

Glass formation and crystallisation in rapidly solidified zirconium alloys

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Abstract

Zirconium-based alloys offer an unique opportunity for studying various aspects of metallic glass, namely glass forming ability, crystallisation modes and kinetics, diffusion mechanisms and formation of glass in bulk. Thermodynamic and kinetic rationale for glass formation have been summarised in binary and ternary metalloid free amorphous alloys rich in zirconium. A comparison has been made between the microstructures of the alloys obtained under different cooling rates in order to understand the process of solidification and the process of phase selection. The different types of nucleation processes and the growth mechanisms of crystals in the undercooled melts of Zr-based glass forming alloys have been investigated. Primary, eutectic as well as polymorphic crystallisation have been observed in the alloys of this class of materials. Crystal nucleation and growth kinetics during crystallisation has been examined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystallisation; Polymorphic; Nucleation

1. Introduction

Zirconium-based alloys show many interesting phase transformations. One of these is the ability to form metallic glasses [1]. The reasons for extensive work carried out in the field of non-crystalline zirconium-based alloys are: (i) ability to form metal–metal metallic glasses; (ii) ability to form glass in wide composition ranges and (iii) interesting glass to crystal transformation modes shown by these amorphous alloys. Many of the Zr-based glasses crystallise to crystalline phases of the same composition. These alloys provide opportunities for examining the effect of atomic arrangement alone on properties without any interference from change in chemistry of the phase [2]. In the Zr–Fe, Zr–Co, Zr–Ni, Zr–Be, Zr–Cu and Zr–Cr systems which have many common features, rapid solidification has yielded amorphous phase over very large composition ranges [3–5]. In some of these systems the as-solidified microstructure has been examined in detail [6–10]. The microstructures resulting from rapid solidification of these alloys have been found to be fully amorphous or partially crystalline depending upon the cooling rate and the glass forming ability of the alloys. Zr-based alloys have also acquired considerable significance because of the fact that these can form bulk metallic glasses. This article describes different criteria for the formation of glass by rapid solidification in binary and ternary Zr-based alloys, cites some examples of bulk metallic glass formation

in multicomponent Zr-based alloys and finally examines kinetics and mechanisms of crystallisation in these alloys.

2. Nucleation and growth of crystals in undercooled melt of alloys

A rapid increase in the melt viscosity leads to glass formation in metallic systems. Nucleation and growth of crystals compete with glass formation in the undercooled melt. A study of glass formation therefore requires a consideration of the rates of both nucleation and growth of crystals in undercooled metallic melts. The conditions under which a “glass” can form are: (i) complete suppression of nucleation; (ii) limited nucleation of crystals but no significant growth of these and (iii) nucleation of a very few isolated crystals followed by their substantial growth while the major part of the matrix vitrifies. The quenched product can be qualified to be an amorphous material if the volume fraction of the crystalline phases present is negligibly small. Condition (i) is difficult to achieve during a process like melt spinning. Condition (ii) leads to the formation of quenched-in-nuclei, which do not get an opportunity to grow. This condition is most readily satisfied during melt spinning in the case of Zr-based glass forming alloys. Consequently, the amorphous matrix usually contains a distribution of quenched-in-nuclei, their density being controlled by the rate of nucleation during the cooling down path. In good glass formers like Zr–Cu, it is possible to minimise the quenched-in-nucleus density by increasing the cooling rate during melt spinning for instance, by increasing

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the wheel speed [8]. The quenched-in-nuclei are very small in size and in volume fraction and hence are very difficult to detect. In order to establish the nature of these nuclei, it is necessary to determine the atomic arrangement and their composition, using high-resolution electron microscopy as has been done by Savalia et al. [11]. These nuclei mostly form in the transient nucleation, stage before the attainment of the steady-state nucleation rate [12,13]. Steady-state homogeneous nucleation frequencies as estimated by the expression due to Turnbull [14] have been found to be much higher in Zr-based alloys compared to that in a very good glass forming system like Pd–Si [10,11,15,16]. In Zr-based alloys, therefore, glass formation is possible only if homogeneous nucleation is avoided. Condition (iii) leads to the formation of a few large crystals in a matrix of the amorphous phase, the crystalline particles being few and far between. A study of the microstructure of these partially crystalline materials yields the following information:

1. The glass forming ability of the alloy can be determined from the measured volume fraction of the crystalline phase in the partially crystalline materials.
2. By determining the identity of the crystalline phase, it is possible to determine the nature of the crystalline phase which competes with glass formation.
3. By studying the morphology of the crystals it is possible to understand the process of solidification during melt spinning.

Once the crystal is nucleated, growth cannot be easily suppressed if growth is through a partitionless solidification process. In comparison, long-range diffusion limited growth rates are much slower due to the partitioning of solutes and the slow rate of attachment kinetics at the crystal/liquid interface [15]. From the studies on partially crystalline ribbons in Zr-based Fe and Ni bearing binary alloys by Dey et al. [17–19] and Savalia et al. [11], the crystalline phases competing with glass formation in these alloys have been identified. The relative glass forming ability has been determined in a range of Zr–Ni alloys by estimating the amount of crystalline phase in the partially crystalline alloys [18]. Dey and Banerjee [19] and Tanner [6] have examined the morphology of the crystals in the partially crystalline alloys. Dey and Banerjee [19] encountered single crystals (Fig. 1(a)) and crystal aggregates (Fig. 1(b)) embedded in the amorphous matrix. Some of these aggregates have been found to show a very interesting sunflower-like morphology (Fig. 1(b)) arising out of twin-relation between the adjacent crystals. Different types of crystal/amorphous interfaces were encountered depending upon the local conditions of solidification [11,19].

In many of these studies, estimates of various nucleation frequencies and of growth rates have been made using the free energy difference between the crystalline phase and that of the liquid phase at different levels of undercooling. This quantity can be estimated by various methods. Savalia et al. [11] were the first to make an attempt to evaluate this quantity from experimentally determined parameters. Their

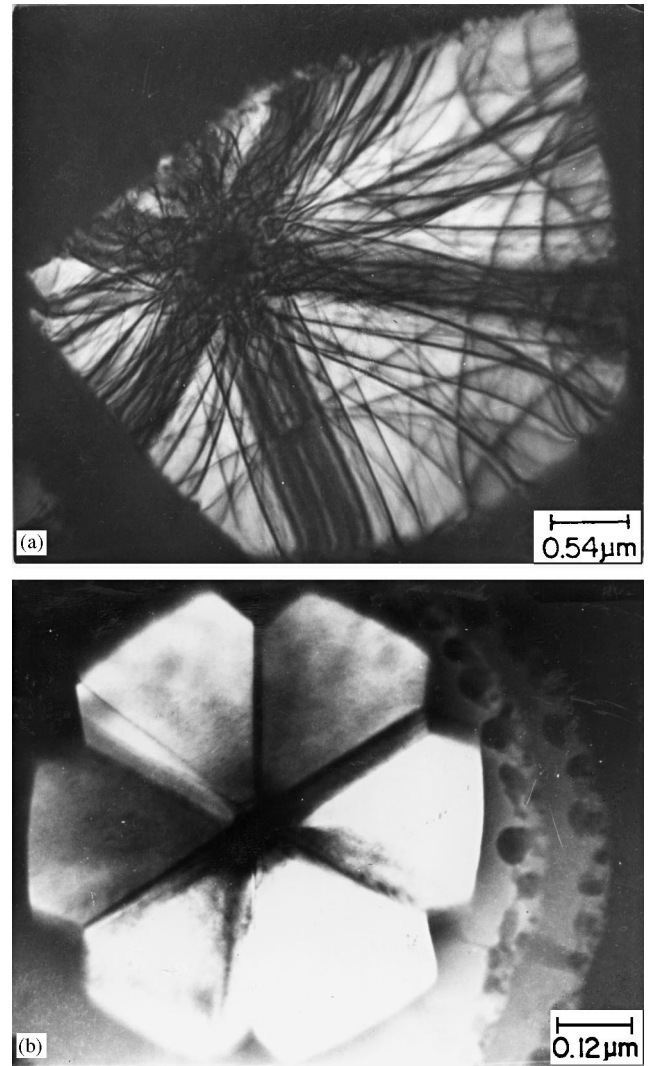


Fig. 1. (a) Single crystal particle embedded in the amorphous matrix. The sharp crystal/matrix interface is consistent with partitionless crystal formation during solidification of $Zr_{76}Fe_{24}$ alloy; (b) crystal aggregate showing sunflower morphology of Zr_3Fe crystals, each petal being twin related with its neighbouring petals.

approach has been elaborated in [11]. Dubey and Ramchandrarao [20] have expressed, ΔG_c , the free energy change associated with the formation of the crystal from the liquid phase in terms of undercooling, ΔT , and the difference in specific heat, ΔC_p , between the liquid and the crystal phase. This relation as given below has been found to be the most appropriate for the estimation of the ΔG_c and has been used by Savalia et al. [11] for evaluation of the nucleation and growth rates of crystals in ternary Zr-based glass forming alloys

$$\Delta G_c = \frac{\Delta H_f \Delta T}{T_m} - \frac{\Delta C_p T^2}{2T} \left(1 - \frac{\Delta T}{6T} \right)$$

The parameters used for evaluation of the free energy are given in [11]. Fig. 2 shows the variation of ΔG_c as a function of temperature.

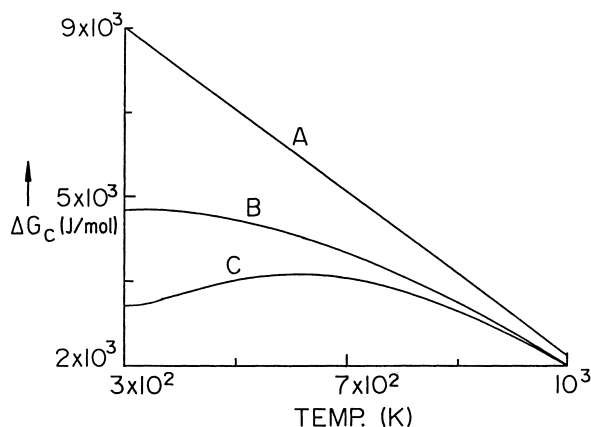


Fig. 2. ΔG_c as a function of temperature. Curve C corresponds to the formulation proposed by Dubey and Ramachandrarao, curve A is on the basis of a linear dependence of ΔG_c on temperature and curve B is based on relation $\Delta G_c = (\Delta H_f \Delta T / T_m)[((1 - \alpha)T_m + (1 + \alpha)T)/(T + T_m)]$ [11,21].

In order to consider glass forming ability, nucleation and growth kinetics of the crystals in the undercooled melt needs to be considered. Three different types of nucleation are important during rapid solidification of alloys. These are homogeneous nucleation in the transient and the steady-state conditions and heterogeneous nucleation. Each of these types of nucleation needs to be considered in assessing the possibility of avoiding nucleation and consequent formation of amorphous structure.

2.1. Transient homogeneous nucleation

The transient nucleation stage persists for a few microseconds till the steady-state is reached. This time scale becomes important in rapid solidification processing where solidification time is of the same order. The calculated values of transient nucleation times in Zr-based ternary glasses as calculated by Savalia et al. [11] based on an approach suggested by Kelton et al. [12,13], have been found to be two orders of magnitude larger than that reported by Ghosh et al. [10]. This is because of the fact that value of ΔG_c used by Savalia et al. [11], which is a better estimate of this parameter, is lower. A larger transient nucleation time corresponds to a lower contribution of steady-state nucleation to the overall nucleation process, thereby improving the glass forming ability.

2.2. Steady-state homogeneous nucleation

The time for the attainment of the steady-state nucleation stage has been calculated by Savalia et al. [11] in the case of Zr-based ternary metallic glasses. They have also calculated the steady-state nucleation frequency using the equation proposed by Turnbull [14] and the values of ΔG_c calculated from experimentally determined parameters. Fig. 3 shows the steady-state nucleation frequency as a function of

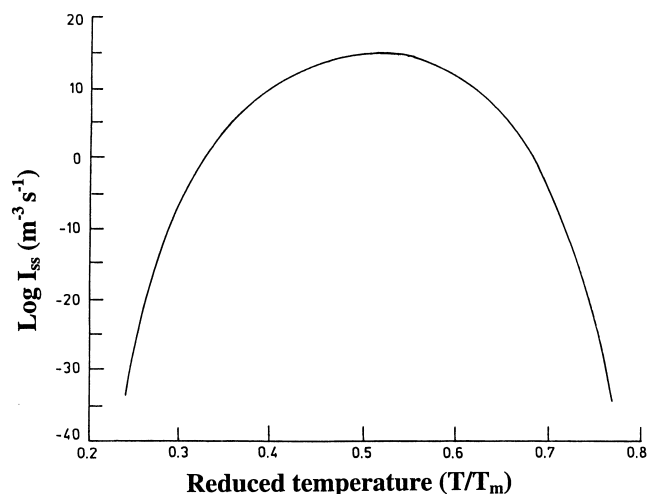


Fig. 3. Homogeneous nucleation frequency as a function of reduced temperature for the alloy $Zr_{76}Fe_{16}Ni_8$.

temperature in the case of a ternary Zr-based alloy. It has been shown [11] that steady-state nucleation rates determined from the modified ΔG_c values are about three orders of magnitude lower than those reported by Thomson et al. [21] and Ghosh et al. [10].

2.3. Heterogeneous nucleation

This mode of nucleation assumes a special significance in determining the possibility of formation of bulk metallic glasses. If heterogeneous nucleation sites have been eliminated and homogeneous nucleation frequencies are low, glass can form at very low cooling rates. The estimated homogeneous nucleation frequency for the Zr-based ternary metallic glasses containing Fe and Ni was quite large as compared that in the case of bulk glass formers like $Pd_{40}Ni_{40}P_{20}$ alloy [11,22]. This is consistent with the fact that the bulk glass does not form in these ternary alloys based on Zr. However, the homogeneous nucleation frequencies are low as compared to many other glass formers suggesting that a suitable modification of the alloy chemistry is likely to produce bulk metallic glasses. Attempts to locate the possible heterogeneous nucleation sites by HREM has been made by Savalia et al. [11], who have shown the presence of the quenched-in-nuclei in the ternary Zr-based glasses. However, it has not been possible to identify the source of heterogeneous nucleation in these alloys.

Dey et al. [23] have examined the structure of bulk metallic glasses using HREM, and have shown that though in bulk metallic glasses, the structures are primarily amorphous a distribution of quenched-in-nuclei is invariably present in the amorphous matrix (Fig. 4).

2.4. Growth

The slow rate of growth of crystals is important for easy glass formation. The rate of growth of crystals may be slow

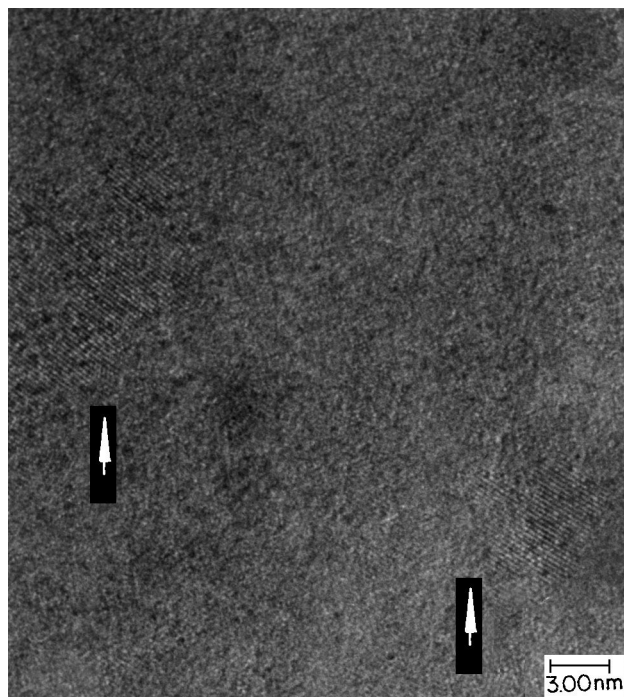


Fig. 4. HREM micrograph showing quenched-in-nuclei in a bulk metallic glass having the composition $\text{Zr}_{56.26}\text{Al}_{9.7}\text{Cu}_{17.46}\text{Ni}_{13.58}\text{Nb}_{3.0}$.

due to either need for partitioning of solutes or due to the need for chemical ordering in the growing phase. Savalia et al. [11] have calculated the interface temperature of a crystal growing in an undercooled melt using the one-dimensional model for crystal growth developed by Greer and Evans [24], and have shown that for a ternary Zr-based alloy $\text{Zr}_{76}\text{Fe}_{16}\text{Ni}_8$ for a very small super heat the interface temperature, drops below T_g before the liquid-to-crystal transformation progresses to a significant extent, indicating easy glass formation in this alloy. Dey et al. [23] have examined the growth of crystals in the bulk glass forming alloys and have drawn similar conclusions.

3. Theoretical estimation of glass forming ability

Numerous factors have been found to influence GFA and there is no single key parameter, which alone can describe GFA [2,4,25,26]. The various types of arguments put forth to explain GFA can be divided into those thermodynamic or kinetic in nature and those based on, size factor and electronic structure. Thermodynamically glass formation is favoured in certain composition ranges of some systems where the free energy difference between the supercooled liquid and the metastable and stable phases competing with glass formation is as little as possible [25].

These concepts have been applied in case of Zr-based glasses. The free energy of the liquid phase and that of the intermetallic compounds have been determined as a function of the composition in binary alloy systems,

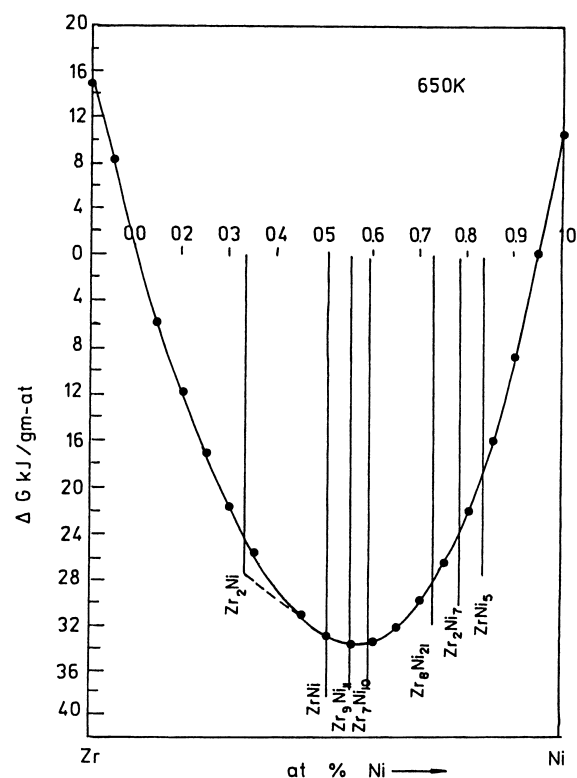


Fig. 5. Free energy–composition diagram showing the free energy hierarchy of the liquid phase and the intermetallic compounds in the Zr–Ni system.

using a thermodynamic analysis of the phase diagram and by incorporating some experimental thermodynamic data [27]. From the free energy hierarchy of several competing phases it could be observed that in the Zr–Ni system, the driving force for crystal formation in Zr-rich alloys was much smaller in case of $\text{Zr}_{67}\text{Ni}_{33}$ as compared to that for $\text{Zr}_{76}\text{Ni}_{24}$ alloy (Fig. 5). This observation is consistent with the fact that thermodynamic glass formation tendency was higher at composition close to that of the first intermetallic compound and not at the first eutectic composition.

A similar approach involving the relative free energies of the liquid and the crystalline phases uses the concept of the T_0 curve. The T_0 curve in the phase diagram is the locus of compositions at each temperature, where the liquid and the solid phases of the same composition have the same value of the integral molar free energy. The importance of the T_0 curves in connection with rapid solidification has been realised quite some time back [28,29]. Predictions about the formation of a single solid solution after rapid solidification can be made for a given alloy system, provided the T_0 line can be calculated in the phase diagram. Dey et al. [30] and Boettinger et al. [31] have examined the conditions for partitionless solidification, based on the position of T_0 , line in the phase diagram. If rapid solidification can suppress alloy partitioning the system tends to behave as a single component system, which can solidify at a temperature below T_0 .

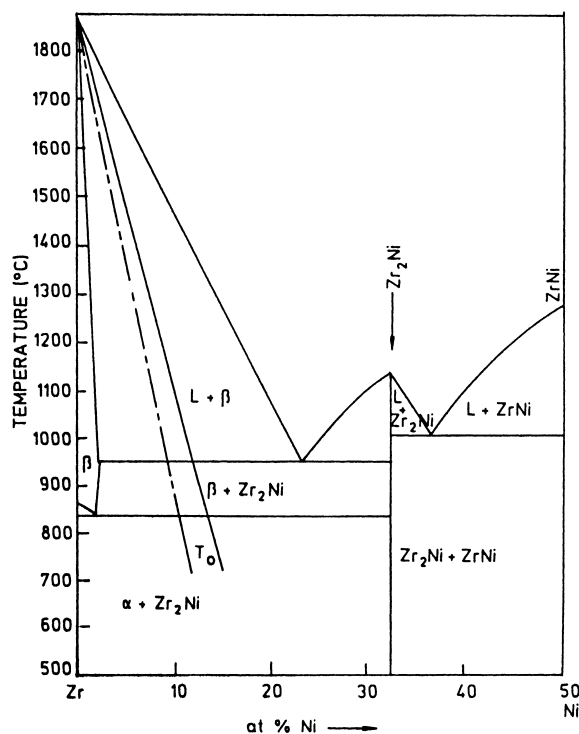


Fig. 6. The zirconium rich part of the phase diagram of the Zr–Ni system with superimposed T_0 line corresponding to the metastable equilibrium between the liquid and the β phase.

into a crystalline phase inheriting the composition of the liquid. In case, T_0 temperature for a given composition is so much depressed that it falls below T_g , the liquid will vitrify. This point is illustrated in the Zr–Ni system in which T_0 , as determined by an approach suggested by Katgerman [32], drops rapidly with increasing Ni content (Fig. 6). It can be seen that exceptionally large undercoolings will be required for the partitionless solidification into the β phase at compositions close to the first eutectic ($Zr_{75}Ni_{25}$). The extrapolated T_0 temperature indeed drops down below T_g at such compositions resulting in the formation of glass.

The destabilisation of the crystalline phase rather than the stabilisation of the glass phase which is important during glass formation [33]. From the kinetic considerations, glass can be obtained in any liquid, which has been so supercooled that crystal nucleation and growth is avoided. The cooling rate required for the avoidance of crystal formation can be estimated from the overall crystal formation kinetics, which is represented by isothermal TTT (time–temperature–transformation) diagrams. Such diagrams were first developed in the context of metallic glasses by Uhlman [34] and subsequently used by Davies [35] to determine the value of the critical cooling rate to just avoid crystallization. Savalia et al. [11] have used this approach and the ΔG_c calculated from experimentally determined parameters for estimating the critical cooling rate for glass formation in the case of $Zr_{76}Fe_{16}Ni_8$ and found it to be close to 10^6 K/min. This value is in good agreement

with that for other alloys in this system [11]. The TTT diagrams for two Zr–Ni alloys, $Zr_{67}Ni_{33}$ and $Zr_{76}Ni_{24}$ were constructed by Dey [9]. It could be seen from these diagrams that critical cooling rate for glass formation is lower for the $Zr_{67}Ni_{33}$ alloy as compared to the $Zr_{76}Ni_{24}$ alloy, though the latter is the eutectic composition. This estimation clearly demonstrated that the eutectic composition need not necessarily be the composition at which glass formation is the easiest. The factors of importance are the viscosity of the melt and the free energy difference between the liquid and solid phases. The Zr-transition metal systems provide opportunities for comparing the glass forming ability of the eutectic compositions such as $Zr_{76}Ni_{24}$ and of intermetallic compounds such as $Zr_{76}Fe_{24}$. The eutectics though generally considered to be better glass formers can in fact have a poorer glass forming ability due to either the presence of metastable phases competing with glass formation or low viscosity of the melt at the eutectic composition due to lack of ordering in the melt. On the other hand glass formation in the intermetallic compounds may be favoured because of the higher viscosity of the melt due to ordering in the liquid phase and/or due to slow nucleation of the intermetallic compounds because of their complex structure.

The formation of bulk metallic glasses can also be based on certain criteria. According to Lieu et al. [36] the important points which need to be noted for bulk metallic glass formation are (a) multicomponent systems consisting of more than three elements; (b) large difference in atomic sizes exceeding 12 pct among the constituent elements and (c) negative heats of mixing among the elements. These factors influence both thermodynamic and kinetic criteria. The foremost requirement is the avoidance of crystallization. Bulk glass formation occurs when crystal nucleation and growth can be avoided even at low cooling rates. Besides other factors, diffusivity in the melt is one important factor controlling the kinetics of crystal nucleation and growth in the undercooled melt. In ceramic and organic systems where bulk glass formation is very easy, melt viscosities below melting point have been found to be very high [2]. In metallic systems as well, the formation of bulk metallic glass would be easy if the melt viscosities are high. A large number of Zr-based alloys have been obtained in the bulk amorphous state [37]. It appears that not only is the melt viscosities high for these alloys, ΔG_c , the free energy difference between the liquid and the crystalline phase competing with glass formation is also low. The lower values of ΔG_c in the case of Zr-based ternary Fe and Ni bearing glasses as compared to estimates made earlier [10,12] has been indicated in the study carried out by Savalia et al. [11].

4. Thermal stability of Zr-based metallic glasses

Zr-based metallic glasses show a variety of crystallization reactions. These have been studied in detail in Zr–Cu, Zr–Cr, Zr–Be, Zr–Ni and Zr–Fe systems [4,5,7,9,38,39].

Primary, polymorphic and eutectic crystallisation reactions have been encountered in these glasses. Studies in Zr-based ternary glasses are fewer in comparison. The overall crystallisation kinetics has been studied in a number of Zr-based binary alloys by differential scanning calorimetry (DSC) [19,38,39]. The crystal, nucleation and growth kinetics have been studied separately by transmission electron microscopy (TEM) in case of $Zr_{67}Ni_{33}$ glass by Dey et al. [38]. This glass undergoes polymorphic crystallisation. A similar study has been carried out in the amorphous alloys $Zr_{76}Fe_{24}$ that also undergoes polymorphic crystallisation [19]. Eutectic crystallisation has been observed in $Zr_{76}Ni_{24}$ amorphous alloy [10]. These are illustrated in Fig. 7.

The products of crystallisation in the $Zr_{76}Fe_{24}$ and the $Zr_{76}Ni_{24}$ glasses have been found to be the Zr_3Fe phase and a mixture of the α and the Zr_2Ni phases, respectively. Since the equilibrium Zr_3Fe and Zr_2Ni phases are not isostructural, a continuous substitution of Fe by Ni is not expected in these intermetallic phases during the crystallisation of amorphous alloys containing progressively increasing amounts of Ni. Earlier investigations on the crystallisation of the binary $Zr_{76}Fe_{24}$ and $Zr_{76}Ni_{24}$ glasses have shown that the base centred orthorhombic (bco) phase crystallises polymorphically from the former while the later decomposes by a eutectic mode resulting in a mixture of phases having bct and hcp structures. Dey et al. [38] in their study of crystallisation of Zr-based ternary glasses containing Fe and Ni have attempted finding answers to the following questions: (a) to what extent Fe and Ni can be mutually substituted in the intermetallic compounds Zr_3Fe and Zr_2Ni ; (b) whether any new phases form in these alloys during crystallisation and (c) how the addition of the third alloying effects the process of crystallisation. Table 1 shows the various crystallisation parameters for Zr-based Ni and Fe bearing binary and ternary glasses as determined by Dey et al. [38].

In addition to the study of the crystal nucleation and growth kinetics, the overall crystallisation kinetics has been examined and the activation energy of crystallisation determined by the Kissinger peak shift method [38–40]. It was observed by Dey et al. [38] that addition of Ni to the Zr–Fe alloys reduces the thermal stability of these glasses. These authors have shown [38] that in compositions where surface crystallisation occurs, the crystallisation temperature comes down substantially. Dey et al. [38] have found that the nucleation density was found to increase with time linearly at all temperatures and that the growth rate of the crystals was constant at each temperature for the alloys showing polymorphic crystallisation.

Crystallisation of metallic glasses can also lead to the formation of nanocrystalline structures. Dey et al. [38] have shown that in the Zr-based ternary alloys having compositions $Zr_{76}Fe_{24-x}Ni_x$ where $x < 12$, nanocrystal formation can occur under suitable conditions of crystallisation. The formation of nanocrystals occurs only in some compositions because of the fact that the steady-state nucleation rates are high. This has been demonstrated by Dey et al. [38] in the

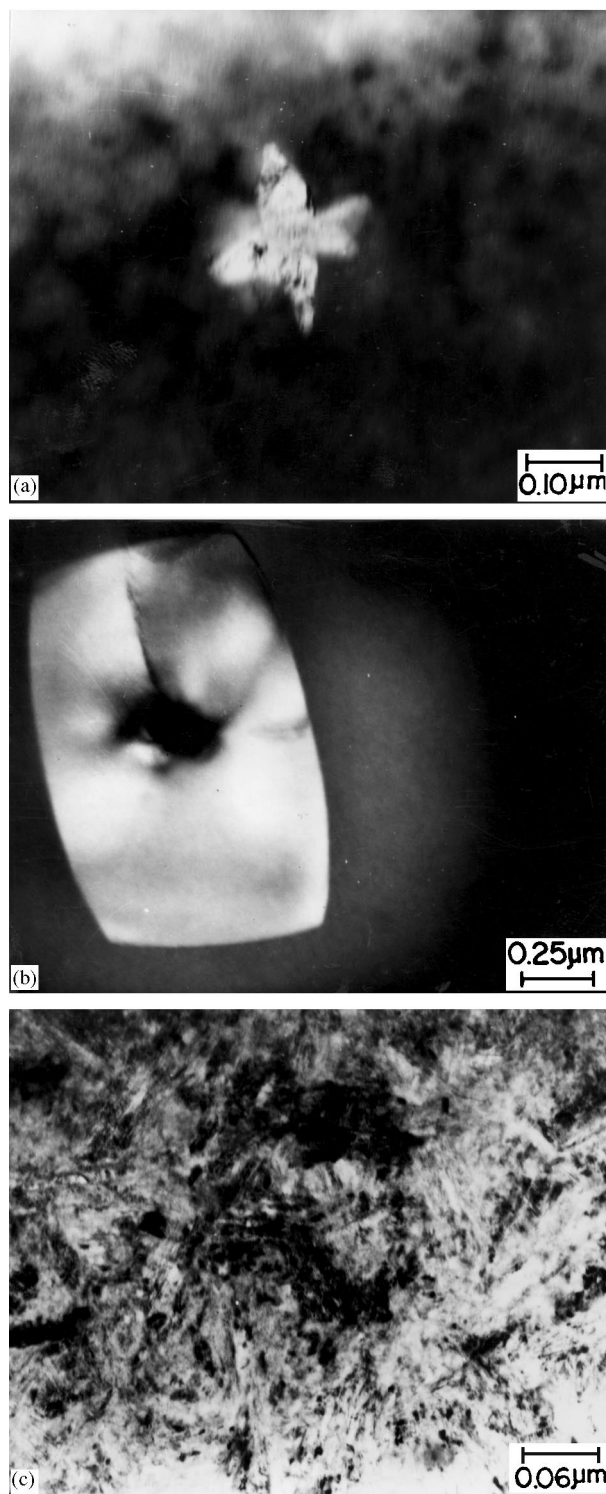


Fig. 7. Morphologies of crystals produced in different modes of crystallisation: (a) primary crystallisation of $Zr_3(Fe,Ni)$ in the $Zr_{76}Fe_{20}Ni_{14}$ glass; (b) polymorphic crystallisation of Zr_3Fe in $Zr_{76}Fe_{24}$ alloy; (c) eutectic crystallisation leading to the formation of $Zr_2Ni + \alpha$ (hcp: Zr rich phase) from the $Zr_{76}Fe_8Ni_{16}$ glass.

Table 1

Crystallisation sequence (mode), glass transition temperature: T_g , crystallisation temperature: T_x , peak crystallisation temperature: T_p , activation energies for (i) overall crystallisation, E ; (ii) nucleation, E_n and (iii) growth, E_g , isothermal annealing temperature, T and Avrami exponent for (i) single step process (n) and (ii) two-step processes (n_1 and n_2)

Composition	Sequence (mode)	Bulk or surface crystallisation	T_g 80 K/min	T_1 (K) 20 K/min	T_p (K) 20 K/min	$E/E_n/E_g$ (kJ/min)	T (K)	n/ n_1/n_2
Zr ₇₆ Fe ₂₄	A → Zr ₃ Fe (polymorphic)	Bulk	650.0	653.5	656.0	272.0 (E)/545.0 (E_n)/168.0 (E_g)	626.0	3.10 (n)
Zr ₇₆ Fe ₂₄ Ni ₄	A → Zr ₃ (Fe, Ni) + A' (primary), A' → α + Zr ₂ Ni (eutectic)	Bulk	641.0	653.0	655.0	286.0 (E)	631.0	2.71 (n)
Zr ₇₆ Fe ₁₆ Ni ₈			639.0	650.7	652.0	278.0 (E)	634.0	2.65 (n)
Zr ₇₆ Fe ₁₂ Ni ₁₂	A → Zr ₃ (Fe, Ni) (polymorphic)	Bulk	627.0	646.0	648.0	275.0 (E)	633.0	2.55 (n)
Zr ₇₆ Fe ₈ Ni ₁₆	A → Fe rich (Fe, Ni) ₃ , Zr(Li ₂) + A' (primary)	Surface	624.0	634.0	647.0	274.0 (E)	631.0	2.21 (n_1)/ 2.73 (n_2)
Zr ₇₆ Fe ₄ Ni ₂₀	A → Zr ₃ (Fe, Ni) + A' (primary), A' → Zr ₂ Ni + α (eutectic)	Bulk	624.0	634.0	647.0	236.0 (E)	634.0	1.98 (n_1)/ 4.00 (n_2)
Zr ₇₆ Ni ₂₄	A → Zr ₂ Ni + α (eutectic)	Bulk	650.0	652.0	654.0	271.0 (E)/ 410.0 (E_n)	631.0	3.20 (n)

Zr-based ternary glasses. The requirement for the formation of the nanocrystalline structures is that a large number density of nuclei should form and these nuclei should grow to the stage of impingement without leaving any untransformed amorphous matrix.

5. Diffusion in Zr-based glasses

Work on the diffusivity of Cu and Al in Zr-based metallic glasses has shown that the diffusivity of Cu is higher than that of Al by an order of magnitude. This observation is indicative of the fact that the diffusivity of the species depends on its atomic size [41]. This point is further established by demonstrating that diffusivities of Cu, Al, and Sb in Zr-based glasses follow the sequence, $D_{Cu} > D_{Al} > D_{Au} > D_{Sb}$ [42], which is consistent with the fact that $r_{Cu} < r_{Al} < r_{Au} < r_{Sb}$ where r is the radius of atom. It is interesting to note that the activation energy of crystal growth in these Zr-based metal–metal glasses is of the same order as the activation energy of diffusion of metal atoms in these amorphous alloys [19]. This is unlike the case of polymorphic crystallisation in metal–metalloid glasses where the activation energy of growth of crystals is very high [19]. This could be because of the fact that atomic transport occurring during polymorphic crystallisation in the metal–metalloid glasses is different from that occurring during diffusion in such amorphous matrix. The activation process in the former may involve a group of atoms. Similar magnitudes of the activation energies of diffusion and for growth of crystals during polymorphic crystallisation in metal–metal glasses suggests the possibility that similarities exist between the mechanism of diffusion and that of atomic jump across the crystal–amorphous matrix interface during this mode of crystallisation.

6. Conclusions

This review highlights the fact that the studies on zirconium base metallic glasses have made important contributions towards a better understanding of several issues connected with amorphous alloys. The glass forming ability of these alloys can be rationalised on the basis of the thermodynamic stability of the liquid phase and the kinetic consideration of avoidance of a competing crystalline phase under a given condition of cooling. The morphology of crystals forming during the crystallisation process and the kinetics of crystallisation can be rationalised in terms of the different modes of crystallisation process encountered in the system. The extent to which homogeneous nucleation — both transient and steady-state and heterogeneous nucleation take part in the overall kinetics and the role of quenched-in-nuclei in the crystallisation process have been elaborated.

References

- [1] K.H.J. Buschow, J. Phys. F. Metal Phys. 14 (1984) 593.
- [2] H.S. Chen, Rep. Prog. Phys. 43 (1980) 355.
- [3] M. Harmelin, R. Calvayrac, A. Oviv, J. Bigot, P. Burnier, M. Fayard, J. Non-Cryst. Solids 61/62 (1984) 931.
- [4] L.E. Tanner, Acta Metall. Mater. 28 (1980) 1805.
- [5] K.H.J. Buschow, Acta Metall. Mater. 31 (1983) 155.
- [6] L.E. Tanner, in: S. Steeb, H. Warlimonts (Eds.), Proceedings of the 5th International Conference on Rapidly Quenched Metals, Vol. 1, Wurzburg, 1984, North Holland, Amsterdam, 1985, p. 67.
- [7] G.K. Dey, S. Banerjee, Mater. Sci. Eng. 73 (1985a) 187.
- [8] S. Kavesh, in: J.J. Gillian, H.J. Leafy (Eds.), Metallic Glasses, ASM, Metals Park, OH, 1978, p. 36.
- [9] G.K. Dey, Rapid Solidification of Zirconium Alloys, Ph.D. Thesis, Banaras Hindu University, Varanasi, 1988.
- [10] C. Ghosh, M Chandrashekar, L. Delaey, Acta Metall. Mater. 37 (1991) 929.

- [11] R.T. Savalia, R. Tewari, G.K. Dey, S. Banerjee, *Acta Metall. Mater.* 44 (1996) 57.
- [12] K.F. Kelton, A.L. Greer, *J. Non-Cryst. Solids* 79 (1986) 295.
- [13] K.F. Kelton, A.L. Greer, C.V. Thompson, *J. Chem. Phys.* 79 (1983) 6261.
- [14] D. Turnbull, *Contemp. Phys.* 10 (1969) 473.
- [15] A.L. Creer, in: *Proceedings of the Workshop on Amorphous and Semiconductors*, E.P.R.I. *Acta Metall. Mater.*, Pergamon Press, San Diego, CA, 1985, p. 29.
- [16] A.J. Drehman, A.L. Greer, *Acta Metall. Mater.* 32 (1984) 323.
- [17] G.K. Dey, R.T. Savalia, E.G. Baburaj, S. Banerjee, in: O.N. Mohanty, C.S. Sivaramakrishnan (Eds.), *Proceedings of the International Conference on Rapid Solidification Processing and Technology*, ICMS 1989, Key Eng. Mater. Trans. Tech. Publishers, Switzerland, 1990, p. 135.
- [18] G.K. Dey, S. Banerjee, in: S. Steeb, H. Warlimonts (Eds.), *Proceedings of the 5th International Conference on Rapidly Quenched Metals*, Vol. 1, Wuzburg, 1984, North Holland, Amsterdam, 1985, p. 67.
- [19] G.K. Dey, S. Banerjee, *Mater. Sci. Eng.* 76 (1985) 127.
- [20] K.S. Dubey, P. Ramachandrarao, *Acta Metall.* 32 (1984) 127.
- [21] C.V. Thompson, A.L. Greer, F. Spaepan, *Acta Metall. Mater.* 31 (1983) 1883.
- [22] A.J. Drehman, A.L. Greer, *Acta Metall. Mater.* 32 (1984) 323.
- [23] G.K. Dey, R.T. Savalia, E.G. Baburaj, S. Banerjee, unpublished results.
- [24] A.L. Greer, P.V. Evans, *Mater. Sci. Eng. Lett.* 98 (1988) 357.
- [25] S.R. Nagel, J. Tauc, *Phys. Rev. Lett.* 35 (1975) 380.
- [26] M. Marcus, D. Turnbull, *Mater. Sci. Eng.* 23 (1976) 211.
- [27] J. Charles, J.C. Gaachon, J. Hertz, *Calphad* 9 (1986) 35.
- [28] I.L. Aptekar, D.S. Kamenetskaya, *Fiz. Metal Metalloved.* 14 (1962) 358.
- [29] J.C. Baker, J.W. Chan, *Solidification*, American Society for Metals, Metals Park, OH, 1971, p. 23.
- [30] G.K. Dey, E.G. Baburaj, S. Banerjee, P. Ramchandra Rao, in: A.K. Bhatnagar (Ed.), *Metallic and Semiconducting Glass*, Vol. II, Key Eng. Mater. Trans. The. Pub., Switzerland, 1987, p. 329.
- [31] W.J. Boettinger, in: T. Masumoto, K. Suzuki (Eds.), *Proceedings of the 4th International Conference on Rapidly Quenched Metals*, Sendai, 1981, Japan Institute of Metals, Sendai, 1982, p. 99.
- [32] L.J. Katgerman, *Mater. Sci. Lett.* 2 (1983) 444.
- [33] H.S. Chen, *Acta Metall. Mater.* 24 (1976) 153.
- [34] D.R. Uhlmann, *J. Non-Cryst. Solids* 16 (1974) 15.
- [35] H.A. Davies, *Phys. Chem. Glasses* 17 (1976) 159.
- [36] C.T. Liu, L. Heatherly, D.S. Easton, C.A. Carmichael, J.H. Schneibel, C.H. Chen, J.L. Wright, M.H. Yoo, J.A. Harton, A. Inoue, *Metal Mater. Trans.* 29 (1998) 1811.
- [37] A. Inoue, *Bulk Amorphous Alloys Preparation and Fundamental Characteristics*, Materials Science Foundations 4, Trans. Tech Publications, Switzerland, 1998, p. 38.
- [38] G.K. Dey, R.T. Savalia, E.G. Baburaj, S. Banerjee, *J. Mater. Res.* 132 (1988) 504.
- [39] G.K. Dey, E.G. Baburaj, S. Banerjee, *J. Mater. Sci.* 21 (1986) 117.
- [40] G.K. Dey, S. Banerjee, *Bull. Mater. Sci.* 156 (1992) 543.
- [41] S.K. Sharma, P. Mukhopadhyay, *Acta Metall.* 38 (1990) 129.
- [42] S.K. Sharma, S. Banerjee, Kuldeep, A.K. Jam, *Acta Metall.* 36 (1988) 1683.