116].

Therefore, matching the microstructural length scales (dendrite size and inter-dendrite spacing) with characteristic length scale (dimension of the crack tip's plastic zone) helps to restrict shear banding and crack propagation [116].

This strategy is not limited only to Zr-based systems. It has been also successfully applied to La-based alloys in which α -La dendritic phase were dispersed in the glassy matrix [117]. Average shear band spacing in the resulting composite structure was estimated to be in the range of 5-20 μm. When inter-dendritic spacing was around 10-40 μm (depending on volume fraction of α -La phase) the dendrites had no effect on the shear band propagation and macroscopic ductility. Decreasing the inter-dendritic spacing (due to higher volume fraction of α -La dendrites) to 2-8 μm caused significant improvement in tensile plastic strain up to 5 % [117].

Interesting results were achieved in Mg-based in situ BMG composites. Hui *et al.* [118] fabricated composites where the primary crystalline phase dispersed in the glassy matrix was soft Mg-rich plates with long period ordered structure. By altering the volume fraction of Mg-phase in the matrix a pronounced value of plastic strain of 18 % was

attained. The change in the properties of these composites depending on the content of Mg-phase is represented in Fig. 2.23(a). Owing to the uniform distribution the flake-shaped phase (Fig. 2.23(b)) promotes multiple shear band formation and thus provides macroscopic plasticity of the composites.

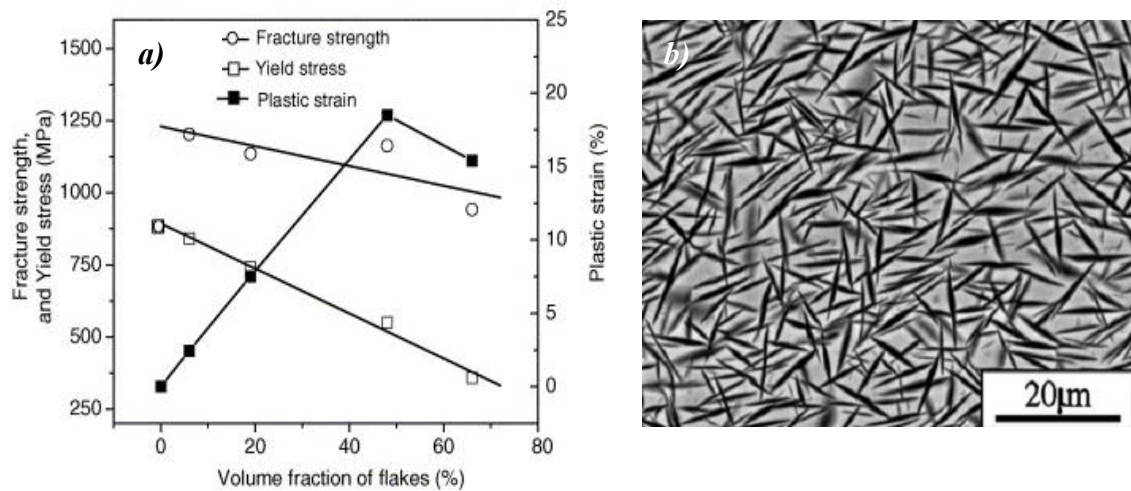


Figure 2.23. (a) Compressive yield strength, fracture strength and plastic strain to failure in the composites as functions of the volume fraction of Mg-rich phase; (b) microstructure of $\text{Mg}_{81}\text{Cu}_{9.3}\text{Y}_{4.7}\text{Zn}_5$ bulk metallic glass composite [118].

Formation of composites with similar morphology of dispersed soft Mg-phase has been observed in other studies of Mg-based BMGs [119-121] though such high values of plastic strain and strength as in Mg-Cu-Y-Zn system were not achieved. Mechanical characteristics for typical in situ BMG composites are listed in Table 2.3.

Table 2.3. Fracture strength σ_f and plastic strain to failure ε_p for monolithic BMGs and in situ composites produced from them.

Alloy	Reinforcement	σ_f, MPa	ε_p, %	Ref.
(Zr ₇₀ Ni ₁₀ Cu ₂₀) ₉₀ Al ₁₀	Monolithic glass	1700	<1	[105]
(Zr ₇₀ Ni ₁₀ Cu ₂₀) ₈₂ Ta ₈ Al ₁₀	Ta-rich particles	2100	~16	[105]
Cu ₆₀ Ti ₂₅ Hf ₁₅	Monolithic glass	2088	1.6	[122]
(Cu ₆₀ Ti ₂₅ Hf ₁₅)Nb ₁₀	Nb-rich dendrites	2232	4.1	[122]
Cu ₅₀ Ti ₃₅ Hf ₁₀ Ag ₅	Monolithic glass	2180	2.1	[123]
(Cu ₅₀ Ti ₃₅ Hf ₁₀ Ag ₅)Ta ₃	Dendrites	2510	9.75	[123]
La ₆₂ Al ₁₄ (CuNi) ₂₄	Monolithic glass	560	0	[117]
La ₇₄ Al ₁₄ (CuNi) ₁₂	α -La dendrites	520	4.1	[117]
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	Monolithic glass	1900	~2	[83]
Zr ₄₇ Ti _{12.9} Nb _{2.8} Cu ₁₁ Ni _{9.6} Be _{16.7}	β -Zr rich dendrites	1700	8	[83]
Zr _{56.2} Ti _{13.8} Nb _{5.0} Cu _{6.9} Ni _{5.6} Be _{12.5}	β -Zr rich dendrites	1700	8.3	[84]
Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₁₀	Monolithic glass	550	0	[124]
(Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₁₀) ₈₇ Fe ₁₃	α -Fe particles	990	~1	[124]
Mg ₇₁ (Cu _{0.667} Y _{0.333}) ₂₄ Zn ₅	Monolithic glass	1250	0	[118]
Mg ₈₁ Cu _{9.3} Y ₅ Zn _{4.7}	Mg-rich phase	1160	18.5	[118]
Mg ₇₅ Ni ₁₅ Gd ₅ Nd ₅	Monolithic glass	870	2	[119]
Mg ₈₀ Ni ₁₂ Gd ₄ Nd ₄	Mg-rich phase	900	4.3	[119]

Properties of monolithic metallic glasses that served as a matrix material for these composites are given for comparison. It is clearly noticeable that alloys with a composite structure outperform monolithic alloys in terms of values of plastic strain to failure. However, a limited number of BMGs have the ability to develop an in situ composite structure containing ductile precipitates. Careful control of the processing conditions and adjustment of the alloy chemistry often including the addition of expensive metals is required for in situ BMG composites. For example, to generate a

composite structure in Zr-based metallic glass, alloying with expensive Nb is usually required.

2.6. SUMMARY AND SCOPE OF THESIS

It is evident that only a limited number of metallic glasses composed from expensive elements possess an adequate combination of plasticity and strength. Nevertheless, intrinsic brittleness of more affordable monolithic BMGs can be alleviated through modification of the glassy structure by intrinsic or extrinsic reinforcing. The effective strategy of in situ precipitation of soft primary crystallites in the glassy matrix can be implemented in alloys with high concentration of base element if composition and cooling rate is correctly adjusted to form the glassy phase. This concept will be applied in this thesis, focusing on the design and fabrication of new amorphous-crystalline composite structures with various types of reinforcing phase in Mg- and Zr-based glass-forming alloys. Mg-based glasses exhibit good glass-forming ability and a high specific strength due to their low density. However, they usually have low Mg contents of 50-75 at.% that results in relatively high densities compared to pure Mg and, consequently, hinders their advantages in lightweight applications. Therefore, the main focus of this thesis is on glass formers containing high Mg concentration (>80 at.%). A number of in situ and ex situ BMG composites have been extensively researched in the Zr-based amorphous system. Nevertheless, systems with a Zr content greater than 70 at.% have received little attention as well as BMG composites produced by inoculation. This fact has served as a motivation for this research to generate composite structures in high Zr-bearing glass-formers using insoluble inoculants and to understand their effect on the structure and properties of these BMG composites.

This thesis investigates BMG composites produced in Mg- and Zr-based glass-forming systems by in situ methods and explores their structural, thermal and mechanical characteristics. The experimental section and associated discussions are divided into four parts.

The first part of the experimental work (Chapter 3) is devoted to the investigation of a new glass-forming system Mg-Ni-Gd-Y with high Mg concentration. The chapter studies various types of heterogeneous morphologies generated in these quaternary alloys, their dependence on alloy chemistry and cooling conditions during solidification.

The second part of the experimental work (Chapter 4) studies the structure of monolithic BMGs and their composites in the Mg-Ni-Gd system produced by methods of regular gravity casting and semi-solid injection casting. The crystallisation behaviour and various properties of amorphous matrix in Mg-Ni-Gd alloys were investigated.

The third part of the experimental work (Chapter 5) describes composites produced by inoculation of Zr-based glass-formers. The influence of inoculating particles and cooling conditions on the morphology of resulting microstructures and their thermal properties are presented.

Chapter 6 provides a general discussion of the results presented in Chapters 3-5 providing a comparison between the different BMG composites in terms of glass-forming ability, morphology and mechanical performance. This chapter is followed by the summary of the main results and findings obtained in this research.

CHAPTER 3 – BMG COMPOSITES

PRODUCED IN MG-NI-GD-Y SYSTEM

3.1. BACKGROUND

Among the variety of BMGs developed and studied during the last two decades, lightweight Mg-based glasses have been known for their low density which translates to high specific mechanical properties. To date, Mg-based BMG alloy systems can be largely classified into three groups depending on the major alloying element: (i) Mg–Cu-based BMGs; (ii) Mg–Ni-based BMGs, and (iii) Mg–Zn-based BMGs. Most researchers have focused on Mg–Cu-based BMGs due to their higher glass-forming ability (GFA) [33, 125, 126]. However, they have a relatively low Mg-content of 50–69 at.% that results in relatively high densities compared to the solvent element, Mg (1.73 g/cm^3) and, consequently, hinders their advantages in lightweight applications. Mg–Ni–RE-based BMGs exhibit lower densities with Mg contents >70 at.% and higher glass transition temperatures [127, 128]. Moreover, they exhibit superior corrosion resistance due to the beneficial effect of Ni on passivation [129].

There are a number of Mg-based glasses discovered in multicomponent alloy systems that exhibit yield strength values about $3\text{--}5\times$ higher when compared with those of conventional crystalline Mg alloys [128, 130–134]. However, their low ductility and fracture toughness inhibit their use as lightweight structural materials. The plasticity of Mg-based BMGs has been shown to be enhanced significantly by incorporating crystalline phases in the high-strength amorphous matrix in BMG-based composites [7–10, 13–16].

Metallic glass/composite structures can be produced by different methods including the ex situ introduction of insoluble particles [78, 98, 135, 136], and in situ formation of reinforcing phase in the amorphous matrix [11–16]. To date, in situ BMG composites in Mg-based systems have been produced by partial crystallisation induced by annealing of glassy precursor [137, 138], or by the adjustment of the cooling rate and chemical composition to precipitate a crystalline phase from the bulk glass during casting [119, 120, 124]. Mg-BMG composites with intermetallic crystalline phases as reinforcement in the glassy matrix exhibit a slight improvement in plastic strain and fracture strength

[11-13]. Significant enhancement in mechanical properties has been achieved in systems with high Mg concentration (>80 at.%) that promoted the formation of a soft Mg-rich phase in the amorphous matrix. Such composites have been fabricated in a limited number of Mg-based systems, including the Mg-Cu-Zn-Y system that generated an impressive maximum fracture strength and fracture strain of 1.2 GPa and 18 %, respectively [118], as well as in Mg-Ni-Zn-Y [120] and Mg-Ni-Gd-Nd alloys [119]. Therefore, design and fabrication of lightweight Mg-based BMG composites is of high interest in terms of attaining improved mechanical properties.

3.2. DESIGN OF COMPOSITE ALLOYS IN MG-NI-GD-Y SYSTEM

Bearing in mind the aforementioned findings in regards to Mg-based metallic glasses, the starting material chosen for exploration in this chapter was the glass-forming Mg-Ni-Gd-Y system. The ternary Mg-Ni-Gd system is known as a good glass former that was studied in the composition range of 70-80 at.% Mg and was found to have critical thickness for glass formation of up to 4 mm. The formation of a homogeneous (monolithic) amorphous phase has also been reported in Mg-Ni-Y alloy ribbons fabricated by melt spinning [139]. However, there have been no reports in the literature regarding the formation of amorphous or composite structures in quaternary Mg-Ni-Gd-Y alloys. The presence of two rear-earth (RE) elements may result in higher value of configuration entropy providing better GFA. This concept was implemented in Mg-Ni-Gd-Nd system [119], where both homogeneous amorphous and composite glassy-crystalline structures have been generated within alloys of high Mg content (up to 80 at%). Applying this strategy with respect to the Mg-Ni-Gd-Y system, one can notice that the elements Y and Nd both exhibit the hcp-structure in their natural crystalline state, identical heats of mixing with Mg (-6 kJ/mole for both Mg-Y and Mg-Nd pairs) and similar atomic radius (0.18 nm for Y and 0.185 nm for Nd, respectively). Therefore, from the perspective of producing an amorphous structure, the Mg-Ni-Gd-Y system is of considerable interest.

Generally, the GFA of amorphous alloys deteriorates with increasing base element concentration. For instance, the maximum Mg content in the Mg-Ni-Gd alloys studied by Park et al. [140] of 80 at.% corresponds to the highest achievable casting thickness

for monolithic glass formation (no crystallites) greater than 1 mm. Nevertheless, this uniquely high solvent element content gives the distinct benefit for generating a glass-crystal structure, as when excessive Mg is added to the alloy melt, it precipitates as the primary crystalline phase in the glassy matrix. At the same time, nucleation and growth of the primary phase does not trigger crystallisation of the remaining glassy phase. It is not always possible to observe the primary crystalline phase formation in the glass-forming melts during solidification since there is a possibility of generating intermetallic phases as precipitates in the glassy matrix depending on chemical composition of alloy and tendency of its elements to form intermediate compounds.

As such, gradually increasing the Mg content in the Mg-Ni-Gd-Y system at concentrations greater than 80 at.% gives a possibility to produce alloys with a composite structure consisting of primary α -Mg crystallites within the glassy matrix. To explore the probable types of two-phase structures in this thesis, the concentration of Mg was varied from 80 to 88 at.%. Table 3.1 lists compositions designed for the Mg-Ni-Gd-Y system with varying amounts of Ni and RE additions.

Table 3.1. Alloys compositions designed in the Mg-Ni-Gd-Y system.

Mg content (at.%)	Alloy composition (at.%)	
80	Mg ₈₀ Ni ₁₂ Gd ₆ Y ₂	-
82	Mg ₈₂ Ni ₁₂ Gd ₄ Y ₂	Mg ₈₂ Ni ₁₀ Gd ₆ Y ₂
84	Mg ₈₄ Ni ₁₂ Gd ₃ Y ₁	Mg ₈₄ Ni ₁₀ Gd ₄ Y ₂
86	Mg ₈₆ Ni ₁₀ Gd ₃ Y ₁	Mg ₈₆ Ni ₈ Gd ₄ Y ₂
88	-	Mg ₈₈ Ni ₈ Gd ₃ Y ₁

Experimental ternary phase diagrams for the Mg-Ni-Gd and Mg-Ni-Y alloy systems are not available in the literature. Prediction of some complex ternary and quaternary phase diagrams can be achieved via thermodynamic modelling. Figure 3.1 shows the thermodynamically calculated liquidus projections of Mg-Ni-Gd system determined by Gibson [141].

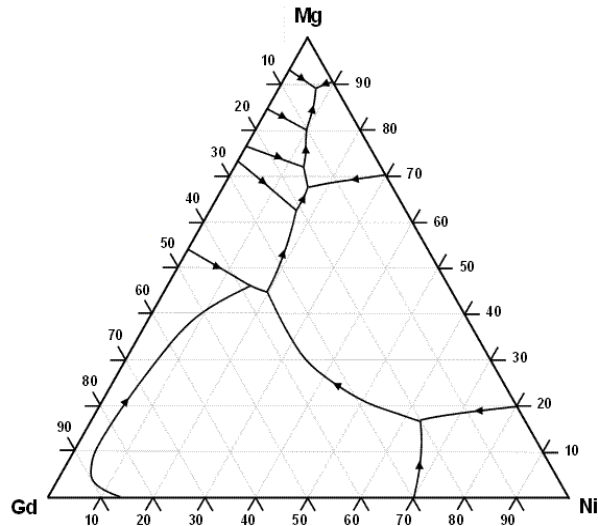


Figure 3.1. Calculated liquidus projections of Mg-Ni-Gd system [141].

For the study the pseudo-ternary liquidus projection of Mg-Ni-(Gd,Y) alloys will be used. Compositions selected for analysis in this section of thesis are located close to the calculated ternary eutectic point. They are marked by red circles in Fig. 3.2.

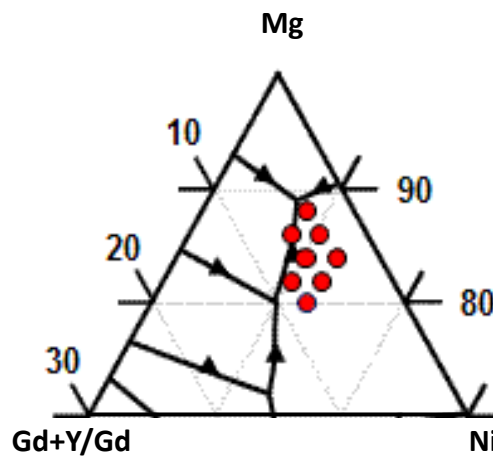


Figure 3.2. Mg-rich side of liquidus projection of pseudo-ternary Mg-Ni-(Gd,Y) system showing the composition range of selected alloys [141].

3.3. PRODUCTION OF MG-NI-GD-Y ALLOYS

Samples of Mg-Ni-Gd-Y alloys were produced by a regular gravity casting technique. High purity elements Mg (99.85 wt.%), Ni (99.9 wt.%), Gd (99.9 wt.%) and Y (99.9 wt.%) were used as starting materials to prepare alloy compositions. Taking into account that melting temperatures of Ni, Gd and Y (1455, 1312 and 1526 °C respectively) are considerably higher compared to Mg (650 °C) and that Mg evaporates

intensively at high temperatures, preliminary Ni-Gd and Ni-Y master alloys were prepared. Figure 3.3 shows phase diagrams with indicated eutectic alloys $\text{Gd}_{68}\text{Ni}_{32}$, $\text{Gd}_{44}\text{Ni}_{56}$ and $\text{Ni}_{57.5}\text{Y}_{42.5}$ (atomic %) that were chosen as master alloy compositions for designed Mg-Ni-Gd/Y samples. Selection of $\text{Gd}_{68}\text{Ni}_{32}$ or $\text{Gd}_{44}\text{Ni}_{56}$ composition was based on the ratio of Ni to Gd in the nominal Mg-Ni-Gd/Y compositions.

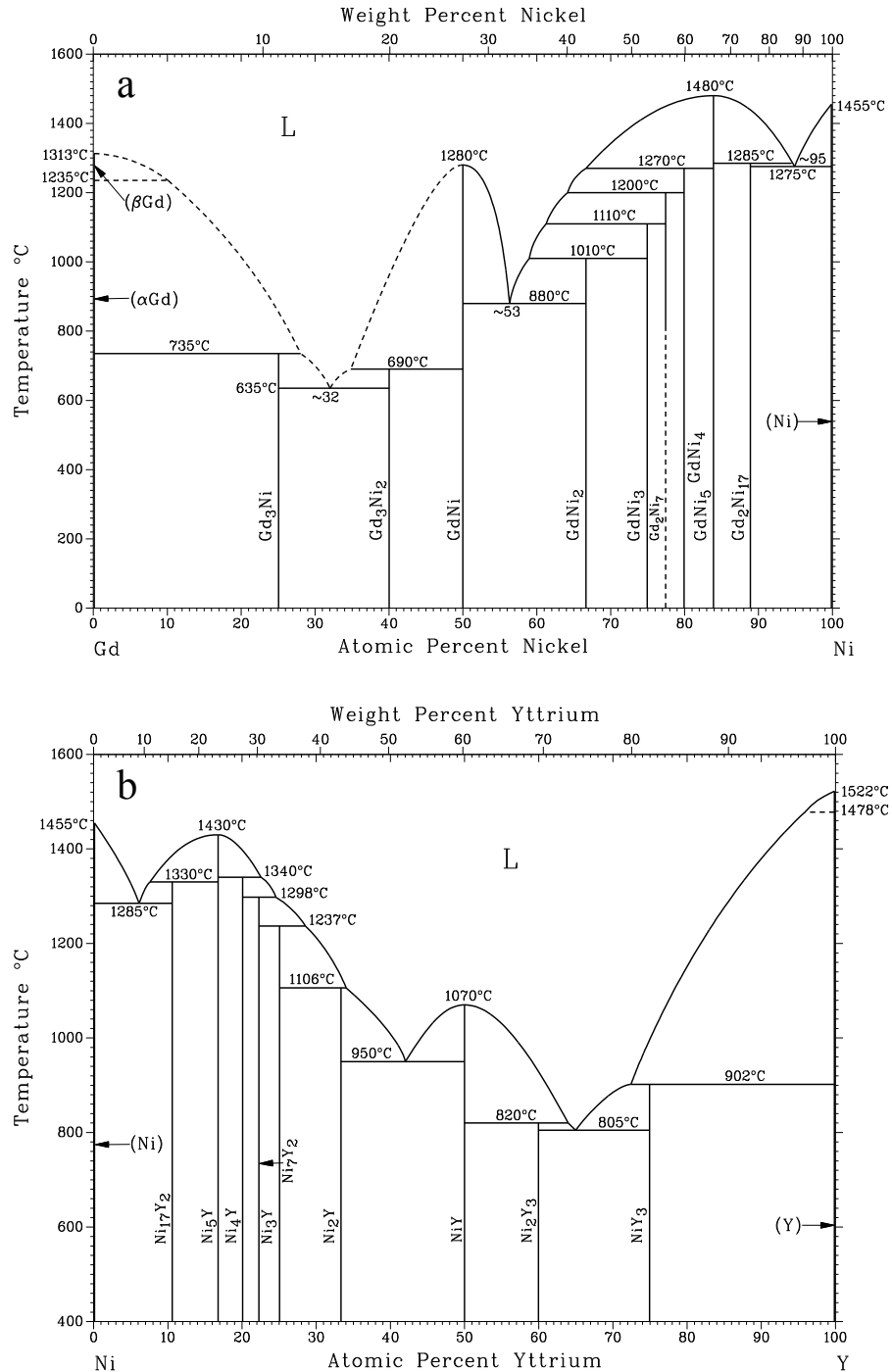


Figure 3.3. Equilibrium phase diagrams [142]: (a) Gd-Ni system; (b) Ni-Y system.

High-temperature Ni-Gd and Ni-Y master alloys were prepared using a Buehler MAM-1 arc melting machine. The raw material charge of 10-20 g weight was placed in the arc-melting chamber that was evacuated typically to 4-5 mPa. Casting was carried out under Ti-gettered argon atmosphere. Each ingot was remelted several times to ensure homogeneity of alloy. The surface of the prepared master alloys was polished mechanically to remove oxides and scum.

Balance of Ni-Gd/Ni-Y master alloys, mechanically cleaned Mg and remaining balance of Ni were placed into a graphite crucible. Inner walls of the crucibles were coated beforehand with a thin layer of boron nitride to minimize any possible chemical reactions between the liquid melt and crucible. Each crucible with the raw materials was placed in a sealed chamber of the casting unit.

Constituent components of the alloy were remelted several times in an induction furnace under a vacuum-purged circulating argon (99.998 wt.%) atmosphere. On the final melt cycle, the alloy charge was heated above its liquidus temperature, cooled to the desired casting temperature (650 °C) and manually poured directly into a naturally cooled wedge-shaped copper mould. The mould has 100 mm cavity length, 40 mm width and maximum wedge thickness of 10 mm. Cooling process in the wedge-shaped mould configuration occurs unevenly and a gradient of effective cooling rate arises throughout the wedge. This generates a range of cooling rates in a single sample during casting and, hence, a range of different structures forms in the wedge. To confirm the reproducibility of the structure, each alloy composition was cast twice into the wedge-shaped copper mould.

The casting temperature, which is the temperature of the melt immediately prior to casting, determines not only the viscosity of the molten alloy but also affects the level of crystallinity of the as-cast sample. Overheating the melt results in a higher degree of crystallinity due to the greater temperature gradient within the casting resulting in a lower sample cooling rate and hence, more time for crystals to nucleate and grow [143]. Casting temperatures were consistently chosen very close to the melting point of alloy so as not to promote the formation of a completely crystalline structure. In this case, due to thermal fluctuations, the melt might contain pre-existing nuclei in its volume which act as nucleation sites and easily trigger crystallisation of the cooling alloy. Thus, the optimal cast temperature was set at 650 °C for all samples which is approximately 100

°C higher than melting temperature of alloys, maintaining a constant casting temperature also infers a constant cooling rate for the wedge-mould configuration, making direct comparisons of microstructures with respect to wedge thickness feasible.

Surfaces of the wedge-shaped samples were highly reflective, particularly in the areas with an amorphous structure closer to the tip of the wedge. Figure 3.4(a) shows a typical wedge sample produced by gravity casting in a copper mould.

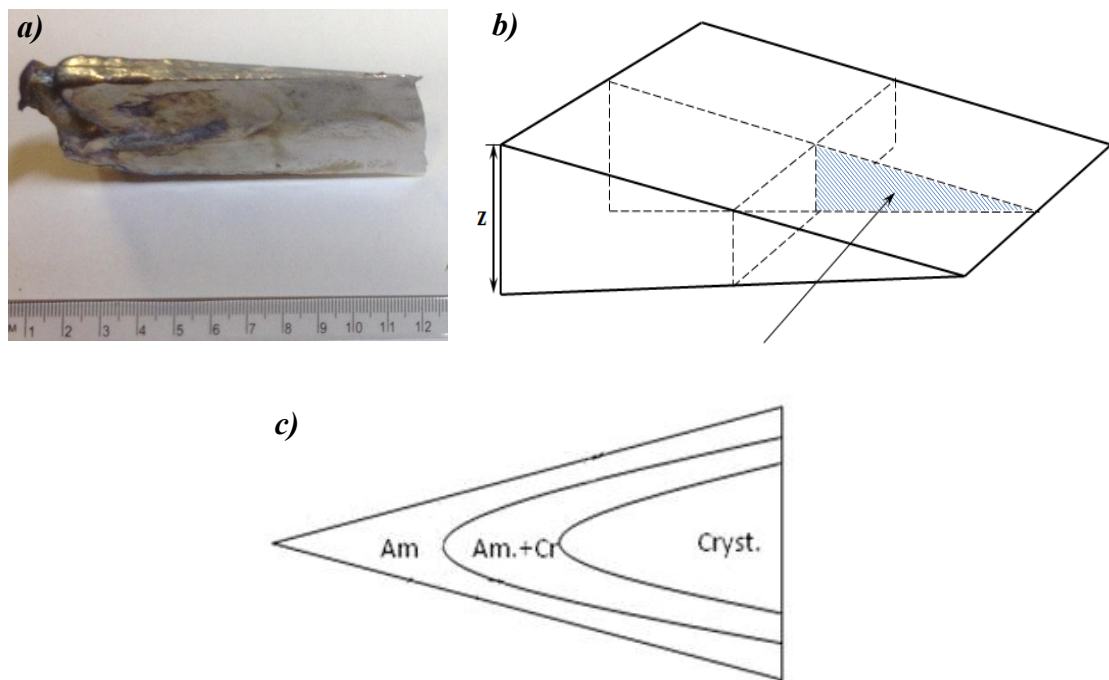


Figure 3.4. Schematic diagram of a wedge-shaped as-cast sample: (a) typical Mg-Ni-Gd-Y casting; (b) wedge sampling dimensions where Z is the wedge thickness (arrow indicates the surface of viewing); (c) schematic distribution of microstructure in the wedge-shaped casting.

Wedge-shaped castings were sectioned through the wedge centreline (as in Fig. 3.4(b)) and mounted in epoxy resin for further structural analysis. At least two midsections from different parts of each wedge were subjected to the microstructural analysis.

Analysis of wedge cross-sections using optical microscope has revealed that there are no sharp boundaries between amorphous and crystalline regions which is schematically depicted in Fig. 3.4(c). The conversion from completely glassy phase to crystalline zone occurs over a range of 0.3-1.8 mm in various samples.

Such a transition zone generated in the wedge-shaped samples is of particular interest in this thesis since it represents typical morphologies of in situ composites which are the

main subject in the given study. Alteration of microstructure in fabricated Mg-Ni-Gd-Y alloys as a function of chemical composition and wedge thickness (which correlates to the cooling rate) is represented in the following sections.

The critical thickness of glass formation was determined as the wedge thickness (Z) at the top of V-shaped transition boundary between amorphous and amorphous-crystalline regions (shown in Fig.3.4(c)), where the onset of crystallisation occurred. The values of critical thickness were taken as an average of at least four separate measurements for each wedge casting.

The size of the crystalline phases has been determined as an average of at least ten measurements from three separate SEM micrographs of each alloy composition over a range of magnifications of 1000-2000x.

Quantitative analysis of the crystalline phase in the base matrix was performed using Adobe Photoshop SC5 software. Binary thresholding of greyscale optical micrographs distinguished crystallites from the surrounding amorphous matrix, thus allowing calculation of their volume fraction. At least five micrographs of each alloy were used for determining the volume fraction.

3.4. STRUCTURAL CHARACTERISTICS OF MONOLITHIC AND COMPOSITE ALLOYS IN MG-NI-GD-Y SYSTEM

3.4.1. Alloy with 80 at.% Mg

Typical SEM images of the $\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$ alloy are given in Fig. 3.5. The microstructure of the wedge for thicknesses of up to 0.7 mm appears featureless, thereby indicating the formation of a single (monolithic) glassy phase, as confirmed by XRD scan with broad halo in Fig. 3.6(a).

A multiphase composite structure was observed at wedge thicknesses from 0.7-1.8 mm and composed of crystallites of 5-10 μm diameter interspersed in the amorphous matrix, as shown in Fig. 3.5(b-c).

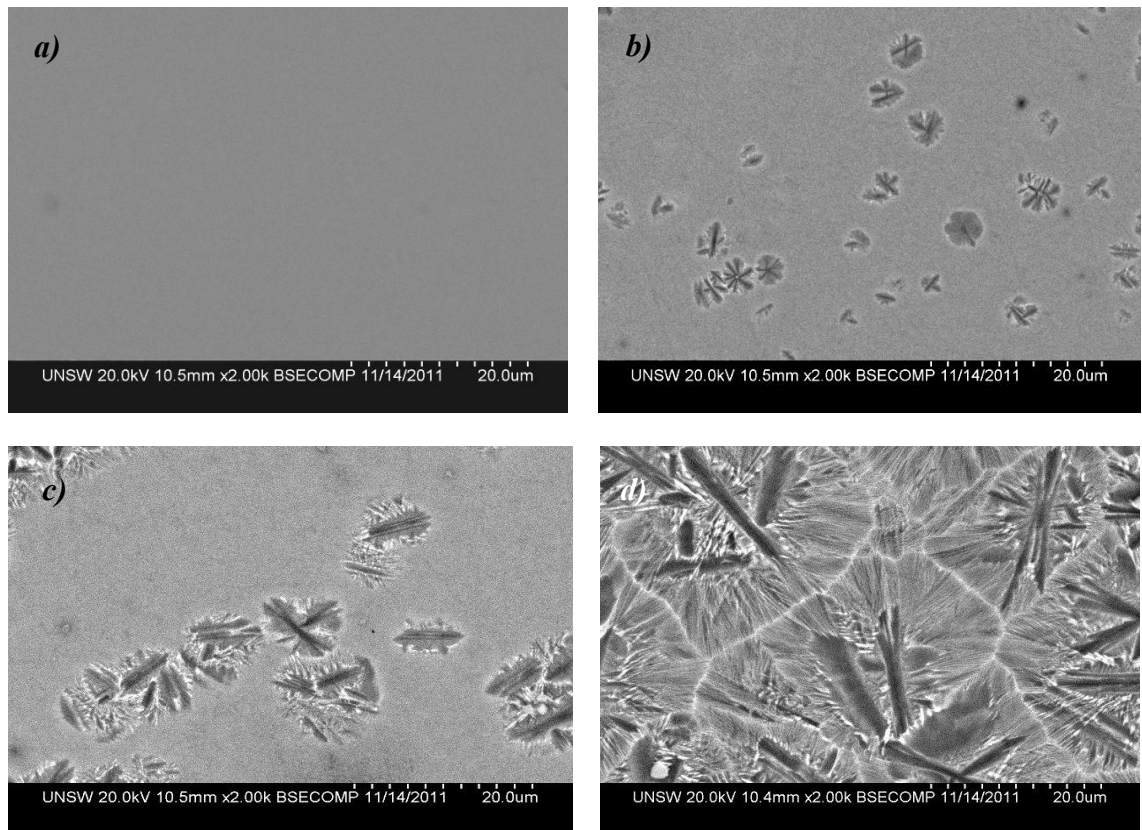


Figure 3.5. SEM backscattered electron images of $\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$ alloy at different wedge thickness (Z): (a) Z=0.6 mm; (b) Z=1 mm; (c) Z=1.7 mm, and (d) Z=2 mm (fully crystalline microstructure).

The presence of a composite microstructure in the $\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$ alloy was confirmed by XRD analysis. Figure 3.6(b) displays an XRD spectrum taken from the centre of the $\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$ wedge at a thickness of 1.7 mm. It has an overlapping broad crest corresponding to the amorphous component of the structure and sharp peaks belonging to the crystalline phases. Crystalline peaks were identified as a mixture of Mg_5Gd , Mg_2Ni and Mg_{25}Y_5 phases. A completely crystalline structure is formed in the wedge at a thickness of 2 mm at which the cooling rate upon solidification is not high enough to retain an amorphous structure from the melt.

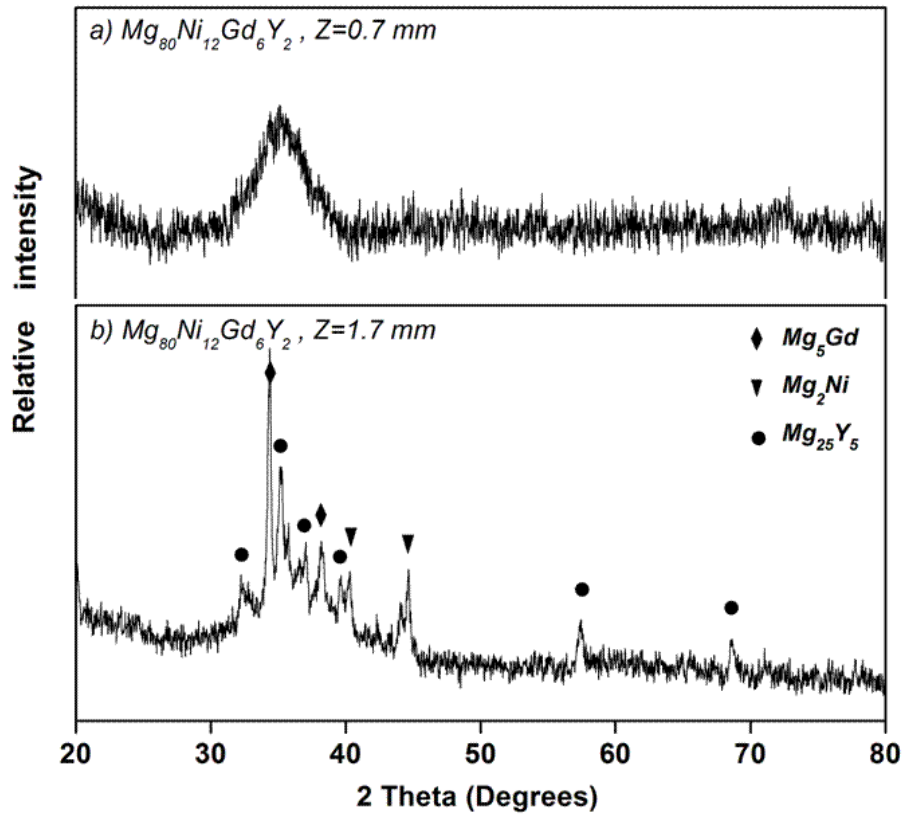


Figure 3.6. XRD pattern for $Mg_{80}Ni_{12}Gd_6Y_2$ alloy at wedge thickness of (a) 0.7 mm and (b) 1.7 mm, respectively.

3.4.2. Alloys with 82 at.% Mg

The observed microstructure of the $\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$ alloy appears similar to that of the $\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$ composition shown in Fig 3.5.

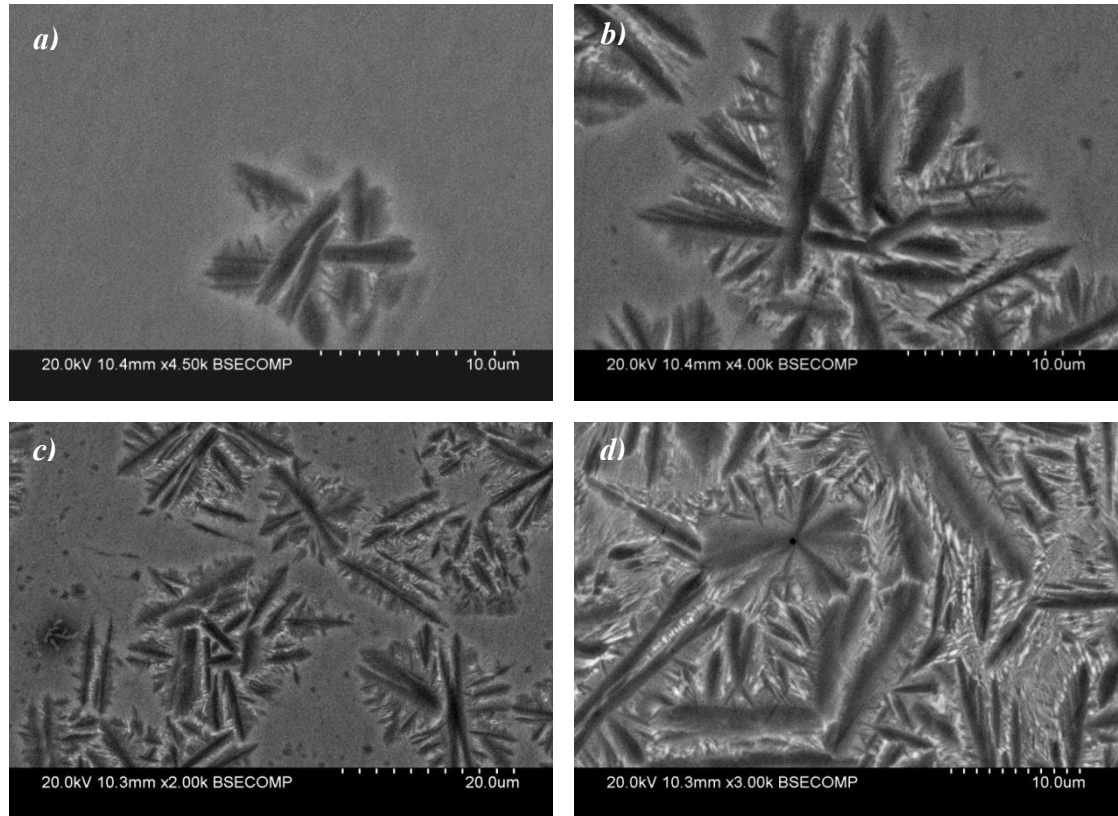


Figure 3.7. SEM backscattered electron images of $\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$ alloy at different wedge thicknesses: (a) $Z=1.2$ mm; (b) $Z=1.5$ mm; (c) $Z=1.8$ mm; (d) $Z=2.1$ mm.

m.

Scattered crystallites were observed in the amorphous matrix at greater wedge thicknesses. Figure 3.7(a-c) shows crystalline agglomerates composed of Mg_5Gd , Mg_2Ni and Mg_{25}Y_5 intermetallics. According to an SEM image taken at a wedge thickness of 2.1 mm no amorphous phase is present in the structure of $\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$ alloy (Fig. 3.7(d)).

Both XRD patterns for a given composition (Fig. 3.8) show the mixture of amorphous and crystalline phases. At wedge thickness of 1 mm, the scan displays a broad halo with overlapping traces of Mg_5Gd and Mg_{25}Y_5 phases. The volume fraction of the crystalline phases is negligible in contrast to the amorphous one. The phase selection at 1.5 mm thickness wedge is represented as a mixture of three crystalline phases (Mg_5Gd , Mg_{25}Y_5 and Mg_2Ni) and amorphous matrix whose volume fraction is considerably smaller compared with that at 1 mm wedge thickness.

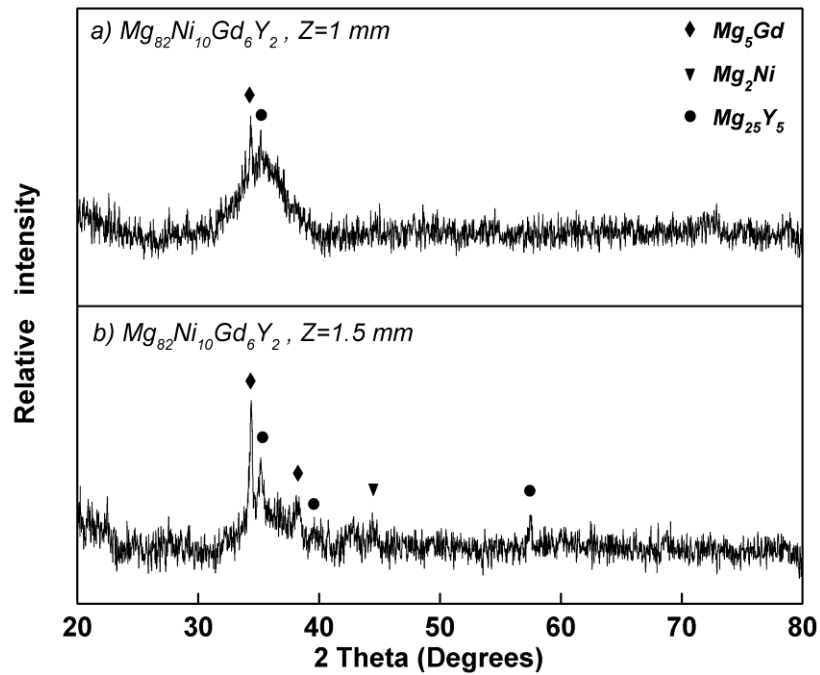


Figure 3.8. Micro XRD scan for $\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$ at wedge thickness (a) 1mm and (b) 1.5mm, respectively.

A similar microstructural distribution was observed for the $\text{Mg}_{82}\text{Ni}_{12}\text{Gd}_4\text{Y}_2$ composition. At wedge thicknesses of 0.5-1.3 mm the alloy has a composite microstructure consisting of the amorphous matrix and crystalline phases. For thicknesses less than 0.5 mm and greater than 1.3 mm the wedge has a single glassy and completely crystalline structure, respectively. An SEM images taken from the $\text{Mg}_{82}\text{Ni}_{12}\text{Gd}_4\text{Y}_2$ alloy at a section of 0.8-1 mm in thickness show elongated flake-shaped and needle-shaped crystals (Fig. 3.9(a-b)).

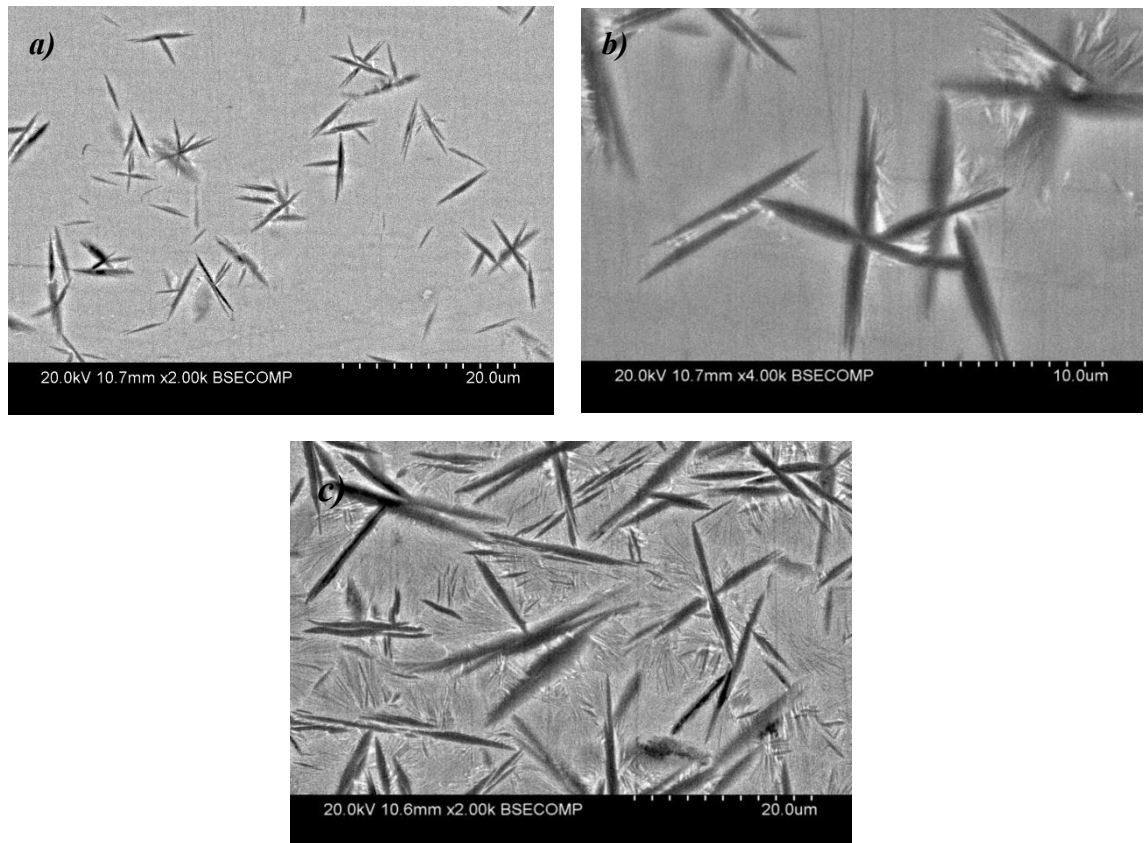


Figure 3.9. SEM backscattered electron images of $\text{Mg}_{82}\text{Ni}_{12}\text{Gd}_4\text{Y}_2$ alloy at different wedge thickness Z : (a) $Z=0.8$ mm; (b) $Z=1$ mm; (c) $Z=1.5$ mm.

Crystalline peaks in the XRD scan (Fig. 3.10(b)) identify those crystals as hcp-Mg-rich phase and Mg_2Ni compound. At 1 mm sample thickness, the average length and width of flake-shaped inclusions dispersed in the amorphous matrix is 8-10 μm and 1-1.5 μm , respectively. Increase in wedge thickness does not provide larger volume fraction of Mg-rich flakes. Instead, it promotes considerable growth of Mg_2Ni intermetallic compound around the flakes. Hence, an increase in Ni content at the expense of RE components raises the propensity of forming Mg_2Ni phase.

In general, both samples with 82 at.% of Mg have a similar structure, especially at larger wedge thicknesses, where they are completely crystalline. However, these alloys exhibit slight differences in the morphology of the crystalline inclusions in amorphous-crystalline region due to various concentrations of Ni and rare-earth elements. Crystallites that form in the amorphous matrix of $\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$ sample represent agglomerates consisting of three phases (Mg_5Gd , Mg_2Ni and Mg_{25}Y_5). Crystalline inclusions in $\text{Mg}_{82}\text{Ni}_{12}\text{Gd}_4\text{Y}_2$ alloy are predominantly Mg-rich flakes, with the

secondary crystalline phase, Mg_2Ni forming around the Mg-flakes. Therefore, the nickel and rare-earth component concentration in the alloy has a great influence on the morphology and growth kinetics of crystallites in the amorphous matrix during solidification.

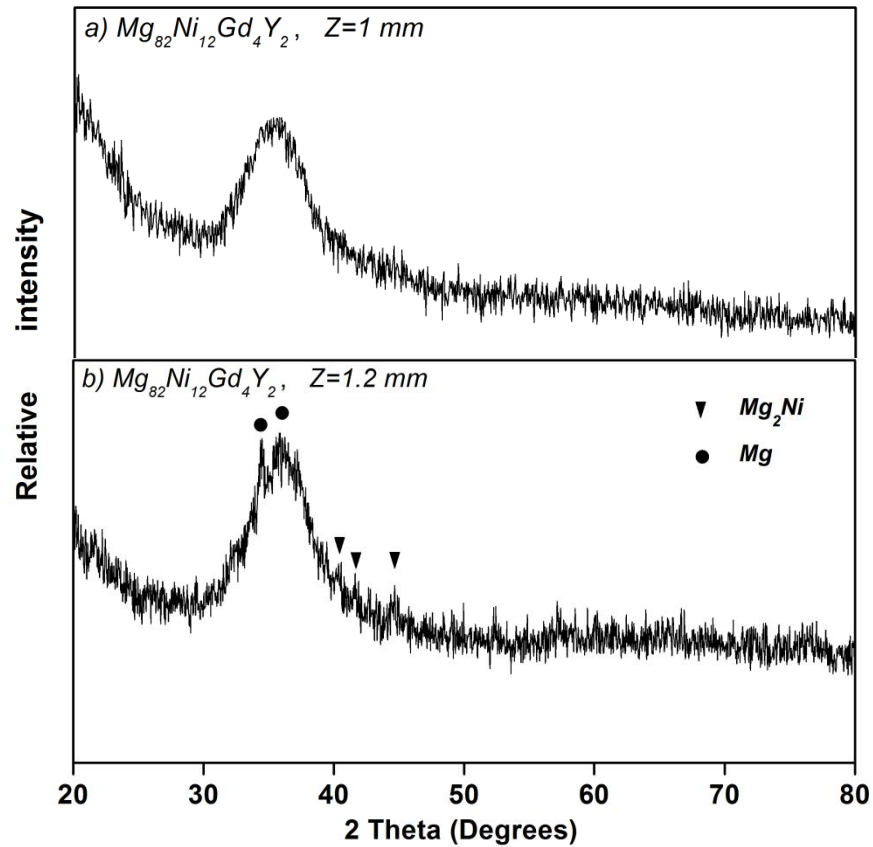


Figure 3.10. XRD pattern taken from the cross-section surface of the $Mg_{82}Ni_{12}Gd_4Y_2$ sample at thickness of (a) $Z=1\text{ mm}$, and (b) $Z=1.2\text{ mm}$.

3.4.3. Alloys with 84 at.% Mg

Both alloys with a Mg-content of 84 at.% ($Mg_{84}Ni_{10}Gd_4Y_2$ and $Mg_{84}Ni_{12}Gd_3Y_1$) have a critical thickness of glass formation of 0.4 mm. They exhibit an amorphous-crystalline structure throughout the interval of 0.5-1.3 mm thickness of the wedge-shaped sample. Diffraction scans recorded from 1 mm wedge thickness for both compositions are shown in Fig. 3.11. The microstructure of the $Mg_{84}Ni_{10}Gd_4Y_2$ alloy was found to be a mixture of the amorphous phase with crystalline hcp-Mg, Mg_5Gd and Mg_2Ni phases present, whereas the $Mg_{84}Ni_{12}Gd_3Y_1$ sample at the same thickness consists of

amorphous matrix with hcp-Mg and the intermetallic Mg_2Ni . XRD scan for $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$ also indicates the presence of Y_2O_3 particles – a likely impurity from the melting process and known inoculant of hcp-Mg in these alloy systems [144]. The volume fraction of the hcp-Mg phase and Mg_2Ni for the given thickness is too small compared with the volume of amorphous phase.

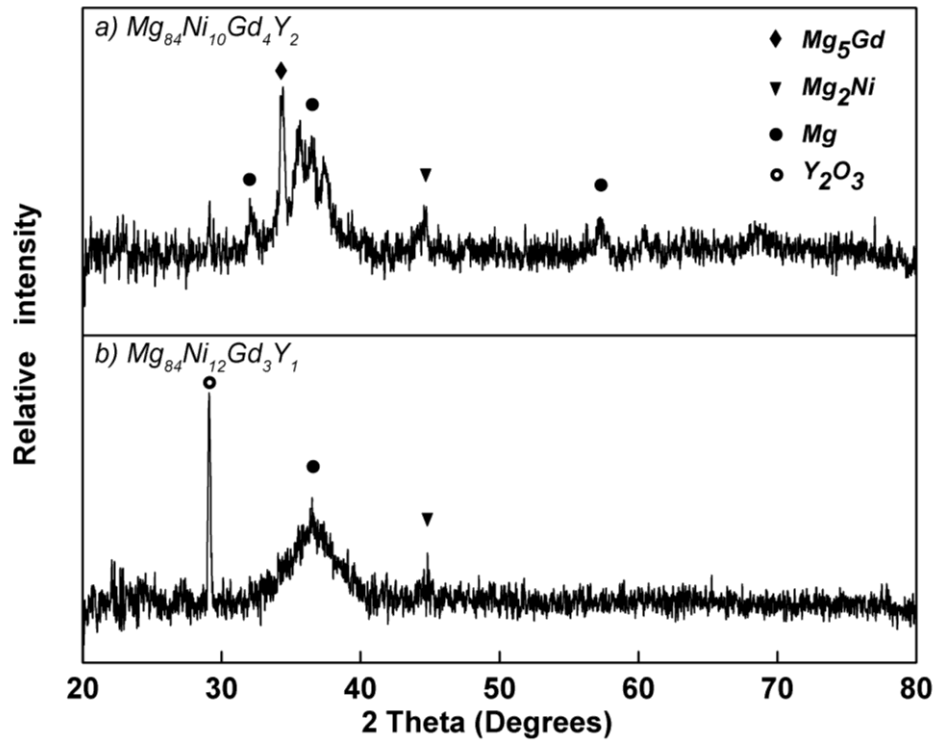


Figure 3.11. XRD patterns taken from the cross-section surface at 1 mm wedge thickness: (a) $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_4\text{Y}_2$; (b) $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$.

Backscattered SEM images of the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_4\text{Y}_2$ structure shows that, at a wedge thickness of 0.4-0.9 mm, only the single crystalline hcp-Mg-phase is present in the amorphous matrix (Fig. 3.12(a)). This phase appears as thin flake-shaped crystallites of 10-20 μm in length. With increase in sample thickness the Mg_5Gd and Mg_2Ni phases are formed between and around these Mg-flakes (Fig. 3.12(b)).

In Fig. 3.12(a) the Mg-flakes of two different size scales are present. In the matrix areas between large crystallites of 10-20 μm in length there are smaller flakes of 1-2 μm . Due to redistribution of components during solidification, these areas are depleted with the Mg. Relatively high cooling rate of the alloy suppresses the formation of the

intermetallic phases in the remaining amorphous matrix, allowing the growth of Mg-flakes of limited size.

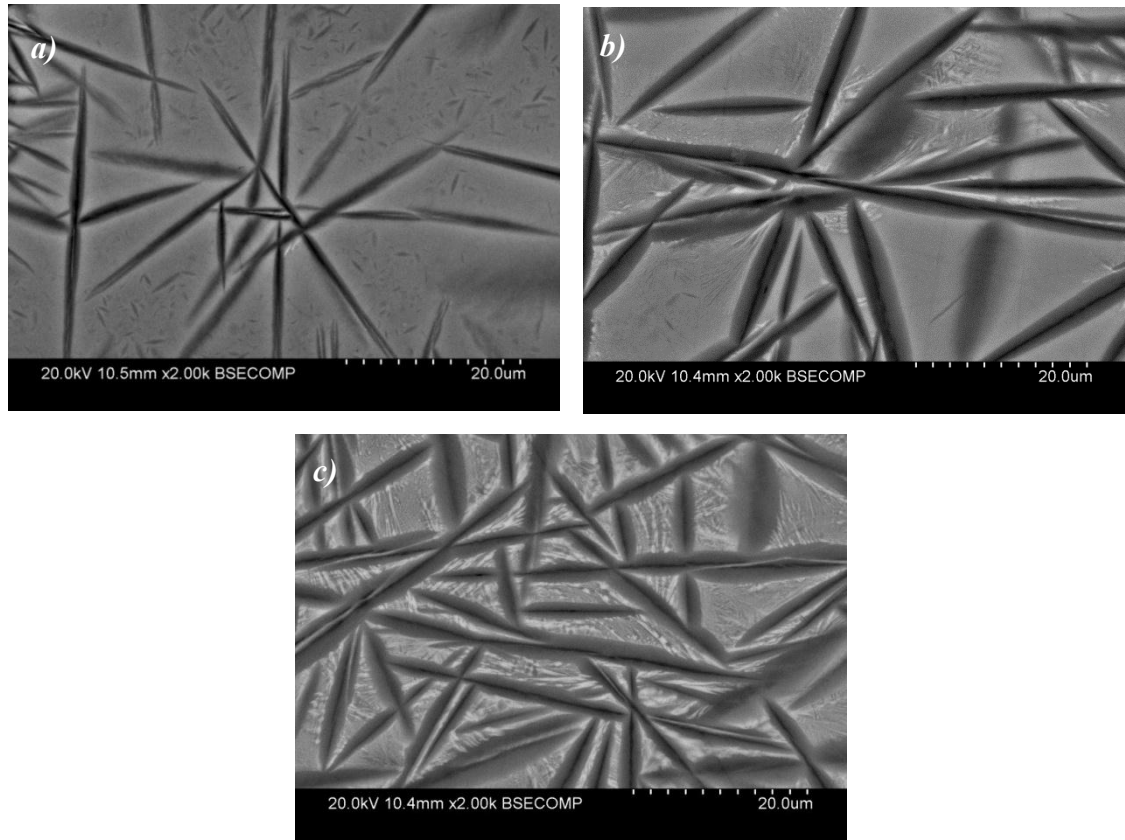


Figure 3.12. SEM backscattered electron images of $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_4\text{Y}_2$ wedge cross sections taken at various thicknesses, Z: (a) Z=0.8 mm; (b) Z=1 mm, and (c) Z=1.5 mm.

At higher thicknesses the cooling rate of the wedge is increased allowing further growth of crystalline phases. Larger and thicker Mg-flakes are formed at 1.5 mm wedge thickness as shown in Fig. 3.12(b-c).

SEM images of the microstructure for $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$ composition are given in Fig. 3.13. Some of the dark flake-like hcp-Mg crystals are oriented at a 90° angle to one another (denoted by circle in Fig. 3.13(a)). From the literature, it is shown that this phenomena is generally associated with the growth of Mg-crystals inoculated from the surface of Y_2O_3 particles that share some specific lattice parameters with hcp-Mg [144]. Starting from the wedge thickness of 0.4 mm the majority of Mg-rich flakes are densely surrounded by a fine dispersion of the Mg_2Ni intermetallic compound. The high Ni-content and low concentration of rare-earth components in the $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$ alloy

appears to promote the formation of the Mg_2Ni phase even at higher cooling rates during casting.

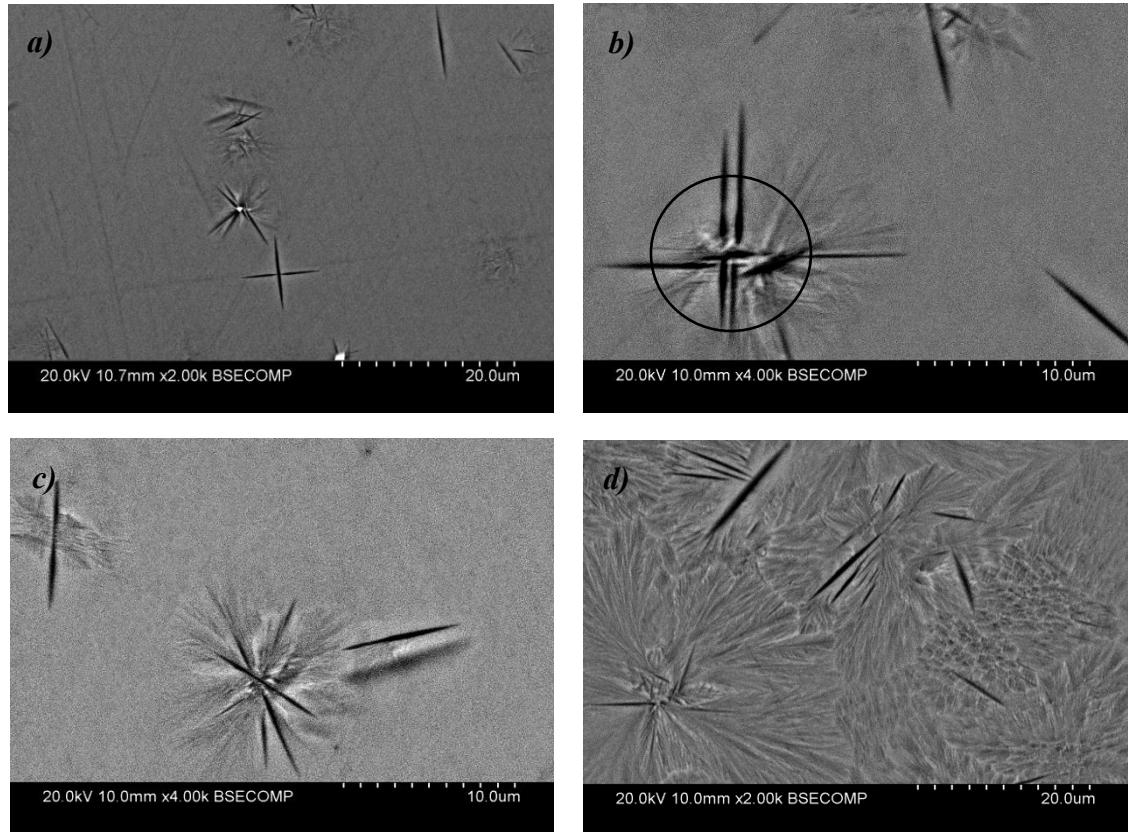


Figure 3.13. SEM backscattered electron images of $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$ wedge cross section at thicknesses Z : (a) $Z=0.5$ mm; (b) $Z=0.8$ mm; (c) $Z=1$ mm, and (d) $Z=1.3$ mm.

By comparing these two alloys with 84 at. % Mg it can be seen that even slight changes in chemical composition lead to significant alteration of crystallite phase morphology in these BMG composites.

3.4.4. Alloys with 86 at.% Mg

Compositions containing 86 at.% Mg are represented by $\text{Mg}_{86}\text{Ni}_8\text{Gd}_4\text{Y}_2$ and $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ alloys. XRD scans for both alloys taken at 0.7 mm wedge thickness are shown in Fig. 3.14 indicating the presence of an amorphous-crystalline structure. The $\text{Mg}_{86}\text{Ni}_8\text{Gd}_4\text{Y}_2$ sample was found to contain the Mg-based amorphous phase and crystalline hcp-Mg, Mg_2Ni and Mg_5Gd phases, whereas the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ alloy consists of amorphous matrix, hcp-Mg and Mg_2Ni (Fig. 3.14(b)) crystalline phases. The

critical thickness for monolithic glass formation is ~ 0.35 mm for both alloys and the composite structure formation occurs in the range of 0.35 – 1.1 mm of wedge thickness.

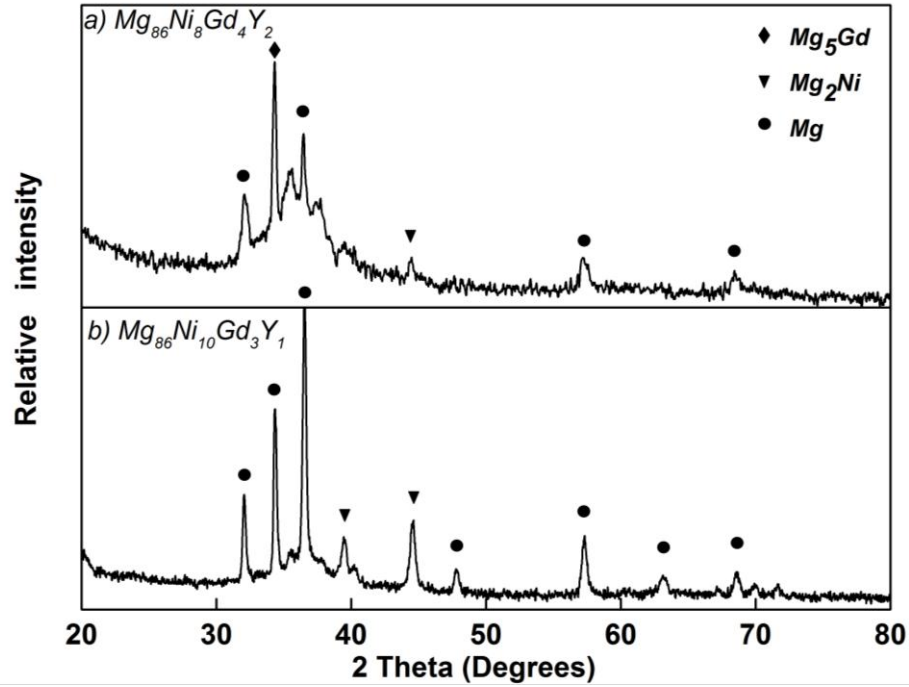


Figure 3.14. XRD patterns taken at 0.7 mm wedge thickness for: (a) $Mg_{86}Ni_8Gd_4Y_2$ alloy; (b) $Mg_{86}Ni_{10}Gd_3Y_1$ alloy.

Backscattered SEM image of the microstructure of the $Mg_{86}Ni_8Gd_4Y_2$ alloy (Fig. 3.15(a)) observed at the wedge thickness of 0.3-0.5 mm demonstrates Mg-rich dendrites with secondary branches dispersed in the amorphous matrix. At sample thickness of 0.6-0.7 mm, a dispersion of the Mg_2Ni and Mg_5Gd phases appears in proximity to the Mg-rich flakes (Fig. 3.15(b)).

The microstructure of the $Mg_{86}Ni_{10}Gd_3Y_1$ alloy is shown in Fig. 3.15(c-d). At thickness of 0.5 mm it consists of the Mg-rich flake-shaped phase dispersed in the amorphous matrix (Fig. 3.15(c)). At larger thicknesses the length and the volume fraction of Mg-flakes increases. Simultaneously thin needle-shaped crystals of the Mg_2Ni -phase appear around the hcp-Mg crystallites. A completely crystalline structure forms at a sample thickness of 1.1 mm.

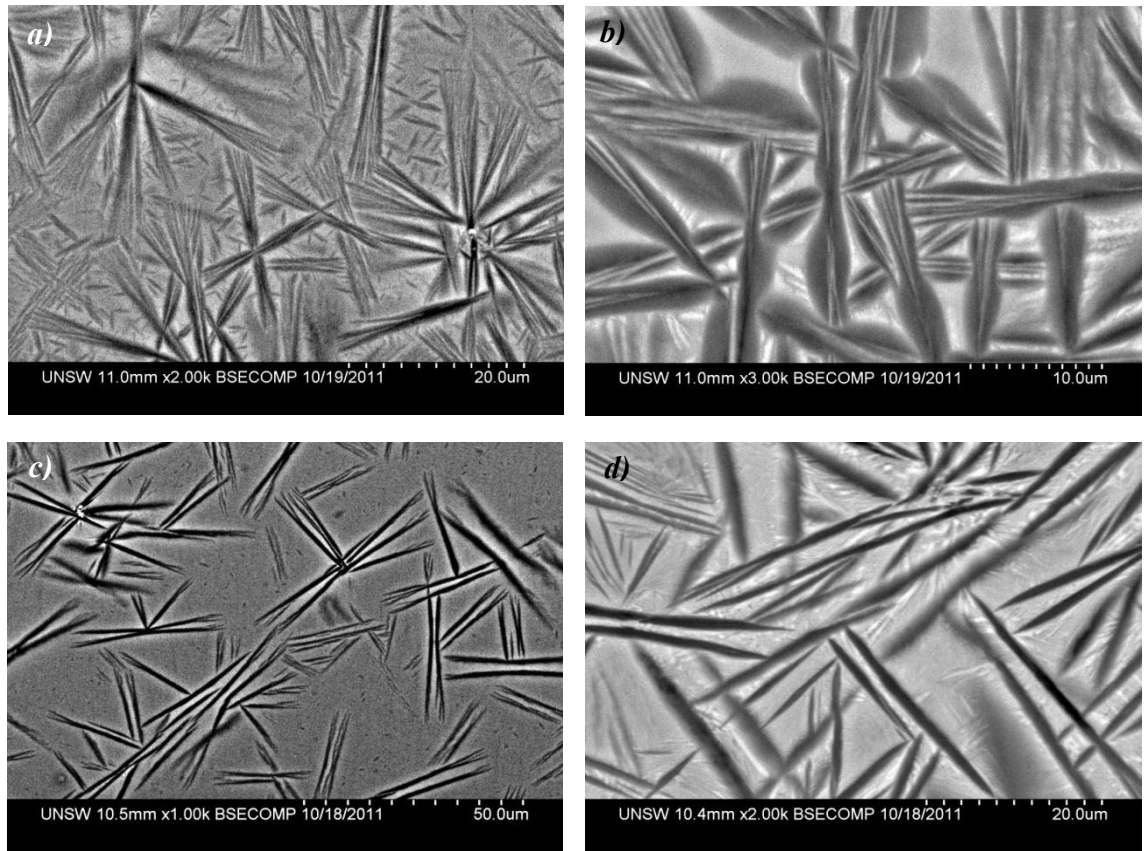


Figure 3.15. SEM backscattered electron images of composite structure at different wedge thickness Z : (a) $\text{Mg}_{86}\text{Ni}_8\text{Gd}_4\text{Y}_2$, $Z=0.5$ mm; (b) $\text{Mg}_{86}\text{Ni}_8\text{Gd}_4\text{Y}_2$, $Z=1$ mm; (c) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$, $Z=0.5$ mm, and (d) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$, $Z=1$ mm.

Thus, analysing images of a given BMG composite with 86 at.% Mg, it may be concluded that an increase in concentration of rare-earth elements promotes the formation of the Mg_5Gd phase around hcp-Mg phase, whereas a higher Ni content results in the precipitation and growth of the Mg_2Ni intermetallic compound.

3.4.5. Alloy with 88 at.% Mg

The maximum Mg concentration examined in this study is for the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$ composition which has a relatively small critical thickness for glass formation of ~ 0.3 mm. However, the amorphous phase is present in the composite structure up to a thickness of 0.8 mm. The XRD pattern for the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ alloy at 0.6 mm wedge thickness indicates the presence of the amorphous phase, hcp-Mg phase and small traces of the Mg_2Ni intermetallic (Fig. 3.16).

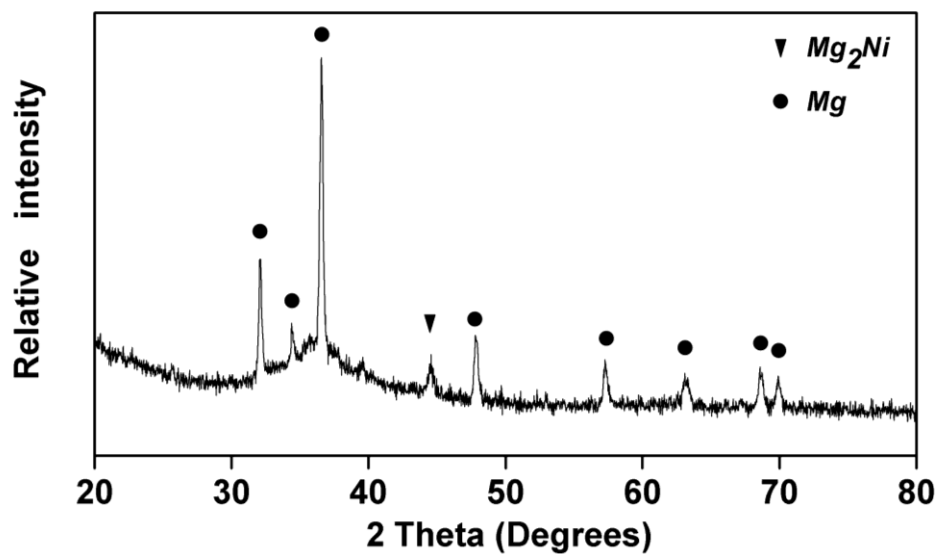


Figure 3.16. XRD scan for $\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$ alloy at thickness of 0.6 mm.

The microstructure of the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$ alloy is depicted in Fig. 3.17. The Mg-rich phase in this composition is represented, not as isolated dendrites of first order but, rather, as a branched dendrite structure. Flake-shaped dendrites with well-defined primary trunks have secondary and sometimes tertiary dendrite arms that intersect with each other. At 0.3-0.5 mm sample thickness these branched dendrites appear as separated groups scattered in the amorphous phase (Fig. 3.17(a)). At greater thicknesses they represent a continuous interwoven network within the remaining glassy matrix (Fig. 3.17(b-c)). Between dendrite arms the Mg_2Ni intermetallic phase is observed which gradually consumes the amorphous matrix with an increase in sample thickness (Fig. 3.17(d)).

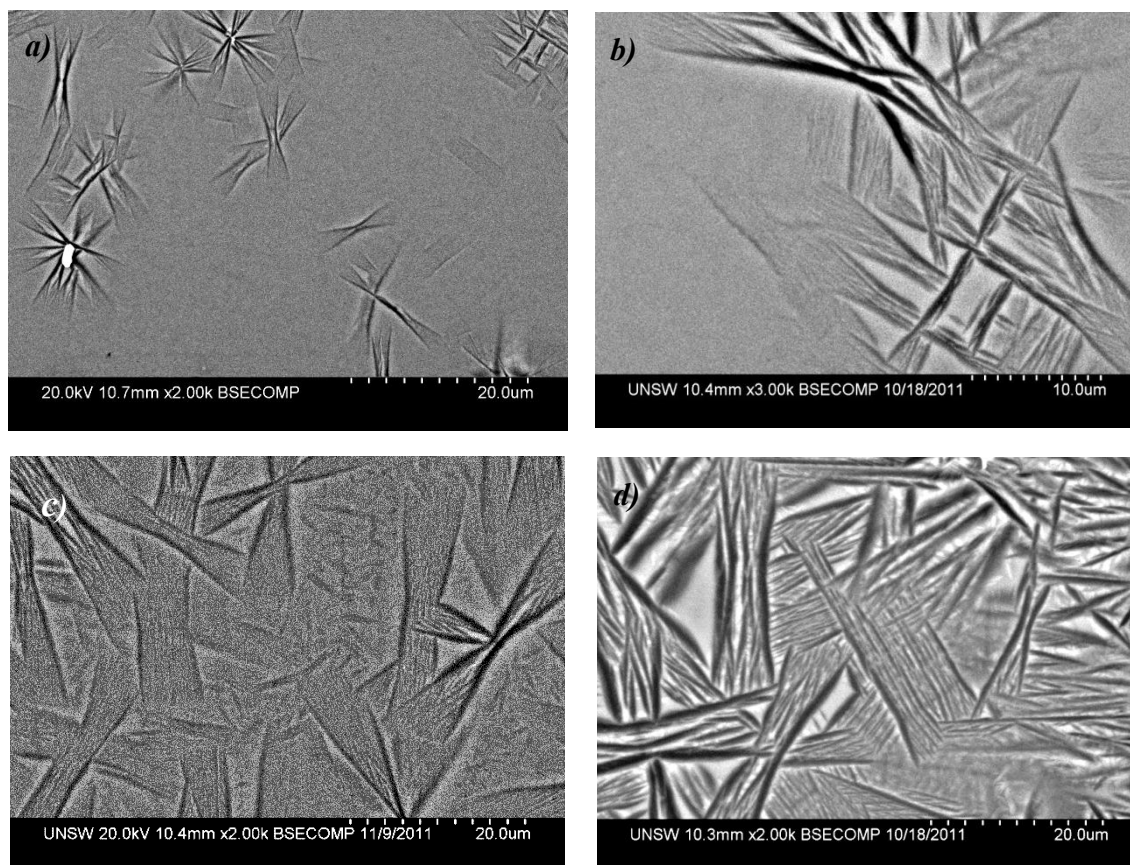


Figure 3.17. SEM backscattered electron images for $\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$ composition at various sample thickness Z : (a) $Z=0.4$ mm; (b) $Z=0.5$ mm; (c) $Z=0.6$ mm, and (d) $Z=0.7$ mm.

3.4.6. Chemical analysis of the microstructure for composite BMG alloy

As noted in the discussion in the previous section, two types of composite structure were produced in the Mg-Ni-Gd-Y alloys. The first type represents a mixture of soft Mg phase and brittle intermetallic compounds distributed in the glassy matrix, whereas the second type represents a single precipitated Mg-rich crystalline phase in the glassy matrix. The latter structure is of particular interest in this thesis since a single ductile phase in the brittle amorphous matrix can provide an enhancement in both the plastic strain to failure and fracture toughness.

As a typical example of an alloy with this type of structure, the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ composition was selected for a careful study of the distribution of elements in both the crystalline inclusions and amorphous matrix using high resolution electron probe microanalysis (EPMA). The analysis was carried out on JEOL JXA-8500F field

emission hyperprobe instrument. Mapping of areas of interest was conducted using 6 kV accelerating voltage, 20 nA probe current, 50 ms dwelling time and step size of 0.1 μm . Figure 3.18 shows EPMA composition concentration profile maps for the constituent elements in the given alloy. Each map represents the distribution of specific elements such as Mg, Ni, Gd and Y within amorphous matrix and the crystalline precipitates. Colour gradients on the right side give a qualitative indication of intensity for each constituent element.

These results indicate that the flake-shaped phase has high Mg concentration (Mg-rich) whereas the surrounding matrix exhibits a local depletion of Mg in the matrix areas in close proximity to the flakes and between them. The distribution of Ni was found to be non-uniform, particularly in the region between Mg-rich flakes where high Ni concentration was observed. Ni was not found in the Mg-flakes since it is not soluble in Mg (<0.04 at.% solubility at 500 °C [142]). Relatively high enrichment of Ni and depletion of Mg in the areas between flakes is likely to promote the formation of the Mg_2Ni compound at the greater wedge thickness, which was found to occur in the majority of the examined compositions. Gd and Y were found to be distributed uniformly in the matrix. Traces of these elements are not observed in the Mg-rich phase although a small amount of Gd can be dissolved in Mg phase (both elements have hcp-structure) due to high cooling rate during solidification.

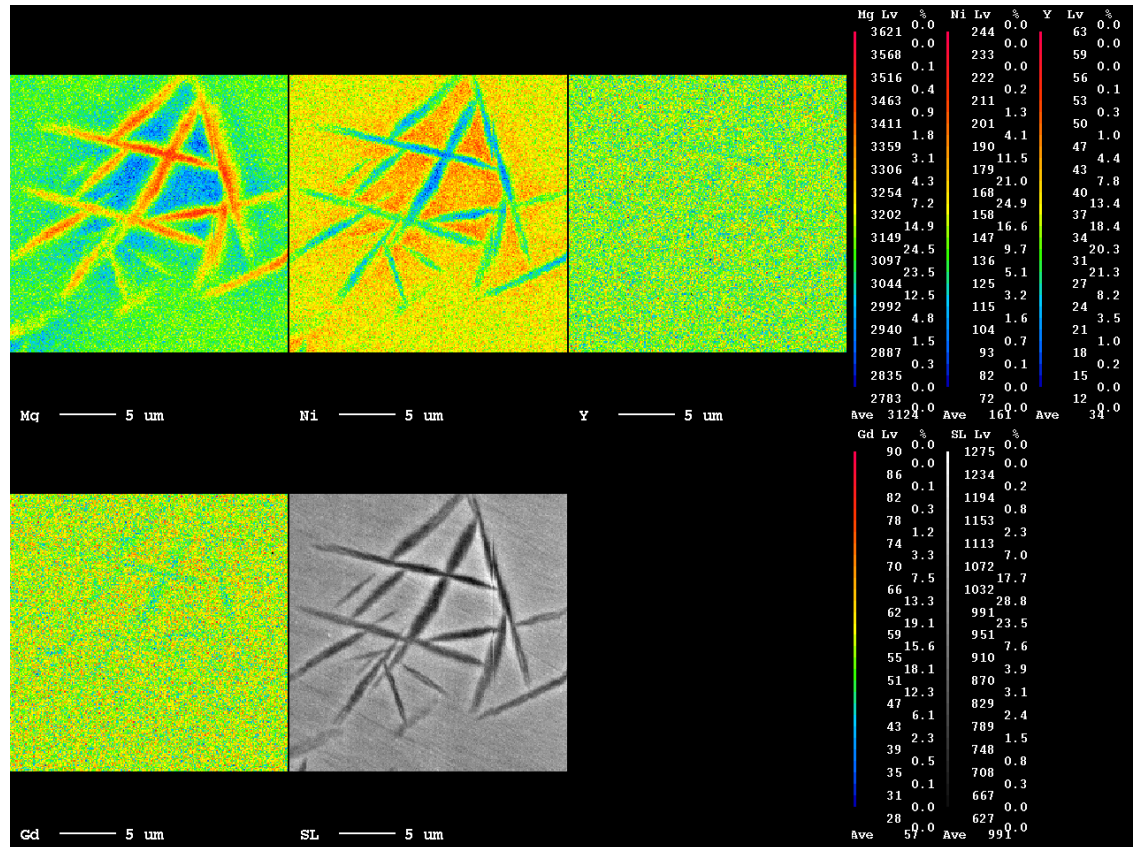


Figure 3.18. EPMA maps of chemical composition for $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ alloy.

3.4.7. Effect of sample chemistry and thickness on phase formation and size of crystallites in amorphous matrix

The study of these Mg-Ni-Gd-Y alloys has demonstrated that small changes in the concentration of rare-earth components, Ni and Mg, defines the glass-forming ability and morphology of crystalline phases generated in the amorphous matrix. In terms of the influence of chemical composition on GFA, it could be said that critical thickness for glass formation descends with increasing Mg content. Table 3.2 summarizes phase selection of composite structures for the alloys examined in this chapter.

Table 3.2. Critical thickness for glass formation and phase selection for Mg-Ni-Gd-Y alloys.

Alloy	Critical thickness for glass formation, mm	Phase selection of the composite structure	Range of sample thickness corresponding to the composite structure, mm
$\text{Mg}_{80}\text{Ni}_{12}\text{Gd}_6\text{Y}_2$	0.7 ± 0.1	AP*+ Mg_5Gd	0.7-1.3
		AP+ Mg_5Gd + Mg_2Ni + Mg_{25}Y_5	1.3-1.8
$\text{Mg}_{82}\text{Ni}_{10}\text{Gd}_6\text{Y}_2$	0.60 ± 0.05	AP+ Mg_5Gd	0.6-1.3
		AP+ Mg_5Gd + Mg_2Ni + Mg_{25}Y_5	1.3-1.8
$\text{Mg}_{82}\text{Ni}_{12}\text{Gd}_4\text{Y}_2$	0.50 ± 0.05	AP+ α -Mg+ Mg_2Ni	0.5-0.8
		AP + α -Mg + Mg_2Ni + Mg_5Gd	0.8-1.3
$\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$	0.4 ± 0.05	AP+ α -Mg+ Mg_2Ni	0.4-1.0
		AP + α -Mg + Mg_2Ni + Mg_5Gd	1.0-1.3
$\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_4\text{Y}_2$	0.4 ± 0.05	AP+ α -Mg	0.4-0.9
		AP + α -Mg + Mg_2Ni + Mg_5Gd	0.9-1.3
$\text{Mg}_{86}\text{Ni}_8\text{Gd}_4\text{Y}_2$	0.3 ± 0.05	AP+ α -Mg	0.3-0.6
		AP + α -Mg + Mg_2Ni + Mg_5Gd	0.6-1.1
$\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$	0.35 ± 0.03	AP + α -Mg	0.35-0.6
		AP + α -Mg + Mg_2Ni	0.6-1.1
$\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$	0.25 ± 0.03	AP + α -Mg	0.25-0.6
		AP + α -Mg + Mg_2Ni	0.6-0.8

*AP – amorphous phase

As seen from Table 3.2, phase selection of composites varies with sample thickness. At lower thickness one or two crystalline phases coexist with the amorphous phase whereas a mixture of at least two crystalline phases is present in the amorphous matrix at greater wedge thickness.

In the alloys with the lowest Mg concentration of 80-82 at.% and high RE content (8 at.%) Mg-based intermetallic compounds are formed in the glassy phase including Mg_5Gd , Mg_2Ni , and Mg_{25}Y_5 . Increasing Mg content to 84 at.% and keeping low concentration of Ni (<10 at.%) and RE elements (<6 at.%) provides the formation of

single Mg-rich phase in the glassy matrix in the range of 0.25-0.9 mm depending on the alloy chemistry.

Figure 3.19 represents the variation in size of the Mg-rich crystalline particles precipitated in the amorphous matrix with increasing thickness of wedge-shaped sample. The size of the crystalline precipitates has been determined as an average of at least ten measurements from three separate SEM micrographs of each alloy composition over a range of magnifications of 1000-2000x. Within the transition zone (glass+crystals) between amorphous and completely crystalline structure the alloys with lower Mg concentration have precipitates of smaller size that gradually increase in size with sample thickness. High Mg-content alloys with 86 and 88 at.% initially have greater sized crystallites (15-20 μm) in the composite region of the wedge. Their size ascends rapidly with increasing wedge thickness due to the lower cooling rate allowing further crystallite growth prior to reaching the temperature at which atomic diffusion is substantially arrested.

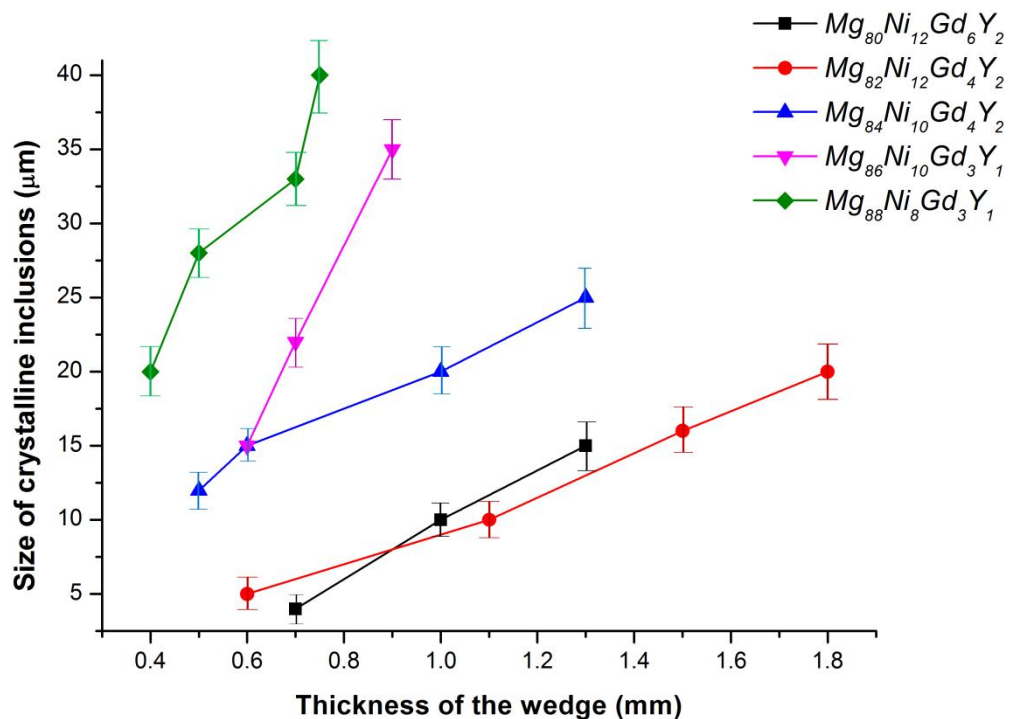


Figure 3.19. Size of Mg-rich crystalline precipitates in glassy matrix as a function of sample thickness.

3.5. THERMAL PROPERTIES OF MG-NI-GD-Y AMORPHOUS ALLOYS

The characteristic thermal properties of the Mg-Ni-Gd-Y glassy alloys were studied by DSC analysis using a Netzch 404 differential scanning calorimeter. To record DSC heating curves, samples from the tip of the wedge were taken where no crystalline phases are observed. Samples placed in the crucible and reference sample (empty crucible) were heated with identical thermal program while the heat flow difference between the sample and reference was recorded. Absorbed and released heat values were plotted as a function of temperature. Figure 3.20 depicts DSC curves for all given Mg-Ni-Gd-Y compositions showing exothermic and endothermic events that occur in the samples during heating due to structural relaxation (the glass transition or T_g), phase evolution (crystallisation), possible phase transformations and melting phenomena. All samples exhibit distinctive glass transition phenomena, some with extended supercooled liquid regions, further indicating that these samples are indeed glassy before heating.

In general, with increasing Mg content and decreasing RE concentration, the glass transition temperature (T_g) and crystallisation temperature (T_x) has a tendency to decline indicating that the glassy structure becomes less thermally stable with increasing Mg concentration. The supercooled liquid region (the difference between crystallisation and glass transition temperatures) for alloys with 86-88 at.% Mg is quite small (7-10 K) indicating the lower resistance to devitrification (tendency of the amorphous phase to crystallise).

DSC curves for each alloy have at least three exothermic peaks denoting multiple phase precipitation from the amorphous structure or transformation from one crystal phase to another during heating. Melting intervals do vary somewhat for the studied alloys based on Mg and RE content. For each of the alloys, multiple endothermic troughs are observed during melting. Ideally, the first major melting trough is attributed to the melting at the nearest eutectic reaction, which, according to the calculated liquidus isosurface is $\alpha\text{-Mg} + \text{Mg}_2\text{Ni} + \text{Mg}_2\text{Gd} + \text{Mg}_{25}\text{Y}_5 \rightarrow \text{Liquid}$. It can be seen from the liquidus traces that the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ and $\text{Mg}_{84}\text{Ni}_{12}\text{Gd}_3\text{Y}_1$ alloys are closest to the quaternary eutectic reaction, as it almost entirely is a single melting trough. It is also notable that alloys with the higher rare-earth content tend to have much larger secondary melting

reactions at higher temperatures, relating to the melting of higher melting-point off-eutectic intermetallics.

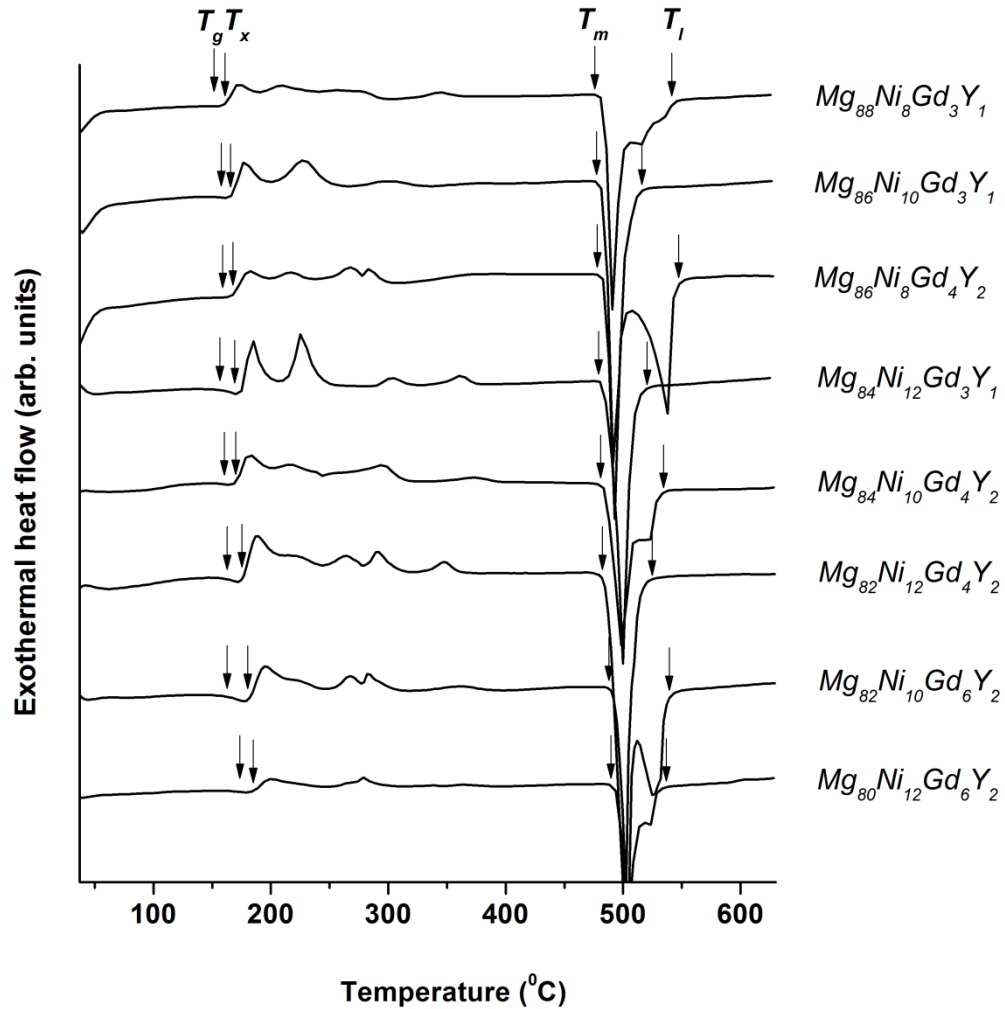


Figure 3.20. DSC scans for the Mg-Ni-Gd-Y alloys recorded at a heating rate of 20 K/min.

A summary of the thermal properties of the Mg-Ni-Gd-Y glassy alloys, as determined from the DSC curves, are given in Table 3.3.

Table 3.3. Thermal properties of Mg-Ni-Gd-Y alloys: T_g – glass transition temperature, T_{x1} – onset temperature of the first crystallisation event, T_m and T_L – onset and offset melting temperatures, respectively.

Alloy	T_g , °C	T_{x1} , °C	$\Delta T_x = T_{x1} - T_g$	T_m , °C	T_L , °C	$T_L - T_m$
Mg ₈₀ Ni ₁₂ Gd ₆ Y ₂	163	180	17	487	540	53
Mg ₈₂ Ni ₁₀ Gd ₆ Y ₂	155	178	23	487	545	58
Mg ₈₂ Ni ₁₂ Gd ₄ Y ₂	156	172	16	481	524	43
Mg ₈₄ Ni ₁₂ Gd ₃ Y ₁	152	172	20	481	520	39
Mg ₈₄ Ni ₁₀ Gd ₄ Y ₂	154	166	12	481	536	55
Mg ₈₆ Ni ₈ Gd ₄ Y ₂	153	163	10	481	550	71
Mg ₈₆ Ni ₁₀ Gd ₃ Y ₁	153	164	11	480	517	37
Mg ₈₈ Ni ₈ Gd ₃ Y ₁	153	160	7	480	544	64

3.6. SUMMARY OF MG-NI-GD-Y BMG COMPOSITES

In summary, the results of investigations into Mg-Ni-Gd-Y alloys showed the variety of amorphous-crystalline morphologies generated in the transition zones between amorphous and crystalline structures. An increase in Mg content from 80 to 88 at.% promotes descending of the limits of full amorphous thickness of samples from 0.7 to 0.25 mm, respectively. The summary range of the amorphous and amorphous-crystalline zones in generated wedges decreases from 1.8 mm to 0.8 mm with increasing Mg concentration.

In regards to the formation of soft crystalline inclusions in an amorphous matrix, the concept of high Mg content was confirmed to be suitable for this purpose. Whilst some compositions form a mixture of intermetallic compounds and hcp-Mg phase in conjunction with glassy phase, few alloys yield single soft Mg-phase as a precipitate in the parent matrix. This fact can be taken further to facilitate the development of new composite structures in metallic glasses.

The thermal properties of alloys are affected by the concentration of Mg and RE elements. A higher RE content increases both the glass transition temperature and crystallisation temperature, whereas an increase in Mg content results in narrowing the supercooled liquid region.

CHAPTER 4 - STUDY OF MG-NI-GD GLASS-FORMING SYSTEM

4.1. BACKGROUND

In light of the experimental results represented in Chapter 3 it is proposed that at least three compositions in the Mg-Ni-Gd-Y system could be potentially considered for the fabrication of ductile BMG composites. The fact that the compositions $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_4\text{Y}_2$, $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_3\text{Y}_1$ and $\text{Mg}_{88}\text{Ni}_8\text{Gd}_3\text{Y}_1$ exhibit a single soft Mg-rich phase as a precipitate in the glassy matrix makes them superior candidates in terms of mechanical performance in comparison with alloys that precipitate intermetallic phases in a glassy matrix. As concluded from the literature assessment of various BMG composite studies, ductile reinforcing particles dispersed in the brittle amorphous matrix can provide an enhancement in fracture toughness and plastic strain to failure. Thus, the aforementioned compositions were selected as a base for further study.

By analysing the morphology of fabricated Mg-Ni-Gd-Y composites it was observed that the microstructure of many compositions contained isolated Y_2O_3 particles or their agglomerates which, to some extent, affected (or inoculated) the formation of crystalline reinforcement in amorphous matrix. Ytria or Y_2O_3 particles were found to be formed in other studies [144, 145] during casting or melt solidification of Mg-Cu-Y-Zn BMG composites and were found to serve as nucleation sites for a crystalline Mg-rich phase similar to that seen in this body of work. In order to exclude the influence of Y_2O_3 particles on the growth of crystalline phase, the concept of simplification of the alloy composition was applied. The Yttrium content in selected Mg-Ni-Gd-Y alloys was entirely substituted with gadolinium and, as a consequence, ternary Mg-Ni-Gd compositions were developed for investigation.

Hence, the aims of this chapter are to: (i) explore the composite microstructure in Mg-Ni-Gd alloys with high Mg content; (ii) determine any differences in morphology and thermal behaviour between the ternary and quaternary alloys containing the same concentration of base element and rare-earth components, and (iii) establish the role of Y in the formation of glassy-crystalline structure in Mg-based glasses.

4.2. BMG COMPOSITES GENERATED IN MG-NI-GD SYSTEM BY GRAVITY CAST METHOD

In order to precipitate the soft and ductile Mg-rich phase from the amorphous matrix/supercooled liquid in Mg-Ni-Gd system, the following compositions were prepared: $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$, $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ and $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$. Wedge-shaped samples were fabricated by the gravity copper mould casting method described in the section 3.3. A casting temperature for all given alloys was 650 °C – this temperature is sufficiently above the determined liquidus temperature. Samples were sectioned and mounted in the epoxy resin then subject to microstructural analysis by OM and SEM.

4.2.1. Structural characteristics of Mg-Ni-Gd composite alloys with 84, 86 and 88 at.% Mg

Up to a certain wedge thickness (critical thickness for glass formation) all compositions have a homogeneous amorphous structure. To compare the glass-forming ability of fabricated alloys, X-ray scans for all compositions were taken from the samples of 0.5 mm thickness as shown in Fig. 4.1. XRD patterns for alloys containing 84 and 86 at. % Mg have a single broad diffraction halo that confirms their glassy nature. XRD scan of composition containing 88 at. % Mg represents a two-phase structure consisting of an amorphous matrix and crystalline precipitates that were identified as a Mg-rich phase with lattice parameters consistent with hcp α -Mg.

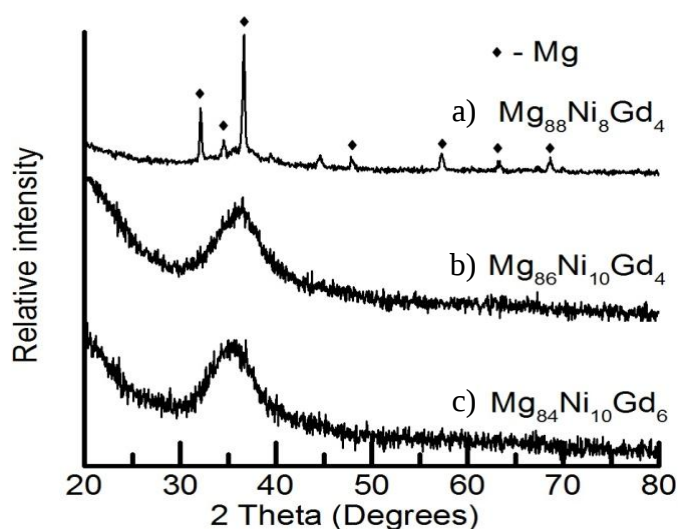


Figure 4.1. XRD patterns taken from the cross-section surface of wedges at 0.5 mm thickness for alloys: (a) $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$; (b) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$; (c) $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$.

Lattice parameters of hcp-Mg phase in alloys with different Mg-content are shown in the Table 4.1. Lattice parameters for compositions with 84 and 86 at.% Mg were estimated by XRD data recorded from the samples of larger thickness where diffraction maxima for hcp α -Mg were clearly prominent.

The microstructure of alloys corresponding to the specific thickness of wedge-shaped sample is given in Fig. 4.2.

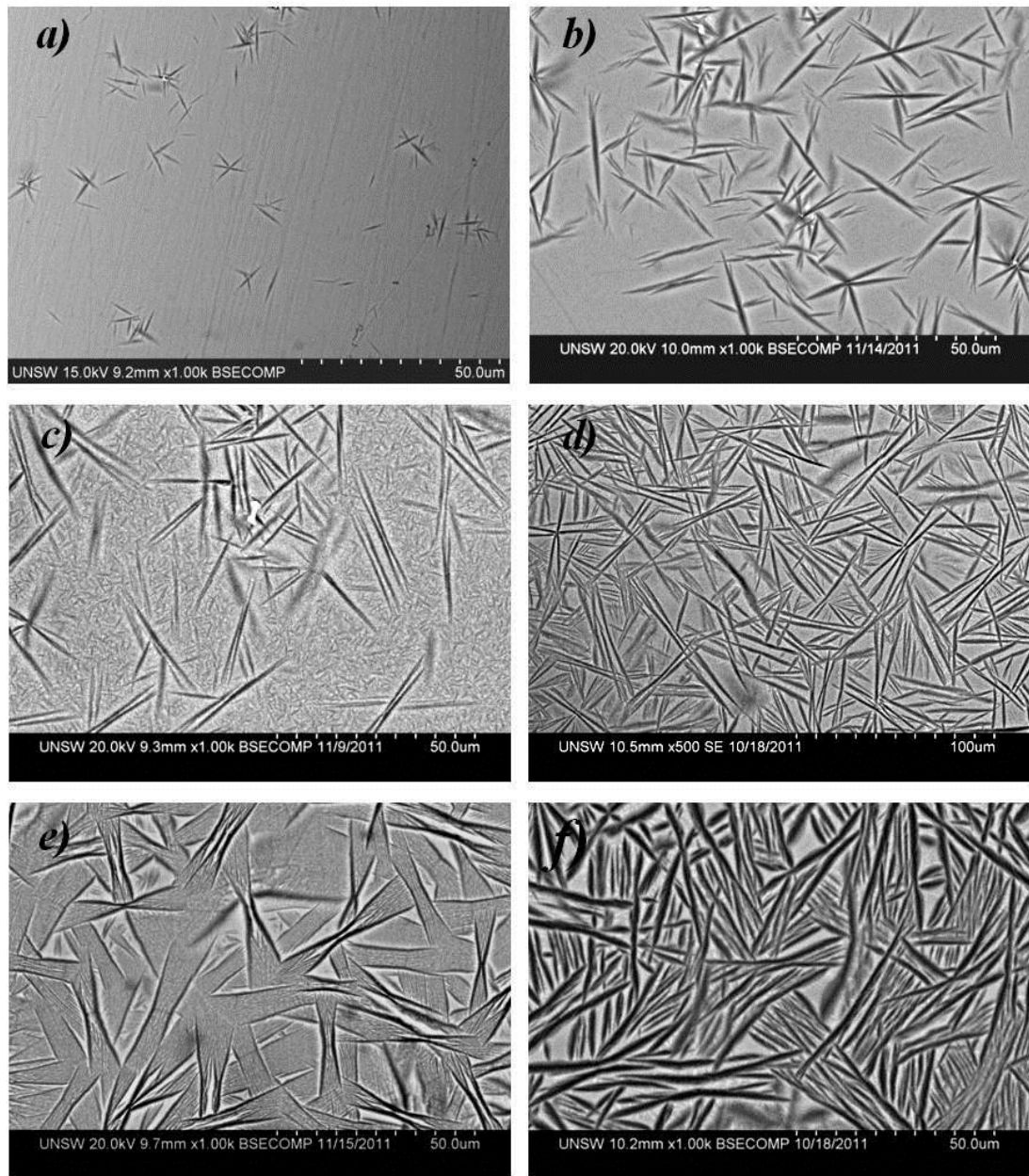


Figure 4.2. SEM backscattered electron images taken from the cross-section surface of as-cast wedges at given thickness, Z , for: (a) $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$, $Z=0.8$ mm; (b) $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$, $Z=1$ mm; (c) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$, $Z=0.8$ mm; (d) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$, $Z=1$ mm; (e) $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$, $Z=0.5$ mm, and (f) $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$, $Z=0.8$ mm.

Table 4.1. Lattice parameters of Mg-rich hcp-phase in Mg-Ni-Gd composite alloys.

Alloy	Lattice parameters, nm	c/a ratio
Mg ₈₄ Ni ₁₀ Gd ₆	$a=0.3209, c=0.5257$	1.638
Mg ₈₆ Ni ₁₀ Gd ₄	$a=0.3209, c=0.5195$	1.619
Mg ₈₈ Ni ₈ Gd ₄	$a=0.321, c=0.5209$	1.623

The morphology of the structure strongly depends on the alloy composition and cooling rate (wedge thickness), which will be discussed in the Section 4.2.2. A featureless amorphous structure is observed for Mg₈₄Ni₁₀Gd₆ and Mg₈₆Ni₁₀Gd₄ alloys at 0.7 and 0.5 mm thickness, respectively.

At a thickness of 1 mm, the structure of the Mg₈₄Ni₁₀Gd₆ composition consists of an amorphous matrix with isolated Mg-crystallites of 15-25 μm in length. The microstructure of the Mg₈₆Ni₁₀Gd₄ composition consists of multiple crystalline precipitates of a few microns in size and larger acicular Mg-rich crystallites dispersed in the amorphous matrix. The structure of the Mg₈₈Ni₈Gd₄ composition also contains crystalline precipitates similar to Mg₈₆Ni₁₀Gd₄, with a lower volume fraction of the amorphous phase. The morphology of the Mg-rich phase now appears as an interwoven network of acicular crystallites. The volume fraction of the (favourable) Mg-rich crystalline phase shown in Fig. 4.2 corresponds to 16, 27 and 52 volume % for alloys with 84, 86 and 88 at.% Mg, respectively. Values of volume fractions were determined by the graphical software Adobe Photoshop CS.

The thickness/cooling rate interval of formation of the two-phase composite structure decreases with increasing Mg concentration. The amorphous-crystalline structure in Mg₈₄Ni₁₀Gd₆ and Mg₈₆Ni₁₀Gd₄ alloys is observed at 0.8-1.5 and 0.4-1.2 mm wedge-thickness, respectively, whereas the formation of a composite structure in the Mg₈₈Ni₈Gd₄ alloy occurs within a narrow thickness range of 0.25-0.9 mm.

4.2.2. Correlation between BMG composite microstructure and solidification rate

The microstructure and phase evolution of samples taken from various wedge thicknesses were found to vary significantly. This is highlighted by the example of the

$\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy. The change in the appearance of XRD patterns for one sample at different thicknesses, Z , indicates structure transformation from single glassy phase to almost completely crystalline containing multiple phases (Fig. 4.3).

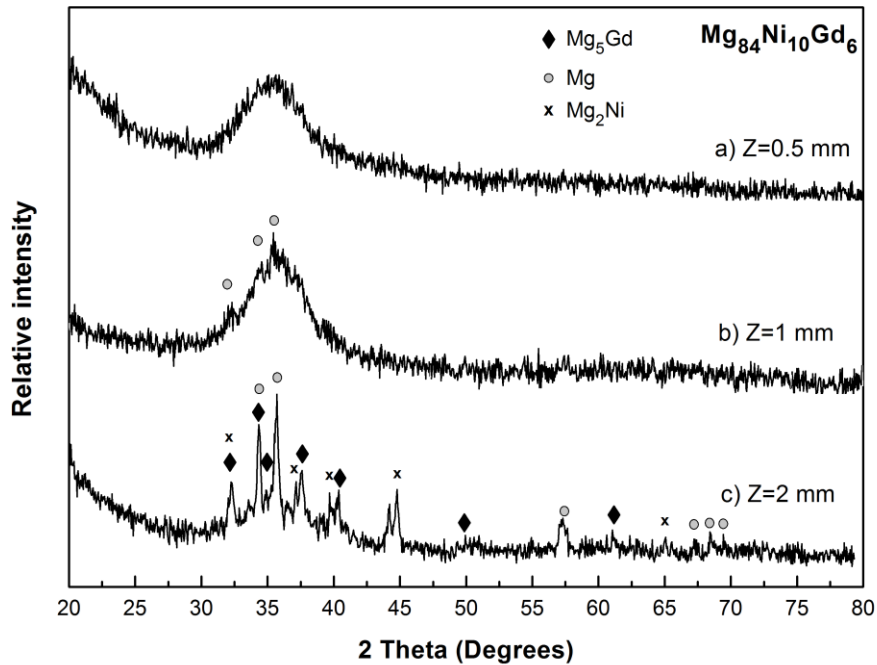


Figure 4.3. XRD patterns taken from the cross-section surface of the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ wedge at various thickness, Z : (a) $Z=0.5$ mm; (b) $Z=1$ mm, and (c) $Z=2$ mm.

SEM images showing the evolution of the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy microstructure are given in Fig. 4.4. Naturally, the microstructure of the entirely amorphous region ($Z < 0.7$ mm) is featureless. With an increase in wedge thickness, Mg-rich flakes (dark contrast phase in Figs 4.4(a) & 4.4(b)) have precipitated from the amorphous matrix. The formation of the primary Mg-rich phase does not lead to the spontaneous crystallisation of the remaining amorphous matrix. In this case the composition of the glassy matrix phase is depleted of ‘excess’ Mg and shifts towards the composition of higher liquid stability and better GFA with a lower Mg-content similar to those observed elsewhere [142].

The volume fraction of the amorphous phase decreases gradually with increasing thickness and completely disappears at ~ 1.5 mm thickness. At a thickness of 1.5 mm, the intermetallic phase, Mg_5Gd , forms around the Mg-rich flakes with the simultaneous growth of the Mg_2Ni (light needle-like phase in Fig. 4.4(b)) in the space between the Mg-rich crystallites. The fact that this alloy lies in the Mg_2Ni liquidus phase field, yet is

the last to precipitate based on cooling rate, indicates that the kinetics of formation of the Mg_2Ni crystallites from the melt/supercooled liquid is much slower than the other phases; this is important for the design of future amorphous alloy/composites.

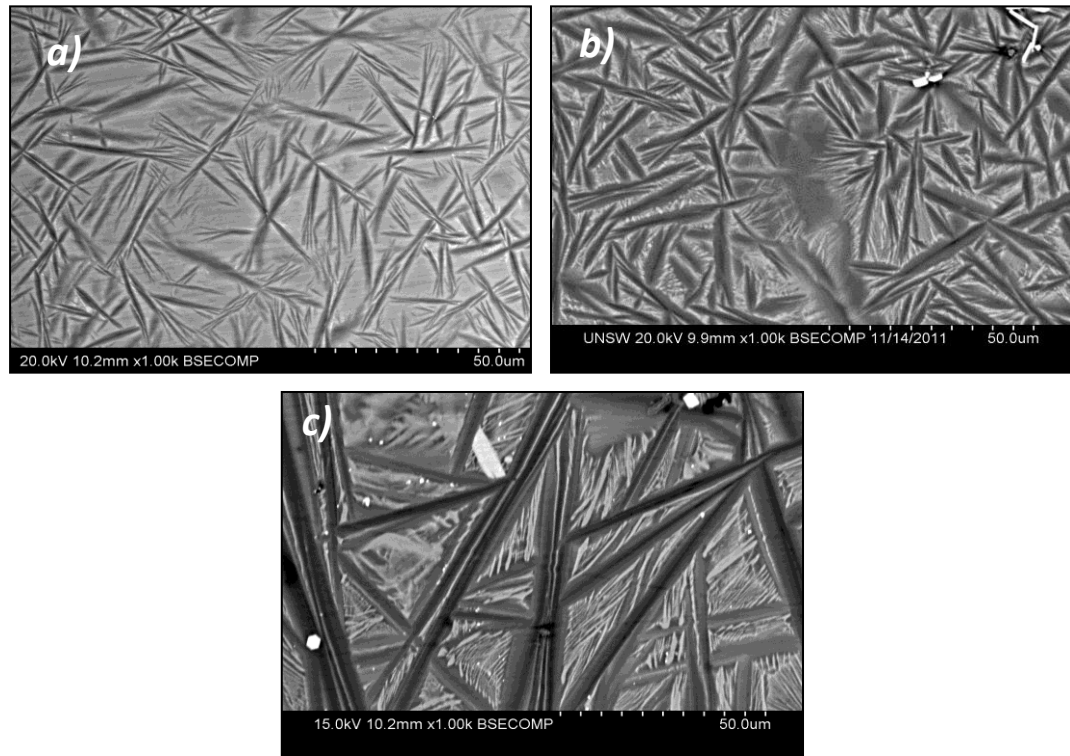


Figure 4.4. SEM backscattered electron images taken from the cross-section surface of as-cast $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ wedge at thickness, Z: (a) Z=1.3 mm; (b) Z=1.5 mm; (c) Z=5 mm.

The sample taken from the 5 mm section (Fig. 4.4(c)) consists of the same phases as the 1.5 mm section (Fig. 4.4(b)). However, due to the much slower cooling rate, the size of Mg-rich and intermetallic phases are 2-3 times larger compared to those depicted in Fig. 4.4(b). The evolution of the microstructures illustrated in Fig. 4.4 shows the strong dependence of microstructure on cooling rate during melt solidification.

4.2.3. Chemical analysis of the microstructure

The distribution of the constituent elements in the structure of the as-cast composite alloy was examined using the electron probe microanalyser (EPMA). Figure 4.5 illustrates iso-intensity maps (using specific X-ray energy dispersion peaks) for Mg, Ni and Gd elements in the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy. The colour gradient bar on the right indicates the relative intensity of each element from low (blue) to high (red). It can be

seen that dark plate-like phase (in the backscattered electron image) consist of almost pure Mg. The Mg-concentration decreases in the area adjacent to the plates and the alloy (amorphous) matrix is depleted in Mg in the areas between plates whereas Ni exhibits a higher concentration in these areas. Due to this fact, the growth of the needle-shaped Mg_2Ni compound occurs in the vicinity of the Mg-plates at larger wedge thickness. Gd appears to be uniformly distributed in the amorphous matrix, although the low concentration of Gd may contribute to a lower signal sensitivity.

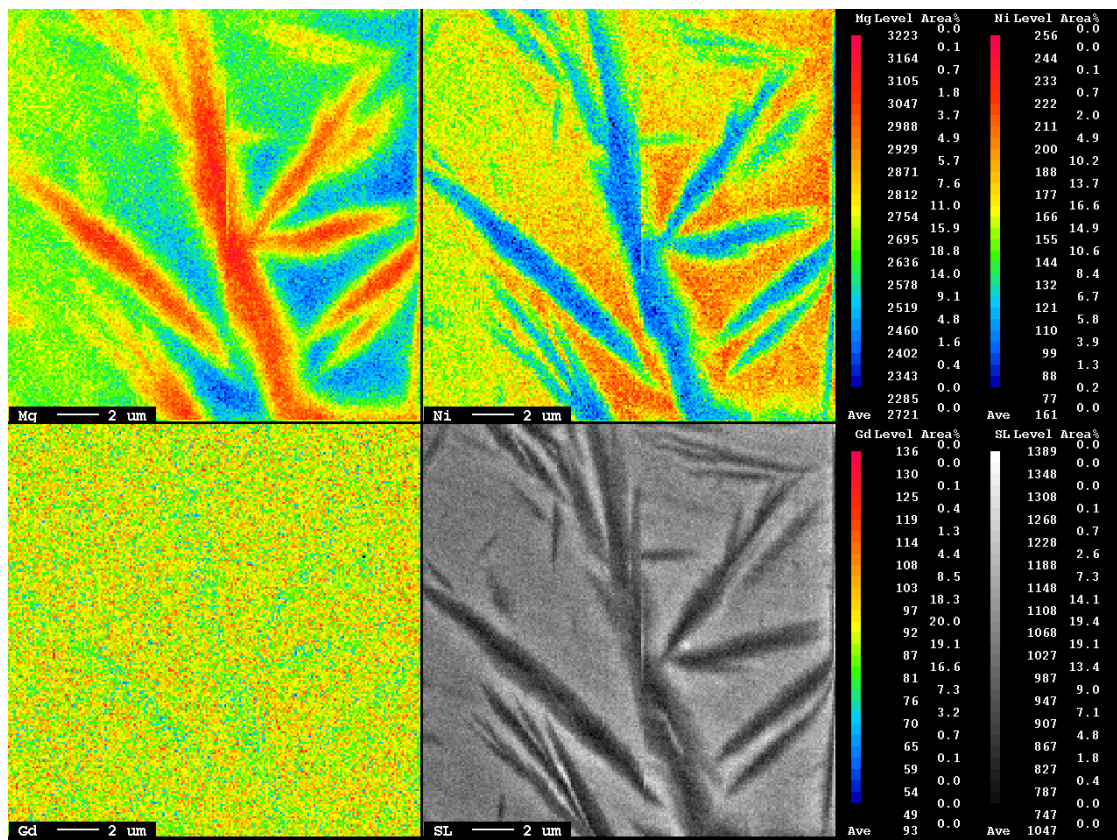


Figure 4.5. EPMA maps of typical structure for as cast $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy at a wedge thickness of 1 mm.

4.3. CRYSTALLISATION BEHAVIOUR OF MG-NI-GD ALLOYS

To understand the thermodynamic and kinetic conditions of non-equilibrium composite structure formation, it is important to understand the crystallisation behaviour of the amorphous component. From a technological or applied perspective, this knowledge can give an estimation of the temperature ranges where BMG composites may maintain their unique properties and microstructures or change or transform them. To determine

the thermal properties of the alloys examined in this study differential scanning calorimetric (DSC) analysis was employed. The crystallisation processes of the amorphous phase during heating were studied for the Mg-Ni-Gd alloys at wedge thickness of 0.3-0.5 mm where no crystalline phases were observed.

4.3.1. Transformation temperatures

DSC isochronal traces for $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$, $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ and $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ compositions recorded at heating rate of 20 °C/min are shown in Fig. 4.6. Alloys containing 84 and 86 at. % Mg, respectively, exhibit both a distinct glass transition and supercooled liquid region. The composition containing 88 at. % Mg exhibits a weaker glass transition yet still reveals exothermic peaks corresponding to the crystallisation processes in the material. This is additional evidence that the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ alloy contains a significant amorphous component in the microstructure prior to heating. A DSC curve for this alloy exhibits multiple endothermic peaks during the melting sequence indicating that this alloy composition resides some distance from the nearest ternary eutectic reaction. The $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy exhibits the narrowest melting interval and a single exothermic peak. This is attributed to the close proximity of this composition to the eutectic point, when compared to the other alloys.

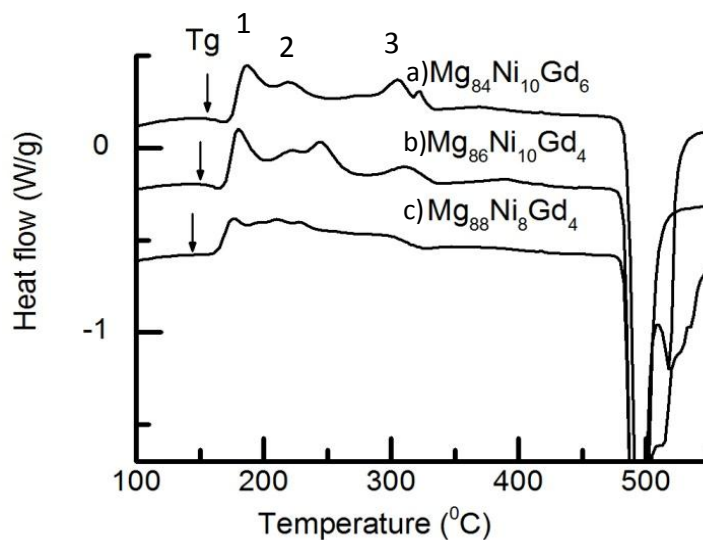


Figure 4.6. Isochronal DSC curve taken from the amorphous region of the as cast Mg-Ni-Gd alloys during heating at 20K/min.

The width of the supercooled liquid interval, which relates to the stability of amorphous phase, is quite small for all compositions, thereby indicating a low level of resistance to crystallisation. The values of the onset glass transition temperature T_g and crystallisation temperature are given in Table 4.2. With increasing Mg content the glass transition temperature (an indicator of thermal stability) decreases as does the size of the supercooled liquid region and the glass-forming ability.

Table 4.2. Thermal properties of Mg-Ni-Gd alloys; T_g denotes the glass transition temperature, T_x the temperature of first exothermic reaction, and T_m and T_L is the onset and offset melting temperatures, respectively.

Alloy	T_g , °C	T_x , °C	$\Delta T_x (=T_{x1}-T_g)$	T_m , °C	T_L , °C
Mg ₈₄ Ni ₁₀ Gd ₆	159	172	13	478	534
Mg ₈₆ Ni ₁₀ Gd ₄	157	168	11	478	525
Mg ₈₈ Ni ₈ Gd ₄	155	160	5	478	550

4.3.2. Structural details of crystallisation products for Mg₈₄Ni₁₀Gd₆ alloy

The products of crystallisation of Mg-rich amorphous matrix were studied in the Mg₈₄Ni₁₀Gd₆ alloy since it had the largest critical casting thickness for glass formation. The DSC curve from the purely amorphous Mg₈₄Ni₁₀Gd₆ alloy (Fig. 4.6) has several exothermal peaks indicating that devitrification occurs in a multistage manner. To determine the phase transformations of the amorphous phase during heating, the alloy was heated to various temperatures corresponding to the DSC curve based on the completion temperatures of exothermic events (peaks 1, 2 & 3 in Fig. 4.6). Purely monolithic samples were heated to temperatures of 210, 240 and 315 °C at a rate of 20 K/min, held isothermally for 60 s and then cooled at a rate of 40 K/min to room temperature to ensure the same thermal history for all alloys. It should be noted that both the heating rate and annealing time considerably affect kinetic parameters of the glassy phase (T_g and T_x) and change its thermal history. Given sufficient annealing

time, any glassy structure can be transformed into a more thermodynamically stable crystalline structure.

Figure 4.7 shows a series of XRD patterns for the heat treated samples including the as-cast alloy for comparison. Splitting of the single diffraction halo on the XRD pattern, which was observed for the alloy heated to 210 °C, is caused by an exothermal reaction corresponding to peak 1 in Fig. 4.6. The two broad peaks in Fig. 4.7(b) may be attributed to the (002) and (101) diffraction reflections of the hcp-Mg phase suggesting that a nanoscale Mg-rich phase forms at the initial stage of devitrification [146].

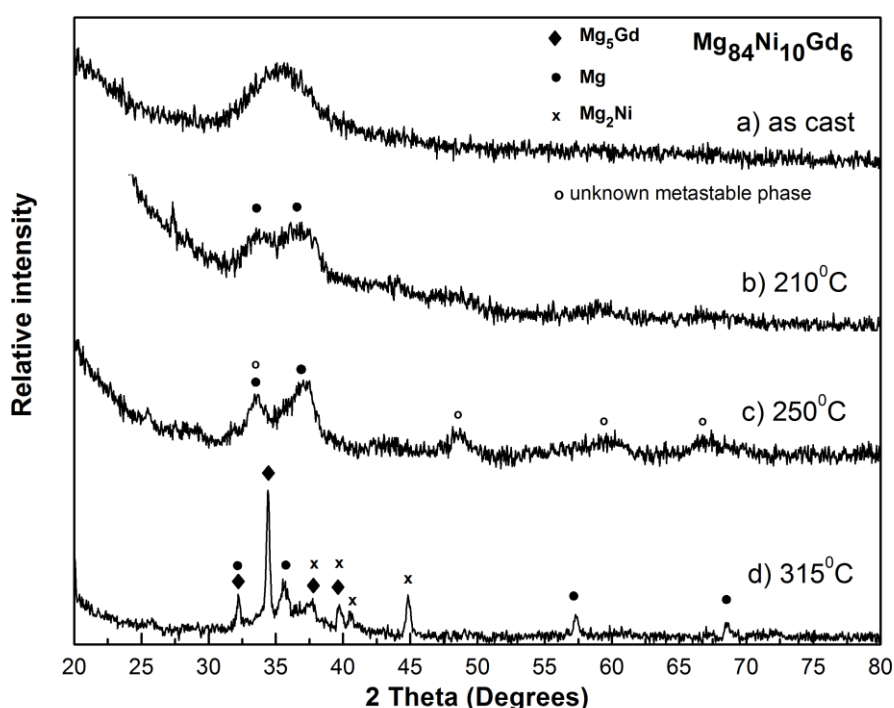


Figure 4.7. XRD patterns taken from the amorphous region of the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ wedge after heating samples at 20 K/min to the temperatures shown as 1-3 in Fig. 4.6, followed by rapid cooling: (a) as cast sample; (b) sample heated to 210°C; (c) sample heated to 250°C; (d) sample heated to 315°C.

The product of the second exothermic reaction (peak 2 in Fig. 4.6) is an unknown metastable phase which decomposes by a subsequent phase transformation.

Figure 4.7(c) represents the diffraction pattern of the sample heated to 250 °C where the hcp-Mg phase and metastable phase coexist. The formation of crystalline precipitates starts at the temperature interval related to the onset of the third exothermal peak.

Comparing XRD scans for alloys heated to 250 °C and 315 °C (Figs 4.7(c) and (d)), it can be seen that (002) and (101) diffraction peaks associated with hcp-Mg phase are shifted to smaller angles at higher heating temperature (from $\sim 37^\circ$ to 35.5° and 33.5° to 32° , respectively). This shift is related to the change in the lattice parameters of hcp-Mg due to its transition to the equilibrium state upon heating.

The XRD pattern corresponding to the sample heated to the completion of the third peak (315 °C) shows the coexistence of Mg-rich, Mg_5Gd and Mg_2Ni crystalline phases, as seen from the SEM image in Fig. 4.8. Dark crystallites correspond to the Mg-rich phase, whereas areas between the Mg phase represent a eutectic mixture of Mg_2Ni and Mg_5Gd compounds. The length and width of the Mg crystallites is 3-5 μm and 0.5-1 μm , respectively. This size is considerably smaller in contrast with the same Mg-phase observed in the crystalline section of the as-cast wedge at a thickness of 5 mm. The same phases that were observed for the as-cast alloy formed at wedge thicknesses greater than 2.5 mm shows that the microstructure after the third phase transformation in the amorphous phase on reheating approaches an equilibrium state.

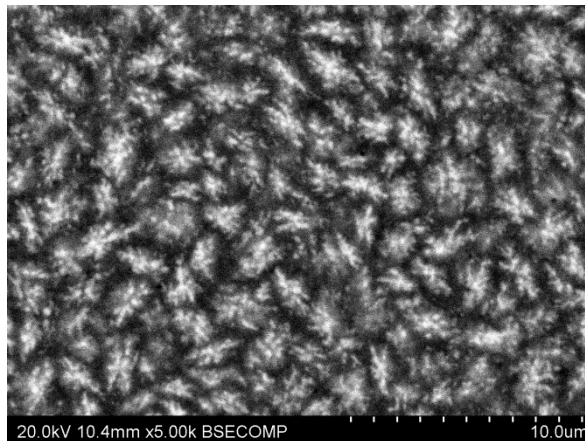


Figure 4.8. Crystalline structure of $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy after annealing to 588 K.

Considering that the first phase that forms in the amorphous $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy consists predominantly of Mg, and according to XRD, the first phase to precipitate from the supercooled liquid during heating corresponds to hcp-Mg, it is likely that the devitrification process occurs via the primary crystallisation mode [147] and α -Mg has the fastest crystallisation kinetics. This process is governed by volume diffusion and requires considerable redistribution of the constituent elements [148], thereby implying

that rearrangement of alloying elements occurs in the amorphous $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy during heating by a similar mechanism to that in the melt upon non-equilibrium cooling.

4.3.3. Thermal stability of glassy phase

Values of T_g and T_x are kinetic parameters that are dependent on the thermal history of the alloy (magnitude of undercooling, cooling rate, heating rate and time at a given temperature). For instance, the higher the cooling rate used for alloy vitrification, the greater is the observed glass transition temperature [8]. In other words, there are no specific values of T_g and T_x that are strictly defined for a given material like melting temperature.

Isochronal DSC scans for amorphous Mg-rich alloys performed at different heating rates indicate that higher heating rates lead to higher values of T_g and T_x . Since the glass transition is a relaxation process from the glassy state to supercooled liquid, the variation of T_g with heating rate reflects time required for structural relaxation. A higher heating rate implies less time for the completion of the relaxation process and consequently, the onset of the glass transition or crystallisation is shifted to higher temperatures.

Figure 4.9 illustrates the heating rate dependence of glass transition and crystallisation temperatures. The stronger dependence of T_g and T_x on heating rate for the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy is an indicator of better GFA and thermal stability.

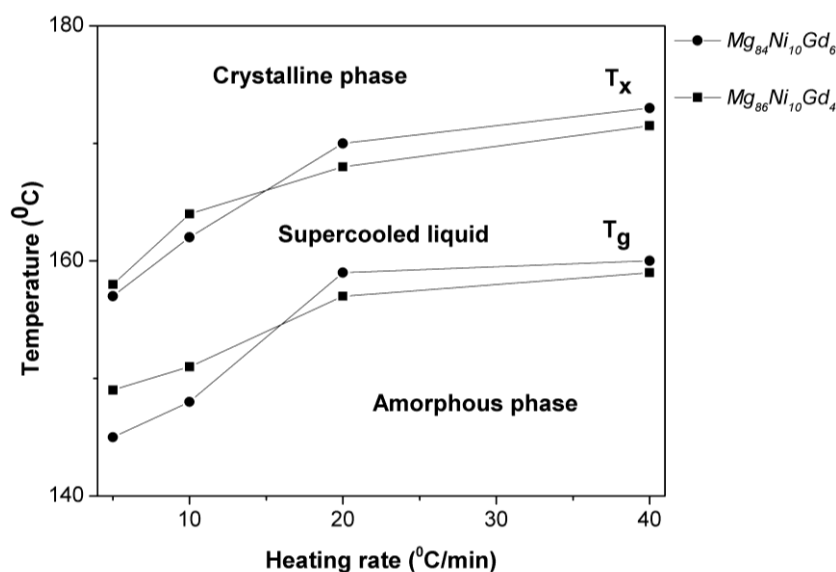


Figure 4.9. Glass transition temperature (T_g) and onset crystallisation temperature (T_x) for the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ and $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloys determined by DSC at heating rates of 5, 10, 20 and 40 °C/min.

4.3.4. Activation energy for crystallisation

The concept of heating rate dependence for T_g and T_x parameters can be used to determine an activation energy for crystallisation. The activation energy shows the value of the energetic barrier that the system needs to overcome in order to proceed with a specific reaction, namely, the transformation from the amorphous to crystalline state. One of the ways to calculate the activation energy is using the Kissinger method. According to this method one needs to determine the temperature of the peaks (or onset temperatures (T_p)) in the DSC data corresponding to a specific event at different heating rates, β . Then, the activation energy E can be obtained from the following Kissinger equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \left(-\frac{E}{RT_p}\right) + \text{const}, \quad (4.1)$$

where R is the universal gas constant; β is the heating rate.

Plotting $\ln\left(\frac{\beta}{T_p^2}\right)$ versus $\frac{1}{T_p}$ usually gives a straight line with a slope $-E/R$. The activation energy E for the transformation can be determined from the data. Data acquired from isochronal annealing experiments at different heating rates of 5, 10, 20 and 40 K/min were used to calculate the activation energy for the crystallisation. Figure 4.10 shows the Kissinger plot for this series of Mg-Ni-Gd alloys.

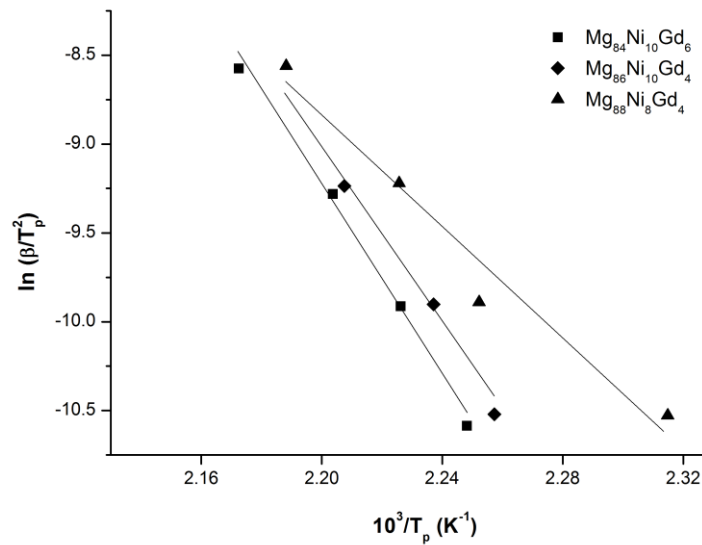


Figure 4.10. Kissinger plot for the Mg-Ni-Gd alloys.

From the slope of linear fitting, the activation energies for the studied alloys were determined and given in Table 4.3. The value of the activation energy of 222 kJ/mole for the onset of crystallisation in $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ composition is higher when compared to the activation energy of 140 kJ/mole for self-diffusion of magnesium [149]. This fact indicates that not only the Mg element is redistributed during the heating process but rearrangement of other constituent elements in the alloy occurs. The smaller values of activation energy for compositions with 86 and 88 at.% Mg assume the growth process of crystals is easier in these alloys and it requires lower activation barrier.

Table 4.3. Activation energy determined for Mg-Ni-Gd alloys.

Alloy	-E/R	Activation energy E, kJ/mole
$\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$	26.70 ± 2.09	222
$\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$	23.10 ± 3.39	192
$\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$	15.63 ± 2.09	129

4.3.5. Determination of fragility

One of the most important kinetic parameters controlling both the glass-forming ability of the melt and its flow behaviour is viscosity. Dependence of viscosity from temperature correlates with the change of glass transition temperature with heating rate and can be used to determine fragility of glass-forming alloy using modified VFT equation [25]:

$$\frac{1}{\beta} = \tau \cdot \exp \frac{D^* \cdot T_0}{T - T_0}, \quad (4.2)$$

where β is the heating rate, D^* is the fragility parameter of the glass-forming liquid, T_0 is the VFT-temperature at which the relaxation time and barriers to viscous flow would become infinite, τ is the fitting parameter.

DSC curves recorded at heating rates of 5, 10, 20 and 40 K/min were used to determine the onset of glass transition. Corresponding data of T_g were plotted versus inverse heating rate and fitted by mathematical iterations to Eq. (4.2) as shown in Fig. 4.11. Fragility parameters were determined only for alloys with 84 and 86 at.% Mg. The

accurate determination of T_g temperature in the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ composition was not possible due to the small size of the supercooled liquid region. Using OriginPro 8.6 software, three unknown parameters from Eq. (4.2) were found as follows for the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy: $D^*=9.1$, $T_0=320$ K and $\tau=9.1\cdot 10^{-12}$ and, similarly for the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy, having parameters of 10, 315 and $2.6\cdot 10^{-12}$, respectively.

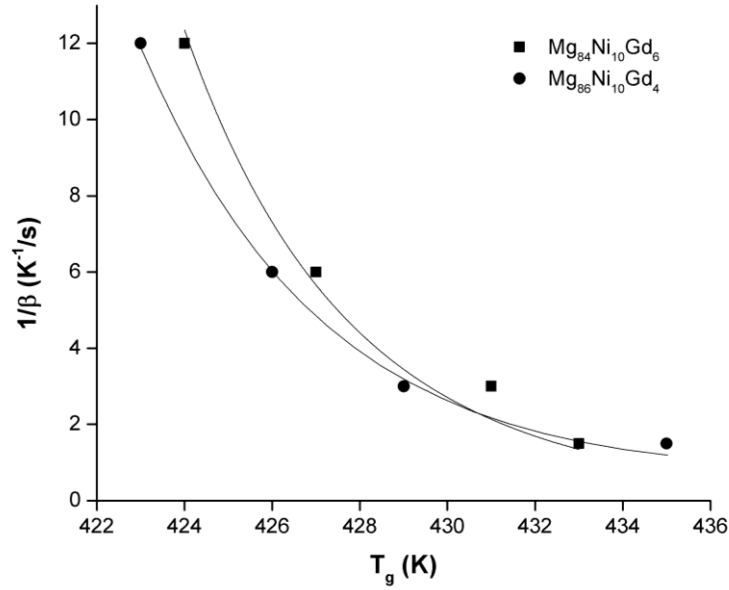


Figure 4.11. Curves fitted to glass transition temperature and inverse heating rate using modified VFT equation (4.2).

The lower value of fragility for alloy with 84 at.% Mg correlates well with the stronger dependence of its T_g and T_x on heating rate compared to the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ composition.

4.4. BMG COMPOSITES PRODUCED BY SEMI-SOLID CASTING IN THE MG-NI-GD SYSTEM

4.4.1. Features of the semi-solid casting technique

The semi-solid casting technique is a well-known near-net-shape casting method widely used for non-ferrous crystalline alloys. During semi-solid processing, an alloy is held between its liquidus and solidus temperatures within the two-phase (liquid + solid 1) region and then injected into a die cavity to form a die-cast component. Recently, for the first time this method has been employed for the fabrication of Zr-based BMG composites by Sun [150] followed by Hofmann's development of highly toughened Zr-

based [116] and Ti-based BMG composites [151]. The semi-solid technique promotes coarsening of dendrites and provides a more homogeneous microstructure. Zr-based BMG composites exhibit remarkable tensile ductility exceeding 10% at room temperature which is explained by a specific length scale distribution of soft inclusions in the amorphous matrix matched with the length scale of the plastic deformation zone [152].

The semi-solid casting method is a way to produce an alternative composite microstructure exhibiting lower aspect ratio crystalline features and a higher volume fraction of these features. This work was carried out purely to determine if the method was applicable to Mg-based glass forming compositions and whether or not it generates an alternative microstructure with altered crystal feature spacing. Similar research on semi solid processing of Zr-based BMGs carried out by Hoffman *et al.* [116] demonstrated that the ability to vary the crystal spacing can dramatically affect the mechanical properties. Due to the high viscosity of the melt during semi-solid casting, the production of high integrity rod-shaped samples suitable for mechanical testing still remains a challenge.

It was reported that the decrease in the semi-solid temperature interval for melting (difference between liquidus and solidus temperatures) improves the GFA of the melt [153]. The reason behind this is that the reduced liquidus temperature leads to a lower magnitude of undercooling required for melt vitrification [143] that can be attained through the semi-solid cast. The $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ composition exhibits the narrowest melting interval and liquidus point among the studied Mg-Ni-Gd alloys and, therefore, was selected for semi-solid processing trials.

4.4.2. Sample preparation

Wedge-shaped samples were fabricated by the inverted injection cast technique designed by Laws [154]. Alloy charges were prepared as described in section 3.3. Crucible with raw materials was placed in a sealed chamber purged with argon and heated to the required casting temperature under protective argon atmosphere. To maintain the maximum fullness of crucible additional amount of charge materials was added to the vessel. Low melt level in the crucible allows more gas to enter the system

which promotes generation of hollow castings. The alloy charge was heated above its liquidus temperature and cooled to the liquidus-solidus temperature interval. Once the melt reached the casting temperature, it was held isothermally for 30 s, remaining entirely below the melting. After that the wedge-shaped copper die and silica tube unit was attached to the vessel. By opening the high pressure gas line, the melt was forced to move up into silica tube and then to the naturally cooled copper mould. Injection pressure was determined experimentally depending on the melt viscosity and casting temperature. Pressure of 1–3 bars was applied to produce samples of Mg-based alloys.

Different casting temperatures within the solidus to liquidus interval and various injection casting pressures were investigated. The $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy was cast from temperature of 515-520 °C which is close to the liquidus temperature (interval of melting is 480-525⁰C) at pressure of 1, 2.5 and 3 Bar. The temperature of the melt determines both the viscosity of the molten metal and the degree of crystallinity of the final casting, whereas the injection pressure affects the velocity of molten metal flow front and velocity at the mould gate.

4.4.3. Morphology of semi-solid cast composite microstructures

The main feature of semi-solid cast alloy structures compared to the regular gravity cast samples is the presence of coarse branched Mg-dendrites randomly distributed in the matrix combined with the presence of the regular non-equilibrium thin flakes developed during the rapid cooling (Fig. 4.12(a-b)). In the semi-solid region the density of pre-existing nuclei is much higher in contrast with the liquid state which results in the formation of coarse Mg-rich dendrites with well-defined secondary branches that have grown prior to final casting. At the same time the cooling rate of the melt is sufficient enough to solidify the majority of the remaining liquid as an amorphous phase and thin flakes, as seen in regularly cast samples. Nevertheless, the composite microstructure is strongly dependent on semi-solid casting parameters. Alloy microstructure generated at 520 °C casting temperature and 1-2.5 bars pressure has Mg-rich dendrites similar to those observed for regular gravity cast samples. As shown in Fig. 4.12(c-d), only some isolated Mg-crystallites have the coarse shape whereas the majority are flake-shaped dendrites. The casting temperature of 520 °C is very close to the liquidus point and deemed not low enough to yield a large volume of coarse dendrites. Instead, it increases

the interval for composite structure formation up to 1.5 mm due to lower level of undercooling required to solidify the melt from 520 °C.

Since viscosity is a strongly temperature dependent parameter, the temperature determines the propensity for the melt to fill the mould cavity. At a casting temperature of 515 °C the melt did not fill completely the tip of the wedge-shaped mould. The minimal wedge thickness achieved under 1 and 3 bars injection pressure was ~1 mm. The sample produced at the higher pressure of 3 bar has a more dense distribution of fine and coarse dendrites in the amorphous matrix. The volume fraction of the crystalline phase in the structure generated at 1 and 3 bars injection pressure is 28% and 32%, respectively (Fig. 4.12(a,b)). Attempts to cast samples from the temperatures lower than 515 °C were not successful due to high viscosity of the melt.

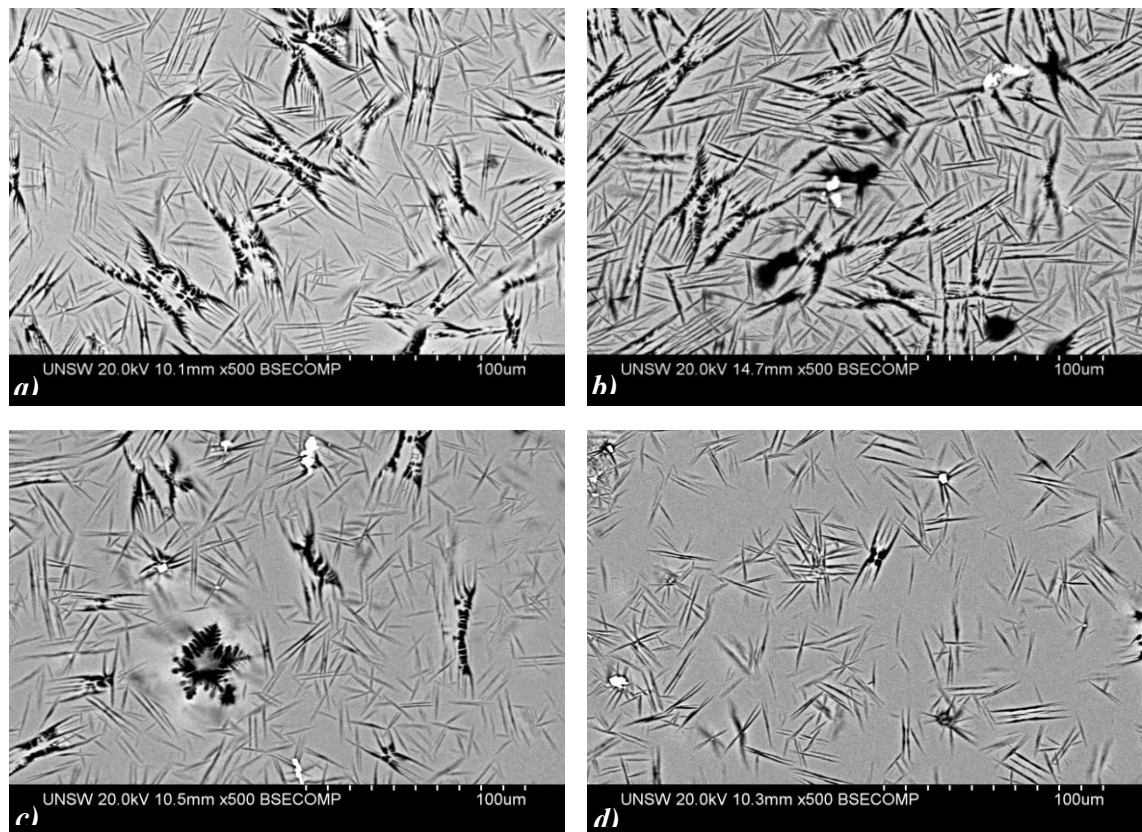


Figure 4.12. Structure of $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy at 1 mm wedge thickness produced by semi-solid injection casting with the following values of casting temperature and injection pressure: (a) 515°C and 1 bar; (b) 515 °C and 3 bars; (c) 520 °C and 1 bar; (d) 520 °C and 2.5 bars.

To summarise, the composite microstructures produced by semi-solid casting have a more homogeneous distribution of crystalline phases in comparison with structure of alloys obtained by regular gravity casting. A lower casting temperature yields larger and coarser dendrites, some with secondary arms and narrower thickness range of composite structure formation. However, the semi-solid casting method at these given casting temperatures does not promote spherical shape crystallites in Mg-Ni-Gd alloys, as was reported for Zr-based BMG composite alloys [150, 155]. Both thermodynamic and kinetic factors are responsible for spheroidisation of crystalline inclusions. Spherical crystallites thermodynamically are more favourable due to lower exposed surface area and, as a consequence, lower interfacial energy. On the other hand, the presence of this driving force is not sufficient to transform dendrite-shaped precipitations into spherical particles. Adequate holding time in the two-phase semi-solid liquid is an essential kinetic parameter to generate spherical morphologies [155]. Insufficient holding time for the alloy studied in this work is a likely reason for the formation of coarse dendrites rather than spheres in the amorphous matrix. There is also a sufficient driving force for crystal growth on the specific crystalline planes. Preferred growth of Mg-rich crystals perpendicular to the basal planes results in the formation of flake-shaped Mg phase in non-equilibrium cooling conditions.

4.5. MECHANICAL PROPERTIES OF MG-NI-GD BMG COMPOSITES

4.5.1. Hardness testing

Vickers hardness testing is a typical and convenient method to reveal the mechanical response of BMG alloys. Hardness is generally associated with the material's resistance to deformation. For non-work hardening materials there is an empirical relationship between yield stress σ_y and hardness H [156]:

$$H = 3 \sigma_y. \quad (4.3)$$

Bulk metallic glasses are usually considered as non-work-hardening materials. Their fracture strength and yield strength are practically the same. In a number of studies it was demonstrated that the Vickers hardness of monolithic BMGs followed this ratio

[44, 88, 157-160]. Therefore, the magnitude of strength for metallic glasses can be roughly estimated using this simple equation.

It was shown experimentally by different research groups [161-163] that Vickers hardness depends on the applied load. It has been found that interfacial friction between indenter and specimen surface has a substantial effect on hardness value in the low load mode, which results in incrementation of hardness with a decrease in applied load. However, no such effects were observed for applied loads greater than 1 N. Therefore, a load of 9.8 N was selected for current microhardness testing of the Mg-Ni-Gd alloys.

Since each wedge-shaped sample contains various types of structure throughout the cross-section, the hardness tests were carried for amorphous, two-phase amorphous-crystalline and crystalline regions. Values of Vickers hardness for different structural states of Mg-Ni-Gd alloys are given in Table 4.4. An increase in Mg content and corresponding decrease in Ni and Gd content resulted in a reduction in hardness for all structural states including the amorphous state. Since hardness of the alloy is correlated to the properties of its constituents, the reduction in the Ni and Gd content of the alloy results in a lower hardness of the amorphous matrix. It can be seen that, for all compositions, amorphous structures were found to exhibit hardness more than 30% higher in contrast with crystalline structure of the same composition. It is logical that hardness values for dual-phase structure lie between those for glassy and crystalline structures. This implies the fractional contribution of the crystalline component to the overall hardness and, therefore, strength of material. The hardness of the two-phase structure also depends on the volume fraction of crystalline component.

Table 4.4. Vickers hardness for Mg-Ni-Gd BMG composites.

Alloy	Hardness of amorphous structure, HV	Hardness of composite amorphous-crystalline structure, HV	Hardness of crystalline structure, HV
Mg ₈₄ Ni ₁₀ Gd ₆	225±12	200±10	165±15
Mg ₈₆ Ni ₁₀ Gd ₄	210±10	180±11	140±13
Mg ₈₈ Ni ₈ Gd ₄	200±14	170±12	130±13
Pure Mg	-	-	30±4

While conducting measurements of hardness it was noticed that continuous semi-loops were formed around edges of indents on the surface of as-cast samples. Such pile-ups around indents have been observed earlier in many studies [119, 160, 164]. This indicates that shear banding occurs around the indent which is considered as the general mechanism of plastic deformation in metallic glasses.

Multiple shear bands formed on the surface of $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ sample are illustrated in Fig. 4.13. Here, the size and the volume fraction of crystalline phase are very negligible and, therefore, crystallites distributed in the amorphous matrix do not contribute to the plasticity of material.

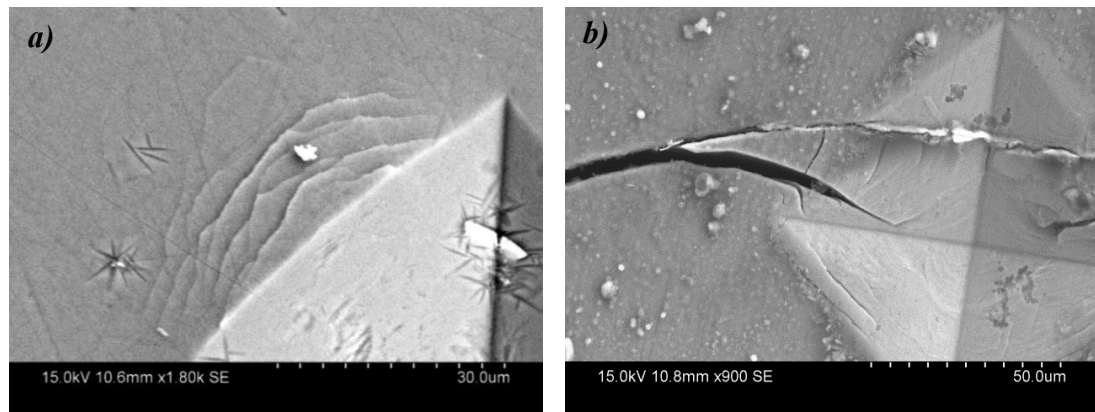


Figure 4.13. SEM image of indentations for $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy: (a) as-cast structure; (b) annealed at 210 °C.

The measurements of microhardness were conducted for annealed samples of the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy. The annealing temperatures correspond to the completion temperatures of phase transformations observed in the glassy phase upon heating. Figure 4.14 compares microhardness values for as-cast and annealed samples.

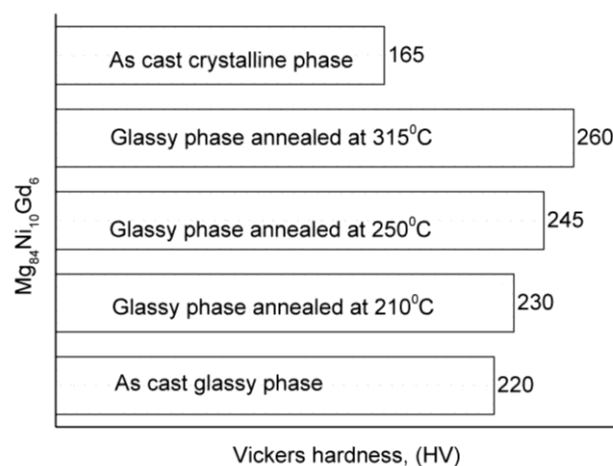


Figure 4.14. Hardness of annealed $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloys.

It can be seen that values of microhardness increase from 220 HV (as cast structure) to 260 HV with increasing annealing temperature. Such an increase is related to the structural changes induced by annealing. Alloys annealed at the temperature of 210 °C no longer contain the glassy component of the microstructure as it is completely transformed into nanoscale hcp-Mg phase. The phenomenon of nanoscale hcp-Mg phase formation during annealing indicates that the primary mode of crystallisation for the as-cast glassy structure requires considerable redistribution of elemental constituents. This structural transformation causes a considerable change in the mechanical response of the material. The improved hardness in the partially devitrified in situ composites is attributed to the compositional change in the glassy matrix and its enrichment by the solute elements [87, 206] even if the crystalline phase is soft [123].

After annealing at 250 °C the metastable phase along with hcp-Mg phase is present in the structure. Phase selection of alloy annealed at 315 °C is represented by the same equilibrium mixture of phases as for the as-cast crystalline structure generated during casting at greater wedge thickness. However, annealed samples exhibit higher hardness compared with as-cast crystalline structure (165 HV). At the same time they all have cracks around impressions (Fig. 4.13(b)). This fact implies that crystallisation of amorphous structure increases the yield stress of the alloy and simultaneously promotes catastrophic embrittlement, which is commonly found in devitrified glasses.

4.5.2. Uniaxial compression testing

The mechanical behaviour of rod-shaped samples of $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$, $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ and $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ alloys was investigated by uniaxial compressive testing at room temperature. Cylindrical samples of 1.5 mm in diameter with 2:1 aspect ratio were fabricated by the injection copper mould cast method described in Section 4.2.2. The ends of the rods were ground and polished to create parallel surfaces.

Compression tests were performed on Instron 5565 SWP machine using a load cell of 5 kN. A strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ and corresponding $3 \times 10^{-4} \text{ mm/s}$ rate of compression was used during experiments. Data from at least 5 samples were collected to ensure reproducibility of the results.

The choice of sample aspect ratio of height to diameter (H/D) for samples undergoing compression tests is important for measuring ductility. Decreasing the aspect ratio results in a considerable increase in plastic strain to failure, however, it is not attributed to the work-hardening of the material. The propagation of shear bands formed in low aspect samples is geometrically restricted due to strong constraints imposed by lateral stresses [165]. Therefore, observed ductility in BMG or their composites is strongly depends on the sample geometry. The mechanical performance of many recently developed metallic glass composites has been tested on the samples with 2:1 aspect ratio. ASTM standards recommend 1.5 or 2.0 length to diameter ratio for high-strength metallic materials (ASTM E9). To compare properties of composite alloys produced in this thesis with alloys reported in the literature, the same aspect ratio was used for mechanical testing.

The diameter of the rods is 1.5 mm which is slightly larger than the 0.5-1.1 mm wedge thickness corresponding to composite structure formation. In the work of Laws *et al.* [143] it was shown, based on heat transfer calculations, that the critical thickness for glass formation in the rod configuration is 1.4× higher compared to that observed in the wedge. To ensure the composite amorphous-crystalline structure is present in the rods, the samples were subjected to SEM imaging. The distribution of the crystalline phase in the amorphous matrix in the central part of the rods is shown in Fig.4.15.

The average volume fraction of crystallite precipitation in the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ rod is 18% which corresponds well with the microstructure of the wedge-shaped sample of 1 mm thickness. Rod sections for $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ and $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ samples have 30 % and 54 % volume fraction of crystalline phase, respectively. In general, Mg-rich crystallites are homogeneously distributed in the matrix throughout the cross-section except at the amorphous skin layer of the cylinders of 50-100 μm thickness. Approximately one quarter of rod-shaped samples had casting defects such as porosity and voids located in the centre of the rods – this is likely due to the degree of shrinkage experienced by the sample on true solidification into a partially crystalline state.

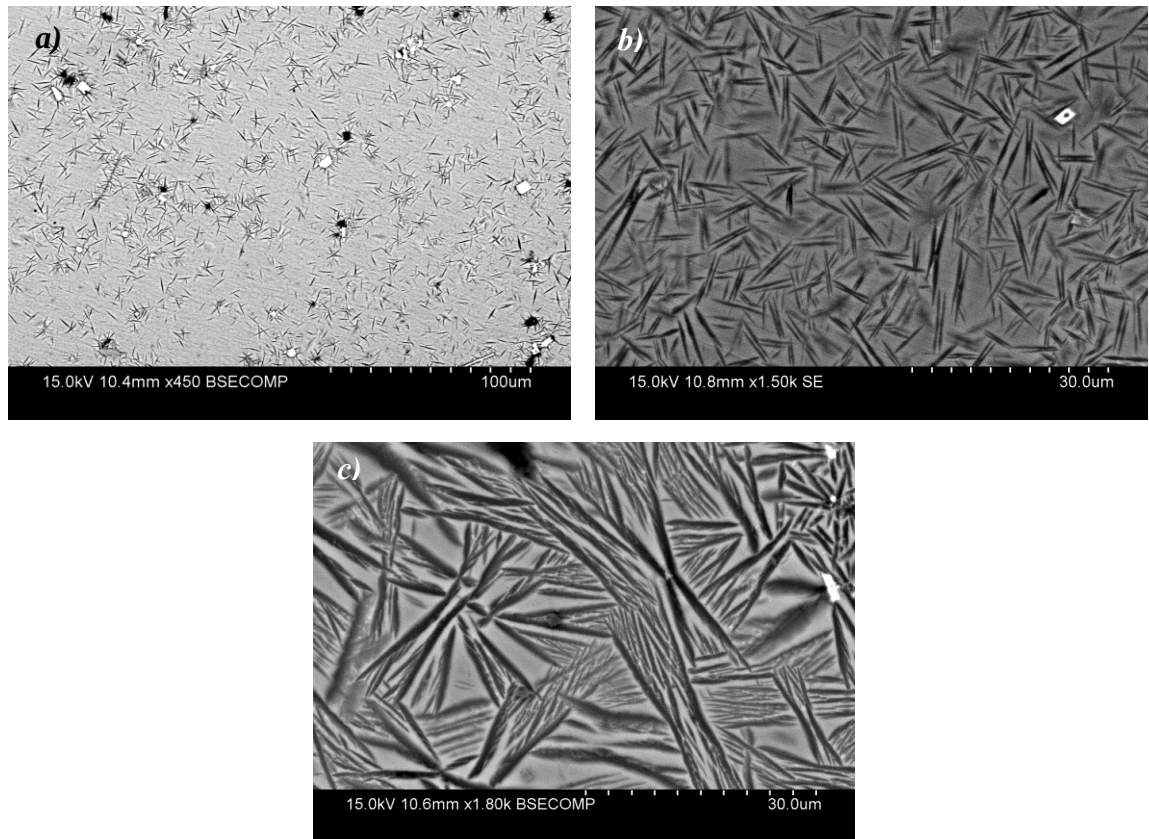


Figure 4.15. SEM images of central part of the rod-shaped samples with 1.5 mm diameter: (a) $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$; (b) $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$, and (c) $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$.

Figure 4.16(a) shows a representative compressive stress-strain curve of $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ sample under quasistatic loading with a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. This sample exhibits elastic behaviour with a yield stress of $\sim 490 \text{ MPa}$ and a corresponding yield strain of $\sim 4\%$. This stage is followed by plastic deformation. At higher stress, serration of the stress-strain curve is observed which is considered to be a characteristic feature of plastic deformation in ductile metallic glasses. The first irregularities on the curve appear at a flow stress of $\sim 580 \text{ MPa}$ which indicates that the material becomes mechanically unstable at this stress level. The formation and propagation of multiple shear bands occur at this stage of deformation. A further increase in load results in a sudden drop of stress rate occurring with certain regularity (Fig. 4.16(b)). The upper limit of the stress during subsequent stressing drops slightly with increasing load whereas the lower stress limit remains nearly constant. A single drop of stress-strain curve serrations is often associated with fast shear band propagation. During deformation, the free volume within a shear band increases which promotes the

reduction in density and, consequently, less resistance to deformation. At a flow stress of ~ 700 MPa, the sample failed by a shear-type fracture mode.

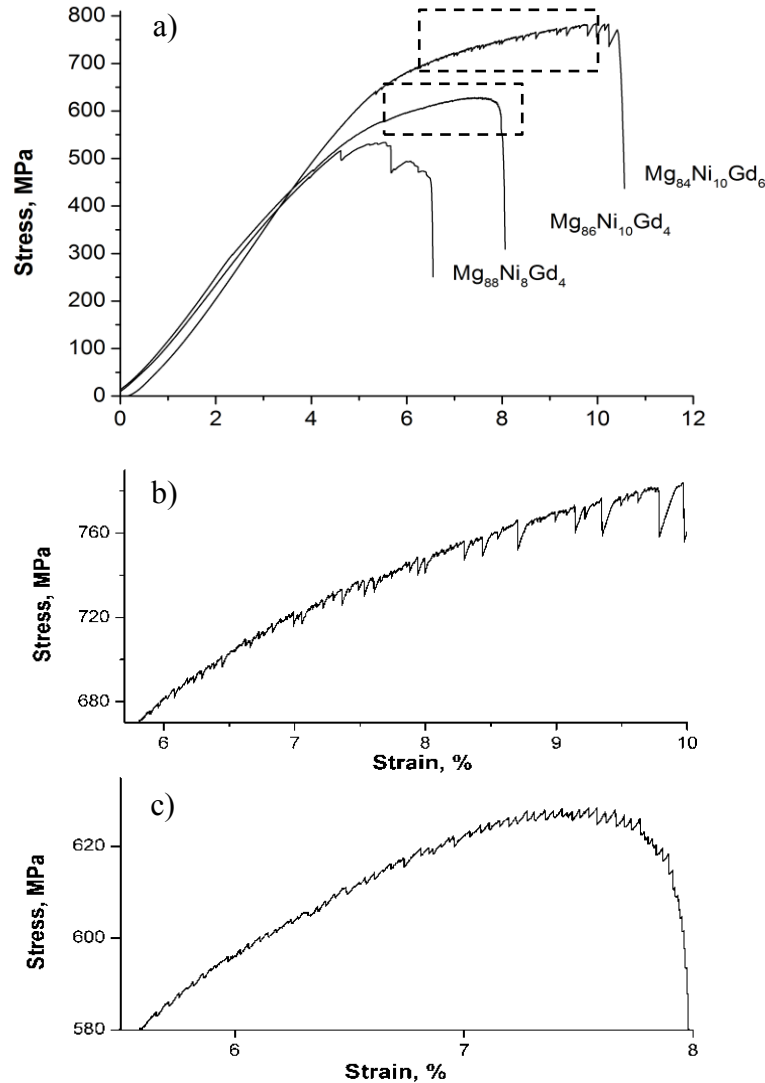


Figure 4.16. (a) Typical stress-strain curve of the as-cast Mg-Ni-Gd rods tested in uniaxial compression; (b) enlarged area of serrations on the stress-strain curve for $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy; (c) serrations on the stress-strain for $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy.

The stress-strain curve for $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ behaves in a manner similar to that for the alloy with 84 at.% Mg. However, this alloy exhibits smaller values of yield and fracture stress (Table 4.5). The transition from elastic to plastic deformation starts at a stress of 353 MPa and 2.6 % strain, respectively. The amplitude of serrations on the stress-strain curve for this alloy is considerably smaller in contrast with $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ as illustrated in Fig. 4.16(c). The sample failed at a stress of 627 MPa.

A typical example of cylindrical samples with 88 at.% Mg under compressive loading is shown in Fig. 4.16(a). The yield strength was determined to be 330 MPa. At 500 MPa stress instabilities in the sample are observed. Steep load drops with an increasing value of stress loss occur in the sample. No regular serrations in the stress-strain curve were observed. The third decrease in load results in sample failure. Such mechanical behaviour of the alloy with 88 at.% Mg was observed for all five samples tested in compression and related to the formation of macro cracks in the material.

The overall ductility of the Mg-Ni-Gd BMG composites containing 84-88 at.% Mg was improved with respect to the monolithic Mg-Ni-Gd BMGs reported in the literature [128, 130]. For instance, the fracture strain and specific strength for the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ BMG composite are 9.6 %, and $2.75 \times 10^5 \text{ Nm/kg}$, respectively, which are much higher than those of respective 3.71%, and $2.66 \times 10^5 \text{ Nm/kg}$ for the monolithic $\text{Mg}_{70}\text{Ni}_{15}\text{Gd}_{15}$ BMG [128]. This suggests that, compared to the BMG with a single glassy structure, the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ BMG composite with a “dual phase” structure displays better mechanical properties, particularly the ductility. The specific fracture strength of the BMG composites studied in this thesis is also higher than conventional cast magnesium alloys such as WE43 ($1.35 \times 10^5 \text{ Nm kg}^{-1}$) and AZ91D ($1.26 \times 10^5 \text{ N m kg}^{-1}$) [166].

The values of the mechanical properties obtained from the stress-strain curves are given in the Table 4.5.

Table 4.5. Mechanical properties of Mg-Ni-Gd BMG composites.

Alloy	σ_y , MPa	ϵ_y , %	σ_b , MPa	ϵ_b , %	$\sigma_{\max}/\rho$, $\times 10^5 \text{ Nm/kg}$
$\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$	474±16	4.1±0.1	713±28	9.6±1	2.75
$\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$	353±13	2.6±0.2	627±25	7.9±1	2.56
$\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$	330±17	2.5±0.2	530±27	4.6±1	2.22
$\text{Mg}_{70}\text{Ni}_{15}\text{Gd}_{15}$ [128]	880	2	959	3.71	2.66

4.5.3. Fracture surface analysis

The morphology of the fracture surface of the composite after straining to failure is shown in Fig. 4.17. It shows well-developed vein patterns that are uniformly arranged

on the flat and smooth main surface. Vein-like patterns are a characteristic of ductile glassy phase [167]. The larger distance between vein cell walls usually correlates to the more ductile alloys. A high magnification SEM image of the smooth zone on the fracture surface shows irregular striations, with many of them appearing to be arrested from further propagation by the Mg-rich crystallites (shown as the dark phase in the image).

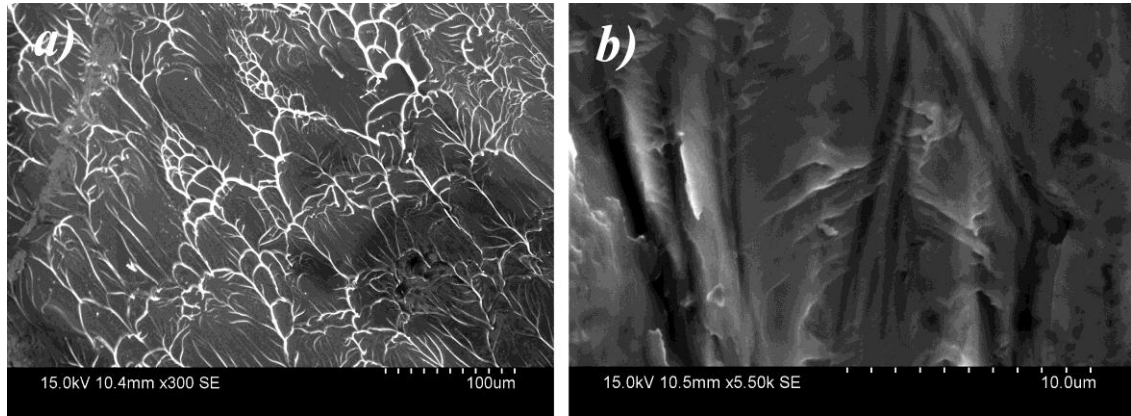


Figure 4.17. SEM images of the fracture surface of as-cast $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy showing: (a) vein patterned zone; (b) high magnification image of the smooth fracture zone.

Smooth regions on the fracture surface of alloys with 86-88 % Mg cover most of the area. They correspond to the areas where the process of dominant shear band sliding is activated before fracture.

Striations observed in these regions (Fig. 4.18(a,c)) are believed to correspond to the stress drops on the stress-strain curves before final fracture [168]. Figure 4.18(b) shows zones with vein-patterns that are located intermittently on the surface and have significantly smaller size scale compared to the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy. These zones usually form at the final stage of fracture when the total elastic energy of sample is released over the short period of time. At this stage, the temperature can increase high enough to promote local softening, which is demonstrated by the formation of melted droplets, as seen in Fig. 4.18(d).

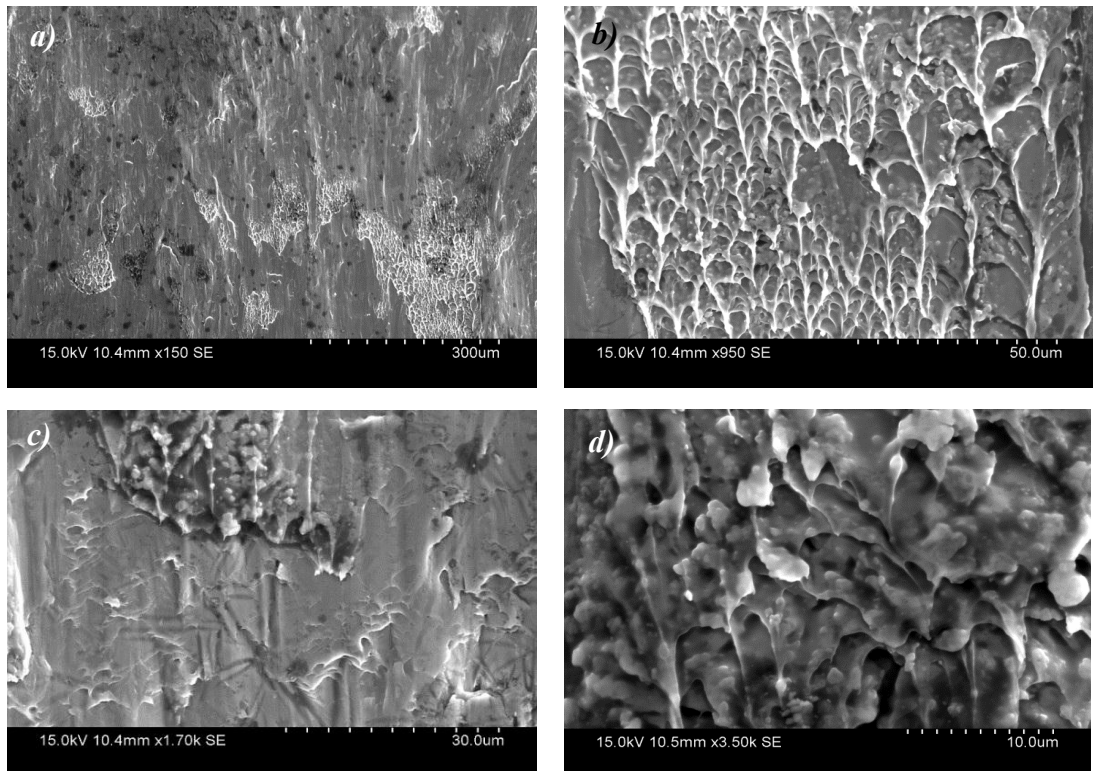


Figure 4.18. Various areas of fracture surface of $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ alloy.

Due to the higher volume fraction of crystalline phase in BMG composite containing 88 at.% Mg, the fracture surface appears somewhat different when compared to the other compositions. Most of the surface is composed of smooth zones with multiple striations, as shown in Fig. 4.19(a). Isolated vein-patterned areas are represented by very rough surface with extensive softening/melting (Fig. 4.19(b)).

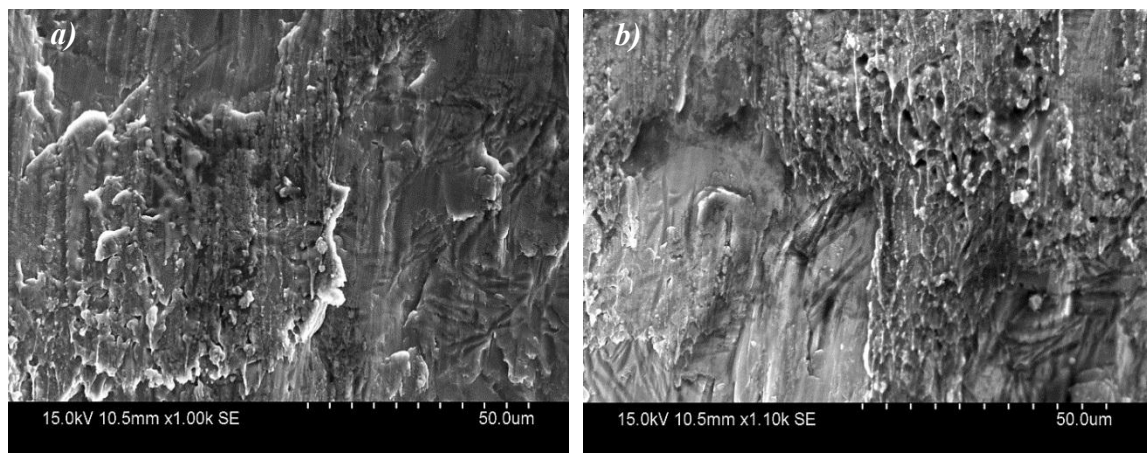


Figure 4.19. Compression fracture surface of $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ alloy.

Overall, with an increase of Mg concentration in the alloy and, therefore, crystalline volume fraction, the length scale and volume fraction of vein-shaped structure descends further.

4.5.4. Evaluation of elastic moduli

A relationship between the elastic constants of crystalline metals and their brittleness or plasticity has been established by Pugh [169]. It was demonstrated that a low ratio of shear modulus to bulk modulus and corresponding high Poisson ratio correlated with plasticity of the polycrystalline metals. The same approach was suggested for metallic glasses in the work of Chen *et al.* [11] and supported in subsequent studies [3, 70, 170].

The elastic properties of glassy alloys, including Poisson ratio, can be estimated from the characteristics of constituent elements [171]. This approximation, based on the rule of mixtures, does not take into consideration enthalpies of mixing for atomic pairs; however it can be used for the prediction of elastic properties of BMGs.

The estimation of Poisson ratio, shear and bulk moduli for Mg-based glassy alloys produced in this thesis has been carried out. The calculation is based on the assumption that modulus of an alloy is an average of moduli of constituent crystalline components in which the applied stress and strain is distributed uniformly [172]. According to this approximation the moduli are computed using the following relations:

$$Y_u = \sum_{i=1}^n \frac{Y_i c_i V_i}{V_{av}}, \quad Y_l = \sum_{i=1}^n \frac{c_i V_i}{Y_i V_{av}}, \quad (4.4)$$

where Y_u and Y_l – is a shear or bulk modulus of the alloy, subscription index u and l denotes upper and lower bound of magnitude calculated in uniform strain and stress assumptions correspondingly; Y_i , c_i , V_i are the modulus, atomic concentration and atomic volume of i -th element; V_{av} is the average atomic volume of the alloy.

The mean of upper and lower bound values gives the final magnitude of modulus for the given alloys. All data required for calculations were taken from the literature [149]. Figure 4.20 shows the shear (a) and bulk modulus (b) calculated for Mg-Ni-Gd and Mg-Ni-Gd-Y alloys plotted as a function of concentration of Mg. Both moduli descend with increasing Mg content in a given alloy. There is no substantial change in moduli for ternary and quaternary alloys although Mg-Ni-Gd compositions exhibit slightly lower

values of shear and bulk modulus. This implies that the addition of a second RE element to the Mg-Ni-Gd alloy causes a small change (<1%) in elastic modulus.

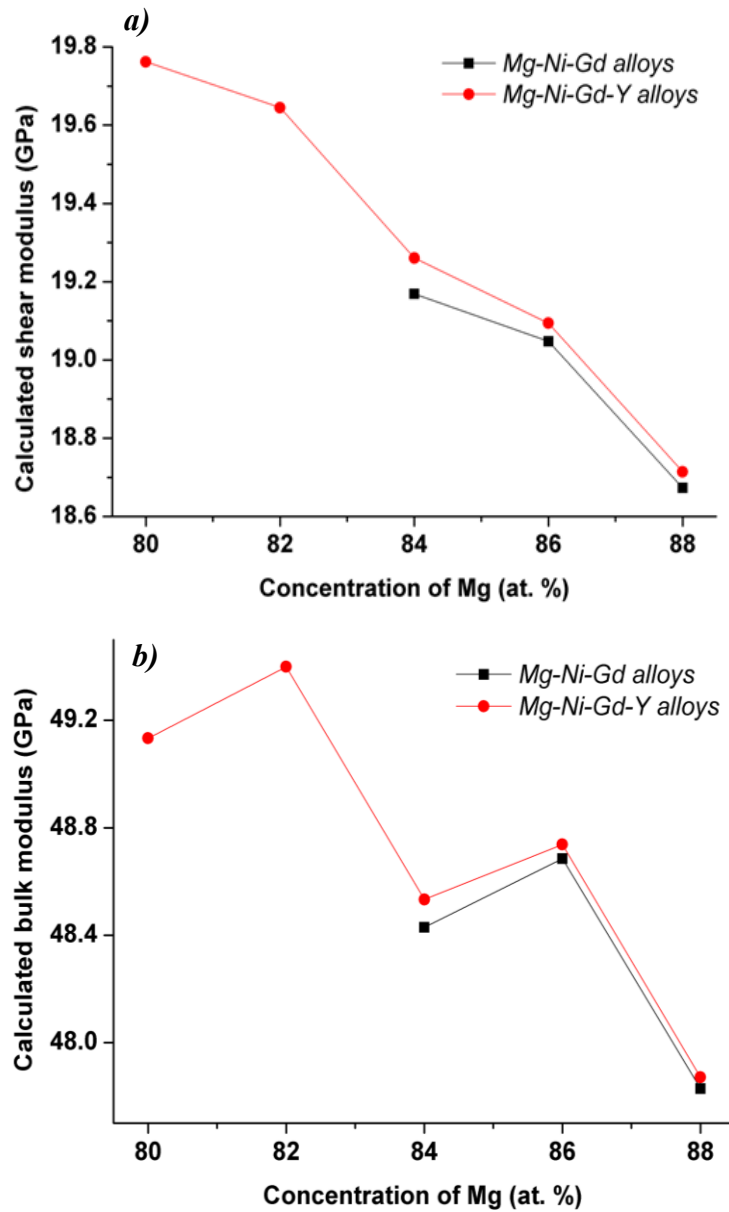


Figure 4.20. Calculated (a) shear and (b) bulk modulus for ternary and quaternary Mg-alloys

4.6. SUMMARY OF MG-NI-GD BMG COMPOSITE ALLOYS

New BMG composites with high Mg content in Mg-Ni-Gd system were produced both by a gravity cast and semi-solid injection method. The structure was found to have a soft Mg-rich crystalline phase precipitated from the monolithic Mg-rich glass. The formation of an amorphous/crystalline composite structure for these alloys was achieved between 0.5 and 1.5 mm of the as-cast sample thickness. The cooling rate and chemical composition are the critical factors affecting the morphology of these BMG composites.

CHAPTER 5 - INOCULATED ZR-BASED BMG COMPOSITES

5.1. BACKGROUND

Monolithic Zr-based BMGs have been explored extensively and characterised in terms of their thermal and mechanical properties. Many researches acknowledge that these metallic glasses can exhibit ductile deformation behaviour, which has been confirmed numerous times with a range of Zr-based alloys showing both significant compressive plasticity and tensile elongation [132, 133, 173, 174]. However, the deformation of monolithic glasses generally occurs in an inhomogeneous deformation mechanism featuring the formation and rapid propagation of shear bands resulting in the sudden rupture of the material. To circumvent the highly localized deformation and improve the limited ductility of Zr-based BMGs, composite structures in Zr-glasses have been developed.

It is well known that a heterogeneous composite structure in Zr-based glass-formers can be achieved through the combination of the amorphous matrix with insoluble reinforcing particulates, such as refractory metals (W, Ta) and ceramic particles (WC, SiC, ZrC) [82, 100, 134, 175]. The formation of the composite structure may also be facilitated via the partial crystallisation of the amorphous matrix by the minor addition of alloying elements. For these purposes refractory elements like Nb, Ta or Hf may be added to promote the formation and stabilization of ductile high-temperature β -Zr phase in the parent glass [83, 84, 116, 176].

In this chapter, two strategies have been applied in an attempt to generate a composite microstructure in Zr-based metallic glasses. The first concept intends to use inoculant particles to encourage the homogeneous formation of the crystalline phase in the glass-former. The inoculation mechanism has been extensively studied in Al-based alloys due to their wide industrial use [177], however, it has received little attention in the field of amorphous alloys. One of the pioneering studies of inoculants action in an amorphous matrix has been done by Schumacher *et al.* for Al-rich metallic glass [178]. They investigated the nucleation of α -Al phase in the Al-Ni-Y-Co glass with added Al-Ti-B

grain refiner alloy and found that α -Al formed on the boride particles TiB_2 covered by the thin layer of Al_3Ti acting as a nucleating substrate.

The second strategy is to increase the concentration of base element in the alloy i.e. Zr. Due to its high abundance, the precipitation of a crystalline phase rich in the base element (which is generally ductile) is anticipated on the inoculating particles distributed in the amorphous matrix. This is the same principle as to which was successfully implemented when increasing the Mg-content in the prior studied Mg-based alloys in Chapters 3-4. Although the higher concentration of Zr reduces the glass-forming ability, it gives the additional advantage of a lighter-weight alloy product.

Whilst detailed studies of in situ composites produced by inoculation have been carried out for Al-based [179-181] and Mg-based glasses [182], the general principles of inoculant-triggered crystallisation in an isotropic amorphous medium that could be extended for different classes of metallic glasses are still not well defined. In this section of thesis, the effect of inoculants on the structure of glass-forming alloys and their thermal properties are discussed.

5.2. DESIGN AND FABRICATION OF COMPOSITE ALLOYS IN ZR-BASED SYSTEM

The glass-forming system selected was Zr-Cu-Ni-Al. Compositions produced in this system are well-recognized BMGs due to excellent combination of their GFA and mechanical characteristics. The interval of glass formation for Zr-Cu-Ni-Al system lies within 50-70 % Zr including eutectic and hypoeutectic alloys. Crude assessment of likely phase evolution in the Zr-Cu-Ni-Al system was achieved by analysing the binary Zr-Cu phase diagram shown in Fig. 5.1 – as Zr and Cu are the two major alloy constituents.

Eutectic alloys for this system are located around the $\text{Zr}_{55}\text{Al}_{10}\text{Cu}_{30}\text{Ni}_5$ composition and have the largest GFA among alloys in the Zr-Cu-Ni-Al system [183]. However, many hypoeutectic compositions were also found to be good glass formers [7]. Moreover, they have higher values of fracture toughness, compressive and tensile plastic strain [184-186] in comparison to the eutectic-type glassy Zr-Cu-Ni-Al alloys.

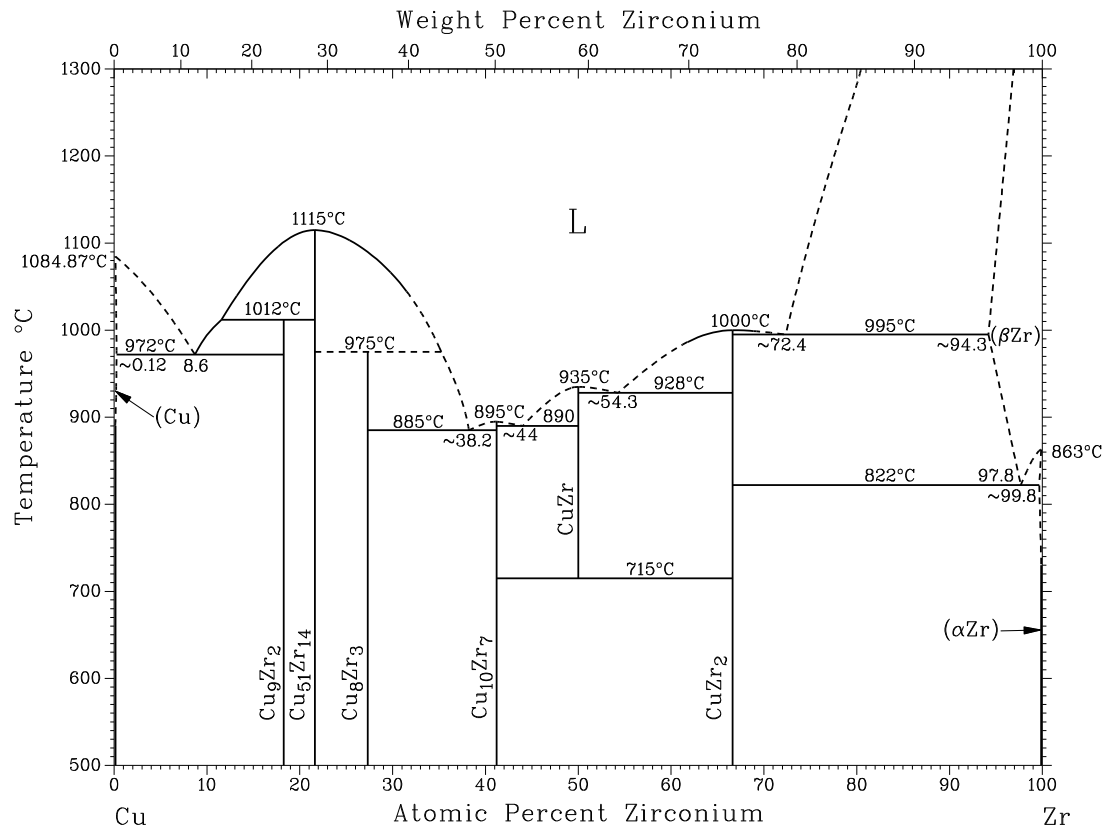


Figure 5.1. Zr-Cu phase diagram [142].

It is believed that improved mechanical properties of hypoeutectic Zr-Cu-Ni-Al compositions originate from the large number of Zr-Zr bonding pairs in alloys with higher Zr concentration. An increase of free volume in the atomic configuration due to the deviation from optimal packing of the amorphous structure may also account for their better mechanical characteristics [7]. Nevertheless, it appears that bulk amorphous alloys in Zr-Cu-Ni-Al system with Zr content more than 70 at.% have not been extensively studied.

To produce a BMG composite in the Zr-Cu-Ni-Al system, the monolithic amorphous alloy was taken as a precursor. Insoluble particles acting as sites for heterogeneous nucleation of crystalline phases in the amorphous matrix were introduced into the melt. In this work, Y_2O_3 (or yttria) powder with a particle size of 2-6 μm was used as an inoculant. The selection of Y_2O_3 powder as the inoculant phase was a result of its thermal and chemical stability (high melting point of 2425 $^{\circ}C$) which implies minimal chemical interaction with the molten alloy. It also exhibits good wettability with the matrix alloy [187] which contributes to the strong interfacial bond strength. The density

of Y_2O_3 is slightly lower when compared to the density of the Zr-Cu-Ni-Al glasses studied herein (4.84 and $\sim 6.6 \text{ g/cm}^3$, respectively).

As a starting point for composite structure generation, a composition of standardised $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ BMG [188] was selected. It has a large supercooled liquid region of 125 K and excellent glass-forming ability (the reported critical diameter is 16 mm). By gradually increasing the Zr concentration in the $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy and keeping the Cu/Ni/Al ratio fixed, the following new compositions were designed:

- $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$
- $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$
- $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5}$
- $Zr_{74}Cu_{13}Ni_{7.4}Al_{5.6}$
- $Zr_{76}Cu_{12}Ni_{6.9}Al_{5.1}$

It should be noted that Cu/Ni/Al ratio in the alloy with 72 at.% Zr is deviated from the fixed ratio. Since the glass forming ability is very sensitive to the chemical composition of the melt, the ratio of Cu/Ni/Al in the alloy with 72 at.%Zr was optimised in the work [183] as a composition nearest to the eutectic point. This composition is $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5}$ which exhibits higher GFA compared to the alloy with fixed ratio ($Zr_{72}Cu_{14}Ni_8Al_6$) and therefore was selected as a precursor for composite structure.

Alloys of the required compositions were prepared using an arc-melter on the water-cooled copper plate. Alloy buttons were then cleaned of any surface oxide layers or impurities and divided into two pieces. Each alloy composition was arc melted and vacuum cast into a copper mould of wedge-shaped configuration without the addition of the inoculant. From the same alloy buttons, alloys were melted with the addition of Y_2O_3 particles in the arc-melter and similarly vacuum-cast into the wedge-shaped copper mould. Castings were cut, cold mounted and polished according to the required surface finish.

In terms of successful rate of fabricated Zr-based BMG alloys, not all attempts were successful, particularly those that may have been remelted several times. Clearly noticeable oxide layers formed on the surface of practically all arc-melted alloy buttons witnessed the presence of oxygen in the operating chamber though all efforts were

undertaken to remove oxides before proceeding to wedge casting. Due to the high oxygen affinity of Zr, oxide precipitates are easily nucleated in the melt during solidification which can act as sites for further nucleation of crystalline phases. This is the case, especially if the melt was overheated to well above its melting point [189]. Though the arc-melter was operated on low/medium currents, overheating of the alloy is not ruled out during the course of melting since the temperature in the arc can reach up to 3000 °C. As a consequence, some of the samples could not reproduce the expected amorphous structure.

5.3. CHARACTERISTICS OF MONOLITHIC AND INOCULATED ALLOYS IN ZR-CU-NI-AL SYSTEM

5.3.1. Alloys with 65 at.% Zr

In terms of the GFA of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ alloys, data available in the literature show a critical thickness for glass formation up to 16 mm [188]. The casting size of the monolithic and composite Zr-based alloys in this work was limited by the size of wedge-shaped mould that could fit the arc-melting chamber. The maximum available thickness of the wedge was 3 mm. Therefore, the amorphous nature of monolithic $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ alloy was confirmed up to 3 mm thickness.

The introduction of Y_2O_3 particles into the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ composition resulted in no notable inoculation effect on the microstructure or GFA up to the 1.9-2 mm wedge thickness achieved in the copper mould. The microstructure of the alloy at 1.5 mm thickness contains single particles of Y_2O_3 distributed in the amorphous phase as shown in Fig. 5.2(a). As can be seen from Fig. 5.2(b), with an increase in wedge thickness (indicative of a lower cooling rate), dark regions around the oxide particles appeared. This implies that the powder particles act as centres of heterogeneous crystallisation and trigger the growth of crystallites around them and hence are effective inoculants.

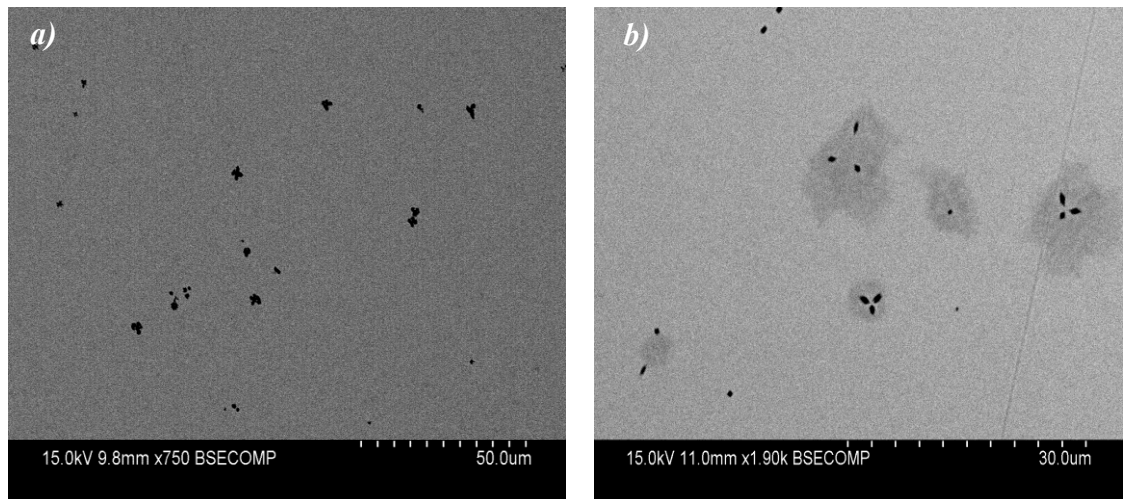


Figure 5.2. SEM images for $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5} + \text{Y}_2\text{O}_3$ wedge at 1.5 (a) and 2 mm (b) thickness.

The XRD pattern of the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ successfully inoculated with Y_2O_3 particles at the thickness of 1.5 mm shows one broad peak representing single amorphous phase, as depicted in Fig. 5.3(a).

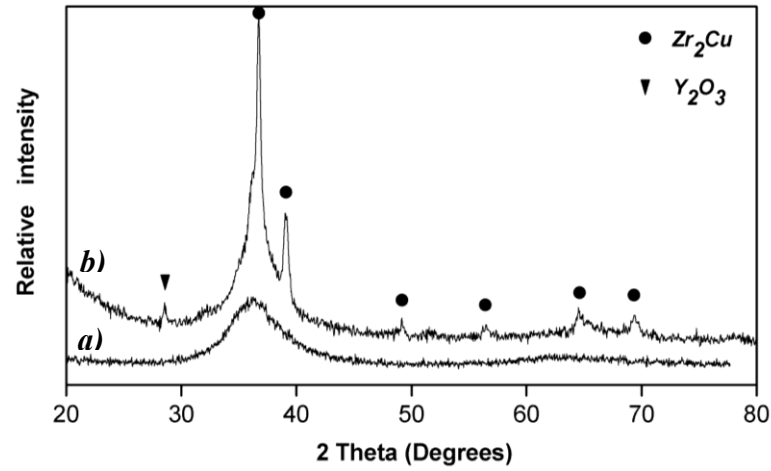


Figure 5.3. XRD scan of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ alloy inoculated by Y_2O_3 particles at various wedge thickness Z : (a) $Z=1.5$ mm; (b) $Z=2.5$ mm.

At larger sample thickness of 2.5 mm, signs of crystalline phase appear on the XRD scan (Fig. 5.3(b)) which was identified as Zr_2Cu . Due to low volume fraction of yttrium oxide (3 wt.%) only slight trace of its strongest diffraction reflex is observed at 29.5° .

5.3.2. Alloys with 70 at.% Zr

The structure of the as-cast monolithic $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_6$ alloy was found to be amorphous with 3 mm critical thickness for glass formation. The XRD scan in Fig. 5.4(a) exhibits a single broad halo confirming the amorphous nature of alloy. Introduction of Y_2O_3 to the amorphous composition with 70 at.% Zr promotes the formation of crystallites around oxide particles at sample thickness greater than 2 mm (Fig. 5.5). Below 2 mm, only a two-phase structure containing the glassy matrix phase and isolated Y_2O_3 particles is present. With ascending sample thickness the volume fraction of the crystalline phase increases (Fig. 5.5(b)) until the amorphous phase completely disappears at 3 mm thickness.

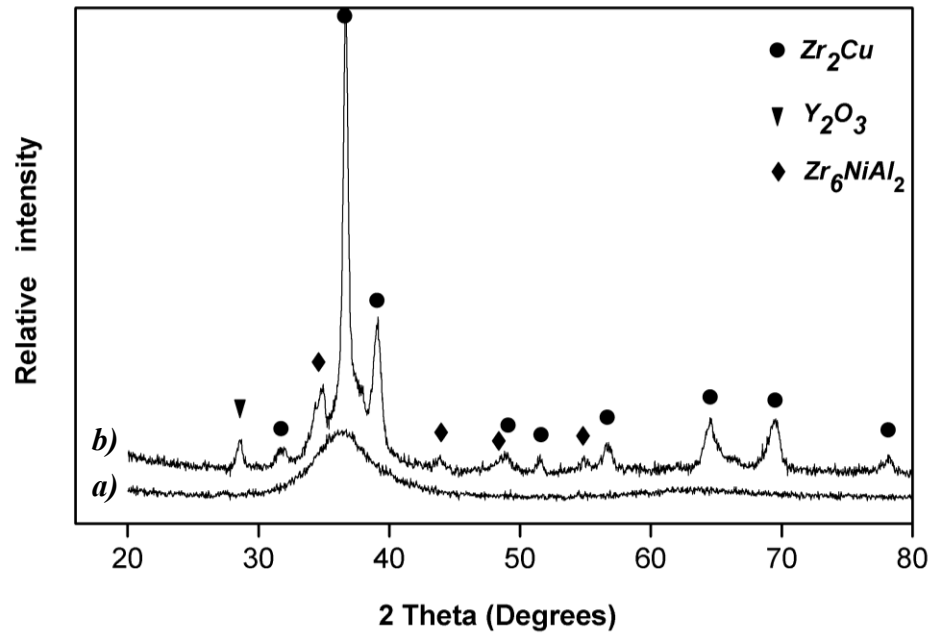


Figure 5.4. XRD scan for $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}$ alloy: (a) monolithic alloy; (b) alloy inoculated by Y_2O_3 , $Z=2.5$ mm

An XRD scan of the $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}+\text{Y}_2\text{O}_3$ composition taken at 2.5 mm wedge thickness is shown in Fig. 5.4(b). Strong diffraction reflections from crystalline phases overlapping with a broadened peak at 37° indicate that the alloy has an amorphous-crystalline microstructure. Again, the crystalline components of the microstructure were identified as Zr_2Cu in addition to the Zr_6NiAl_2 phase.

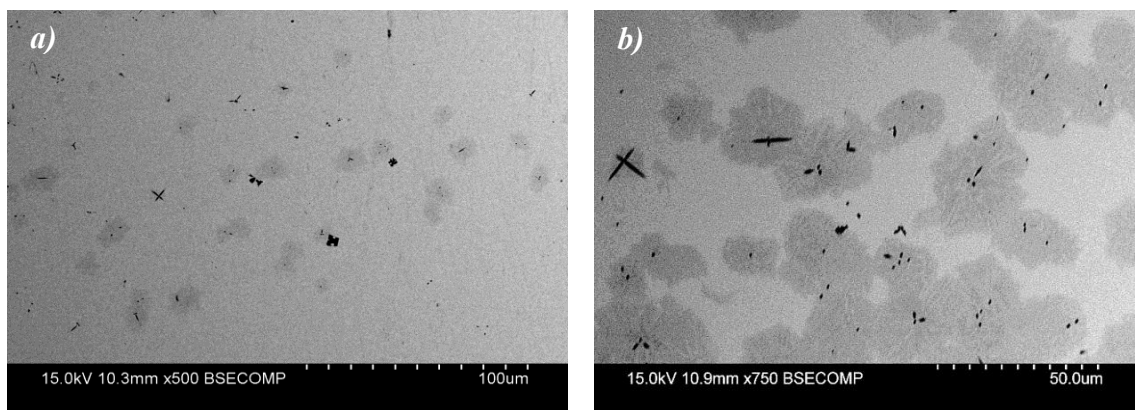


Figure 5.5. SEM images for $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}+\text{Y}_2\text{O}_3$ showing evolution of the microstructure with increase of wedge thickness, Z : (a) $Z=2$ mm; (b) $Z=2.3$ mm.

5.3.3. Alloys with 72 at.% Zr

To produce a glassy alloy with 72 % Zr and to consequently inoculate it using Y_2O_3 particles, a composition $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5}$ was selected as a precursor. The formation of an amorphous structure in this alloy with a critical casting diameter of 2 mm was reported in the work of Hui *et al.* [184].

The as cast $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5}$ sample has an amorphous structure with critical thickness for glass formation of 2 mm confirmed by XRD analysis (Fig. 5.6(a)). The introduction of 3 wt.% of Y_2O_3 into the given alloy considerably decreased the GFA of the alloy to 0.6-0.7 mm critical thickness.

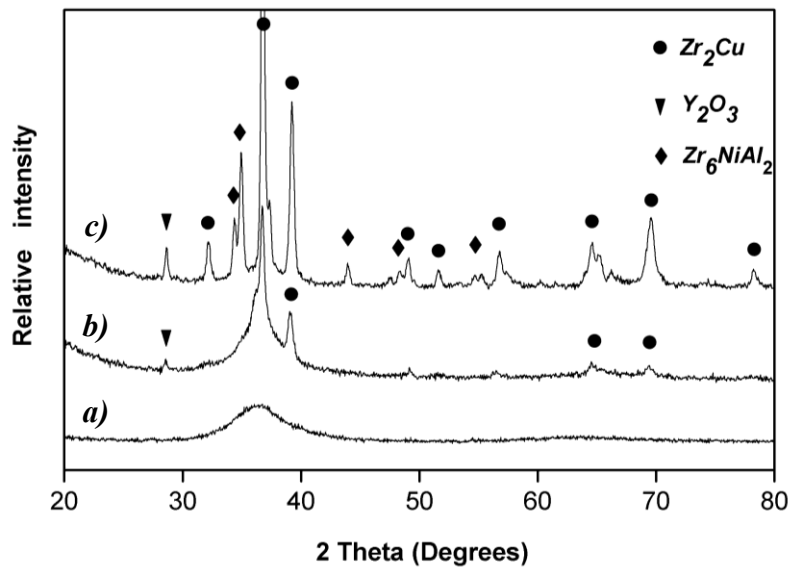


Figure 5.6. XRD scans of $Zr_{72}Ni_{7.5}Cu_{13}Al_{7.5}$ alloys at various wedge thickness Z : (a) monolithic alloy at $Z=2$ mm; (b) alloy inoculated by Y_2O_3 particles, $Z=1.2$ mm; (c) alloy inoculated by Y_2O_3 particles, $Z=1.5$ mm.

As shown in Fig. 5.7(a), darker crystallites of 10-15 μm in size are formed around black Y_2O_3 particles at the sample thickness greater than 0.6 mm. The XRD pattern for this microstructure is shown in Fig. 5.6(b) and defines a mixture of the glass and Zr_2Cu phase. Wedge thickness increase is accompanied by an ascending size of the crystallites up to 25-30 μm and a concurrent decrease of amorphous volume fraction (Fig. 5.7(b)). A completely crystalline microstructure is observed for a 1.5 mm sample thickness.

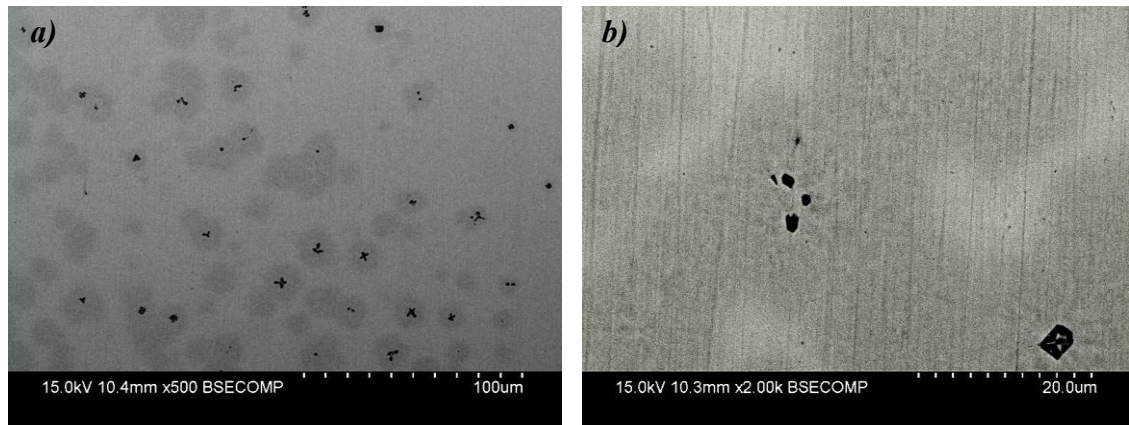


Figure 5.7. SEM images of $\text{Zr}_{72}\text{Ni}_{7.5}\text{Cu}_{13}\text{Al}_{7.5}$ alloy inoculated by Y_2O_3 particles at various wedge thickness Z : (a) $Z=1$ mm; (b) $Z=1.2$ mm.

5.3.4. Alloys with 74 at.% Zr

XRD analysis of the $\text{Zr}_{74}\text{Cu}_{13}\text{Ni}_{7.4}\text{Al}_{5.6}$ alloy confirms that this composition has an amorphous structure at 2 mm thickness, as indicated by the broad diffraction halo shown in Fig. 5.8(a).

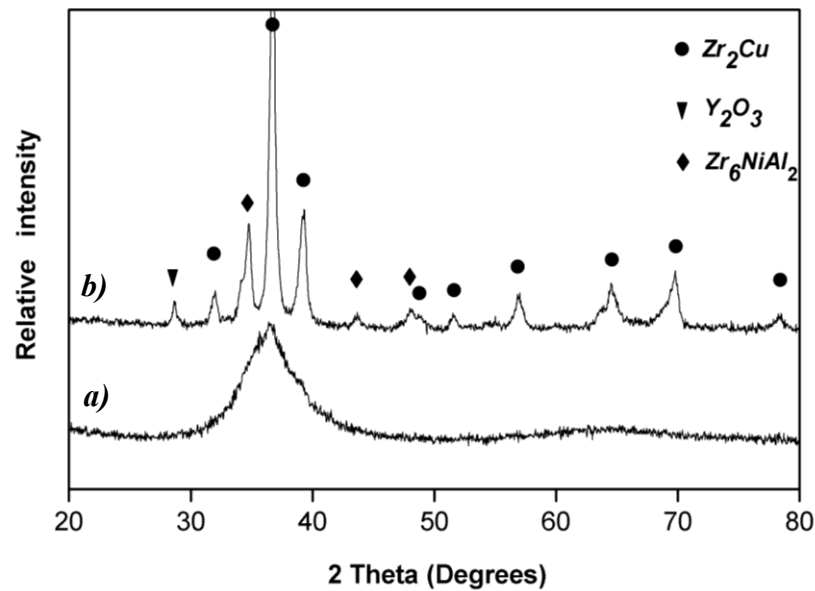


Figure 5.8. XRD scans for $\text{Zr}_{74}\text{Cu}_{13}\text{Ni}_{7.4}\text{Al}_{5.6}$ alloys taken from various sample thickness Z : (a) monolithic alloy at $Z=2$ mm; (b) alloy inoculated by Y_2O_3 oxide particles, $Z=1.5$ mm.

No amorphous phase is observed in the alloy melted with 3 wt.% Y_2O_3 . The introduction of oxide particles subsequently resulted in the formation of a completely crystalline morphology consisting of fine grains of Zr, Zr_2Cu and Zr_6NiAl_2 phases which was confirmed by XRD (Fig. 5.8(b)). As seen in Fig. 5.9, inoculated particles do not affect the formation of crystalline phases since there is no change in microstructure in the areas adjacent to the particles. This could have been due to the addition of excess oxygen to the alloy through the dissolving of the Y_2O_3 particles, destroying the alloys glass-forming ability.

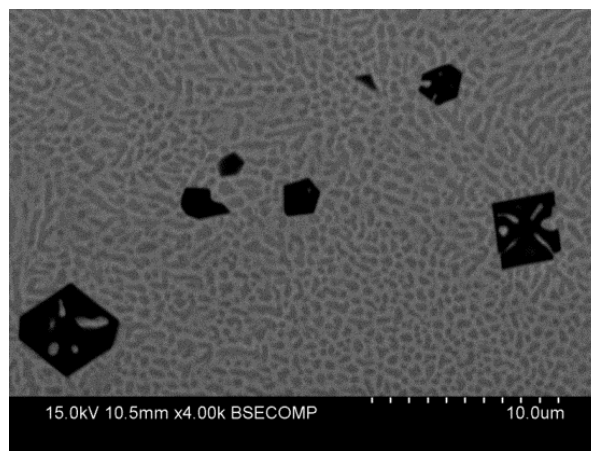


Figure 5.9. SEM images for composition $Zr_{74}Cu_{13}Ni_{7.4}Al_{5.6}$ inoculated by Y_2O_3 particles.

5.3.5. Alloys with 76 at.% Zr

The maximum Zr concentration of 76 at.% in the Zr-Cu-Ni-Al system still allowed the formation of a glassy phase, albeit, with significantly deteriorated GFA. According to the XRD analysis, the $Zr_{76}Cu_{12}Ni_{6.9}Al_{5.1}$ alloy has a monolithic amorphous structure at the sample thickness less than 1 mm and amorphous-crystalline structure at larger thicknesses, which is shown in Fig. 5.10(a-b). The composite structure consists of the glassy matrix and the crystalline Zr_2Cu phase.

Inoculation of $Zr_{76}Cu_{12}Ni_{6.9}Al_{5.1}$ alloy with Y_2O_3 particles was found to completely suppressed formation of glass across the whole wedge. The XRD pattern of the given alloy is represented as a mixture of Zr_2Cu and Zr_6NiAl_2 phases (Fig. 5.10(c)). The microstructure of the inoculated alloy appears identically to the structure of $Zr_{74}Cu_{13}Ni_{7.4}Al_{5.6}$ composition shown in Fig. 5.9.

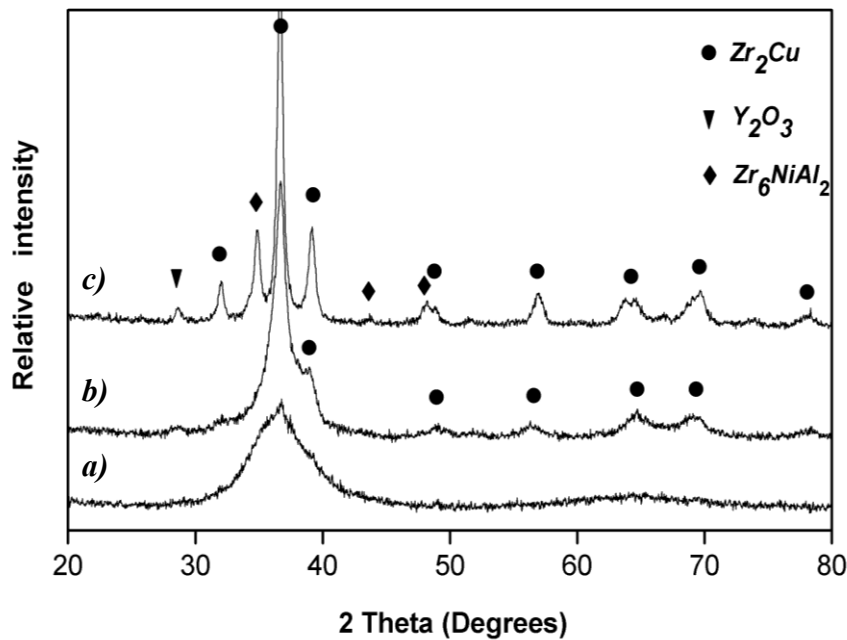


Figure 5.10. XRD patterns for $\text{Zr}_{76}\text{Cu}_{12}\text{Ni}_{6.9}\text{Al}_{5.1}$ alloys taken at various thickness Z : (a) monolithic alloy, $Z=0.5$ mm; (b) monolithic alloy at $Z=2$ mm; (c) alloy inoculated by Y_2O_3 , $Z=0.5$ mm.

5.3.6. Chemical analysis of composite structure

To confirm the stoichiometry and morphology of the intermetallic phases and inoculant particles a chemical analysis of the samples structure has been carried out. A typical EPMA map for the studied Zr-based composites represented by the $\text{Zr}_{72}\text{Ni}_{7.5}\text{Cu}_{13}\text{Al}_{7.5}$ alloy is shown in Fig. 5.11(a). The composition of amorphous matrix and the volume fractions of amorphous and crystalline components will vary between different alloy compositions. Intensity maps for Y and O elements confirm that the black particles located in the centre of crystallite regions (shown in black & white image) are Y_2O_3 . While the SEM BSE image of the structure shows good contrast between the glassy matrix and crystalline phase (Fig. 5.11(b)), no visible contrast can be seen on the maps of the individual elements of Zr, Cu, Ni and Al.

This fact indicates that there is no significant redistribution of components during melt solidification. Heterogeneous nucleation and growth of crystallites around Y_2O_3 particles occurs via a eutectic reaction. In this case the overall chemical composition of the amorphous matrix and crystalline phase are, within resolution, very similar. In addition, the amorphous phase does not appear to change its local composition when the

glass-crystal interface moves through it, unlike the depleted regions observed for the Mg-based composites (e.g. Fig. 4.5).

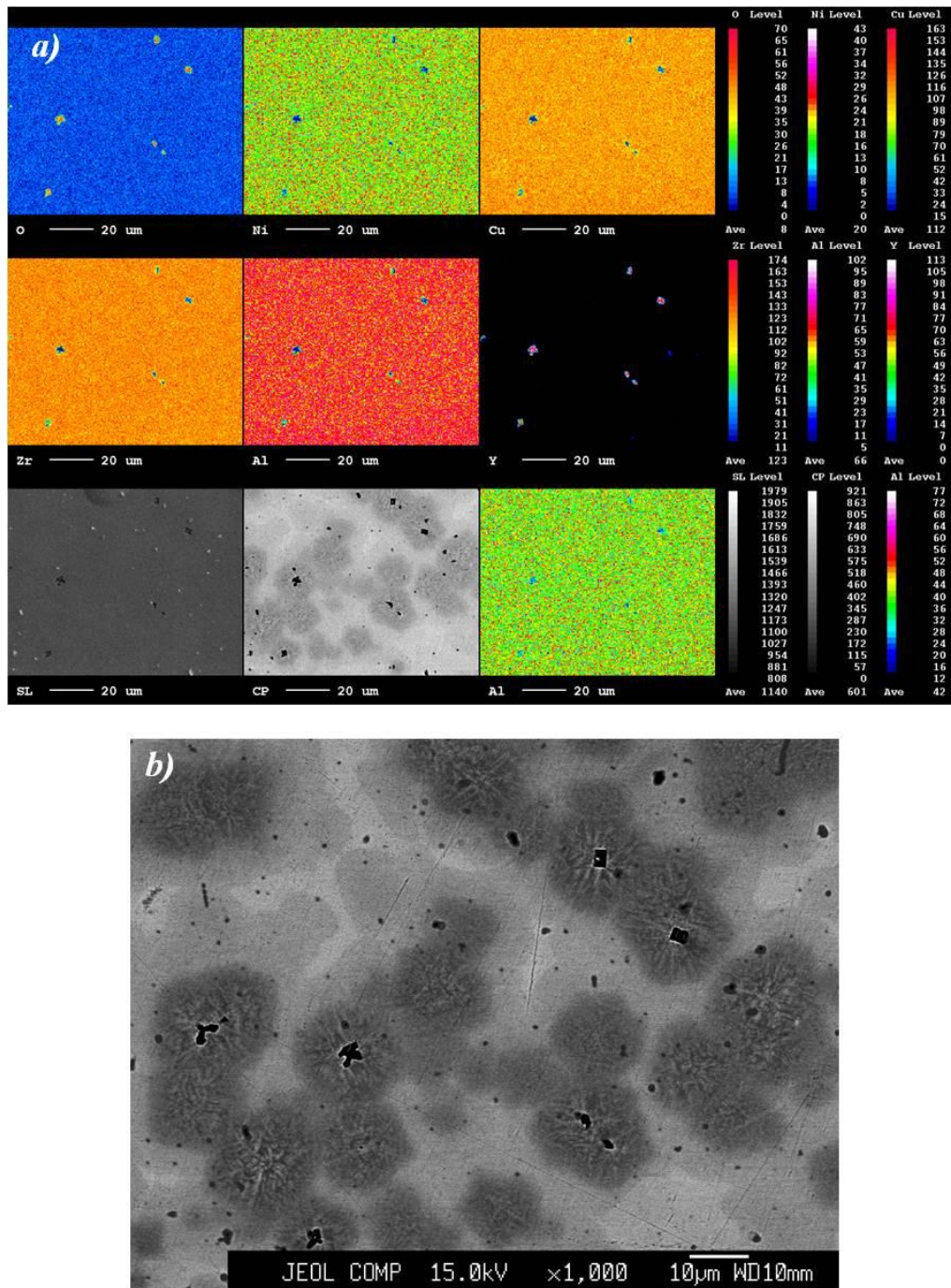


Figure 5.11. EPMA maps of typical structure for as cast $\text{Zr}_{72}\text{Ni}_{7.5}\text{Cu}_{13}\text{Al}_{7.5}$ alloy inoculated by Y_2O_3 particles; sample thickness is 1 mm; (b) magnified SEM image for $\text{Zr}_{72}\text{Ni}_{7.5}\text{Cu}_{13}\text{Al}_{7.5}$.

5.3.7. Thermal properties of Zr-based BMG composites

The thermal properties of the monolithic and inoculated alloys were investigated using DSC. Fig. 5.12 shows isochronal DSC curves for Zr-based alloys recorded at the heating rate of 20°/min. They feature clear endothermic relaxation troughs indicating the onset of glass transition and large supercooled liquid region.

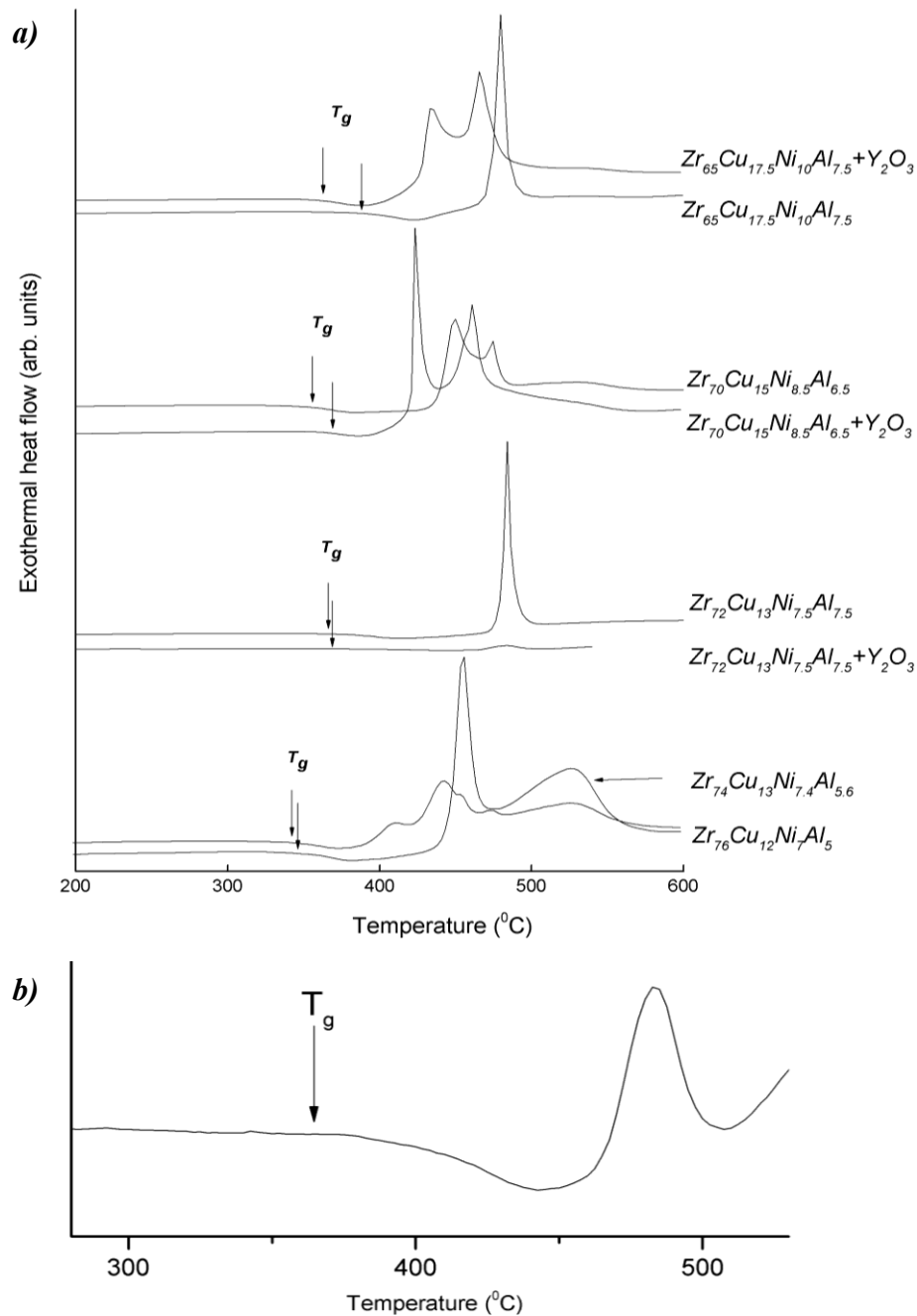


Figure 5.12. (a) DSC scans of as-cast monolithic and composite alloys inoculated by Y_2O_3 ; (b) magnified Tx region for $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5} + Y_2O_3$ composition.

The glass transition and crystallisation temperatures have a general tendency to decline with an increase in Zr concentration. Meanwhile, the width of the SCLR does not follow this trend and exhibits a maximum magnitude of 110 °C for the alloy with 72 at.% Zr indicating its strong resistance to crystallisation. Thermophysical data for the selected Zr-based alloys determined by DSC in conjunction with GFA data are given in Table 5.1.

Table 5.1. Values of the onset of the glass transition temperature (T_g), crystallisation temperature (T_x) and supercooled liquid region ($T_x - T_g$).

Alloy	Critical thickness for glass formation, mm	T_g , °C	T_x , °C	$T_x - T_g$, °C
Zr ₆₅ Cu _{17.5} Ni ₁₀ Al _{7.5}	3.0±0.2	380	468	88
Zr ₆₅ Cu _{17.5} Ni ₁₀ Al _{7.5} +Y ₂ O ₃	2.0±0.1	355	420	65
Zr ₇₀ Cu ₁₅ Ni _{8.5} Al _{6.5}	3.0±0.2	340	430	90
Zr ₇₀ Cu ₁₅ Ni _{8.5} Al _{6.5} +Y ₂ O ₃	1.8±0.1	360	391	31
Zr ₇₂ Cu ₁₃ Ni _{7.5} Al _{7.5}	2.5±0.2	360	470	110
Zr ₇₂ Cu ₁₃ Ni _{7.5} Al _{7.5} +Y ₂ O ₃	0.7±0.1	360	460	100
Zr ₇₄ Cu ₁₃ Ni _{7.4} Al _{5.6}	2±0.1	330	430	100
Zr ₇₆ Cu ₁₂ Ni _{6.9} Al _{5.1}	1±0.1	325	382	57

5.4. THE EFFECT OF YTTRIA PARTICLES ON SUPERCOOLED LIQUID REGION IN INOCULATED ZR-BASED ALLOYS

As reflected by the results of associated microstructure and morphology analysis for the inoculated alloys, only three compositions with 65, 70 and 72 at.% Zr appeared to have an amorphous-crystalline microstructure after introduction using Y₂O₃ powder. In regard to the effect of yttria particles on the thermal behaviour of the alloys, it can be seen that the addition of these particles during processing significantly reduces the size of the interval of the SCLR, which was likewise observed in other studies [190, 191]. It also promotes shift in the onset of the glass transition, particularly, to the lower value

for $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ and to the higher temperature for $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}$. The variation of the glass transition temperatures and width of the SCLR as a function of Zr concentration is shown in Fig. 5.13. This phenomenon might be attributed to different reasons.

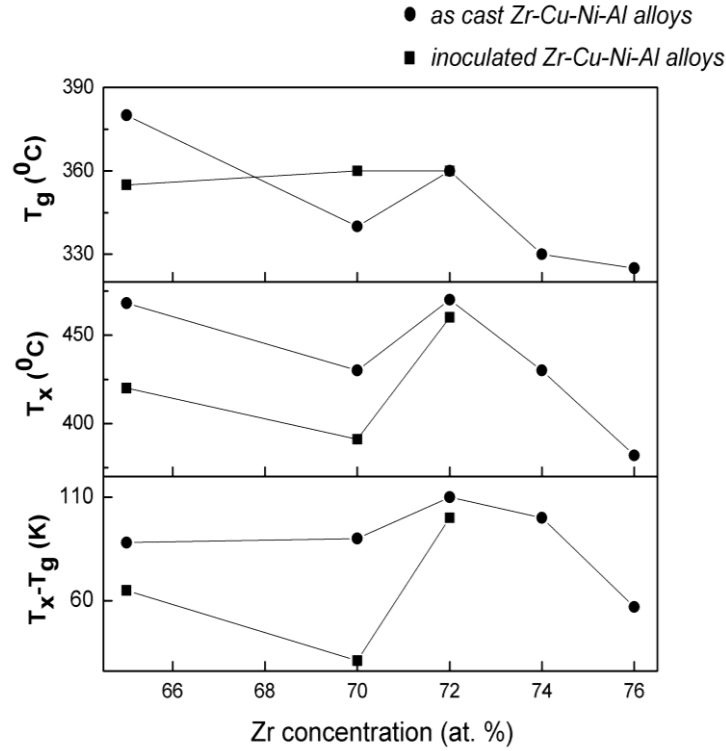


Figure 5.13. Effect of composition on glass transition temperature (T_g), onset of crystallisation (T_x) and supercooled liquid region ($T_x - T_g$) for as-cast Zr-Cu-Ni-Al alloys and alloys inoculated by Y_2O_3 oxide particles.

A possible rationale for this occurrence is the higher oxygen content in the alloys inoculated by Y_2O_3 compared to the monolithic glasses. During the course of alloying glass with Y_2O_3 powder, the vacuum in the operation chamber was of order of 10^{-4} mbar. For comparison, monolithic alloys have been prepared under vacuum 10^{-5} mbar. This difference implies the variation of oxygen concentration in finish products. As it was reported earlier, the oxygen content strongly affects phase formation and thermal stability in Zr-based BMGs [189]. It was noticed that whilst the oxygen stabilizes the amorphous phase in binary Zr-Cu alloys, it deteriorates glass resistance to the crystallisation in Zr-Cu-Ni-Al systems [189] which is clearly seen in the inoculated alloys with 65, 70 and 72 at.% Zr (Fig. 5.12). The oxygen is far more likely to come from the dissolved Y_2O_3 particles themselves. The alloy dissolves Y_2O_3 , so oxygen and

metallic yttrium is dispersed in the alloy, then, as it solidifies, Y_2O_3 is precipitated first. However, the alloy will retain some of the oxygen and yttrium in solution, hence, the change in crystallisation mechanisms occurs.

During heating, $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ and $Zr_{72}Cu_{13}Ni_{7.5}Al_{7.5}$ compositions crystallise through a single exothermic peak with concurrent precipitation of two crystalline phases: Zr_2Cu and Zr_6NiAl_2 (Fig. 5.14).

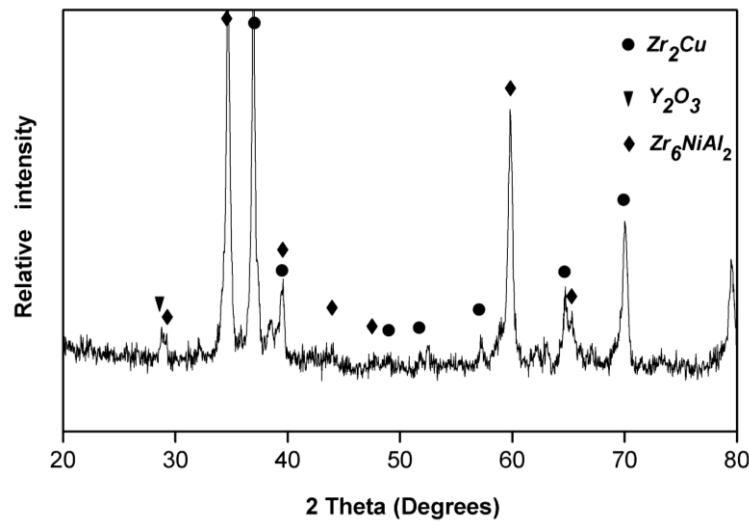


Figure 5.14. XRD scan of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy heated to 600 °C.

The alloy with 65 at.% Zr inoculated by Y_2O_3 transforms to the equilibrium state through two exothermic reactions. Such a transition from a one-step to two-step devitrification mechanism for the same $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glass composition was observed by Gebert and Eckert *et al.* [189, 192]. The first exothermal DSC peak was attributed to the formation of a metastable fcc- Zr_2Ni , whereas the second reaction was believed to originate from the subsequent transformation to the mixture of stable crystalline Zr_2Cu and Zr_6NiAl_2 phases. It is reasonable to apply this transformation sequence in regard to the devitrification mechanism of the inoculated $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy and both $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$ alloys (monolithic and composite).

On the other hand, the inoculated alloy with 72 at.% Zr retains a single step crystallisation process. Generally, one exothermic peak is related to the eutectic reaction type of devitrification when multiple crystalline phases are precipitated simultaneously. Since this composition has a comparatively lower Ni content of 7.5 at/%, it may be

deduced that shift in Zr/Ni ratio suppresses the oxygen-induced formation of the metastable Zr_2Ni phase and results in single crystallisation event.

5.5. MECHANICAL PROPERTIES OF ZR-BASED MONOLITHIC AND COMPOSITE BMGS.

The mechanical behaviour of Zr-based BMGs was investigated in uniaxial compression at room temperature. Cylindrical samples of monolithic $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ and $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$ alloys, and their corresponding composites inoculated by Y_2O_3 , were fabricated by the vacuum casting method. Here, alloys of the required compositions were prepared using an arc-melter on the water-cooled copper plate. Alloy buttons were then cleaned of any surface oxides and impurities and cut into two pieces. Each alloy composition was vacuum-cast into a copper mould of rod-shaped configuration without the addition of the Y_2O_3 inoculant particles. From the same alloy buttons, alloys were melted with the addition of the Y_2O_3 particles in the arc-melter and vacuum-cast into the same rod-shaped copper mould. The ends of the 2 mm diameter as-cast rods of 2:1 aspect ratio (i.e. 4 mm in length) were ground and polished to create parallel surfaces needed for uniaxial compression testing.

Compression tests were performed on an Instron 5565 SWP machine using a 5 kN load cell. The samples were strained to failure at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$, which corresponds to a cross-head speed of $3 \times 10^{-4} \text{ mm/s}$. Data from at least three samples were collected for ensuring reproducibility of the results. Figure 5.13 shows the comparison of representative compressive stress-strain curves for both the monolithic and inoculated BMGs of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ and $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$ compositions, respectively. There is a clear trend of ascending plastic strain and descending yield strength with increasing Zr content. All samples show noticeable yielding followed by plastic deformation. However, only BMGs inoculated with Y_2O_3 exhibit significant plastic strain at failure. The yield strength of the BMGs is also slightly increased with the addition of Y_2O_3 , as shown in Table 5.2. Inoculation of the BMGs with Y_2O_3 also results in considerable increase in strain to failure (Table 5.2). For example, the $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ BMG and composite has a fracture strain of 7 % and 12.4 %, respectively.

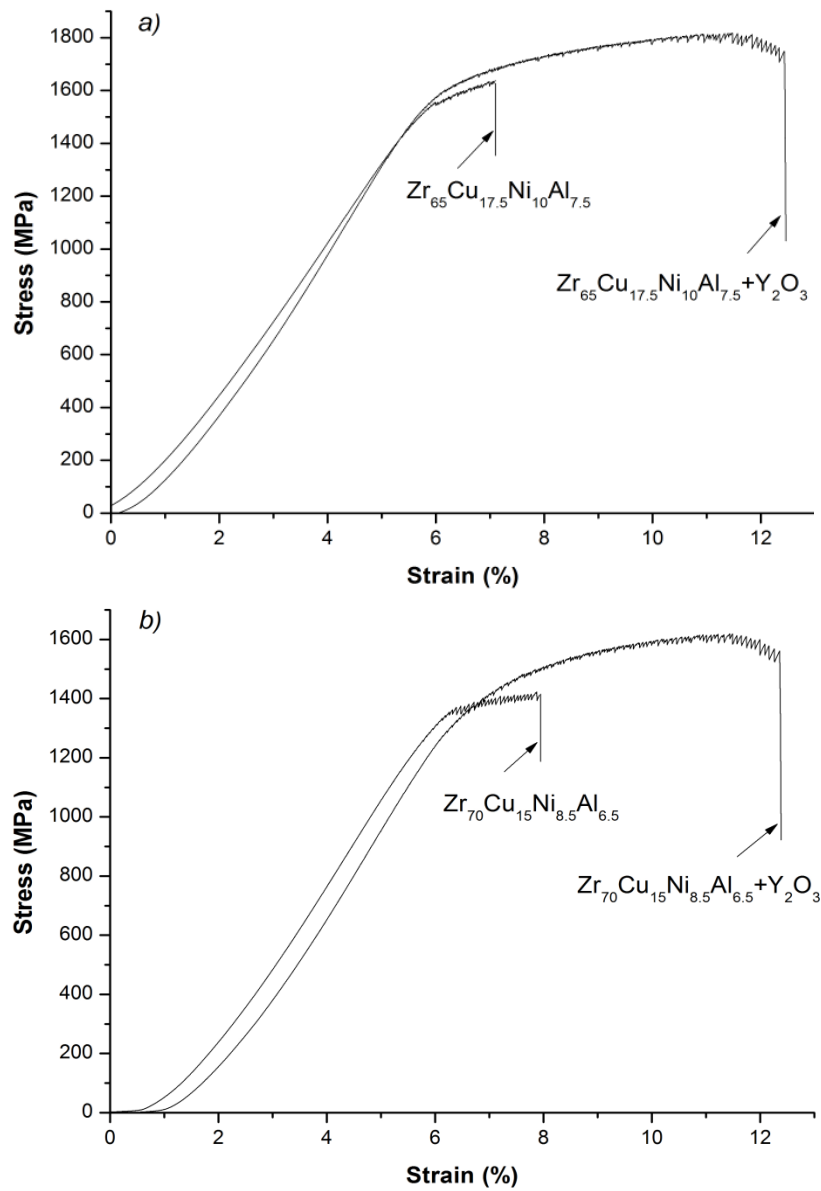


Figure 5.15. Typical stress strain of the monolithic and composite Zr-based alloys tested in uniaxial compression: (a) $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$; (b) $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$.

Table 5.2. Mechanical properties of monolithic and composite Zr-based alloys.

Alloy	σ_y , MPa	ϵ_y , %	σ_b , MPa	ϵ_b , %	σ_{max} , MPa
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	1460	5.5	1620	7	1620
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}+Y_2O_3$	1490	5.6	1750	12.4	1800
$Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$	1250	5.8	1400	7.9	1400
$Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}+Y_2O_3$	1300	6.1	1550	12.4	1600

Therefore, the Y_2O_3 inoculant particles and crystallites that nucleate and grow around these particles (as shown in Fig. 5.2 and 5.5) also have a pronounced reinforcing effect on the Zr-based BMGs. For the present $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ and $Zr_{70}Cu_{15}Ni_{8.5}Al_{6.5}$ composites, both the ductility and fracture strength were effectively improved with respect to the monolithic alloys.

5.6. SUMMARY OF ZR-BASED BMG COMPOSITE ALLOYS

Monolithic glasses with a Zr content greater than 70 at.% and their composites with incorporated Y_2O_3 particles were successfully fabricated by an arc-melting - vacuum casting technique. With the increase of Zr concentration, the glass-forming ability of alloys appears to deteriorate down to a critical thickness of 1 mm at maximum Zr-concentration of 76 at.%. Inoculation of the alloy using Y_2O_3 particles affected the microstructure of the monolithic glasses by promoting the growth of crystallites around the inoculants. However, the growth of any crystalline phases was suppressed at the lower sample thickness correlating to higher solidification rates. The process of incorporating the Y_2O_3 powder into the amorphous alloy provoked the contamination of the composite structure by oxygen. As a result, the thermal relaxation properties (i.e. the glass transition) and the crystallisation paths associated with the devitrification of the alloy were dramatically altered in some cases.

CHAPTER 6 – DISCUSSION

6.1. STABILITY OF THE AMORPHOUS STRUCTURE

As reflected and confirmed in numerous studies on metallic glasses, the glass-forming ability (GFA) is a function of many factors including chemical composition of the alloy, purity of raw materials, cleanliness of the melt, presence of the oxygen, the production techniques and process-related variables such as cooling rate and casting temperature.

6.1.1. Glass-forming ability of Mg-based alloys

The Mg-based glass-formers described in chapters 3 and 4 exhibit a wide range of GFA depending on the chemical composition and solidification rate. To compare GFA of Mg-rich alloys produced in this thesis and with the alloys reported in the literature, it is useful to use critical thickness of glass formation in the wedge-shaped castings as an indicator of GFA. Figure 6.1 shows the intervals of amorphous, composite and crystalline structures through the wedge length for the Mg-Ni-Gd-Y and Mg-Ni-Gd alloys with the different Mg content. The ternary Mg-Ni-Gd compositions have slightly higher glass formation thickness in contrast to the quaternary alloys. In both systems glassy and composite structure regions descend with the increment of Mg concentration which is related to the deterioration of the glass-forming ability. For instance, the $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$ alloy has critical thickness for glass formation 4 mm [128], whereas this value for the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ alloy does not exceed 0.25 mm. As noted earlier, GFA of an alloy is determined by the thermodynamic and kinetic properties which, in turn, are affected by the atomic structure. The Mg-Ni-Gd alloy system consists of elements having negative heat of mixing between atomic pairs (-12 kJ/mol for Mg-Ni, -27 kJ/mol for Mg-Gd, -161 kJ/mol for Ni-Gd [194]). The large difference in the heat of mixing between atomic pairs in the Mg-Ni-Gd alloy system and resulting attraction in the liquid allow elements to effectively mix at the atomic level. The strong chemical affinity between the atomic pairs and high packing density lead to a low potential energy and high stability of the short range ordered clusters (SRO) [193]. These favoured SRO clusters may compete with intermetallic compounds, enhance the viscosity and prolong the structural relaxation time resulting in relatively good GFA for the $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$ composition. An increase in Mg content leads to the lower number of

heterogeneous atomic pairs and results in a less efficient packing of the structure and, consequently, deteriorates the GFA of the alloy.

The GFA of the alloy cannot be estimated by a single parameter with specific value. Generally, all established relationships and parameters show trends for potential glass-forming systems. Earlier criteria for the prediction of GFA developed for rapidly solidified ribbons are applicable to the bulk glass-formers. One of the universal ratios is the reduced glass transition temperature [26] that depends on the liquidus temperature T_l and the glass transition temperature T_g . Figure 6.2 compares these values for the Mg-Ni-Gd-Y and Mg-Ni-Gd alloys. T_g in both systems is reduced with increasing Mg content, which is associated with the formation of less stable structure configuration. The ternary alloys have higher T_g in the entire concentration interval compared to those for the Mg-Ni-Gd-Y alloys. The liquidus temperature has a stronger dependence on the composition in contrast to T_g . According to the data obtained from DCS measurements, both ternary and quaternary alloys with 86 at.% of Mg exhibit the lowest T_l and narrowest melting interval. This indicates the close proximity of these alloys to the eutectic compositions, which are expected to be better glass-formers in comparison with the off-eutectic alloys. However, these compositions do not exhibit an improved GFA among other compositions in Mg-Ni-Gd-Y/Mg-Ni-Gd systems. This correlates with other studies that have reported better glass formation in the off-eutectic alloys [194, 195], including $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$ composition with the critical thickness of 4 mm located far away from the eutectic point [128].

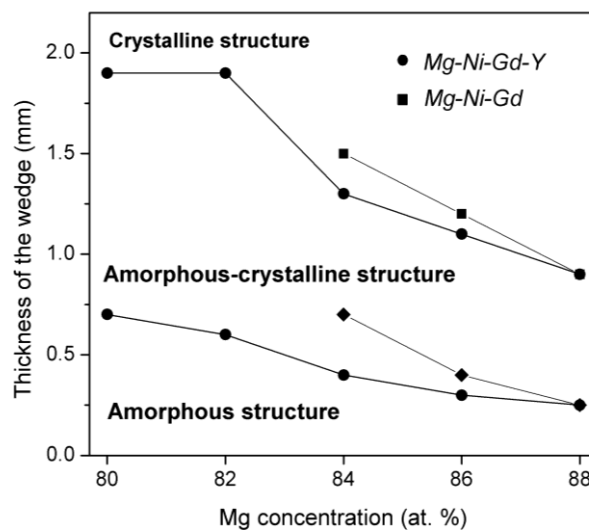


Figure 6.1. Structure distribution in the wedge-shaped samples of Mg-Ni-Gd-Y/Mg-Ni-Gd alloys as a function of wedge thickness and concentration of Mg.

A wide interval of the supercooled liquid region (SCLR) often indicates good GFA. For instance, $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ BMG alloy with 4 mm critical thickness has SCLR value of 65 K [143]. The width of the SCLR for the studied alloys is quite low and ranges from 5 to 23 K. It decreases for the alloys with higher Mg content in both systems indicating that they become less resistant to crystallisation of the amorphous phase.

The ternary and quaternary Mg-based systems exhibit similar T_{rg} in the range of 0.52–0.54. Typically, a minimum value of 0.4 is required to observe glass formation. It can be noted that alloys with the highest values of T_{rg} such as compositions with 86 at.% Mg do not correspond to the best glass-formers among the studied alloys.

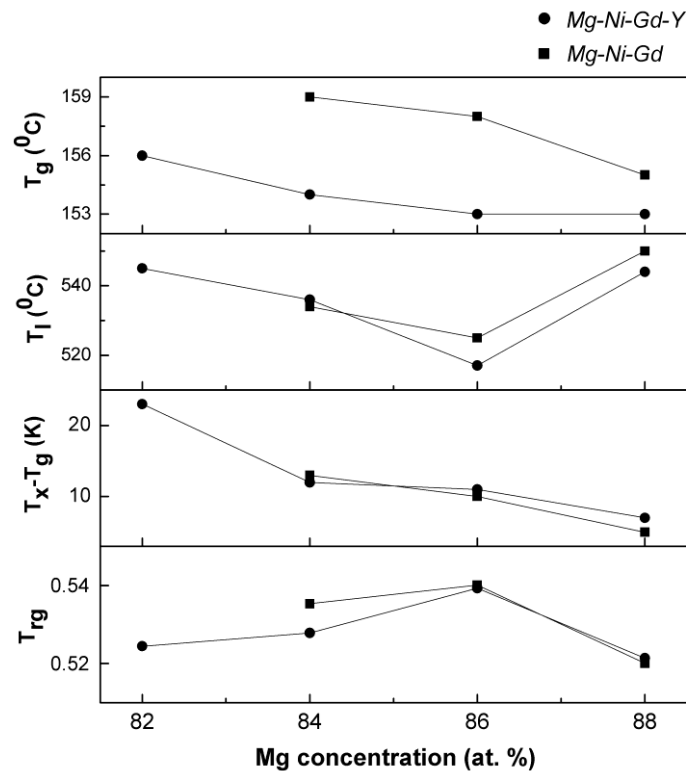


Figure 6.2. Effect of composition on glass transition temperature (T_g), liquidus temperature, supercooled liquid region ($T_x - T_g$) and reduced glass transition temperature (T_{rg}) for Mg-Ni-Gd-Y/Mg-Ni-Gd glass-forming alloys.

There is no substantial difference in the microstructure between ternary Mg-Ni-Gd and quaternary Mg-Ni-Gd-Y alloys at the fixed Mg concentration. The shape, size and distribution of the primary Mg crystalline phase in the amorphous matrix are the same for both ternary and quaternary compositions. Alloys containing one rare-earth (Gd) or

two elements (Gd and Y) have similar thermal properties. This leads to the conclusion that in a given type of Mg-based BMG composite (Mg-Ni-Gd/Y), the element Y does not contribute considerably to microstructure formation and thermal behaviour.

6.1.2. Glass-forming ability of Zr-based alloys

The GFA of Zr-based alloys undoubtedly outperform the Mg-based compositions. Nevertheless, as reflected in the results from the section 5.3.7, it significantly reduces for compositions with higher Zr-content. Figure 6.3 demonstrates a steady decrease in critical casting thickness for glass formation in the Zr-alloys produced in this thesis with increasing Zr concentration.

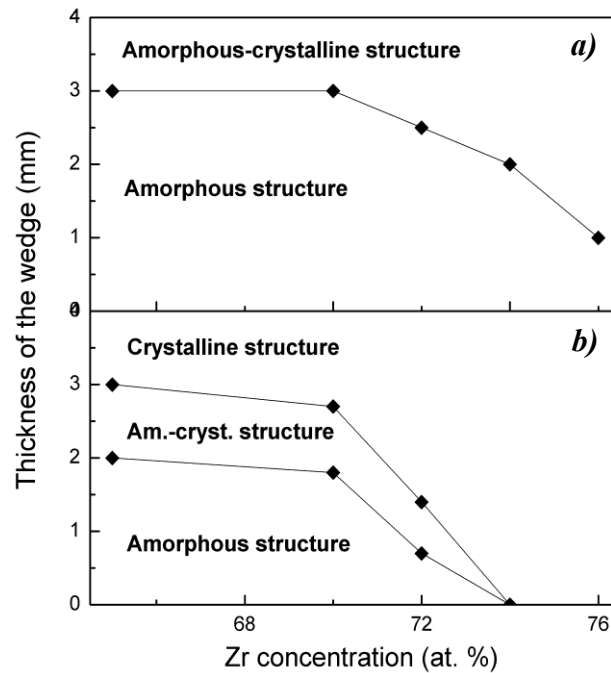


Figure 6.3 Structure distribution in the wedge-shaped samples of Zr-Cu-Ni-Al alloys as a function of wedge thickness and concentration of Zr: (a) as cast alloys; (b) alloys inoculated by Y_2O_3 particles.

It is widely accepted that GFA is attributed to the randomly packed dense structures in the liquid state. Strong atomic bonding is required to form these structures. According to Niessen *et al.* [196], estimated heats of mixing for Zr-Ni, Zr-Cu and Zr-Al pairs are -165, -78 and -164 kJ/mole, respectively, which means the easiness to generate the densely packed structures with the constituent element that are strongly attracted to Zr. An increase in Zr concentration gives a larger number of homogeneous pairs and can consequently result in weakening of the bonding energy between the clusters [184].

Therefore, deterioration in bonding effect may be a reason for the sluggish formation of the dense random structures and, as a consequence, the lower GFA.

The noticeable reduction of GFA in alloys with inoculating particles, which is represented by reduced thickness of glass formation in Fig.6.3(b), may be mainly attributed to the effect of the oxygen that destabilizes amorphous structure. Apparently, the oxide particles also contribute to the GFA deterioration since they activate heterogeneous nucleation and growth of crystalline phases.

6.2. FORMATION OF A COMPOSITE STRUCTURE IN BULK METALLIC GLASSES

6.2.1. Nucleation in Mg-based composites

As discussed in chapters 3 and 4, all Mg-based alloys produced in this thesis form a composite structure during a single processing casting step. Study of the composite structure formation in BMGs provides an opportunity to understand the nucleation and growth of crystals in an isotropic environment of an amorphous matrix. In general, this process can be described as follows. When the liquid is cooled the crystals of favourable phase are formed first at a higher temperature. Often crystalline precipitations have dendritic structure since high undercooling is involved. The remaining liquid is cooled down further until it is supercooled below the glass transition temperature and, subsequently, turns into the amorphous state. However, the nucleation mechanisms and the factors affecting the nucleation and growth of crystallites in the undercooled melt are not completely understood.

6.2.1.1. *Nucleation of the crystalline phase*

A large number of studies have been devoted to the solidification of conventional alloys. The crystalline phases here are nucleated heterogeneously on the walls of the mould or at inoculants. In contrast, very little research has been carried out on crystal growth in an amorphous phase during the solidification process. Typically, the high cooling rate of the glass-forming alloys is the main obstacle to obtain information on phase transformations in the rapidly solidifying melt. Various theoretical approaches

have been applied to describe the kinetics of phase transformations in metallic glasses [26, 197-200]. Homogeneous nucleation and growth of crystal phase in glass-formers has been observed in some BMG composites [118, 119]. However, classical theory of homogeneous nucleation does not generally fit with the experimental data since, in the real conditions during solidification of the glass-forming alloy, heterogeneous nucleation always occurs first [201]. For instance, the nucleation of Mg-rich flakes in the amorphous Mg-Cu-Y-Zn matrix has been shown to originate substantially from the surface of Y_2O_3 particles that form in the melt during casting [144, 145].

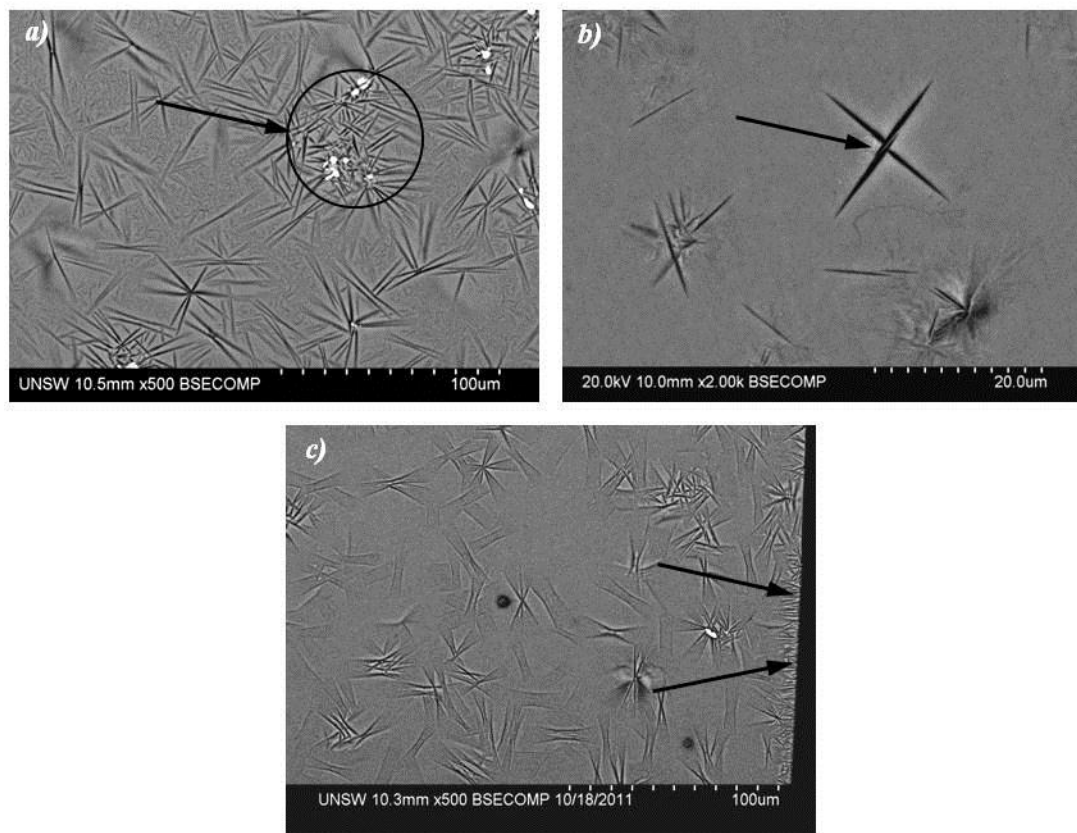


Figure 6.4. Examples of nucleation (marked by arrows) of Mg-rich phase in the glassy matrix: (a) $Mg_{86}Ni_{10}Gd_3Y_1$ alloy; (b) $Mg_{84}Ni_{12}Gd_3Y_1$ alloy; (c) $Mg_{88}Ni_8Gd_3Y_1$.

In regards to crystalline phase formation in the amorphous matrix in the studied Mg-Ni-Gd/Y systems, heterogeneous nucleation always occurs. The heterogeneous mechanism is especially evident in the alloys containing Y. Images of the composite microstructures do not always directly reveal the presence of impurities such as Y_2O_3 particles. As exemplified in Fig. 6.4(a), the dark Mg-rich flakes are radiating away from the particle cluster which appears to act as a preferred nucleation site. The group of

flake-shaped Mg crystallites in Fig. 6.4(b) also appear to originate from a point source (i.e. particle), which is not visible in the figure as it is likely to be located in the front or behind the polished sample surface. However, the Mg flakes have a preferential direction of growth and oriented perpendicular to each other. This may serve as an indicator of Mg-crystal growth on the surface of a Y_2O_3 particle which has cubic lattice structure [202]. Y_2O_3 particles are possibly formed due to the interaction of a small fraction of yttrium with residual oxygen during the melting of the charge. The finer precipitation of the Mg-rich phase located between the large-sized flakes (Fig. 6.4(a)) do not appear to originate from particles. Their sizes are 1-3 μm , and they do not exhibit a preferential direction of growth and are also not grouped. The formation of these small flakes may be facilitated by heterogeneous nucleation at inhomogeneities present in the cooling melt.

Another example of heterogeneous nucleation of crystals during cooling of the melt was observed at the surfaces of the Mg-based castings. The direct contact of the melt with faceted surface of copper mould has promoted directional growth of crystals normal to the mould surface, as illustrated in Fig. 6.4(c). It is worth noting that recent experiments on heterogeneous nucleation in the Mg-Cu-Y-Zn glassy matrix demonstrated that the Mg-rich phase does not nucleate directly on the surface of inoculating particles. Instead, Mg-flakes were found to form at intermediate copper layer between the matrix and inoculant [182]. In light of these results it can be assumed that copper plays some special role in the nucleation of the Mg-phase. As such, this fact may serve as a further consideration for developing BMG composites with preferential/specified orientation of precipitates in an isotropic matrix.

6.2.1.2. Structural features of the crystalline phase in amorphous matrix

The study of the crystalline Mg-rich phase formed in the Mg-Cu-Y-Zn and Mg-Ni-Gd-Nd BMG composites has revealed that this phase is characterized by a long period ordered structure (LPOS) [118, 119, 144]. LPOS represents an hcp-structure distorted by the embedded heavy elements such as Y, Zn, Gd and Nd. However, as noticed in recent work [144], the flake-shaped Mg-phase does not consist completely of a long period ordered structure. Also, the LPO structure observed in the Mg-based BMG composites is typical in alloys containing at least four elements.

The Mg-rich flakes that formed in the Mg-Ni-Gd/Y BMG composites in this thesis were found to have a regular α -Mg hcp-structure. According to the XRD results, hcp-Mg phase in the $\text{Mg}_{88}\text{Ni}_8\text{Gd}_4$ composite has lattice parameters a and c that are very close to those for pure Mg (Fig. 6.5). The slightly different values of a and c in the alloys containing 86 and 84 at.% Mg is evidence of the formation of hcp-Mg solid solution. Ni has very limited solubility in Mg (< 0.04 at.% at 500°C) and, therefore, it partitions to the surrounding liquid. In contrast, Gd exhibits a maximum solubility of 4.53 at.% and 0.61 at.% at 548°C and 200°C respectively. Since the partial solidification of the composites occurs at high cooling rates, the maximum solubility in the solid-state alloy at ambient temperature can exceed the limited equilibrium values. The atomic radius of Gd and Y atoms (0.18 nm) is higher compared to Mg (0.16 nm) [202]. Therefore, it is likely that hcp-Mg solid solution with the increased lattice parameters contains Gd in its structure. According to the EPMA results in section 4.2.3, the flake-shaped crystallites of larger size (10-20 μm) have uneven distribution of the components. The concentration of Mg is higher in the central part of the flakes along the length and gradually reduces towards the edges, thereby indicating the greater amount of solute Gd away from the centre.

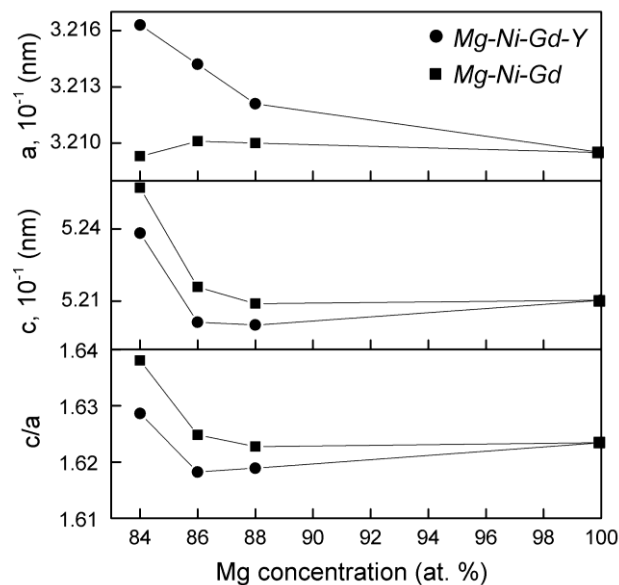


Figure 6.5. Correlation between the lattice parameters for Mg hcp-phase and Mg concentration in Mg-Ni-Gd/Y glass-forming compositions

The type of crystallites that formed in the glassy matrix of the Mg-Ni-Gd/Y alloys is dendritic in nature, which is the most common during solidification of the melt. It can be noted that Mg concentration in both the ternary and quaternary Mg-Ni-Gd/Y alloys affects the appearance of Mg-rich dendrites. Compositions with maximum Mg content of 88 at.% have Mg-dendrites with secondary and tertiary branches whereas the other alloys have dendrite arms of the maximum second order.

6.2.2. Nucleation in Zr-based composites

In contrast to the composites produced by the single-step process in the Mg-based glasses, Zr-containing composites were fabricated by the two-stage routine. Over the course of first step the monolithic glass was cast, whereas the second melting step was used to introduce the oxide particles into the glassy structure. It is known that Zr and its alloys are highly susceptible to the smallest quantities of oxygen. Due to this fact every consecutive cycle of remelting is expected to increase the oxygen content in the structure of the final composite. Therefore, apart from decrease in GFA of the amorphous matrix, the oxygen presence may also affect the formation of the crystalline structures in inoculated Zr-based BMG alloys.

The phase selection of composite structures generated by the inoculating Y_2O_3 powder was a mixture of $Zr_2Cu + Zr_2Ni$ or $Zr_2Cu + Zr_6NiAl_2$ compounds distributed in the amorphous structure. Although the formation of soft Zr-rich phase was anticipated due to the abundant concentration of Zr in the produced alloys, only brittle intermetallics were found to precipitate that was observed likewise in other partially crystallised composites with considerably smaller Zr content [99, 203, 204]. Although in previous studies intermetallic phases were confirmed to be detrimental to the plasticity of BMGs [205, 206], their effect on mechanical properties still remains a controversial question since the opposite phenomenon has been reported by Chen in Zr-Cu-Ni-Al BMG composites [203].

A morphological examination of the inoculated composite structures showed that the inoculating particles do not promote growth of the crystalline phase at the reduced wedge thickness, particularly less than 2 mm for the compositions containing 65 and 70 at.% Zr and ≤ 0.5 mm for the alloy containing 72 at.% Zr. Samples of the smaller thickness are exposed to the higher cooling rate upon casting and their structure appears

to be resistant to heterogeneous nucleation at the surface of the Y_2O_3 particles. The investigation of the mechanism responsible for the formation of crystallites at the particle surfaces or their suppression as a function of solidification rate might be a potential consideration for further research. For instance, the inoculation of metallic glasses by various oxide/carbide particulates resulted in the generation of reaction layers at the interface between the matrix and particles. For example, for SiC/WC particles embedded in the Zr-based BMG a weak ZrC layer was formed with no subsequent inoculation of crystalline phase [82]. In contrast, in an inoculated Al-based glass, a thin metastable Al_3Ti layer was formed around inoculating particles that served as a preferred site for nucleating Al-crystals [178]. It was also shown that, at the early stages after nucleation, crystallisation can be suppressed by rapid quenching. Therefore, the microstructure of the alloy with inoculants can be controlled and optimised by the solidification rate.

6.3. MECHANICAL PROPERTIES OF COMPOSITES

As shown in the sections 2.5.2 and 2.5.3, a composite structure is known to significantly alter the mechanical characteristics of bulk amorphous alloys. Apart from the influence of the amorphous matrix, the contribution from all constituent phases of the composite alloy, including their volume fraction, size and chemical stability, is anticipated.

6.3.1. Correlation between hardness and strength in BMG composites

It is well-known that hardness of a metallic material is approximately $3\times$ greater than its compressive yield strength [207], and this assumption is also accurately fulfilled for the monolithic metallic glasses [88, 157, 159, 208]. However, as reported in the works [160, 161], this empirical relationship is not always valid for BMG composites. The relationship between Vickers hardness (H_V) and the yield or fracture strength (σ_y , σ_f) for a range of the monolithic metallic glasses and few composites is given in Fig. 6.6.

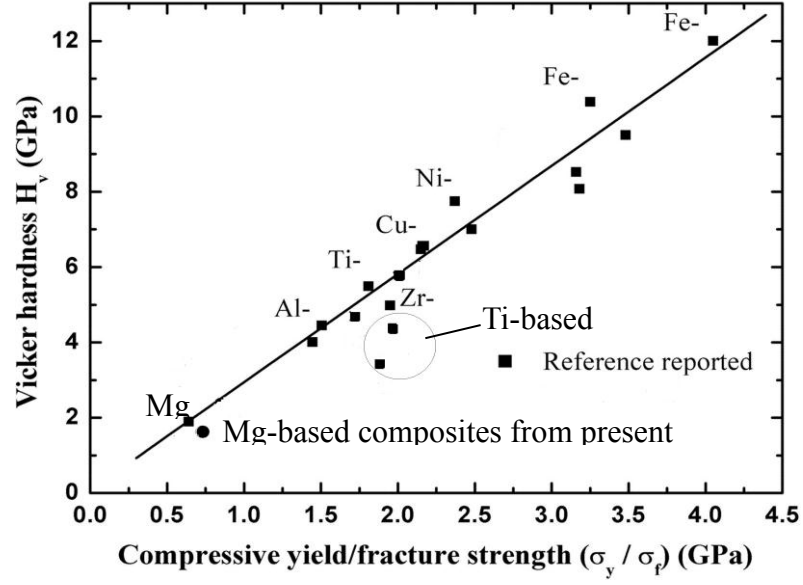


Figure 6.6. Relationship between Vickers hardness and compressive yield/fracture strength reported for monolithic glasses and BMG composites [160].

Since BMG composites exhibit a certain degree of plasticity in contrast to most monolithic metallic glasses (section 2.5.3), the values of yield and fracture strength are different. Therefore, this imparts a deviation from the ratio $H_v/3 = \sigma_f$. As suggested by Pan [160], the hardness of BMG composites can be expressed as a function of several parameters:

$$H_v/3 = \sigma_y + f(\sigma_f, \delta_E, \delta_T, n) \quad (6.1)$$

where δ_E is the elastic energy density, δ_T the total energy density, and n the hardening rate of material. However, a detailed understanding of these parameters and their relations are not completely clear and further research is required.

The values of Vickers hardness converted to MPa units (by multiplying by 9.81 [156]) and yield/fracture strength for Mg-Ni-Gd alloys (determined in section 4.5.2) were used to generate the graph in Fig. 6.7. For the monolithic amorphous alloys the ratios of $H_v/3\sigma_y$ and $H_v/3\sigma_f$ should be close to the unity, but all three studied compositions exhibit deviation from the unity. As such, the hardness of the composite structure generated in the Mg-Ni-Gd alloys can be expected to follow the modified relationship:

$$\sigma_y < H_v/3 < \sigma_f \quad (6.2)$$

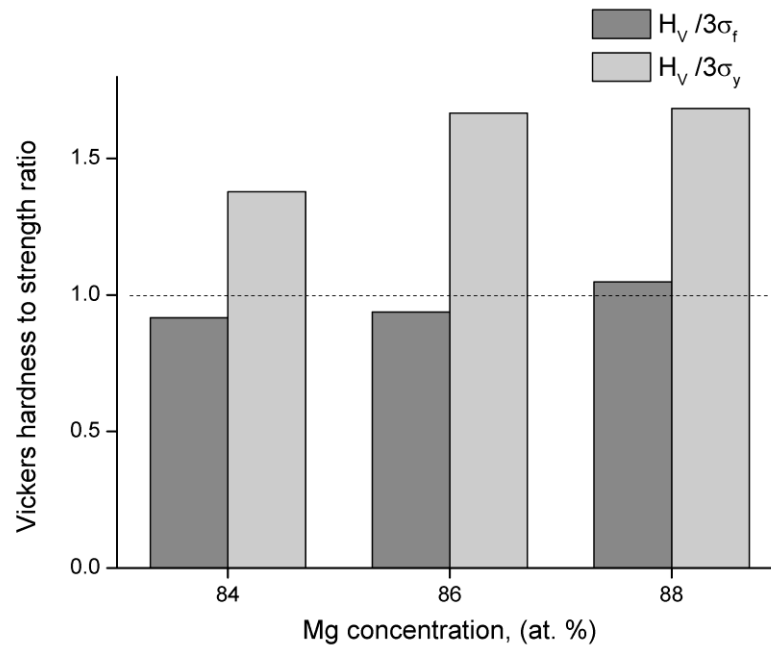


Figure 6.7. Ratio of Vickers hardness to strength in $Mg_{84}Ni_{10}Gd_6$, $Mg_{86}Ni_{10}Gd_4$ and $Mg_{84}Ni_{10}Gd_6$ composite alloys.

As described in the section 4.5.1, the hardness of the composite structure in the BMG alloys was lower than the monolithic amorphous zone. The opposite effect of strengthening in the ex situ and in situ composite structures has been reported in several studies [78, 87, 106, 123, 135, 136, 209]. Understandably, higher hardness of ex-situ composites is observed due to the nature of reinforcement materials represented by hard ceramics, carbides or refractory metals particles [78, 106, 135, 136]. The improved hardness in the partially devitrified in situ composites is attributed to the compositional change in the glassy matrix and its enrichment by the solute elements [87, 209] even if the crystalline phase is soft [123].

In regards to the amorphous-crystalline Mg-Ni-Gd alloys produced in this thesis, the Mg-rich phase acts as a softening phase. The process of formation of this phase, morphology and size do not induce homogeneous compositional alteration in the amorphous matrix, but rather, causes a local change in the areas adjacent to the Mg-crystallites according to the EPMA analysis (Fig. 4.5). Therefore, the overall hardness of Mg-Ni-Gd composite structure is an additive value of the two phases.

6.3.2. Role of the amorphous matrix in the overall plasticity of BMG composites

The hardness and compression tests carried out on the Mg-based BMG composites in this thesis indicate a reasonably level of plasticity in the samples. Considering that the monolithic amorphous alloy $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$ [128] was reported to exhibit a large plastic strain (up to 2 %), it can be assumed that the amorphous matrix in the Mg-Ni-Gd composites produced herein contributes significantly to the overall plasticity with achieved yield strain of 2.5-4.0 %, depending on the composition.

Generally, the plasticity observed in monolithic BMGs is attributed to the chemical and structural inhomogeneity on the atomic scale. To attain the chemical inhomogeneity the components of the glass-former need to have positive enthalpy of mixing between atomic pairs. The structural irregularity is related to the formation of free volume that acts as sites for shear band initiation and branching. In the case of the Mg-Ni-Gd system, all atomic pairs of the components have a negative enthalpy of mixing. However, the difference in relative magnitude, for instance between Mg-Ni and Gd-Ni is quite large (-12 kJ/mol and -161 kJ/mol, respectively [210]) and can give the same effect on inhomogeneity as atomic pairs with positive heat of mixing. The fraction of the free volume can be increased by the higher cooling rate of the melt during casting. However, within the bounds of the gravity casting method, which was used to produce samples, the cooling rate cannot be altered.

6.3.3. G/B and Poisson's ratio

The ratio of shear modulus to bulk modulus (G/B) for metallic glasses has been shown to correlate with their brittleness or plasticity. Figure 6.8 shows the dependence between G/B ratio for a series of different BMGs and their fracture energy [70]. The fracture energy, defined as a maximum energy that the material can sustain upon impact, gives a good basis for comparison of BMGs in terms of their resistance to crack propagation [40]. It can be seen that there is a certain range of G/B ratio dividing glasses with high and low fracture energy that can be used to quantify mechanical behaviour of these materials [70]. Glasses with $G/B > 0.41$ -0.43 exhibit intrinsically brittle behaviour whereas the lower G/B ratio corresponds to the more ductile BMG alloys.

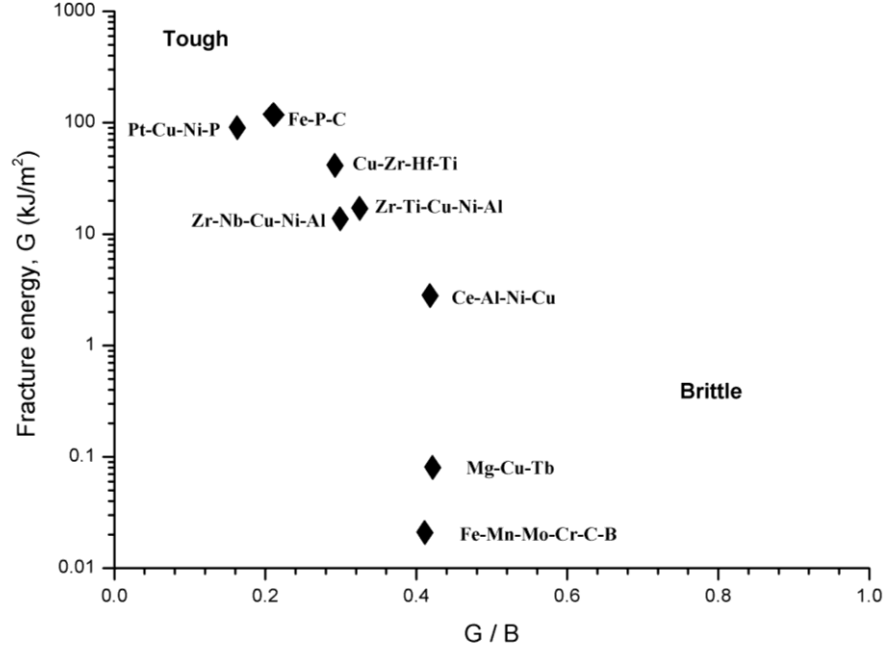


Figure 6.8. Relationship between fracture energy and elastic modulus ratio for different metallic glass systems (adopted from [70]).

Shear and bulk moduli determined for Mg-Ni-Gd and Mg-Ni-Gd-Y alloys in section 4.5.4 yield the G/B ratios in Table 6.1. Values of 0.40 for compositions containing 84 at.% Mg and 0.39 for the other alloys are located on the boundary between ductile and brittle glasses. It implies that there is a potential to circumvent the brittleness of Mg-Ni-Gd compositions by alloying with the constituent elements that have low G/B ratio.

In addition to the G/B ratio there is another indicator for ductile BMGs. The dimensionless Poisson's ratio ν , defined as a ratio of relative transverse expansion to the relative longitudinal compressive strain in the direction of applied load, is high for ductile BMGs [3, 42, 70, 170]. A higher Poisson's ratio correlates with the larger fracture energy for various BMG alloys and gives a critical range of 0.31-0.32 [70] dividing brittle and ductile glasses. Table 6.1 gives the ν -values for the Mg-based BMG composites produced in this thesis, as determined using the following relation [156]:

$$\nu = \frac{3-2(G/B)}{6+2(G/B)}. \quad (6.3)$$

A value of 0.33 for studied Mg-Ni-Gd/Y alloys indicates their ability to withstand plastic deformation.

Table 6.1. Calculated shear to bulk modulus ratio and Poisson's ratio for Mg-Ni-Gd/Y alloys.

Alloy	G/B	Poisson ratio
Mg ₈₄ Ni ₁₀ Gd ₆	0.40	0.33
Mg ₈₆ Ni ₁₀ Gd ₄	0.39	0.33
Mg ₈₈ Ni ₈ Gd ₄	0.39	0.33
Mg ₈₄ Ni ₁₀ Gd ₄ Y ₂	0.40	0.32
Mg ₈₆ Ni ₁₀ Gd ₃ Y ₁	0.39	0.33
Mg ₈₈ Ni ₈ Gd ₃ Y ₁	0.39	0.33

The correlation between ν and kinetic fragility D^* , as established by Novikov [211], suggests that a larger D^* value induces larger ν ratio. D^* indicates how closely the alloy obeys the Arrhenius flow behaviour and is ~ 2 for the most fragile glasses and can reach 100 for the strong glass formers such as SiO₂ [25]. The fragility parameter for the Mg₈₄Ni₁₀Gd₆ composition determined in section 4.3.5 is ~ 12 that can be compared with other Mg-based glass-forming alloys. The given value of D^* is less than 22.1 determined for Mg₆₅Cu₂₅Y₁₀ alloy [25] which is considered to be a strong liquid with high GFA but exhibiting brittle behaviour. The fragility of Mg₇₅Ni₁₅Gd₁₀ and Mg₇₅Ni₁₅Gd₅Nd₅ alloys was estimated using the same method as described in section 4.3.5 and found to have values of 58 [128] and 67 [130], respectively. These BMG alloys have large plastic strain during compression (up to 2%) which authors ascribe to the high D^* and consequently high ν value. The estimated value of ~ 12 for the as-cast Mg₈₄Ni₁₀Gd₆ composition assumes that this alloy has a low viscosity at the melting temperature which rises sharply when approaching T_g . It also predicts that the alloy is a marginal glass-former with low resistance to the crystallisation. Indeed, it has 0.7 mm critical thickness for glass formation and small supercooled liquid region of 13 K. In terms of mechanical performance, most of the Mg-based BMG alloys reported are brittle rather than ductile. However, the intermediate value of Poisson's ratio of 0.33 for the alloys produced herein provides some space for further improvement in plasticity.

In general, the overall plastic strain in BMGs has a complicated origin and cannot be associated only with high Poisson's ratio and low G/B values of the constituent elements, though these parameters are more universal for the glassy alloys rather than for crystalline metals in terms of a plasticity indicator [170].

6.3.4. Effect of crystalline inclusions on the plasticity of BMG composites

As shown in the compression test results (section 4.5.2), the yield and fracture strength declined with increasing Mg concentration in the BMG composites. In spite of the larger volume fraction of crystalline phase in the alloys containing 86-88 at.% Mg, they do not exhibit improved plasticity. For instance, the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ and $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ compositions have similar average size of crystallites of 10 μm in length but a different volume fraction of $\sim 16\%$ and $\sim 30\%$, respectively. Nevertheless, the $\text{Mg}_{86}\text{Ni}_{10}\text{Gd}_4$ composite loses 35 % of yield stress and more than 10 % of fracture strength compared to the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ alloy. As such, the composition with 84 at.% Mg is deemed to be the most attractive in regards to mechanical performance. The soft Mg-rich phase with the volume fraction of $\sim 16\%$ additionally enhances plasticity of the material where $\sim 9\%$ strain to failure was observed.

Overall, the plastic strain to failure for the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ composite is greater than the aforementioned monolithic $\text{Mg}_{75}\text{Ni}_{15}\text{Gd}_{10}$ amorphous alloy [128]. However, it is considerably lower than the 18.5 % strain to failure achieved in the Mg-Cu-Zn-Y-based BMG composite [118]. In earlier work [83, 85] it was noted that mechanical properties of BMG composites are sensitive not only to the volume fraction of primary crystalline phase but to the scale of the microstructure. Furthermore, it was highlighted by Hoffman *et al.* [116] that, for optimising plastic behaviour, the microstructural scale of the crystalline phase/s should have the same order but smaller value than size of plastic zone which is responsible for shielding the structure from the high stress concentration in the metallic glasses [40]. Therefore, according to the mechanical tests results reported in section 4.5.2, it may be concluded that the Mg-rich phase in the Mg-Ni-Gd BMG composites is too fine, particularly in the alloys containing 86 and 88 at.% Mg. This causes a reduction in the amount of the interfaces between the Mg flakes and the amorphous matrix and, thus, a decreased number of sites to significantly obstruct the propagation of shear bands. As a result, the ductility of BMGs with 86 and 88 at.% of Mg is not significantly improved compared to the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ BMG composite.

CHAPTER 7 – CONCLUSIONS

In this thesis, hyper-eutectic BMG composites in the Mg- and Zr-based alloy systems were designed and successfully fabricated by die casting and arc-melting casting. The glass-forming ability (GFA) for both alloy systems does not exceed corresponding well-known metallic glasses due to the high content of the main component (Mg and Zr, respectively), with the resulting compositions located away from the range of concentration favourable for glass formation.

This behaviour was exploited for designing Mg- and Zr-based BMG composites. A range of composite morphologies, containing either primary soft crystalline phases or intermetallic compounds dispersed throughout an amorphous matrix, were generated.

The major findings of the thesis are now summarised below:

Mg-based compositions

- Based on gravity casting experiments into a wedge-shaped mould, it found that GFA of the Mg-Ni-Gd/Y alloy systems deteriorated with increasing Mg concentration. The maximum Mg content of 88 at.% yielded an alloy with a critical thickness of 0.25 mm for glass formation.
- This initial work was important as BMG composites in Mg-Ni-Gd-Y and Mg-Ni-Gd systems were successfully designed and fabricated for the first time. Here, intervals and limits for amorphous, amorphous-crystalline and crystalline structures as a function of sample thickness and composition were determined.
- For the wedge-cast Mg-Ni-Gd system, the hardness of the amorphous and amorphous-crystalline zones was found to be 30-50% higher in comparison with completely crystallised structure of identical composition.
- Both the type and morphology of the crystalline phases that form in the Mg-Ni-Gd-Y BMG composites was influenced by both the rare-earth content and cooling rate. A range of targeted compositions generated optimal composite structures containing a dispersion of soft Mg-rich crystalline flakes throughout the amorphous matrix.

- A semi-solid casting method was explored for producing Mg-Ni-Gd composites. This technique promoted the formation of coarse dendrite morphology in the amorphous matrix with a more homogeneous distribution, as compared to the gravity cast samples.
- The thermal stability of the Mg-Ni-Gd/Y systems, as determined by the glass transition temperature of the amorphous matrix, was found to vary between 153-163 °C, depending on the Mg content. Furthermore, the devitrification of the amorphous matrix in the Mg-Ni-Gd composites was found to occur in a multistage manner with the formation of several intermediate metastable phases.
- In the Mg-Ni-Gd composites, the soft Mg flakes dispersed throughout the amorphous matrix contributed to an enhancement in the plastic strain to failure but slightly reduced the strength. The maximum fracture strength and plastic strain to failure of 713 MPa and 9.6 %, respectively, was reached in the $\text{Mg}_{84}\text{Ni}_{10}\text{Gd}_6$ composite.

In light of the foregoing conclusions, further optimisation of chemical composition and casting parameters are needed for controlling the morphology of the final structure in these composites and balancing their strength and ductility.

Zr-based compositions

- Alloys with high Zr-content were designed and fabricated in the Zr-Cu-Al-Ni glass-forming system. An amorphous structure was achieved in compositions with 65, 70, 72, 74 and 76 at. % Zr. The GFA of the alloys varied with Zr concentration. The maximum Zr content of 76 at.% reduced critical thickness for glass formation to 1 mm.
- Monolithic alloys with 65-76 at. % of Zr were successfully inoculated by Y_2O_3 particles by arc-melting and vacuum casting. The GFA of the inoculated alloys was also found to be affected by the Y_2O_3 inclusions. Here, the Y_2O_3 particles acted as preferred nucleation sites for the Zr_2Cu phase in the $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$, $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}$ and $\text{Zr}_{72}\text{Cu}_{13}\text{Ni}_{7.5}\text{Al}_{7.5}$ compositions. Indeed, the particles generated a completely crystalline structure in $\text{Zr}_{74}\text{Cu}_{13}\text{Ni}_{7.4}\text{Al}_{5.6}$ and $\text{Zr}_{76}\text{Cu}_{12}\text{Ni}_{6.9}\text{Al}_{5.1}$ compositions.

- The nucleation of the crystalline phase at the inoculant particles was dependent on the cooling rate during casting. The particles were found not to nucleate the Zr_2Cu phase for a casting thickness of less than 2 mm in $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ and $\text{Zr}_{70}\text{Cu}_{15}\text{Ni}_{8.5}\text{Al}_{6.5}$ compositions and less than 0.6 mm in $\text{Zr}_{72}\text{Cu}_{13}\text{Ni}_{7.5}\text{Al}_{7.5}$ composition. Unlike the Mg alloys, the nucleated crystallites did not grow in preferential directions, but via a eutectic mode without substantial redistribution of the constituents.

CHAPTER 8 - REFERENCES

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