Devitrification kinetics and phase selection mechanisms in Cu-Zr metallic glasses

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ABSTRACT

Metallic glasses have been a promising class of materials since their discovery in the 1960s. Indeed, remarkable chemical, mechanical and physical properties have attracted considerable attention, and several excellent reviews are available. Moreover, the special group of glass forming alloys known as the *bulk* metallic glasses (BMG) become amorphous solids even at relatively low cooling rates, allowing them to be cast in large cross sections, opening the scope of potential applications to include bulk forms and net shape structural applications. Recent studies have been reported for new bulk metallic glasses produced with lower cooling rates, from 0.1 to several hundred K/s. Some of the application products of BMGs include sporting goods, high performance springs and medical devices. Several rapid solidification techniques, including melt-spinning, atomization and surface melting have been developed to produce amorphous alloys. The aim of all these methods is to solidify the liquid phase rapidly enough to suppress the nucleation and growth of crystalline phases. Furthermore, the production of amorphous/crystalline composite (ACC) materials by partial crystallization of amorphous precursor has recently given rise to materials that provide better mechanical and magnetic properties than the monolithic amorphous or crystalline alloys. In addition, these advances illustrate the broad untapped potential of using the glassy state as an intermediate stage in the processing of new materials and nanostructures. These advances underlie the necessity of investigations on prediction and control of phase stability and microstructural dynamics during both solidification and devitrification processes.

This research presented in this dissertation is mainly focused on Cu-Zr and Cu-Zr-Al alloy systems. The Cu-Zr binary system has high glass forming ability in a wide compositional range (35-70 at.% Cu). Thereby, Cu-Zr based alloys have attracted much

attention according to fundamental research on the behaviors of glass forming alloys. Further motivation arising from the application of this system as a basis for many BMGs and ACC materials; the Cu-Zr system warrants this attention and offers great potential for the development of new materials. However, the prediction and control of microstructural evolution during devitrification remains challenging because of the complex devitrification behavior of the Cu-Zr binary alloy which is arising from the competition of metastable and stable phases and diversity of crystal structures. This dissertation details a systematic fundamental investigation into the mechanisms and kinetics of the various crystallization transformation processes involved in the overall devitrification response of Cu-Zr and Cu-Zr-Al glasses. Various isothermal and nonisothermal treatments are employed, and the structural response is characterized using bulk X-ray and thermal analysis methods as well as nano-scale microscopic analysis methods, revealing structural and chemical details down to the atomic-scale.

By carefully combining techniques such as differential scanning calorimetry (DSC), in-situ synchrotron high energy X-ray diffraction (HEXRD), and transmission electron microscopy (TEM) to quantify the characterization transformations, this research has uncovered numerous details concerning the atomistic mechanisms of crystallization and has provided much new understanding related to the dominant phases, the overall reaction sequences, and the rate-controlling mechanisms. As such this work represents a substantial step forward in understanding these transformations and provides a clear framework for further progress toward ultimate application of controlled devitrification processing for the production of new materials with remarkable properties.

CHAPTER 1: OVERVIEW

General Introduction

Metallic Glasses

The term amorphous (or glassy) state can be described as a metastable state lacking in long-range atomic order, dislocations or grain boundaries, thereby different from crystalline solids. In this sense, metallic glasses are basically the metal systems having no long-range atomic order. Since the synthesis of first metallic glass (Au-Si) by Duwez et al [1] in 1960, there has been much effort given to the investigation of new metallic glass systems. Attributed to their amorphous and metallic characters, metallic glasses possess good chemical, physical and mechanical properties such as high tensile and fracture strengths, high hardness, good ductility, high corrosion resistance, and high elastic energy [2-5]. Metallic glasses can be produced by rapid solidification of a liquid melt with a high cooling rate to suppress the nucleation and growth of crystalline phases.

Formation of Metallic Glasses

The amorphous phase can be produced if the nucleation and growth of crystalline phase are suppressed by cooling the liquid alloy rapidly enough [6, 7]. The formation of metallic glasses can be explained using time-temperature-transformation (TTT) diagram from the kinetics aspect. C-curve shaped TTT diagram indicates the competition between the increasing driving force for crystallization and the slowing down kinetics of the atomic movement. When the liquid is rapidly quenched, it will not touch the nose of the C-curve of any possible crystalline phase (Fig.1 [8]). The liquid will then eventually freeze with a disordered atomic configuration. Due to the sharp increase in the viscosity, the liquid will

behave as a solid. This metastable solid state which is structurally similar to a liquid is named as glassy state. The temperature below which the glassy solid exists is called glass transition temperature (T_g). It should be noted that, T_g is a kinetic parameter therefore it depends on melt cooling rate and thermal history of the glass. It is widely accepted that the T_g is the temperature at which the viscosity increases up to 10^{13} poise [9].

Glass formation in metallic systems has been widely investigated and many theories have been proposed in order to understand the glass forming ability (GFA) term. According to Turnbull [6], glass formation will be favored and the amorphous structure can be obtained relatively at low cooling rates when the reduced glass transition temperature ($T_{rg} = T_g/T_l$ where T_l is the liquidus temperature) is 2/3 or higher. This criterion predicts that such a liquid will be sluggish in crystallization and crystal nucleation will be suppressed during quenching because of the lowered driving force for nucleation and mobility. Some of the reported critical cooling rate, R_c , values of metallic glasses and bulk amorphous alloys are given in Fig.2 [3, 10]. R_c values are varying from one system to another and basically depends on the position of C-curve in the T-T-T diagram. The closer the C-curve to the left, the more highly metastable will be the glass as time for the crystallization becomes shorter. On the other hand, the glass will be highly stable against crystallization when the C-curve is far away from the left side.

Glass formation in metals systems should be considered separately from that in ordinary glasses such as polymers. Fig.3 [11] illustrates the differences in the structural changes of conventional amorphous alloys and metallic glasses during the continuous heating. In the metallic glassy systems different from ordinary glasses, another important parameter in determining the GFA and the stability of the glass against crystallization is the

supercooled liquid region. This region is the gap between the glass transition and the melting temperatures of liquid and generally defined by the difference between the T_g and crystallization temperature (T_x) as ΔT_x . In the supercooled liquid region, glass first relaxes into a highly viscous liquid and eventually crystallizes. Therefore, the alloy is accepted as a good glass former with a high GFA if the ΔT_x is wide. On the contrary, Lu and Liu [12] claimed that ΔT_x is not sufficient alone to determine the GFA of alloys and introduced a new parameter, γ ($=T_x/(T_g+T_l)$). Based on the reported experimental results for different systems, they proposed a relationship between γ , R_c and critical thickness of amorphous section for glass forming alloys which indicated that the parameter γ has a stronger connection with GFA than that of T_{rg} .

Inoue and coworkers [13-16] reported three empirical rules required to achieve high GFA in metallic systems, such as the multicomponent alloys with more than three elements, at least 12% atomic size difference between the constituent elements and negative heats of mixing among these elements. The satisfaction of these rules will increase T_{rg} , thereby increase the GFA of the alloy. Furthermore, Greer's confusion principle predicted that the addition of elements will confuse the alloy to create crystal structures [17]. Therefore, they suggested that the higher the GFA will be achieved when the more the elements involve in the alloy. However, recent advances have elucidated that multi-component systems are not required for high GFA which can exist even in the binary such as Cu-Zr and Ni-Zr or ternary metallic systems. Based on the three empirical rules, the eutectic systems are accepted as good candidates with a deep valley in their melting temperature. Furthermore, Inoue and Louzguine-Luzgin [18] suggested a new criterion which proposed that the specific volume of

the liquid must be larger than that of the corresponding crystal for an achievement of high GFA of pure metals.

Recent studies have shown the relationship between the eutectic coupled zone and the GFA of alloys. Boettinger [19, 20] reported that when the liquid is undercooled below the T_0 lines (at which the free energies of liquid and the crystal phases of an alloy are equal to each other), the partitionless crystallization of an alloy becomes thermodynamically possible. They mentioned that it is unlikely to obtain a glassy composition where $T_g < T_0$. But, if the cooling rate is sufficiently high enough to prevent the partitionless crystallization then the glass formation will be possible as the undercooled melt will be frozen in to a glassy state. The calculations of T_0 curves have been performed in many systems, for example very recently, Yao and Napolitano et al [21] calculated the T_0 values for several Al-rare earth binary alloys. Beside these studies, others have focused on the relationship between the coupled zone and the glass forming ability. Li [22] proposed that the eutectic compositions should be the best glass formers for the alloys with a symmetric coupled zone while the off-eutectic compositions have the highest GFA for the alloys with an asymmetric coupled zone. These two types of coupled zones; symmetric and asymmetric were presented in Fig.4 (a) and (b), respectively.

Based on thermodynamics aspects, GFA is related to the free energy of formation from liquid to crystalline phase (ΔG_f). The lower ΔG_f will result in the higher GFA. Therefore, in Eq.1, for low ΔG_f value, entropy of fusion, ΔS_f , should be large and enthalpy of fusion, ΔH_f , should be low. The increase in ΔS_f which is proportional to the number of microscopic states will increase the degree of dense random packing. This increase will decrease ΔH_f of the system and increase solid/liquid interfacial energy.

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (1)$$

For a given undercooling, thermodynamics predict the formation of both stable and possible metastable phases. However, kinetics will give the information about the sequence of these metastable phase formation. According to the kinetics point of view, homogeneous nucleation and growth of a spherical crystalline phase from the undercooled liquid, I and U , can be defined as

$$I = \frac{10^{30}}{\eta} \exp\left[-16\pi\alpha^3\beta/3T_r(1-T_r)^2\right] \quad (2)$$

$$U = \frac{10^2 f}{\eta} \left[1 - \exp\left[-\beta\Delta T_r/T_r(T/T_m)\right]\right] \quad (3)$$

where, T_r (T/T_m) is the reduced temperature, η is a viscosity, f is the nucleation site fraction at the growth interface, ΔT_r is the temperature difference between T and T_m , α and β dimensionless parameters related to the liquid/solid interface energy (σ), expressed by the following equations

$$\beta = \Delta S_f / R \quad (4)$$

$$\alpha = (N_0 V)^{1/3} \sigma / \Delta H_f \quad (5)$$

where N_0 is the Avagadro's number and V is the atomic volume of the crystal. The above relationships indicate that the increase in β and α values will increase the ΔS_f and decrease the ΔH_f , respectively. It is concluded that if the $\alpha\beta^{1/3}$ term in Eq.2 is above 0.9, crystallization will not take place at any cooling rate, however it will not be possible to prevent the crystallization of liquid when $\alpha\beta^{1/3}$ is below 0.3.

Rapid Solidification

Rapid solidification term requires solidification of a liquid into a solid phase at a high cooling rate and in a very short time interval. High cooling rates will result in large undercoolings which defines the nucleation time for crystalline phase. Thermodynamically, phase formation can only occur when the free energy of the system decreases. Therefore, the possible phases to form can be determined by comparing the Gibbs free energies under equilibrium conditions. Phase diagrams are good source to determine the stability of phases under equilibrium conditions however in non-equilibrium case, the system will be metastable and there will not be enough time to reach the equilibrium. Therefore, thermodynamics will not be sufficient alone and the solidification kinetics will be useful to get the information about phase formation, phase selection and microstructure under far from equilibrium conditions. Ostwald [23] suggested that the metastable phase has larger nucleation frequency compared to the stable one under large undercoolings therefore metastable phase is predicted to nucleate first. Fig.5 (a) shows the free energy concentration diagram where C_0 indicates the undercooled liquid composition [24]. As seen from the plot, the free energy of the system will be lowered when the solid phase forms in the composition range of a to b. At the composition of c, the free energy will be at its lowest value. At that point, as mentioned previously, the nucleation frequency is important to determine the composition of the first nuclei. Furthermore, kinetics predicts the formation of metastable phase under two conditions. The metastable phase may nucleate before the more stable ones or its crystal growth exceeds that of the stable one. The relationship between the growth rate and the undercooling can be determined by the Jackson equation:

$$U = U_0(\Delta T)^\beta \quad (6)$$

The analysis of the above equation indicates that the growth rate of metastable phase will be larger than the stable one when the β value of metastable phase is higher than that of the stable one. Fig.5 (b) shows the hypothetical relationship between the growth rate of metastable and stable phases.

Rapid Solidification Techniques

High cooling rates and large undercoolings can be achieved by several rapid solidification techniques including melt atomization [25, 26], melt spinning [27], thermal spray coatings [28], laser melting [29] and splat quenching [30]. Fig.6 indicates the critical thicknesses, cooling rates and reduced glass transition temperature for various metallic glass-forming alloys correlated with the various quenching techniques [31]. Among these methods, spinning mostly known as melt spinning or melt extrusion is generally preferred to achieve extremely high cooling rates in the range of 10^4 – 10^7 K/s [32]. In a single roller melt spinner, as seen in Fig.7, a thin melt stream is dripped on the internally cooled metal drum. Solidification stabilizes the liquid stream when emerging from the orifice and prevents the breaking of stream into the droplets. Rapidly solidified ribbons with a thickness of 10-50 μm can be obtained as a product. In some cases, twin roller melt spinner is used to increase the cooling rate and homogenize the structure of the as-quenched ribbons.

Devitrification of Metallic Glasses

Devitrification term can be described as controlled crystallization of metastable glassy to subsequent crystallization states under continuous heating as functions of temperature and time. Recent studies have shown the importance of devitrification as mechanical and physical properties of metallic glasses are improved with annealing treatments. Crystallization in rapidly solidified systems are thermally activated and occurred

by nucleation and subsequent growth and impingement of crystalline particles. The free energy difference between the metastable and stable states will be the driving force for nucleation. During annealing process, the structural relaxation will occur first before the crystallization takes place. Structural relaxation can be defined as the structural change occurs in the single amorphous phase due to the change in the density and the viscosity. Cohen and Turnbull [33] proposed a free volume theory which suggests a randomly distributed excess volume in the undercooled liquid. The theory assumes that this excess volume may move above T_g but is trapped at T_g . Following the structural relaxation, crystallization will start with nucleation which occurs either heterogeneously or homogeneously. Heterogeneous nucleation generally occurs at nucleation sites such as on the container walls, phase boundaries or any other impurities. On the other hand, homogeneous one takes place without requiring of any nucleation sites. Therefore, heterogeneous type nucleation occurs more often than the homogeneous one.

Following the nucleation, the growth of nuclei occurs in two manners; parabolic or linear. However, in some cases, such as in-situ phase transformations, kinetics may be changed by some surface interactions and neither of them can be observed. Linear growth can be seen during the diffusionless transformations or during the long-range diffusional transformations. The growth rate of particles is generally determined by microstructural analysis under isothermal annealing conditions. For example, the growth of a nucleus in polymorphous reaction which is a linear type can be expressed as

$$u = u_0 \exp\left(-\frac{Q_s}{RT}\right) \left(1 - \exp\left(-\frac{\Delta G}{RT}\right)\right) \quad (7)$$

where Q_s is the activation energy for growth, u_0 is in the order of 5×10^3 m/s for polymorphous reactions.

On the other hand, parabolic growth occurs during diffusion controlled processes. These reactions might be primary crystallization, precipitation or peritectoid where the growth rate of the spherical particle can be determined as

$$U = \frac{1}{2} \alpha D r^{-1} \quad (8)$$

where $r = \alpha \sqrt{Dt}$, D is diffusion with Arrhenius relationship ($D = D_0 \exp\left(-\frac{Q_D}{RT}\right)$) where D_0 is the diffusion coefficient, Q_D is the activation energy for growth.) α is a dimensionless parameter related to the composition of the particle and composition at the interface of the particle. It should be noted that the growth rate is time dependent; growth will be slower when the particles are getting larger.

Diffusionless transformations occur by the small displacements of atoms without requiring any long-range atomic arrangements. The atoms will keep their neighbor relationships. In polymorphous transformation, the newly formed phase will have the same composition as the matrix but a different structure. As predicted from the Ostwald's step rule [23], phase transformation might be occurred step by step to reach more stable phases. In polymorphous phase transformation, starting from the unstable phase, the first nucleating phase can probably be the metastable one which is more stable than the starting phase but not the most stable one. In the martensitic type transformation which occurs as a result of rapid cooling, the growth rate will be high. This type of transformation is mostly controlled by

nucleation and shear where the product martensites will have the same composition with the parent phase.

Diffusion controlled transformations where the transformation is occurred by diffusion rather than heat flow includes eutectoid, precipitation or primary crystallization and peritectoid reactions. In eutectoid reaction, two crystalline phases grow cooperatively by a discontinuous coupled growth process. The growth rate will be dependent on the diffusivity of these two phases and therefore will be slower compared to diffusionless transformations. In the precipitation or primary crystallization case, crystalline precipitates with a different composition than the parent phase will be formed by primary crystallization process. Peritectoid reaction is rarely seen in rapidly solidified alloy systems during the decomposition of quasicrystalline phase where the microstructure is the mixture of metastable and a stable phase transforms into a more stable one by a peritectoid reaction. The final microstructure will consist of metastable crystals surrounded by a secondly formed stable phase embedded in the stable parent phase.

In order to analyze the isothermal crystallization process, the kinetics of phase transformation including the nucleation and growth can be modeled using Johnson-Mehl-Avrami (JMA) [34-36] equation

$$x(t) = 1 - \exp[-k(t - \tau)^n] \quad (9)$$

where $x(t)$ is the transformed volume fraction at annealing time t , τ is the incubation time before transformation begins, n is the Avrami exponent, which reflects the crystallization mechanisms of nucleation and growth. The reaction rate constant, k , is related to the activation energy by the following Arrhenius equation;

$$k = k_0 \exp\left(\frac{E}{RT}\right) \quad (10)$$

where k_0 is the reaction rate constant, E is the activation energy and R is the gas constant. The Avrami exponent, n , and reaction rate constant, k can be calculated from the slope and the intercept of the linear fitting to the JMA plot using the equation;

$$\ln\left[\ln\left(\frac{1}{1-x}\right)\right] = \ln k + n \ln(t - \tau) \quad (11)$$

This parameter reflects the transformation/reaction mechanisms. The explanations of Avrami exponent values for different conditions are listed in Table 1 [37]. However, it has been proposed that the local Avrami exponent, expressed in Eq.12, should be used for more detailed information about the changes in the nucleation and growth rates of crystals during the whole crystallization process.

$$n(x) = \frac{\partial \ln[-\ln(1-x)]}{\partial \ln(t - \tau)} \quad (12)$$

JMA equation was developed for isothermal annealing conditions. In order to get information about the kinetics and growth mechanisms for temperature and time dependent conditions, or named as isochronal (or continuous heating), Kissinger equation [38, 39] is generally used. Kissinger relationship is based on the JMA equation, and has been commonly used in activation energy calculations in dynamic mode. The activation energies can be calculated by means of the Kissinger model by

$$\ln \phi / T^2 = -\frac{E}{RT} + \text{const.} \quad (13)$$

where ϕ is the heating rate, T is the specific temperature varying with heating rate, E is the apparent activation energy for the process and R is the gas constant. The apparent

activation energy, E , can be estimated using the variations in the corresponding T from the slope of Kissinger plot under continuous heating conditions.

Literature Review

Metallic Glasses

The first metallic glass reported by Klement and Duwez was only produced as thin strips and required to be cooled at a rate of 10^6 K/s. In the late 1960's, glassy Pd-Si-Cu alloy was formed relatively at lower cooling rate (100-1000 K/s). Later in 1976, Lieberman and Graham synthesized a new method and produced thin ribbons of amorphous Fe-Ni-P-B metal alloy on a supercooled fast spinning wheel. Since 1980's, various number of metallic glass alloys in different systems have been produced with low cooling rates.

Recently, in 1990's, new alloys were synthesized and named as bulk amorphous as they can be cast into a bulk form with a several centimeters in thickness. More recently, new bulk amorphous alloys with low cooling rates have been reported in many multicomponent systems, such as Mg-Lanthanide metals (Ln)-Transition metals (TM) [40], Zr-Al-TM [41, 42], La-Al-TM [43, 44], Pd-Cu-Si [44, 45], Pd-Cu-Ni-P [46], Ti-Zr-TM [47] and in ferrous systems such as Fe-based [48-50] and Co based [50] alloys. The first commercial amorphous alloy, $Zr_{41.2}Be_{22.5}Ti_{13.8}Cu_{12.5}Ni_{10}$, named as "Vitreloy 1" was developed in 1992's at Caltech. Following Vitreloy1, other commercial alloys were developed with low cooling rates and named as Vitreloy 4, Vitreloy 105, Vitreloy 106a for $Zr_{46.75}Be_{27.5}Ti_{8.25}Cu_{7.5}Ni_{10}$, $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ compositions, respectively. In 2004, a collaborative group of Oak Ridge National Laboratory and University of Virginia produced bulk amorphous steel named as "glassy steel", which has higher strength than conventional steels and non-magnetic at room temperature [51, 52].

Binary Cu-Zr Metallic Glasses

Cu-Zr based amorphous alloys are particularly interesting for mechanical and structural applications because of their good glass forming ability and appreciable compressive plasticity which prevents any catastrophic failures [53-55]. Based on Inoue's three empirical rules expectations, Cu-Zr system favors the glass formation as the difference in the atomic sizes between Cu (0.128 nm) and Zr (0.160 nm) is over 10 %, and the heat of mixing between Zr and Cu is -23 kJ/mol. This large chemical mixing enthalpy stabilizes the efficient cluster packing structure. Besides these properties, the constituent elements are relatively cheap compared to the other good glass former binaries. Among these binary systems, Cu-Zr has known to have a wide composition range of GFA; starting from 35 to 70 at% Cu in alloys where Fig.8 shows the equilibrium Cu-Zr phase diagram [56].

Glass formation in Cu-Zr binary alloy series have been investigated previously and it is known that GFA of this system is strongly composition dependent. Xia et al. [57] have shown this dependency by thermodynamic calculations based on Miedema's model. They introduced a new parameter, γ^* , to evaluate GFA of systems. γ^* can be expressed as

$$\gamma^* = \frac{-\Delta H_{\text{amorphous}}}{\Delta H_{\text{amorphous}} - \Delta H_{\text{intermetallic}}} \quad (14)$$

where $\Delta H_{\text{amorphous}}$ and $\Delta H_{\text{intermetallic}}$ are the enthalpies of formation of amorphous phase and intermetallic compound, respectively. Fig.9 (a) and (b) show the γ^* parameters and critical diameters of fully amorphous structure as functions of Zr concentration in Zr-Cu binary system, respectively. It is clear that, both plots show the similar tendency with Zr concentration where they both point out $\text{Cu}_{64}\text{Zr}_{36}$ and $\text{Cu}_{50}\text{Zr}_{50}$ as best glass formers. Besides these compositions, $\text{Cu}_{63.5}\text{Zr}_{36.5}$ is another good glass former which can be cast into 2 mm in

diameter fully amorphous rods, as seen in Fig.9 (b). Furthermore, Xu et al [58] studied on the glass formation in Cu-rich Cu-Zr binaries (in the range starting from 34 at.% to 40 at.% Cu). Their results supported Xia's [57] analysis where they reported that $\text{Cu}_{64}\text{Zr}_{36}$ is the best glass former composition in that range as it can be cast into fully amorphous 2mm diameter rod. Wang et al. [59] also studied the glass forming ability of the Cu-Zr binary system and reported the best glass former composition as $\text{Cu}_{64.5}\text{Zr}_{35.5}$ which can be cast into 2mm diameter glassy rod. Tang et al.[60] and Wang et al. [61] focused on understanding the GFA of $\text{Cu}_{50}\text{Zr}_{50}$ alloy. They reported that binary $\text{Cu}_{50}\text{Zr}_{50}$ alloy can be cast into 2 mm diameter fully amorphous rod. Their results showed the metastable $\text{Cu}_{51}\text{Zr}_{14}$ to be the main competing phase with increasing the rod diameter (>2mm). They concluded that the GFA of $\text{Cu}_{50}\text{Zr}_{50}$ alloy can be interpreted in terms of a deep metastable eutectic between $\text{Cu}_{51}\text{Zr}_{14}$ and $\beta\text{-Zr}$. It should be also noted that contrary to deep eutectic rule, two best glass formers of Cu-Zr system; $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{64.5}\text{Zr}_{35.5}$ are at off eutectic compositions.

Li et al [62] have studied on the relationship between the density of the amorphous phase and glass formation using several Cu-Zr binary alloys, in the composition range of $\text{Cu}_{47}\text{Zr}_{53}$ to $\text{Cu}_{68}\text{Zr}_{32}$. They have reported that distinct peaks in the density of the amorphous phase were found to correlate with specific maxima in the critical thickness for glass formation. Their results showed three compositions named as $\text{Cu}_{64}\text{Zr}_{36}$, $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$ have these maxima, as presented in Fig.10 (a) and (b).

GFA of Cu-Zr system has been found to increase significantly with an addition of third element, especially one of the transition metals (TM), such as Al, Ti, Ni or Ag. In accordance with the confusion principle discussed in the previous sections, an addition of the third element decreases the liquidus temperature of the alloy and thereby increases T_{rg} which

leads to an increase in GFA. It has been reported that Cu-Zr based ternaries can be produced in the form of 3-6mm diameter rods [63]. Among the Cu-Zr-TM ternaries, Cu-Zr-Al and Cu-Zr-Ti alloys have shown the most enhanced properties. Cheung et al [64] reported the results on addition of a minor amount of Al to $\text{Cu}_{50}\text{Zr}_{50}$ bulk metallic glasses. Their results showed that the highest thermal stability was seen for the 8 at.% of Al addition while highest hardness was obtained for the 10 at.% of Al addition. On the other hand, addition of Ti was found to improve the mechanical strength exceeding 2 GPa in $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ system [4]. Using the other impurity element, Ag, Zhang et al [65] reported that the $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ glassy alloy has a critical diameter of 6 mm and a high mechanical strength of 1.8 GPa.

Recent analyses of amorphous/crystalline composite (ACC) materials produced by partial crystallization of amorphous precursor have elucidated the significant enhancement in mechanical and magnetic properties compared to that of the monolithic amorphous or crystalline alloys. Inoue et al [66] reported that amorphous/crystalline $\text{Cu}_{50}\text{Zr}_{50}$ composite can sustain a compressive plastic strain of more than 50% at room temperature. Recent studies have also shown the importance of introducing the primary crystallization phase to form a glass/crystalline composite to improve the mechanical properties. There have been several studies reported the effect of geometry, size, microstructure and volume fraction of primary crystallizing phases on mechanical properties of bulk metallic glass composites [67-69]. Jiang et al [67] showed that $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ bulk metallic glass composite with a distribution of reinforced martensitic type CuZr phase yields at 1733 MPa, fails at 1964 MPa and exhibits a plastic strain of 3.7 %. It has also been reported that the mechanical properties such as macroscopic deformability can be enhanced in partial crystallization of amorphous

Cu-Zr alloys [53, 70, 71]. Das et al [53] showed that the nanometer size crystalline precipitates embedded in the amorphous $\text{Cu}_{50}\text{Zr}_{50}$ matrix enhance the fracture strain of 7.9 %.

Thermal Stability and Crystallization Studies in Cu-Zr Metallic Glasses

Devitrification studies are important in both understanding the structure, thermodynamic and kinetics during the crystallization of metallic glasses and improving the technological applications. Devitrification studies provide a chance to test several nucleation, growth and thermodynamic models and simulations. On the other hand, by the help of crystallization studies, applicability limit of metallic glasses can be determined, for example, ductility and corrosion resistance of metallic glasses are deteriorated upon crystallization while some of the mechanical properties are improved when the metallic glass is partially crystallized. Therefore, crystallization studies especially in the best glass former Cu-Zr binary system which serves as a base for many multi-component glassy alloys is significantly important to determine the devitrification path under both isothermal and continuous heat treatment conditions. With complex crystalline dynamics arising from the competition of a number of stable and metastable phases, explicitly a variety of crystal structures, the crystallization kinetics and thermal stability of Cu-Zr based alloys have attracted much attention with respect to fundamental research on the behaviors of glass forming alloys.

As mentioned in previous sections, $\text{Cu}_{50}\text{Zr}_{50}$ alloy is one of the best glass former in Cu-Zr binary system. The crystallization of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy was first proposed by Altounian [72] who performed $\text{CuK}\alpha$ X-ray diffraction studies on crystallized melt spun ribbons to determine the structure of final phases and reported that the crystallization sequence of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy has only one step and two products; high amount of $\text{Cu}_{10}\text{Zr}_7$ phase with a low amount of Zr_2Cu phase. Kneller et al. [73] reported the most

detailed findings using Dynamic Temperature X-ray diffraction (DTXD). They reported that cubic CuZr (B2) phase is a first crystallizing phase which is then decomposed immediately into the $\text{Cu}_{10}\text{Zr}_7$ and Zr_2Cu phases at its crystallization temperature. One of the interesting results of their study is that they introduced a new Cu-Zr phase, Cu_5Zr_8 , which formed during the crystallization of $\text{Cu}_{50}\text{Zr}_{50}$ alloy. However, Cu_5Zr_8 is still under investigation as some of studies did not confirm its stability [74]. Recently, Louzguine-Luzgin et al [75] reported the primary formation of a metastable CuZr martensite during crystallization of glassy $\text{Cu}_{50}\text{Zr}_{50}$ alloy.

$\text{Cu}_{64.5}\text{Zr}_{35.5}$ alloy is also known as one of the best glass former Cu-Zr binary systems. The investigations around $\text{Cu}_{64.5}\text{Zr}_{35.5}$ composition have revealed that this part of Cu-Zr phase diagram has an asymmetric eutectic type of coupled zone, as seen in Fig.11 (a), which determines the glass and glass composite regions [59]. In this study, Wang et al. reported that the change in the primary phase from $\text{Cu}_{10}\text{Zr}_7$ (in $\text{Cu}_{64}\text{Zr}_{36}$) to Cu_8Zr_3 (in $\text{Cu}_{65}\text{Zr}_{35}$) nails down the best glass forming ability in between at $\text{Cu}_{64.5}\text{Zr}_{35.5}$, as shown in Fig.11 (b).

$\text{Cu}_{56}\text{Zr}_{44}$ alloy is one of the other best glass formers in Cu-Zr system. Freed [76] investigated the crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ glass using differential scanning calorimetry (DSC), X-ray energy dispersive analysis and transmission electron microscopy (TEM) and reported that $\text{Cu}_{10}\text{Zr}_7$ phase nucleated primarily which was then followed by the formation of CuZr when the equilibrium fraction of $\text{Cu}_{10}\text{Zr}_7$ was obtained. Wang et al [77] investigated the crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ glass under isothermal annealing conditions. They reported that Cu_8Zr_3 phase nucleated primarily, and then decomposed into $\text{Cu}_{10}\text{Zr}_7$, later CuZr_2 formed and Cu_8Zr_3 re-precipitated at the final stage where they stayed in equilibrium with

$\text{Cu}_{10}\text{Zr}_7$. Literature on the devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy shows that a crystallization mechanism of this system is still unclear.

Due to the contradictions in the literature on the crystallization studies of the best glass former Cu-Zr binaries, comprehensive study is required to understand both the thermal stability and devitrification kinetics in this system. Therefore, in the present work, Cu-Zr binary alloys were selected and investigated in terms of their thermal stability, devitrification dynamics, and the evolution of structural hierarchy, phase stability, and competitive growth. Accordingly, the critical issues have been selected as; characterize the dynamical evolution of structural hierarchy during devitrification, assess the thermal stability of the amorphous structure and quantify the kinetics of devitrification for various heating profiles and predict and control of phase transformation kinetics and stability and competitive growth of devitrification microstructures in Cu-Zr alloys. We investigated the thermal stability, crystallization kinetics, and dynamic characterization of structure evolution during devitrification using in-situ high energy synchrotron X-ray diffraction (HEXRD), differential scanning calorimetry (DSC), high-temperature DSC and transmission electron microscopy (TEM).

Experimental Methods

Sample Production

Ingots with nominal compositions of Cu-Zr alloys were prepared from high purity constituents (0.9999 Cu and 0.999(3) Zr, by weight) using arc melting under an argon atmosphere. Alloy ingots were remelted and quenched on water-cooled copper hearths three times to obtain good chemical homogeneity. Amorphous ribbons were produced by rapid solidification using a Copper block single roller melt spinner (Fig.12) in Ames Laboratory of

DOE with a tangential wheel velocity of 25 m/s under 1/3 atm He using graphite crucibles. The cooling rate achieved with melt spinning was in the order of $10^4 \sim 10^7$ K/s.

Specimen Preparation for Characterization

Several characterization techniques were used to analyze the as-quenched and annealed ribbons. These techniques include differential scanning calorimetry (DSC), high-temperature differential scanning calorimetry, transmission electron microscopy (TEM) and in-situ high energy X-ray diffraction (HEXRD).

Differential Scanning Calorimetry (DSC) and High-Temperature DSC: Thermal analysis of as-quenched ribbons was carried out using DSC (Perkin Elmer Pyris 1 DSC) with platinum sample holders under continuous heating (isochronal) and isothermal conditions. The isochronal DSC traces were obtained at heating rates ranging from 10 to 60 K/min under high purity Ar atmosphere with the accuracy of ± 0.1 K and $0.2 \mu\text{W}$. For isothermal studies, melt spun ribbons were first heated with a heating rate of 100 K/min to a fixed temperature below T_x , and then maintained at that temperature for a certain period of time until the crystallization was completed. A sample weight of 8.00 mg or 10.00 mg was used for each continuous (isochronal) and isothermal heating runs. The specific heat capacity measurements were performed using step-scan method and the data were calculated and corrected based on the specific heat calculations of a standard sample (sapphire). The details of relaxation and specific heat capacity measurements were given in the fifth chapter. High-temperature DSC was preferred to reach higher temperatures compared to DSC for continuous heating experiments. For each high-temperature DSC run, a sample weight of 30-40 mg was used. The sample pans were selected as aluminum and alumina for DSC and high-temperature DSC, respectively.

Transmission Electron Microscopy (TEM) - Energy Dispersive Spectroscopy

(EDS): The microstructural analysis of as-quenched and isothermally annealed ribbons were done using transmission electron microscopy (TEM) in bright field (BF), selected area diffraction (SAED) and high resolution (HRTEM) modes. The samples were initially polished mechanically and then thinned by chemical etching (electropolishing or electrochemical polishing) technique. In electropolishing technique, the current passes through a flow of etchant and hits on the sample where the impingement forms a small hole in the center. The optimum conditions of electropolishing process were obtained after several trials. The samples were thinned using a mixture of 67 vol. % methanol and 33 vol. % nitric acid (HNO₃) polishing solution (electrolyte) at an accelerating voltage of 15 V and a temperature of -241 K.

In-situ synchrotron high energy X-ray diffraction (HEXRD): Synchrotron radiation is a powerful tool in investigation of local structures of amorphous and crystalline materials. The wavelength is constant in synchrotron radiation, but the scattering angle is continuous and the image plate detects the scattering pattern in a range of scattering angles. Continuous tunability, high intensity and excellent collimation because of the relativistic effect such as small angular divergence of the beam, high level of polarization and high brilliance and excellent monochromaticity are some of the characteristics of synchrotron radiation (SR). Furthermore, SR provides good resolution and high signal to noise ratio (S/N). On the other hand, high energy of X-rays (HEXR) provides some advantages compared to conventional ones. The particles can transmit through the bulk material; therefore the information is collected from the whole sample not just from the surface of it. Small scattering angles and short wavelengths can be obtained using HEXR which allow the detailed structural

investigations. Photo-absorption cross section is reduced by HEXR which provides the better penetration into materials. Moreover, rapid data collection can be achieved by the extremely high photon flux property of HEXRD. Based on these advantages, SR with HEXR is a powerful tool for X-ray crystal structure investigations.

In-situ high energy synchrotron X-ray diffraction (HEXRD) studies of as-quenched ribbons were performed at Advanced Photon Center in Argonne National Laboratory, Fig.13. In-situ HEXRD data was collected using the energy of 99.586 keV corresponding to a wavelength of 0.01245 nm. For preparation to HEXRD experiments, the ribbons were first cut into 12 mm lengths and then inserted as a stack of 40 into 2 mm diameter thin walled quartz capillaries which were sealed under Ar atmosphere, as shown in Fig.14 (a). The capillaries were then inserted into the furnace which was designed to meet some requirements such as inert oxidizing, sample rotation for improved powder averaging, sample containment, uniform heating, Eulerian Cradle, very low lateral and radial thermal gradient ($\sim \pm 2^\circ\text{C}$ over 4 mm distance). The diffraction data were collected with the exposure time of 15 s using a charge coupled device (CCD) having Deby-Scherrer geometry, as indicated in Fig.14 (b). In-situ HEXRD data of amorphous ribbons were collected using a heating rate of 10 K/min for continuous heating case. For the isothermal annealing experiments, as-quenched ribbons were initially heated to a fixed temperature below T_x with a heating rate of 100 K/min and then maintained at that temperature for a certain period of time until the alloy was completely crystallized. The diffraction data were then analyzed using Rietveld refinement where the lattice parameters, atomic coordinates, occupancies, thermal parameters, phase fractions, background and peak profiles were refined simultaneously during pattern modeling.

Rietveld Refinement: The correlation in atomic scale is significant in analysis of scattering patterns of crystalline samples, measured in high Q ($=2\pi/d$) range. For precise analysis of phase information, the intensity is critical parameter therefore modeling is required to fit the patterns. Rietveld technique [78, 79] was first modeled for the monochromatic diffraction where the Bragg angle is used to determine the peak positions. Rietveld uses the least squares approach for the refinement of theoretical profile until it matches to the measured profile. Rietveld method provides an effective separation of overlapping, enables quantitative determination of lattice parameters, atomic coordinates, occupancies, and thermal parameter and phase fractions, and thereby allows an accurate structure determination.

Thesis Organization

This thesis is written in the alternate paper format which is divided into seven chapters. The first chapter is the general introduction including introduction, literature review and experimental methods.

The second chapter, entitled as “*High-accuracy X-ray diffraction analysis of phase evolution sequence during devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass*” focuses on the analysis of phase selection and devitrification kinetics in an amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy using differential scanning calorimetry (DSC) and in-situ high energy X-ray diffraction (HEXRD) under constant heating rate conditions.

The third chapter, entitled as “*Isothermal Crystallization and Phase Selection Dynamics in $\text{Cu}_{50}\text{Zr}_{50}$ Metallic Glass*” discusses the phase selection sequence and crystallization kinetics during isothermal annealing of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ using DSC,

HEXRD, conventional and high-resolution transmission electron microscopy (TEM and HRTEM).

The fourth chapter, entitled as “*Crystallization Kinetics and Phase Transformation Mechanism in Cu₅₆Zr₄₄ glassy alloy*” presents the results on the devitrification kinetics and phase selection dynamics in eutectic Cu₅₆Zr₄₄ alloy using DSC, HRTEM and TEM under both isothermal and isochronal conditions.

The fifth chapter entitled as “*Glass Forming Ability of Binary Cu-Zr and Ternary Cu-Zr-Al Glassy Alloys*” focuses on the glass forming ability and the thermal stability of binary Cu-Zr and ternary Cu-Zr-Al alloys using high-temperature DSC. The effect of Al addition on the primary crystallization in Cu₅₀Zr₄₅Al₅ and Cu_{47.5}Zr_{47.5}Al₅ were also discussed in this chapter.

The sixth chapter entitled as “*Structural Relaxation and Specific Heat in the Vicinity of Glass Transition in Cu₅₀Zr₅₀ Metallic Glass*” concentrates on the relaxation and specific heat calculations in Cu₅₀Zr₅₀ amorphous alloy in the vicinity of glass transition using DSC and high-temperature differential scanning calorimetry (DSC).

The seventh chapter is the “General Conclusion” which summarizes the findings in the current study and gives the suggestions for future studies.

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Fig.1. TTT diagrams showing the cooling curves for ordinary amorphous, conventional crystal and metallic glasses [8].

Fig.2. Relationship between (a) the critical cooling rate and reduced glass transition temperature, ($T_g = T_g / T_m$) and maximum thickness of glass (t_{max}) [3], (b) Critical casting thickness for glass formation and their discovery year [10].

Fig.3. Phase transitions in conventional amorphous alloys and bulk metallic glasses [11].

Fig.4. Glass formation region in alloy systems with (a) a symmetric and (b) an asymmetric (skewed) coupled zone [22].

Fig.5. (a) Free energy-concentration diagram (b) Growth rate-temperature diagram [24].

Fig.6. Critical thicknesses, d_c , and cooling rate, R_c , vs reduced glass transition temperature T_g/T_{liq} for various metallic glass-forming alloys and correlated with the various quenching techniques [31].

Fig.7. Single roller melt spinner

Table 1. The values of Avrami exponent (n) for various crystallization conditions [37].

<i>(i) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth, etc.</i>	
Conditions	
n	
Increasing nucleation rate	>4
Constant nucleation rate	4
Decreasing nucleation rate	3-4
Zero nucleation rate (site saturation)	3
Grain edge nucleation after saturation	2
Grain boundary nucleation after saturation	1
<i>(ii) Diffusion controlled growth</i>	
Conditions	
n	
All shapes growing from small dimensions	
Increasing nucleation rate	>2.5
Constant nucleation rate	2.5
Decreasing nucleation rate	1.5-2.5
Zero nucleation rate	1.5
Growth of particles of appreciable initial volume	1-1.5
Needles and plates of fine long dimensions, small in comparison with their separation	1
Thickening of long cylinders (needles)	1
Thickening of very large plates	0.5
Precipitation on dislocations	~ 0.67

Fig.8. Cu-Zr phase diagram [56].

Fig.9. Concentration dependence of the (a) GFA parameter γ^* and (b) experimentally determined maximum diameter D_{max} in Cu–Zr binary alloys [57].

Fig.10. (a) Density change of amorphous phase in several Cu-Zr binary alloys, (b) critical thickness of glass formation of several Cu-Zr binary alloys [62].

Fig.11. (a) Schematic phase diagram showing a skewed type coupled zone and glass and composite forming zones **(b)** Part of Cu-Zr phase diagram around $\text{Cu}_{64.5}\text{Zr}_{35.5}$ [59].

Fig.12. Copper block single roller melt spinner, Ames Laboratory of DOE.

Fig.13. In-situ high energy synchrotron[†] X-ray diffraction at Argonne National Laboratory

Fig.14. (a) Sample inserted quartz capillary, (b) a charge coupled device (CCD) having Debye-Scherrer geometry

CHAPTER 2: HIGH-ACCURACY X-RAY DIFFRACTION ANALYSIS OF PHASE EVOLUTION SEQUENCE DURING DEVITRIFICATION OF **Cu₅₀Zr₅₀ METALLIC GLASS**

A paper accepted by *Metallurgical and Materials Transactions A*

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Abstract

Real time high-energy X-ray diffraction (HEXRD) was used to investigate the crystallization kinetics and phase selection sequence for constant-heating-rate devitrification of fully amorphous Cu₅₀Zr₅₀. In-situ HEXRD patterns were obtained by the constant-rate heating of melt-spun ribbons under synchrotron radiation. High accuracy phase identification and quantitative assessment of phase fraction evolution through the duration of the observed transformations were performed using a Rietveld refinement method. Results for 10 K/min (10 °C/min) heating show the apparent simultaneous formation of three phases, orthorhombic Cu₁₀Zr₇, tetragonal CuZr₂ (C11_b) and cubic CuZr (B2), at 706 K (433 °C), followed immediately by the dissolution of the CuZr (B2) phase upon continued heating to 789 K (516 °C). Further heating results in re-precipitation of the CuZr (B2) phase at 1002 K (729 °C), with the material transforming completely to CuZr (B2) by 1045 K (772 °C). The Cu₅Zr₈

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phase, previously reported to be a devitrification product in $C_{50}Zr_{50}$, was not observed in the present study.

Introduction

While the investigation of glass formation in metallic systems has uncovered numerous systems with high glass forming ability, leading to the development of several so-called bulk metallic glasses (BMGs) with noteworthy mechanical, electrical, and chemical properties [1-4], the effective application of these materials is somewhat hindered by our limited ability to control the complex phase transition dynamics that give rise to crystalline structures during solidification of a highly undercooled melt or devitrification of a glassy solid. Moreover, there are several recently reported examples of amorphous-crystalline composite (ACC) materials that illustrate the great potential value of controlled devitrification as a means to obtain novel structures of metastable phases [5-7]. In such cases, in-situ and ex-situ methods have been investigated with respect to their utility in enabling control of phase selection and composite structure [8-10]. Here, we focus on devitrification behavior in Cu-Zr, a binary system upon which several BMG alloys are based. Of course, reliable prediction and control of phase selection and structural dynamics requires quantification of system thermodynamics as well as an understanding of the kinetic mechanisms involved in solidification/devitrification processes, and advances in the thermodynamics and structure of Cu-Zr liquids, glasses, and crystalline phases have recently been reported [11-13]. Indeed, with numerous stable and metastable crystalline phases, this system offers an immense spectrum of potentially accessible structures and properties and has attracted much attention related to BMGs [14-16], crystallization structures [17-19], and ACC materials [20, 21].

A review of prior thermodynamic treatments for the Cu-Zr system was recently reported, and the assessed phase diagram is shown in Fig.1 [22]. The crystalline phases observed in this system are summarized in Table 1. We focus the present investigation on the $\text{Cu}_{50}\text{Zr}_{50}$ composition, for which several stable and metastable phases have been observed upon solidification from the melt and devitrification from the glass [17-19]. The first systematic study of crystallization from the glass in this alloy was reported by Freed et al. [46], who used X-ray diffraction (XRD), differential scanning calorimetry (DSC) and Transmission electron microscopy (TEM) to investigate the crystallization of splat quenched glassy alloy, reporting primary crystallization involving an unidentified metastable phase. Using XRD to investigate phase transitions in melt-spun ribbons on heating, Altounian subsequently reported that devitrification occurs in a single reaction from an amorphous phase to a two-phase structure, with $\text{Cu}_{10}\text{Zr}_7$ being the major phase and CuZr_2 being the minor phase [19]. Attempting to resolve this complex transformation path using dynamic temperature X-ray diffraction (DTXRD), Kneller et al. reported that the formation of a transient cubic CuZr (B2) phase precedes the formation of the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases during continuous heating at a rate of 0.835 K/min (0.835 °C/min) [17]. They also reported that a Cu_5Zr_8 phase forms upon heating through an eutectoid invariant temperature of 985 K (712 °C), above which a mixture of $\text{Cu}_{10}\text{Zr}_7$ and Cu_5Zr_8 are observed until the completion of the transition to the CuZr (B2) phase, which is stable from 1003 K (730 °C) to its melting temperature. While this intermediate temperature range of stability for the Cu_5Zr_8 phase is consistent with the phase diagram reported by Okomato [47], it does not agree with the findings of Zhou and Napolitano [22], and additional work may be needed to clarify this issue. In addition to the stable phases that may play a role in the devitrification response of

the $\text{Cu}_{50}\text{Zr}_{50}$ alloy, it should be noted that several metastable CuZr phases have been observed. For example, the CuZr (B2) phase has been shown to undergo a martensitic transition to a two-phase structure, reported to be composed of a B19' phase [40] and a B33 phase [48]. Whether such phases play any role in devitrification response and, if so, under what conditions, remains unclear at this time.

In the work presented here, in-situ high energy X-ray diffraction (HEXRD) is employed to investigate phase selection and devitrification kinetics in an amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy, examining specifically the competition of phases observed under constant heating rate conditions. While a systematic set of isothermal treatments at various temperatures with time resolved phase identification is called for to facilitate complete quantification of the devitrification kinetics, we leave that for a later analysis and employ here constant heating rate experiments for the purpose of resolving the uncertain crystallization sequence, as reported in prior investigations [17, 19, 46]. Accordingly, all diffraction data are analyzed using a Rietveld refinement technique [49, 50], providing reliable phase identification and high accuracy quantification of phase fractions. Herein lies the principal difference between the present work and prior reports, which rely only on the indexing of the XRD patterns by fitting the interplanar spacings. By incorporating lattice parameters, atomic coordinates, atomic site occupancies, phase fractions and isotropic thermal displacement parameters into a model of the overall diffraction pattern, the Rietveld refinement method used here provides a means for deconvolution and interpretation of the many overlapping peaks, enabling a reliable quantitative analysis of X-ray diffraction patterns obtained from multiphase structures observed throughout the course of the devitrification process.

Experimental Methods

Alloy specimens were prepared from high purity constituents (0.9999 Cu and 0.9995 Zr, by weight) by arc melting under an argon atmosphere and were remelted and chill-quenched three times for chemical homogeneity. Amorphous alloys were produced from the liquid by free-jet melt spinning [51, 52] on a copper wheel at a tangential velocity of 25 m/s, under 0.33 atm He using a graphite crucible, yielding ribbons that were nominally 1mm wide and 38 μm thick. Each X-ray diffraction specimen was prepared by cutting the melt-spun ribbons into 12 mm lengths, stacking 40 lengths together, placing the stack into a 2 mm diameter thin walled quartz capillary tube, and sealing under an Ar atmosphere.

The amorphous nature of the as-quenched $\text{Cu}_{50}\text{Zr}_{50}$ specimens was verified using DSC, HEXRD, and TEM. Each DSC specimen (8.00 mg) was sealed in an aluminum pan and placed in a platinum sample holder. DSC scans were performed using a constant heating rate of 10, 20, 30, 40, 50 and 60 K/min (10, 20, 30, 40, 50 and 60 $^{\circ}\text{C}/\text{min}$), from room temperature to 843 K (570 $^{\circ}\text{C}$), with temperature and power input accuracies of ± 0.1 K (± 0.1 $^{\circ}\text{C}$) and 0.2 μW , respectively. For each specimen analyzed, multiple scans were performed and the second scan was taken as an instrument baseline.

In-situ HEXRD was used to investigate the devitrification process during constant-rate (10 K/min (10 $^{\circ}\text{C}/\text{min}$)) heating. Synchrotron X-rays of 99.586 keV ($\lambda=0.0124(5)$ nm) were employed, and diffraction patterns were collected in Deby-Scherrer geometry using a charge-coupled device (CCD) with an exposure time of 15 s and a temperature range between 423 and 1264 K (150 and 991 $^{\circ}\text{C}$). Diffraction data were analyzed using a Rietveld refinement (fitting) scheme, where the approach is to minimize the function

$$M = \sum_i^n w_i [I_i^E(Q) - I_i^M(Q, \phi)]^2, \quad (1)$$

which quantifies the integral difference between the experimentally measured diffracted intensity, $I_i^E(Q)$, and a model intensity function, $I_i^M(Q, \phi)$, where w_i is a weighting factor, Q is defined as $4\pi \sin \theta / \lambda$, ϕ represents a set of model parameters that are optimized in the fitting process, and the sum is taken over all (n) measured points along Q . The adjustable and nonadjustable parameters included in this model are defined in Table 2, and the details of the refinement scheme are given an Appendix.

Results

The HEXRD pattern for the as-quenched ribbon is shown in Fig.2 (a), where the broad diffuse scattering peaks indicate that the structure is amorphous. This is further supported by the featureless bright-field TEM image in Fig.2 (b) and the corresponding selected area electron diffraction (SAED) pattern in Fig.2 (c), showing only broad halo rings. The continuous heating DSC traces for the $\text{Cu}_{50}\text{Zr}_{50}$ as-quenched ribbon at 10, 20, 30, 40, 50 and 60 K/min (10, 20, 30, 40, 50 and 60 °C/min) are shown in Fig.2 (d), revealing a distinct glass transition feature and exothermic peaks associated with crystallization. The expanded scale inset shows the DSC trace for 10 K/min (10 °C/min), clearly exhibiting (i) the glass transition (T_g) at 668 K (395 °C), (ii) the onset of crystallization (T_x) at 703 K (430 °C), and (iii) the temperature of maximum (peak) crystallization rate (T_p) 708 K (435 °C). In addition, the thermograph shows a second broad exothermic peak with an onset of 738 K (465 °C).

All three of these characteristic temperatures (T_g , T_x and T_p) were clearly identifiable for all heating rates and each was found to increase with heating rate, as shown in Fig.3. As a

means for considering the mechanisms involved in the crystallization process, we apply a Kissinger analysis [53] to model the rate-dependent crystallization temperature (T_x) as

$$\ln \phi / T_x^2 = -\frac{E}{RT_x} + \text{const.} \quad (2)$$

where ϕ is the heating rate, R is the gas constant, and E is an apparent *net* activation energy associated with all of the mechanisms that contribute to the observed crystallization process. Based on our DSC results, this is evaluated as 383 kJ/mol, which is in a reasonable agreement with the analyses of Buschow [18] and Eifert [54], who reported values of 396 and 396.6 kJ/mol, respectively.

The time-resolved HEXRD data are shown in Fig.4, for heating amorphous CuZr from 423 to 1264 K (150 to 991 °C) at a rate of 10 K/min (10 °C/min). Based on the indicated transitions, we identify several temperature regimes to examine more closely using a quantitative Reitveld refinement scheme, and refined HEXRD patterns are shown in Fig.5 for temperatures of 706, 789, 1002 and 1045 K (433, 516, 729 and 772 °C). Corresponding fitted model parameters and the refined structural data for each phase are listed in Table 3 and Table 4, respectively.

This quantitative analysis facilitates more complete and reliable interpretation of the experimental data. First, the optimized pattern for 706 K (433 °C), in Fig.5 (a), confirms that the amorphous Cu₅₀Zr₅₀ initially devitrifies into three phases, Cu₁₀Zr₇, CuZr₂ and CuZr (B2). We note here that the CuZr (B2) phase is metastable at this temperature and only stable from 1002 K (729 °C) to its melting temperature [22]. Fig.5 (b) shows the fitted pattern at 789 K (516 °C), where the sharper peaks for the Cu₁₀Zr₇ and CuZr₂ phases indicate that the increase in phase fraction is accompanied by an increase in crystallite size. This pattern also shows

that the CuZr (B2) phase dissolution is completed at approximately 789 K (516 °C) for this heating rate. Additionally, we note that only the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases are present, with no evidence to suggest that the Cu_5Zr_8 phase appeared at any subsequent time. Fig.5 (c) shows the fitted pattern for 1002 K (729 °C) and the appearance of weak peaks for the CuZr (B2) phase supports our preliminary observation that the CuZr (B2) phase forms in this temperature range, where it becomes stable. After the precipitation of the CuZr (B2) phase, the three phases ($\text{Cu}_{10}\text{Zr}_7$, CuZr_2 , CuZr (B2)) coexist until the transformation is complete, with the phase fraction of the CuZr (B2) phase increasing to unity at 1045 K (772 °C), as shown in Fig.5 (d), The alloy then melts congruently at 1233 K (960 °C).

Discussion

Based on our experimental findings, the constant-heating-rate devitrification sequence is summarized below and in Fig.6 (with specific temperatures associated with a heating rate of 10 K/min (10 °C/min)).

- (i) The onset of crystallization ($T_x=706$ K (433 °C)) involves the simultaneous (within the limits of temporal resolution) formation of three phases, including $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2). This initial crystallization event occurred within a 15 second interval, too rapid to differentiate and resolve the rates of formation associated with the individual phases. After the initial event, the material was completely crystalline with phase fractions of 0.399, 0.223 and 0.378 (by weight) for $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2), respectively.
- (ii) The initial rapid crystallization event is immediately followed by a slower transition process over the range from 706 K (433 °C) to 789 K (516 °C), characterized by a gradual increase in the fractions of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 , coupled with the simultaneous

complete decomposition of the CuZr (B2) phase. At the end of this period, the phase fractions are 0.636 and 0.364 (by weight) for $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 , respectively.

- (iii) Upon continued heating from 789 K (516 °C) to 1002 K (729 °C), the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases remain in equilibrium with no observable changes in phase fractions.
- (iv) At 1002 K (729 °C), the re-precipitation of the CuZr (B2) phase is observed. On continued heating, the growth of this phase is accompanied by the dissolution of both $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 until the fraction of CuZr (B2) reaches unity at 1045 K (772 °C).
- (v) The CuZr (B2) melts congruently at 1233 K (960 °C).

Experimental limitations regarding temporal resolution in the collection of HEXRD patterns do not permit deconvolution of the initial complex crystallization event, involving the formation of three phases. However, Reitveld analysis of the HEXRD patterns does allow reliable determination of the resulting crystallized phase fractions, as listed in item (i) above. Coupled eutectic-type growth of a three-phase structure is not expected in the binary system, even under these far-from-equilibrium conditions. However, it is likely that there is some catalytic effect between the phases that promotes rapid nucleation and growth after the initiation of a single phase. As stated previously, detailed elucidation of these nanoscale structural and chemical interactions are beyond the scope of the present study. Focusing on the devitrification sequence, we note that while the initial crystallization event remains unresolved from a temporal perspective, our in situ HEXRD studies, coupled with quantitative Reitveld analysis, permit reliable deconvolution of the secondary phase transformations that follow the primary crystallization process. Indeed, the growth of the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases and the simultaneous dissolution of the CuZr (B2) phase were well resolved in time, for the heating rate of 10 K/min (10 °C/min), as shown in Fig.6 (a).

Moreover, analysis of the DSC traces obtained for heating rates from 10 to 60 K/min (10 to 60 °C/min) indicate that while the characteristic temperatures exhibit a shift with heating rate, the transformation appears to remain isokinetic over this range, with a well defined net activation energy, suggesting that a common set of crystallization mechanisms are operative over this range. Accordingly, while the specific temperatures are influenced by heating rate, the HEXRD data collected at 10 K/min (10 °C/min) can be considered as representative of all rates in this range, from a mechanistic standpoint.

The sequence of metastable and stable phase formation, indicated by the DSC and HEXRD results, is consistent with the recently reported thermodynamic description of the CuZr system [22], as described in Fig.6 (b), where the Gibbs free energies of CuZr (B2), CuZr (B33), and the two-phase $\text{Cu}_{10}\text{Zr}_7 + \text{CuZr}_2$ mixture, are plotted as a function of temperature for the $\text{Cu}_{50}\text{Zr}_{50}$ composition. All free energies are given with respect to the liquid free energy, and the free energy of the glass is shown schematically to illustrate the devitrification sequence. It is clear that the driving force for all crystallization processes becomes rather large upon heating above T_x and T_g . The decomposition reaction producing $\text{Cu}_{10}\text{Zr}_7 + \text{CuZr}_2$ is the most strongly driven, but this process requires chemical partitioning and diffusion and is sluggish. The process with the second highest driving force is the partitionless transition to the CuZr (B2) phase, requiring only short-range atomic rearrangements. It is likely therefore that the nucleation of the CuZr (B2) phase initiates the crystallization response, but that chemical, interfacial, and volume effects associated with formation of the CuZr (B2) phase very quickly reduce the kinetic barriers that inhibit the highly driven formation of the stable $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases.

We now raise and briefly discuss three specific points. First, we assert that the structural similarity between CuZr_2 and CuZr ($B2$) provides an avenue for epitaxial-type transitions from one phase to the other during growth from the glass. This type of devitrification response has been suggested by previously reported experiments involving this system [17, 46] and other related alloys, such as Cu-Zr-Ti [55] and Cu-Zr-Ti-Pd [56]. Some of these observations involve “quenched in” nuclei, but we report that no such crystallites were observed in the melt-spun alloys investigated presently. Second, the structural similarity between the two phases would also serve to reduce the barrier to the re-precipitation of the CuZr ($B2$) phase from the $\text{Cu}_{10}\text{Zr}_7 + \text{CuZr}_2$ two phase structure, observed upon heating above 1002 K (729 °C), where this phase becomes stable (see Fig.5). Third, while Kneller reported [17] the formation of Cu_5Zr_8 during the continuous heating of $\text{Cu}_{50}\text{Zr}_{50}$ glass with a heating rate of 0.835 K/min (0.835 °C/min), this phase was not observed in the present work, consistent with the recent findings of Zhou and Napolitano [22]. These differing reports suggest that, while the presently reported devitrification sequence was consistently observed for heating rates from 10 to 60 K/min (10 to 60 °C/min), much lower heating rates may give rise to a very different phase selection response. Recently, Louzguine et al. [57] reported the formation of monoclinic martensitic type CuZr phase primarily in $\text{Cu}_{50}\text{Zr}_{50}$. However, in this study, neither of the previously reported [40, 48] CuZr martensitic transformation product phases ($B2 \rightarrow B19' + B33$) were observed under the devitrification conditions examined here. In addition to heating rate effects, such differences in observed crystallization products may arise from small differences in trace impurity content.

Conclusions

This analysis has provided a thermodynamically self-consistent description of devitrification in a $\text{Cu}_{50}\text{Zr}_{50}$ glass under constant-heating-rate (10 K/min (10 °C/min)) conditions, and the experimental observations are strengthened by quantitative modeling of the measured diffraction data. The sequence involves the formation of CuZr (B2), $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases from the amorphous precursor at 706 K (433 °C), decomposition of B2 into more stable $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 upon heat to 789 K (516 °C), re-precipitation of B2 upon heating above 1002 K (729 °C), accompanied by dissolution of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 until the transformation to B2 is complete at 1045 K (772 °C).

While several details have been quantitatively revealed, three important questions remain. First, how can the discrepancy be reconciled between our results and the reported finding of Kneller et al, where the Cu_5Zr_8 phase was observed in the devitrification sequence for this alloy (at the much lower heating rate of 0.835 K/min (0.835 °C/min))? This will require a more comprehensive investigation into the influence of heating rate. Secondly, can the rapid multiphase crystallization event be resolved sufficiently to distinguish the individual contributing phenomena? Third, what are the relative influences of chemical partitioning, diffusion, strain, and defect accommodation in phase selection and the evolution of structural? These are topics of ongoing investigation.

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Appendix

The modeled intensity, $I^M(Q, \phi)$ where Q is $\left(Q = \frac{4\pi \sin \theta}{\lambda}\right)$ for the general case can be written as

$$I^M(\lambda, \theta, \phi) = L(\lambda, \theta) \sum_p A_p(\lambda) s_p P_p(\lambda) PV_p(\theta) m_p(\theta) [F_p(\theta)]^2 \quad (2)$$

where the sum is taken over all phases (p), and where $L(\lambda, \theta)$ is the Lorentz polarization factor $\left(L(\lambda, \theta) = \frac{P_h(\lambda) + (1 - P_h(\lambda)) \cos^2 2\theta}{2 \sin^2 \theta \cos \theta}\right)$, $A(\lambda)$ is an absorption factor, which is not refined for constant wavelength data because the correction is indistinguishable from thermal motion effects, s_p is phase fraction weighting factor, P_p is a preferred orientation factor, $PV_p(\theta)$ is a pseudo-Voigt shape function (Type-2) which is a linear combination of Gaussian and Lorentzian functions, $m_p(\theta)$ is a multiplicity factor, $F_p(\theta)$ is the structure factor, and $P_h(\lambda)$ is the polarization fraction. For the work described here, we use a constant wavelength and set $P_h = 0.950$. In addition, we take P_p and m_p as unity. Thus, for the case described here, the model becomes

$$I(\theta) = L(\theta) \sum_p A_p s_p PV_p(\theta) |F_p(\theta)|^2 + I_b(\theta) \quad (3)$$

where the optimization simply involves fitting the remaining three parameters, s_p , $PV_p(\theta)$, and $F_p(\theta)$, where s_p is a scalar,

$$PV_p(\theta) = \eta L(\theta) + (1 - \eta)G(\theta) \quad (4)$$

and

$$\left| F_p(\theta) \right|^2 = \left| \sum_p f_p(\theta) e^{2\pi i(k \cdot \vec{r}_n)} \right|^2 \quad (5)$$

where η is a mixing parameter determines the mixture of Gaussian ($G(\theta)$) and Lorentzian ($L(\theta)$) components, f_p is an atomic scattering factor, $\vec{r}_n$ gives the atomic positions and the sum is taken over the unit cell. The background intensity, $I_b(\theta)$ were modeled using the sixth background profile function as

$$I_b(\theta) = B_1 + \sum_{j=1}^N \left(B_{2j} \frac{(4\pi \sin \theta / \lambda)^{2j}}{j!} + B_{2j+1} \frac{j!}{(4\pi \sin \theta / \lambda)^{2j}} \right) \quad (6)$$

where B_1 is a constant, N is number of coefficients and the values of B_j are determined by least squares during Rietveld refinement of pattern.

An example of profile fitting using Rietveld refinement is shown by the sequence in Fig.7 for three diffraction peaks corresponding to the CuZr (B2) structure with a space group of Pm-3m having atomic positions of Cu ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and Zr (0, 0, 0) at 1216 K (943 °C). The refinement is started from the raw data (Fig.7 (a)) and done in proper order of applying Lorentz-polarization and background functions (Fig.7 (b)), scale factor (Fig.7 (c)), structure factor including lattice parameters (Fig.7 (d)), Gaussian and Lorentzian peak profile functions (Fig.7 (e)) and structure factor including thermal motion using isotropic thermal displacement parameters (Uiso) (Fig.7 (f)).

Rietveld refinement provides an accurate determination of structural properties. After achieving a satisfactory profile fitting, the lattice parameter of B2 is found to change from 3.2810 Å (at room temperature) to 3.29616 Å when heated up to 1216 K (943 °C). A specific

benefit of the Rietveld analysis is that the refined model provides a quantitative phase analysis, where the weight fraction, w_i , of each crystalline constituent phase can be determined from the corresponding phase scale parameter, s_i according to the relationship

$$w_i = \frac{s_i Mu_i}{\sum_j s_j Mu_j} \quad (7)$$

where Mu_i is the unit cell mass. This analysis is based on the normalization condition $\sum w_i = 1.0$.

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Figure 1. The equilibrium Cu-Zr Phase Diagram [22].

Figure 2. (a) HEXRD diffraction pattern, (b) BF image with (c) corresponding SAED and (d) isochronal DSC plots at 10, 20, 30, 40, 50 and 60 K/min (10, 20, 30, 40, 50 and 60 $^{\circ}\text{C}/\text{min}$) with inset shows the DSC trace at 10 K/min (10 $^{\circ}\text{C}/\text{min}$) of the as-quenched $\text{Cu}_{50}\text{Zr}_{50}$ ribbons.

Figure 3. Characteristic temperatures determined for melt spun $\text{Cu}_{50}\text{Zr}_{50}$ from DSC traces at different heating rates (ϕ).

Figure 4. Two dimensional representations of diffraction pattern of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy during devitrification at 10 K/min (10 $^{\circ}\text{C}/\text{min}$).

Figure 5. Rietveld refined diffraction patterns for the data collected at (a) 706 K (433 °C), (b) 789 K (516 °C), (c) 1002 K (729 °C) and (d) 1045 K (772 °C). The vertical marks indicate the reflections for the $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases below the XRD plots in (a) and (c), $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases below the XRD plot in (b), and B2 phase below the XRD plot in (d) from top to bottom, respectively.

Figure 6. (a) Weight fractions of $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases during continuous heating of $\text{Cu}_{50}\text{Zr}_{50}$ alloy at 10 K/min (10 °C/min). (b) Free energy curves of metastable and stable phases in $\text{Cu}_{50}\text{Zr}_{50}$ system in the same temperature range [22].

Figure 7. An example of Rietveld refinement sequence of CuZr (B2) phase at 1216 K (943 °C) (a-f); starting with (a) raw data, and refining with (b) Lorentz-polarization factor and background function, (c) phase scalar factor, (d) structure factor including lattice parameters, (e) Gaussian and Lorentzian peak profile functions and (f) isotropic thermal displacement parameters. The goodness of fit factors are given inset the figures.

Table 1. Stable and metastable (*) phases reported in the Cu-Zr system.

<i>Stoichiometry</i>	<i>Prototype</i>	<i>Structural Designation</i>	<i>Space Group</i>	<i>Ref.</i>
Cu	Cu	A1	$Fm\bar{3}m$	[23]
Cu ₅ Zr	AuBe ₅		$F\bar{4}3m$	[24-27]
Cu ₉ Zr ₂				[28]
Cu ₅₁ Zr ₁₄	Ag ₅₁ Gd ₁₄		$P6/m$	[29, 30]
Cu ₇ Zr ₂ *			$C2/m$	[31]
Cu ₃ Zr*			$P6_3/mmc$	[32]
Cu ₈ Zr ₃	Cu ₈ Hf ₃		$Pnma$	[29, 33]
Cu ₂ Zr			$Fd\bar{3}m$	[34]
Cu ₂₄ Zr ₁₃				[35]
Cu ₁₀ Zr ₇			$Aba2$	[27, 29]
Cu ₁₀ Zr ₇	Ni ₁₀ Zr ₇		$Cmca$	[36]
Cu ₁₀ Zr ₇			$Pbca$	[37]
Cu ₁₁ Zr ₉			$I4/m$	[38]
CuZr	CsCl	B2	$Pm\bar{3}m$	[39]
CuZr*		B19'	$P2_1/m$	[40]
CuZr*		B33	$Cmcm$	[41]
CuZr*	γ -CuTi	B11	$P4/nmm$	[42]
CuZr*	AuCu-I	L1 ₀	$P4/mmm$	[42]
CuZr*	β -AuCd	B19	$Pmma$	[42]
Cu ₅ Zr ₈			$R3m$	[43]
Cu ₅ Zr ₈			$I\bar{4}3m$	[44]
Cu ₅ Zr ₈				[35]
β CuZr ₂	MoSi ₂	C11 _b	$I4/mmm$	[45]
β Zr	W	A2	$Im\bar{3}m$	[42]
α Zr*	Mg	A3	$P6_3/mmc$	[43]

Table 2. Summary of model intensity parameters for Reitveld refinement

<i>Parameters</i>	<i>Symbol</i>	<i>Equation</i>
<i>Lorentz-polarization factor</i>	$L(\lambda, \theta)$	$\left(L(\lambda, \theta) = \frac{P_h(\lambda) + (1 - P_h(\lambda)) \cos^2 2\theta}{2 \sin^2 \theta \cos \theta} \right)$
<i>Pseudo-Voigt shape function</i>	$PV_p(\theta)$	$PV_p(\theta) = \eta L(\theta) + (1 - \eta) G(\theta)$
<i>Structure factor</i>	$F_p(\theta)$	$\left F_p(\theta) \right ^2 = \left \sum_p f_p(\theta) e^{2\pi i(k \cdot \vec{r}_n)} \right ^2$
<i>Polarization fraction</i>	$P_h(\lambda)$	
<i>Background intensity</i>	$I_b(\theta)$	$I_b(\theta) = B_1 + \sum_{j=1}^N \left(B_{2j} \frac{(4\pi \sin \theta / \lambda)^{2j}}{j!} + B_{2j+1} \frac{j!}{(4\pi \sin \theta / \lambda)^{2j}} \right)$
<i>Preferred orientation</i>	P_p	$P_p = \frac{1}{N} \sum_{i=1}^N \left[1 + (\tau^2 - 1) \cos^2 \phi \right]^{-1/2} *$
<i>Absorption</i>	$A(\lambda)$	$\left(A = \frac{1}{V} \int_V \exp(-\mu_{\text{eff}} l) dV \right) **$
<i>Phase fraction weighting factor</i>	s_p	
<i>Multiplicity</i>	$m_p(\theta)$	

* The sum is taken over a systematically equivalent reciprocal lattice points and τ is preferred orientation parameter.

** In the equation, V is volume of the sample, l is the total path of both incident and diffracted beam through the sample, μ_{eff} is an effective linear absorption coefficient.

See appendix for details.

Table 3. Fitted model parameters during Rietveld refinement

<i>Profile Parameters</i>			<i>706 K (433 °C)</i>	<i>789 K (516 °C)</i>	<i>1002 K (729 °C)</i>	<i>1045 K (772 °C)</i>
<i>Phase Scale Factor</i>	<i>Cu₁₀Zr₇</i>		0.0015 <u>3</u>	0.0024 <u>3</u>	0.0025 <u>0</u>	—
	<i>CuZr₂</i>		0.008 <u>8</u>	0.014 <u>4</u>	0.014 <u>4</u>	—
	<i>CuZr (B2)</i>		0.047 <u>8</u>	—	0.001 <u>8</u>	0.15 <u>0</u>
<i>Background Coefficients</i>	<i>B1</i>		0.4065E+02	0.4066E+02	0.3930E+02	0.3599E+02
	<i>B2</i>		0.9389E+01	0.8750E+01	0.1121E+02	0.1746E+02
	<i>B3</i>		-0.1643E-01	-0.1378E-01	-0.1792E-01	-0.9859E-02
	<i>B4</i>		-0.8928E+00	-0.8310E+00	-0.9286E+00	-0.1628E+01
	<i>B5</i>		0.1207E-05	0.1103E-05	0.1372E-05	0.7277E-06
	<i>B6</i>		0.5815E-01	0.544E-01	0.5217E-01	0.9526E-01
	<i>B7</i>		-0.5891E-11	-0.5437E-11	-0.6727E-11	-0.3555E-11
	<i>B8</i>		-0.1818E-02	-0.1712E-02	-0.1454E-02	-0.2647E-02
<i>Profile Functions</i>	<i>Cu₁₀Zr₇</i>	<i>GW</i>	0.4706E-01	0.2068E+00	0.1551E+00	—
		<i>LX</i>	0.2474E+01	0.1667E+01	0.1705E+01	
		<i>LY</i>	0.3886E+02	0.2996E+02	0.8943E+01	
	<i>CuZr₂</i>	<i>GW</i>	0.3247E-01	0.1310E+00	0.2090E+00	—
		<i>LX</i>	0.5753E+01	0.1901E+01	0.1700E+01	
		<i>LY</i>	0.2766E+02	0.3607E+02	0.1417E+00	
	<i>CuZr (B2)</i>	<i>GW</i>	0.6489E+00	—	0.2110E+00	0.2273E+00
		<i>LX</i>	0.7521E+00		0.7330E+00	0.1364E+01
		<i>LY</i>	0.6568E+02		0.2891E+02	0.4896E+01

Table 4. Structural parameters refined during Rietveld modeling

<i>Structure Parameters</i>				<i>706 K (433 °C)</i>	<i>789 K (516 °C)</i>	<i>1002 K (729 °C)</i>	<i>1045 K (772 °C)</i>
<p><i>Cu₁₀Zr₇</i></p> <p> Zr Cu </p>	<i>Lattice parameters</i>	<i>a</i>		12.714 [†]	12.717	12.7249	—
		<i>b</i>		9.415	9.411	9.442	—
		<i>c</i>		9.414	9.415	9.450	—
	<i>Atomic sites</i>	<i>Atom</i>	<i>Wyckoff</i>	x, y, z	x, y, z	x, y, z	x, y, z
		<i>Cu</i>	<i>16 g</i>	0.144, 0.020, 0.209	0.144, 0.018, 0.201	0.143, 0.024, 0.210	—
			<i>16 g</i>	0.358, 0.294, 0.008	0.358, 0.287, 0.009	0.357, 0.295, 0.010	
			<i>8 f</i>	0.000, 0.105, 0.390	0.000, 0.106, 0.393	0.000, 0.103, 0.398	
		<i>Zr</i>	<i>8 f</i>	0.000, 0.309, 0.200	0.000, 0.309, 0.200	0.000, 0.309, 0.199	
			<i>8 e</i>	0.250, 0.264, 0.250	0.250, 0.264, 0.250	0.250, 0.269, 0.250	
			<i>8 d</i>	0.3074, 0.000, 0.000	0.3076, 0.000, 0.000	0.3076, 0.000, 0.000	
			<i>4 a</i>	0.000, 0.000, 0.000	0.000, 0.000, 0.000	0.000, 0.000, 0.000	
	<i>Uiso</i>	<i>Cu</i>	<i>16 g</i>	0.010	0.012	0.038	—
			<i>16 g</i>	0.013	0.021	0.022	
			<i>8 f</i>	0.031	0.035	0.035	
		<i>Zr</i>	<i>8 f</i>	0.031	0.027	0.028	
			<i>8 e</i>	0.013	0.015	0.029	
			<i>8 d</i>	0.024	0.021	0.028	
			<i>4 a</i>	0.028	0.026	0.046
<p><i>CuZr₂</i></p>	<i>Lattice parameters</i>	<i>a, b</i>		3.2426	3.2354	3.2419	—
		<i>c</i>		11.163	11.231	11.2651	—
	<i>Atomic sites</i>	<i>Atom</i>	<i>Wyckoff</i>	x, y, z	x, y, z	x, y, z	x, y, z
		<i>Cu</i>	<i>2 a</i>	0.000, 0.000, 0.000	0.000, 0.000, 0.000	0.000, 0.000, 0.000	—
		<i>Zr</i>	<i>4 e</i>	0.000, 0.000, 0.3467	0.000, 0.000, 0.3463	0.000, 0.000, 0.3464	—
	<i>Uiso</i>	<i>Cu</i>	<i>2 a</i>	0.029	0.029	0.047	—
		<i>Zr</i>	<i>4 e</i>	0.018	0.017	0.029	—
<p><i>CuZr (B2)</i></p>	<i>Lattice parameters</i>	<i>a, b, c</i>		3.2778	—	3.2880	3.28952
	<i>Atomic sites</i>	<i>Atom</i>	<i>Wyckoff</i>	x, y, z	x, y, z	x, y, z	x, y, z
		<i>Cu</i>	<i>1 b</i>	0.500, 0.500, 0.500	—	0.500, 0.500, 0.500	0.500, 0.500, 0.500
		<i>Zr</i>	<i>1 a</i>	0.000, 0.000, 0.000	—	0.000, 0.000, 0.000	0.000, 0.000, 0.000
	<i>Uiso</i>	<i>Cu</i>	<i>1 b</i>	0.036	—	0.01 [†]	0.062
		<i>Zr</i>	<i>1 a</i>	0.021	—	0.02 [†]	0.047

CHAPTER 3: ISOTHERMAL CRYSTALLIZATION KINETICS AND PHASE SELECTION DYNAMICS IN $\text{Cu}_{50}\text{Zr}_{50}$ METALLIC GLASS

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Abstract

The crystallization kinetics and microstructural dynamics associated with devitrification of a $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass were investigated using isothermal (671 K) treatments of melt-spun amorphous ribbons, in-situ high-energy synchrotron X-ray diffraction (HEXRD), conventional and high resolution transmission electron microscopy (TEM and HRTEM), and differential scanning calorimetry (DSC). Consistent with previously reported constant-heating raret (CHR) experiments, the isothermal devitrification response was found to involve the $\text{Cu}_{10}\text{Zr}_7$, CuZr (B2), and CuZr_2 phases. However, the observed microstructural dynamics are very different from the CHR behavior. Under the conditions studied here, the isothermal transformation starts with the formation of the $\text{Cu}_{10}\text{Zr}_7$ phase, which grows in a generally equiaxed morphology. At a size of approximately 100 nm, the growth of the $\text{Cu}_{10}\text{Zr}_7$ particles is interrupted by the precipitation of a thin layer

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of the CuZr_2 phase upon which the metastable CuZr (B2) grows epitaxially. Crystallization kinetics are quantified here through in-situ measurements (HEXRD, DSC) and post-situ microstructural analysis (TEM, HRTEM). The overall transformation kinetics are modeled using a JMAK approach, and a related isothermal-transformation diagram is reported. Finally, the influence of chemical partitioning, diffusion, and crystallographic orientation on this sequence are examined.

Introduction

The Cu-Zr binary system has been observed to exhibit several remarkable characteristics, including very good (even “bulk”) glass-forming ability [1-6], a large glass-forming composition range (~35-70 at% Cu) [1, 2, 7], and a variety of possible devitification pathways [8-12] during which numerous stable and metastable phases may compete and contribute to a broad spectrum of complex nano-scale crystalline and amorphous-crystalline structures [13-19]. Moreover, the Cu-Zr binary system has served as a base system for the development of several “bulk” metallic glass alloys, as shown in Table 1, which exhibit low critical cooling rates and, therefore, can be cast as amorphous alloys even in relatively large cross sections [20-24]. Motivated by the potential technological benefits of attaining new or enhanced properties through the control of nano-scale devitrification structures, the Cu-Zr binary system represents both an excellent model for scientific discovery as well as a starting point for new alloys intended for specific functionality.

We have previously reported that constant-heating-rate treatments give rise to a rapid crystallization response, where the essentially simultaneous formation of three phases ($\text{Cu}_{10}\text{Zr}_7$, CuZr (B2) and CuZr_2) [25]. While our previous study revealed several details concerning post-crystallization transformations involving these phases, the kinetics

associated with the crystallization of the individual phases were not resolved. In the work reported here, we use isothermal treatments to probe the mechanisms of crystallization and to systematically investigate the transformation kinetics and nano-scale dynamics associated with devitrification of the $Cu_{50}Zr_{50}$ glass[†]. With differential thermal analysis (DSC), we quantify the kinetics over a range of temperatures. Using synchrotron-based high energy X-ray diffraction (HEXRD), we identify the relevant phases and isolate the transformation kinetics of each. Through transmission electron microscopy (TEM), we examine the nano-scale structures at different stages of the devitrification process and uncover the details related to the complex transformation sequence such as the orientation relationships between the participating phases and the extent of chemical partitioning and diffusion.

The Cu-Zr binary phase diagram has recently been assessed, as shown in Fig.1 [26]. For compositions near the $Cu_{50}Zr_{50}$ alloy, the most relevant phases to consider as possible contributors to the devitrification behavior are $Cu_{10}Zr_7$, CuZr (B2), $CuZr_2$ phases, which appear on the equilibrium phase diagram, as well as the CuZr (B19' and B33) phases which do not. Important characteristics of these phases are summarized in Table 2 [27-34].

Reported studies [8, 11, 35, 36] of devitrification in $Cu_{50}Zr_{50}$ suggest that the decomposition and/or structural relaxation of the glass may occur through a range of transformation pathways, where phase selection, growth morphology, and final microstructure all depend on the thermal history. Early reports by Altonuian, based on XRD patterns for melt-spun ribbons isothermally annealed at 823 K, suggested that devitrification

[†] The italics used here are intended to distinguish an alloy composition from a specific stoichiometric compound or alloy phase.

occurs in a single-step reaction involving the simultaneous formation of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 [8]. Lu et al. used Field Ion Microscopy (FIM) to study CHR treatment of $\text{Cu}_{50}\text{Zr}_{50}$ melt spun ribbons, reporting a two-step process in which $\text{Cu}_{10}\text{Zr}_7$ precipitates first from the amorphous alloy at 723 K, followed by the CuZr_2 phase at 773 K [35]. For constant heating at a very low rate (0.835 K/min), Kneller et al. later reported that the nucleation of the CuZr (B2) phase, which is metastable at low temperature, precedes the formation of the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases [11]. According to CHR HEXRD analysis at 973 K, Pauly et al. reported that $\text{Cu}_{50}\text{Zr}_{50}$ glass devitrifies in a single step into $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 [36]. One of the challenges associated with investigating these transformations is that the X-ray diffraction patterns for the relevant phases are largely overlapping and difficult to deconvolute. Apply a quantitative modeling approach to analyze the diffraction patterns, we recently reported that, at a constant heating rate of 10 K/min, the initial devitrification event result in the rapid formation of the CuZr (B2), $\text{Cu}_{10}\text{Zr}_7$, and CuZr_2 phases (in the relative amounts of 37.8, 39.9, and 22.3 wt %), followed by the gradual decomposition of the metastable CuZr (B2) into the two more stable phases [25]. Following our previous work [25], the present analysis employs isothermal treatments, where low temperatures can be utilized to show the crystallization reaction, permitting more detailed analysis of kinetics and structural dynamics.

Experimental Methods

An ingot of $\text{Cu}_{50}\text{Zr}_{50}$ nominal composition was prepared from high purity constituents (0.9999 Cu and 0.999(5) Zr, by weight) by arc melting under an argon atmosphere. The alloy ingot was remelted and quenched on a water-cooled copper hearth three times to obtain good chemical homogeneity. The rapidly solidified amorphous ribbons with a width of 2.5 mm and a thickness of 45 μm were produced using Cu-block single-roller free-jet melt spinning

[37, 38] with a tangential wheel velocity of 25 m/s under 1/3 atm He. Thermal analysis of the as-quenched ribbons was done using DSC under isothermal annealing conditions. For each DSC analysis, a sample weight of 10.00 mg was used where the second run with an empty sample pan was served as a baseline. For the isothermal studies, amorphous ribbons were initially heated with a heating rate of 100 K/min to a fixed temperature below T_x and then maintained at that temperature for a certain period of time until the crystallization was completed.

In-situ HEXRD was used to examine the as-quenched alloy and to investigate the devitrification sequence under isothermal heating conditions at 673 K. HEXRD patterns were collected using synchrotron X-rays of 99.586 keV ($\lambda=0.0124(5)$ nm) in Debye-Scherrer geometry using a charge-coupled device (CCD) with an exposure time of 15 s. For the HEXRD experiments, the as-quenched ribbons were first cut into 12 mm lengths, and then stacked as a group 40 and placed into a thin walled quartz capillary tube. Each tube was sealed under an Ar atmosphere to prevent any oxidation or contamination during in-situ HEXRD runs. The samples were heated up to 673 K with a rate of 100 K/min and kept at that temperature for a certain period of time until crystallization was complete. The analysis of HEXRD data was performed using Rietveld refinement [25]. Rietveld refinement was performed on the HEXRD pattern of the fully crystallized ribbons. Furthermore, microstructural analysis of the isothermally annealed ribbons was performed using transmission and high resolution electron microscopy (TEM, HRTEM). The TEM samples were first heated up to a certain temperature with a heating rate of 100 K/min, maintained at that temperature isothermally for different periods of time and then quenched rapidly to the R.T using DSC. Then, the samples were thinned using double jet polishing at 242 K and a

voltage of 10 V with an etching solution of 33 vol. % HNO_3 and 67 vol. % methanol. Quantitative microchemical analysis was performed using energy dispersive X-ray spectroscopy (EDS).

Results

The isothermal DSC curves obtained at different annealing temperatures are shown in Fig.2 (a), where each DSC scan exhibits a single apparent exothermic peak related to the overall multiphase crystallization process. The basic characteristics of these data are that peak height increases, peak width decreases, and onset time decreases with increasing annealing temperature. The crystallized volume fraction, x , is plotted as a function of annealing time in Fig.2 (b) obtained by integrating the area under the exothermic DSC peak. The corresponding isothermal transformation (IT) diagram is plotted in Fig.3 (a), summarizing the observed overall crystallization response. In the IT diagram, 1, 50 and 99 % of crystallization were shown as functions of time and temperature. The transformation time $t(x)$ has an Arrhenius relationship with annealing temperature due to a following equation;

$$t(x) = t_0 \exp[E(x) / RT] \quad (1)$$

where $E(x)$ is the local activation energy for nucleation, t_0 is a constant, R is the gas constant and T is the isothermal annealing temperature. The local activation energy of amorphous to crystallization phase transformation is calculated from the slopes of the Arrhenius plots given in Fig.3 (b). The dependence of activation energy on crystallized fraction was given in Fig.3 (c). It is seen that the activation energy is changing throughout the crystallization.

The in-situ diffraction patterns measured during isothermal annealing at 673 K are shown in Fig.4. The patterns were indexed due to correlate interplanar spacing values for the three phases; $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2). However, because of the overlapping and common diffraction peaks, Rietveld refinement was used to model the most crystallized HEXRD diffraction pattern taken at 75 min. The optimized HEXRD pattern is shown in Fig.5, yielding computed phase fractions of 0.38, 0.22 and 0.40 (by weight) for $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) respectively.

While DSC analysis indicates a single step crystallization under isothermal annealing conditions, Rietveld analysis of HEXRD pattern shows the formation of three phases; $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2). The questions arising from these analyses are; can multi-phase crystallization be resolved and can the pathway of phase selection be determined? To answer these questions; microstructural analysis was performed on isothermally annealed and interrupted quench ribbons using TEM and HRTEM. The annealing times of the TEM samples were indicated on the isothermal DSC curve at 671 K in Fig.2 (b). Fig.6 (a) indicates the HRTEM image of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons that were annealed at 671 K for 23 min. The inset figures show the corresponding fast Fourier transform (FFT) patterns taken from different regions of HRTEM image. Even though the annealing time is very short (see Fig.2 (b)) relative to the overall transformation time, FFT pattern taken from region “a1” detects fine nanocrystals with a size of 3-5 nm embedded in the amorphous matrix which is confirmed by the diffuse scattering peaks obtained from “a2”, “a3” and “a4” regions. These nanocrystals in “a1” were identified as $\text{Cu}_{10}\text{Zr}_7$ which indicates that $\text{Cu}_{10}\text{Zr}_7$ is a primary crystallization phase during the isothermal annealing of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons at 671 K. Fig.6 (b) shows the growth of $\text{Cu}_{10}\text{Zr}_7$ crystal upon annealing up to 30 min. No other crystal structure was

detected up to this annealing time which further confirms the primary formation of $\text{Cu}_{10}\text{Zr}_7$ phase.

Fig.7 shows the BF image with corresponding SAED pattern and EDS mapping of $\text{Cu}_{10}\text{Zr}_7$ crystal after 37 min. of annealing. EDS mapping clearly shows the chemical partitioning where Cu concentration is high within the crystalline region with respect to $\text{Cu}_{50}\text{Zr}_{50}$ amorphous matrix which results an accumulation of Zr atoms around the $\text{Cu}_{10}\text{Zr}_7$ crystals. Besides $\text{Cu}_{10}\text{Zr}_7$ crystals, plate-like structures with a size of 10-20 nm in length were detected in the amorphous matrix. Because of their small sizes, it is difficult to determine the exact nucleation time for plate-like nanocrystals however, during earlier annealing time, those structures were not be observed or identified.

BF-image of isothermally annealed $\text{Cu}_{50}\text{Zr}_{50}$ alloy for 37 min, in Fig.8 (a), shows the nucleation of nodular-like crystals around $\text{Cu}_{10}\text{Zr}_7$. The analysis of corresponding HRTEM image in Fig.8 (b) taken from the area “A” in Fig.8 (a) indicates that the growth of $\text{Cu}_{10}\text{Zr}_7$ crystal was restricted by the nucleation of CuZr_2 which facilitates the nucleation of CuZr (B2) phase. This is further supported by the composition profile data collected by EDS along the line (A-A’) on the HAADF image of isothermally annealed $\text{Cu}_{50}\text{Zr}_{50}$ alloy for 44 min, as shown in Fig.9 (a). The line profile analysis in Fig.9 (b) clearly demonstrates that the $\text{Cu}_{10}\text{Zr}_7$ crystal was surrounded by a thin layer of CuZr_2 and then CuZr (B2). It is clear that CuZr_2 crystals nucleated when the composition at the interface of $\text{Cu}_{10}\text{Zr}_7$ crystal with a size of 100-150 nm range approached to that of CuZr_2 . From the Fig.8 (a) which shows the crystallographic relationship between $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) crystals, a special epitaxy were found between CuZr_2 and CuZr (B2) crystals which facilitates the nucleation of CuZr (B2) crystals.

Further annealing for 49 min. indicates the growth of CuZr (B2) phase on CuZr₂ crystals, as seen in Fig.10 (a). Fig.10 (b) shows the distribution of these crystals in the amorphous matrix and Fig.11 indicates the impingement of the crystals at the end of the crystallization.

Discussion

The DSC analysis of isothermally annealed $Cu_{50}Zr_{50}$ amorphous alloy at different temperatures indicates a single crystallization peak, as seen in Fig.2. Even though only one crystallization peak is observed in DSC thermograph, Rietveld refined HEXRD pattern, in Fig.5, indicates formation of three phases; Cu₁₀Zr₇, CuZr₂ and CuZr (B2) for the isothermally annealed $Cu_{50}Zr_{50}$ amorphous alloy at 671 K for 75 min. Our previous results [25] on the devitrification of $Cu_{50}Zr_{50}$ have also showed the formation of these three phases under continuous heating conditions. The variation of activation energy throughout the whole crystallization process (Fig.3 (c)) also indicates that crystallization kinetics is not constant.

Herein, the microstructural analysis were performed using TEM in several modes helped us to characterize the early stage crystallization mechanism and phase selection pathway. The microstructural analysis has been carried out at different annealing stages, which are indicated on the DSC crystallization plot at 671 K, in Fig.2 (a). HRTEM analysis in Fig.6 (a) reveals the nucleation of fine Cu₁₀Zr₇ crystals with a size of 3-5 nm in the amorphous precursor. Primary nucleation of Cu₁₀Zr₇ in the isothermally annealed $Cu_{50}Zr_{50}$ amorphous alloy is not surprising because it is one of the phases expected from the HEXRD analysis for both isothermal (present work) and continuous heating [25] conditions. It is known that Cu is a rapid diffuser than Zr which may facilitate the initial nucleation of Cu₁₀Zr₇ in $Cu_{50}Zr_{50}$ glass. Thermodynamically, phase selection dynamics are greatly related

to the Gibbs free energies of potential phases. Zhou and Napolitano [26] recently evaluated the model parameters used in the calculation of Gibbs free energies of formation in Cu-Zr system. Based on these parameters, the Gibbs free energies were calculated for several related Cu-Zr phases at 671 K, as listed in Table 3. Among these phases, $\text{Cu}_{10}\text{Zr}_7$ has the highest negative free energy which further indicates the highest driving force for the formation of this phase.

Further annealing of $\text{Cu}_{50}\text{Zr}_{50}$ alloy indicates the growth of $\text{Cu}_{10}\text{Zr}_7$ until the average size of the crystals reaches to 100-150 nm. The quantitative analysis indicates the Cu-depletion at the interface of these $\text{Cu}_{10}\text{Zr}_7$ crystals which facilitates the nucleation of CuZr_2 . From the Cu-Zr phase diagram, $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 might be expected to nucleate in a coupled eutectoid manner; however, here we showed the sequence of formation starts with $\text{Cu}_{10}\text{Zr}_7$. Then, the thin layer of CuZr_2 prefers to nucleate when the interface composition of the $\text{Cu}_{10}\text{Zr}_7$ crystals reaches to that of CuZr_2 . Here we should note that, we did not observe the Zr-rich Cu_5Zr_8 phase either from TEM or HEXRD analysis. This also supports our previous results on continuous heating analysis for $\text{Cu}_{50}\text{Zr}_{50}$ alloy [25] and Napolitano and Zhou's findings [26]. Besides $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 , HRTEM analysis under both isothermal and isochronal conditions pointed out the contribution of large amount of CuZr (B2) phase during the devitrification of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy. The Rietveld refined diffraction plot in Fig.5 determined the CuZr (B2) with a phase fraction of 0.394 (by weight) for the isothermally annealed ribbons at 673 K for 78 min. The HRTEM analysis has revealed that CuZr (B2) prefers CuZr_2 as a nucleation site. Indeed, the similarity between the atomic configurations and the lattice parameters of CuZr_2 and CuZr (B2) helps to explain why CuZr (B2) takes CuZr_2 as a preferential nucleation site. This is further explained by the special

epitaxy determined between the CuZr_2 and CuZr (B2) crystals from the HRTEM in Fig.8 (b). Possible relationship between these phases is shown in Fig.12, schematically. Here it is clearly seen that CuZr_2 and CuZr (B2) phases prefer to share the interface coherently using the Cu atoms in [010] direction which requires only short range arrangements. Thus, during the atomic rearrangements, the lattice parameter of CuZr_2 (3.24 Å) enlarges to that of the CuZr (B2) (3.28 Å) which creates strains on the lattices of CuZr (B2) structure. Consequently, the crystallographic orientation between CuZr_2 and CuZr (B2) phase can be written from the HRTEM image, in Fig.8 (b) as $[001]_{\text{B2}} // [001]_{\text{CuZr}_2}$; $(100)_{\text{B2}} // (100)_{\text{CuZr}_2}$. It is widely known that the metastable phases nucleate with a high rate because of their smaller surface energies [39]. Here, we believe that this epitaxy decreases the surface energy and facilitates the nucleation and growth of CuZr (B2) without long range diffusion.

In both of our studies on the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ amorphous alloy under constant heating rate and isothermal annealing conditions, we determined three phases; $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) take place during the initial crystallization of $\text{Cu}_{50}\text{Zr}_{50}$ glass. Kneller [11] reported that CuZr (B2) initiates the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ amorphous alloy which is immediately followed by the precipitation of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 using HEXRD. Here, we revealed the phase pathway by microstructural analysis that the crystallization started with $\text{Cu}_{10}\text{Zr}_7$, followed by CuZr_2 and then continued with CuZr (B2). Yamamoto et al. [40] reported the precipitation of metastable CuZr (B2) phase during the crystallization of $\text{Cu}_{50}\text{Zr}_{50}$ and ternary alloys of $\text{Cu}_{50-x}\text{Zr}_{50}\text{Al}_x$ ($x=4,6$). Their XRD results on rapidly heated metal plates of these three compositions indicate the formation of $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) at 800 K which is well below the stability of CuZr (B2) (which is 1002 K) [25, 26]. They concluded that CuZr (B2) precipitates primarily in ternary alloys and precipitates in $\text{Cu}_{50}\text{Zr}_{50}$

metallic glass while rapidly heated up to 800 K and cooled down. On the contrary, Louzguine et al. [41] reported the primary nucleation of monoclinic martensitic type CuZr phase in $Cu_{50}Zr_{50}$ glass, however, this phase were not observed in this study. Another finding of the current work is the nucleation of high population of platelike structures in the amorphous matrix, seen in Fig.7. These platelike crystals might be another metastable or one of a stable phase already observed during devitrification sequence. However, because of their small sizes and common diffraction data, they could not be detected with HEXRD or resolved by TEM, well. Therefore, the incubation time for platelike crystals is not very well defined. These structures are still under investigation. Based on the HEXRD and TEM analysis, the crystallization and phase selection mechanism in isothermally annealed $Cu_{50}Zr_{50}$ amorphous alloy is shown schematically in Fig.13. This analysis has determined the devitrification pathway of amorphous $Cu_{50}Zr_{50}$ alloy under isothermal annealing conditions. The analysis results show that $Cu_{50}Zr_{50}$ glass devitrifies into $Cu_{10}Zr_7$ primarily, and followed by platelike structures embedded in the amorphous matrix, and $CuZr_2$ nucleates on $Cu_{10}Zr_7$ and finally CuZr (B2) crystal nucleates around $CuZr_2$ at the end of the crystallization process.

Conclusions

The current study investigated the devitrification mechanism and phase selection pathway in $Cu_{50}Zr_{50}$ amorphous alloy under isothermal annealing conditions. We previously reported that glassy $Cu_{50}Zr_{50}$ alloy initially devitrifies into metastable CuZr (B2), $Cu_{10}Zr_7$ and $CuZr_2$ by in-situ HEXRD analysis during constant-heating rate conditions. The present analysis reveals the sequence of phase formation using TEM with HEXRD under isothermal annealing conditions. The results indicate the primary nucleation of $Cu_{10}Zr_7$ in the amorphous precursor which is followed by the nucleation of $CuZr_2$. A special epitaxy

determined between CuZr_2 and CuZr (B2) results in the nucleation of CuZr (B2) on CuZr_2 crystals. During the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ glass, the nano-size plate-like structures embedded in the amorphous matrix were observed under TEM studies.

This study has revealed and resolved the details of rapid multiphase crystallization event in $\text{Cu}_{50}\text{Zr}_{50}$ glass under isothermal annealing conditions. The analysis indicates that the phase selection mechanism during crystallization is similar in both isothermal annealing and continuous heating rate cases. The effects of nano platelike crystals on the crystallization pathway need further investigations.

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Table 1. Thermal parameters (supercooled liquid region, $\Delta T_x (=T_x - T_g$ where T_x is the crystallization temperature and T_g is the glass transition temperature) and reduced glass transition temperature, $T_{rg} (=T_g/T_l$ where T_l is the liquidus temperature)) and critical sample diameters (d_c) of several Cu-Zr based bulk metallic glass alloys.

Alloy	ΔT_x	$T_{rg}(=T_g/T_l)$	d_c (mm)	Ref.
$\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$	76	0.61	3	[20]
$\text{Cu}_{50}\text{Zr}_{43}\text{Al}_7$	71	0.613	4	[21]
$\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$	73	0.60	6	[22]
$\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$	100	0.60	10	[20]
$\text{Cu}_{38}\text{Zr}_{46}\text{Ag}_8\text{Al}_8$	103	0.604	20	[24]
$\text{Cu}_{34}\text{Zr}_{48}\text{Ag}_8\text{Al}_8\text{Pd}_2$	99	0.611	30	[23]

Table 2. Important characteristics of $\text{Cu}_{10}\text{Zr}_7$, CuZr (B2), CuZr_2 phases.

Stoichiometry	Prototype	Structural Designation	Space Group	Ref.
$\text{Cu}_{10}\text{Zr}_7$	$\text{Ni}_{10}\text{Zr}_7$		<i>Aba2</i>	[27, 28]
$\text{Cu}_{10}\text{Zr}_7$			<i>Cmca</i>	[29]
$\text{Cu}_{10}\text{Zr}_7$			<i>Pbca</i>	[30]
CuZr	CsCl	B2	$Pm\bar{3}m$	[31]
CuZr^*		B19'	$P2_1/m$	[32]
CuZr^*		B33	<i>Cmcm</i>	[33]
βCuZr_2	MoSi_2	C11_b	<i>I4/mmm</i>	[34]

Table 3. Gibbs free energy of formation of some of the Cu-Zr phases [26]

<i>Phase</i>	<i>Parameter</i>	<i>kJ/mol (at 671K)</i>
Cu ₁₀ Zr ₇	$\Delta G^{Cu_{10}Zr_7}$	-17.41
CuZr ₂	ΔG^{CuZr_2}	-13.40
CuZr (B2)	ΔG^{B2}	-14.26
B33	ΔG^{B33}	-13.81
B19'	$\Delta G^{B19'}$	-13.85

Fig.1. The equilibrium Cu-Zr Phase Diagram [26].

Fig.2. (a) Isothermal DSC plots and (b) corresponding crystallization curves at different annealing temperatures of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy. The letters on the crystallization curve at 671 K indicate the annealing times of the TEM samples.

Fig.3. (a) Isothermal transformation (IT) diagram, (b) Arrhenius plots of the transformation time as a function of temperature and (c) the variation of local activation energy with crystallized fraction for amorphous $Cu_{50}Zr_{50}$ alloy.

Fig.4. In-situ HEXRD patterns of isothermally annealed amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy at different annealing times at 673 K.

Fig.5. Rietveld refined diffraction data of annealed $\text{Cu}_{50}\text{Zr}_{50}$ alloy at 673 K for 78 min. The observed and the calculated data are represented by “•” and “—” symbols, respectively. A difference curve and the vertical marks giving the reflections for $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) type structures (from top to bottom, respectively) are displayed below the HEXRD plot.

Fig.6. (a) HRTEM image of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons isothermally annealed at 671 K for 23 min.

Inset: Corresponding Fourier transform FFT patterns where a1 shows the $\text{Cu}_{10}\text{Zr}_7$ nanocrystals at $[334]$ zone axis and a2, a3, a4 indicate amorphous regions. (b) BF image of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons isothermally annealed at 671 K for 30 min with corresponding SAED pattern of $\text{Cu}_{10}\text{Zr}_7$ crystal at $[-2,3,3]$ zone axis.

Fig.7. BF image of Cu₅₀Zr₅₀ ribbons isothermally annealed at 671 K for 37 min. Inset: EDS mapping and SAED pattern of the Cu₁₀Zr₇ crystal at [100] zone axis.

Fig.8. (a) BF image showing the heterogeneous nucleation of CuZr_2 and CuZr (B2) on $\text{Cu}_{10}\text{Zr}_7$ crystal for the isothermally annealed $\text{Cu}_{50}\text{Zr}_{50}$ alloy at 671 K for 37 min. (b) HRTEM image showing the $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases and the interface between them. Inset: The corresponding FFT images of the selected areas by squares named as b1 from [100] zone axis of $\text{Cu}_{10}\text{Zr}_7$, b2 from [100] zone axis of CuZr_2 , b3 and b4 from [100] zone axis of CuZr (B2).

Fig.9. (a) STEM image of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons isothermally annealed at 671 K for 44 min with a line indicating the corresponding EDS analysis (b).

Fig.10. BF images of Cu₅₀Zr₅₀ ribbons isothermally annealed at 671 K for 49 min. (a) BF image showing the heterogeneous nucleation of CuZr (B2) type structure on Cu₁₀Zr₇ and CuZr₂ crystals. Inset shows the corresponding CBED taken from CuZr (B2) crystal at [111] zone axis. (b) BF image showing the distribution of these crystals in the amorphous matrix.

Fig.11. BF images of $\text{Cu}_{50}\text{Zr}_{50}$ ribbons isothermally annealed at 671 K for 75 min.

Fig.12. Two dimensional schematic projection showing the coherent interface between Cu_2Zr and CuZr (B2) structures.

Fig.13. A schematic graph showing the crystallization pathway of isothermally annealed $\text{Cu}_{50}\text{Zr}_{50}$ amorphous alloy

CHAPTER 4: CRYSTALLIZATION KINETICS AND PHASE TRANSFORMATION MECHANISMS IN $\text{Cu}_{56}\text{Zr}_{44}$ GLASSY ALLOY

A Paper to be submitted to *Acta Metallurgica*

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Abstract

The crystallization kinetics and phase selection mechanism of eutectic $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy were investigated using in-situ high-energy X-ray diffraction (HEXRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) under isothermal and isochronal conditions. In-situ HEXRD results for 10 K/min heating indicate that the amorphous alloy devitrifies into CuZr_2 and mainly $\text{Cu}_{10}\text{Zr}_7$ at the crystallization temperature of 725 K. The sequence continues with the precipitation of CuZr (B2) at 1008 K, where these three phases coexist until the decomposition of CuZr_2 is observed at 1030 K. The two equilibrium phases $\text{Cu}_{10}\text{Zr}_7$ and CuZr (B2) remain present on further heating, until melting at the eutectic temperature for the $\text{Cu}_{56}\text{Zr}_{44}$ alloy. TEM analysis of the $\text{Cu}_{56}\text{Zr}_{44}$ initially amorphous alloy, isothermally annealed at 705 K, revealed the primary nucleation and growth of $\text{Cu}_{10}\text{Zr}_7$. The growth of the $\text{Cu}_{10}\text{Zr}_7$ crystals was observed to be initially planar

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with a transition to a cellular morphology, associated with partitioning of Zr at the growth front. Related cellular structures and composition profiles are quantified.

Introduction

Since their discovery in 1960s [1], metallic glasses have attracted much more attention due to their unique properties compared to their crystalline metallic systems. Recent investigations on metallic glasses have pointed out the high potential of glass formation in binary metallic systems. Among these systems, the Cu-Zr binaries are of the main interest due to wide range of glass forming ability (35-70 at.% Cu in binary Cu-Zr alloys), high enthalpy of mixing between constituents (-23 kJ/mol) and ability to be cast into bulk dimensions of fully glassy structures [2-6].

In this study, we focus on $\text{Cu}_{56}\text{Zr}_{44}$ eutectic alloy in order to understand the devitrification behavior and crystallization kinetics under both continuous heating and isothermal annealing conditions. Although, for some of the alloys, off eutectic compositions were reported to have higher GFA [7], eutectic systems have been widely accepted as best glass formers. According to Turnbull's criteria [8], higher GFA is expected for higher reduced glass transition temperature, T_{rg} ($=T_g/T_l$ where T_g is glass transition and T_l is liquidus temperatures) parameter which predicts the eutectic compositions be the best glass formers. This is mainly because; the liquid at the eutectic will be stable to a lower temperature and thereby the nucleation of crystals will be prevented. Glass forming ability of some of the Cu-Zr binaries has been studied previously. For example, Li et. al. [9] reported that the analysis of critical amorphous thickness in Cu-Zr alloys has revealed three maxima of 1.14 ± 0.04 mm at $\text{Cu}_{64}\text{Zr}_{36}$, 1.02 ± 0.04 mm at $\text{Cu}_{56}\text{Zr}_{44}$ and 1.14 ± 0.04 mm at $\text{Cu}_{50}\text{Zr}_{50}$ compositions. We previously investigated the devitrification of one of these good glass

formers; $\text{Cu}_{50}\text{Zr}_{50}$ alloy and reported the formation of $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and metastable CuZr (B2) phases under constant heating rate conditions using in-situ high energy X-ray diffraction (HEXRD). Additional microstructural analysis under isothermal annealing conditions revealed the primary formation of $\text{Cu}_{10}\text{Zr}_7$ crystals which is then followed by CuZr_2 . Furthermore, we reported a special epitaxy between the CuZr_2 and CuZr (B2) crystals from high resolution transmission microscopy (HRTEM) analysis which facilitates the nucleation of CuZr (B2) on CuZr_2 crystals. Here, we focus on $\text{Cu}_{56}\text{Zr}_{44}$, a neighbor composition of $\text{Cu}_{50}\text{Zr}_{50}$, to investigate the phase selection mechanism and crystallization kinetics. The crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ alloy were investigated previously Freed et al [10] using differential scanning calorimetry (DSC), X-ray energy dispersive analysis and transmission electron microscopy (TEM). They reported the initial formation of $\text{Cu}_{10}\text{Zr}_7$ via nucleation and growth mechanism which is then followed by the formation of equilibrium phase CuZr when the $\text{Cu}_{10}\text{Zr}_7$ reached the equilibrium fraction during isothermal annealing of the glassy alloy below T_g . Later, Wang et. al [11] studied the microstructure and crystallization of amorphous $\text{Cu}_{56}\text{Zr}_{44}$ alloy under isothermal annealing conditions and reported the devitrification sequence including the primary crystallization of Cu_8Zr_3 , decomposition of Cu_8Zr_3 when the $\text{Cu}_{10}\text{Zr}_7$ phase precipitates, formation of CuZr_2 and re-precipitation of Cu_8Zr_3 where they stay in equilibrium with $\text{Cu}_{10}\text{Zr}_7$. Based on these inconsistencies, the devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy was remained unclear. Therefore, in this study we focused on the crystallization and phase selection mechanism in amorphous $\text{Cu}_{56}\text{Zr}_{44}$ under isochronal and isothermal heating conditions using several characterization techniques including DSC, high-temperature DSC, HEXRD and TEM.

Experimental Methods

$\text{Cu}_{56}\text{Zr}_{44}$ ingot was prepared from high purity constituents (0.9999 Cu and 0.999(3) Zr, by weight) by arc melting under an argon atmosphere. The ingot was remelted three times for a good chemical homogeneity and quenched on a water-cooled copper hearth. The amorphous ribbons, 2.5 mm wide and 45 μm thick, were produced by Cu-block single roller free jet melt spinning [12, 13] using a tangential wheel velocity of 25 m/s under 1/3 atm He within graphite crucibles. The thermal analysis under both isothermal and isochronal conditions was carried out using DSC on as-quenched ribbons with a sample weight of 10.00 mg. After each DSC sample run, the second one at the same conditions was used as an instrumental baseline. For constant-heating rate DSC, the as-quenched ribbons were heated at 10, 20, 30, 40, 50 and 60 K/min from ambient temperature to 808 K. The isothermal studies include the initial heating of amorphous ribbons from room temperature to a fixed temperature which is below crystallization temperature of the amorphous alloy with a heating rate of 100 K/min and maintained at that temperature until the completion of crystallization. For high temperature continuous heating analysis, high-temperature DSC was used with a heating rate of 10 K/min.

In-situ high-energy X-ray diffraction (HEXRD) was used to examine the as-quenched alloy and to investigate the devitrification sequence under continuous heating rate conditions at 10 K/min from 369 to 1131 K. Synchrotron X-rays of 99.586 keV ($\lambda=0.0124(5)$ nm) were used, and diffraction data were collected in Deby-Scherrer geometry using a charge-coupled device (CCD) with an exposure time of 15 s. X-ray diffraction specimens were prepared by cutting the melt-spun ribbons into 12 mm lengths, stacking 40 lengths together, placing the stack into thin walled quartz capillary tube and sealed under an Ar atmosphere. HEXRD data

were analyzed using a Rietveld refinement technique where the details given in elsewhere [14]. Microstructural analysis of the as-quenched, partially and fully crystallized ribbons was performed by transmission and high resolution electron microscopy (TEM, HRTEM). The devitrified TEM samples were initially prepared using DSC by heating the as-quenched ribbons up to two isothermal temperatures; 692 and 705 K with a heating rate of 100 K/min, annealed for a period of time and quenched to room temperature. The as-quenched and annealed ribbons were thinned using double jet polishing at 242 K and using an etching solution of 33 vol. % HNO_3 and 67 vol. % methanol. The further quantitative chemical analysis of the samples were performed using energy dispersive X-ray (EDX).

Results

Thermal Analysis (DSC and high-temperature DSC)

The amorphous nature of rapidly solidified $\text{Cu}_{56}\text{Zr}_{44}$ ribbons was investigated and confirmed by HEXRD, DSC, high-temperature DSC and TEM analysis. Fig.1 (a) indicates the HEXRD pattern of as-quenched ribbons which shows only the diffuse scattering peaks related to the amorphous structure. Furthermore, the featureless matrix in the BF image in Fig.1 (b) and the corresponding selected area diffraction (SAED) pattern in Fig.1 (c), showing only broad halo rings confirm the glassy structure of the melt-spun ribbons. This is further supported by the continuous heating DSC analysis collected at heating rates of 10, 20, 30, 40, 50 and 60 K/min, in Fig.1 (d) where the inset shows the DSC trace taken at 10 K/min. Each DSC plot shows a characteristic glass transition which is followed by an exothermic peak corresponding to the crystallization of alloy. In the inset plot, three characteristic temperatures; glass transition, T_g , onset of crystallization, T_x , and peak of crystallization, T_p , were marked on the DSC trace and measured as 688, 725 and 727 K, respectively for 10

K/min. These three temperatures were determined for each heating rate and plotted in Fig.2. T_g , T_x and T_p values are found to shift to higher temperatures with increasing the heating rate. Kissinger analysis [15, 16] was used to model these variations as follows;

$$\ln \phi / T^2 = -\frac{E}{RT} + \text{const.} \quad (1)$$

where ϕ is the heating rate, R is the gas constant, T is the corresponding temperature varying with heating rate, and E is an activation energy corresponding to the crystallization mechanisms. The Kissinger analysis yields the activation energies of E_x and E_p as 401.7 and 399.7 kJ/mol for $\text{Cu}_{56}\text{Zr}_{44}$ alloy, respectively. The activation energies are slightly higher than the reported value of 385 kJ/mol by Wang et al. [11] for $\text{Cu}_{56}\text{Zr}_{44}$ alloy.

Thermal analysis of the $\text{Cu}_{56}\text{Zr}_{44}$ alloy at higher temperatures was carried out using high-temperature DSC under continuous heating conditions with a heating rate of 10 K/min, as shown in Fig.3. The high-temperature DSC analysis indicates a strong glass transition signal at 688 K, an exothermic peak associated with a crystallization event at an onset of 725 K, an eutectoid reaction with an onset temperature of 1004 K, and an endothermic peak associated with melting at an onset of 1177 K. T_g and the T_x as determined from DSC and high-temperature DSC, are in good agreement with each other. The high-temperature DSC analysis also indicates only one exothermic crystallization peak.

Fig.4 (a) shows the isothermal DSC analysis of $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy at different annealing temperatures. All the DSC scans exhibit single exothermic peak where the incubation period increases with decreasing the annealing temperature. The crystallized volume fraction, x , curves as functions of annealing time at different temperatures, were obtained by integrating the exothermic peaks in Fig.4 (a) and plotted in Fig. 4 (b). It is clear

that all plots display typical sigmoid shape. Generally, the isothermal crystallization process is modeled using well-known Johnson-Mehl-Avrami (JMA) equation [17-19];

$$x(t) = 1 - \exp[-k(t - \tau)^n] \quad (2)$$

where $x(t)$ is the transformed volume fraction at time t , τ is the incubation time before transformation begins and taken up to 0% crystallized volume fraction, t is the annealing time and n is the Avrami exponent, which reflects the crystallization mechanisms of nucleation and growth. The Avrami exponent, n , and reaction rate constant, k can be calculated from the slope and the intercept of the linear fitting to the JMA plot using the equation;

$$\ln \left[\ln \left(\frac{1}{1-x} \right) \right] = n \ln k + n \ln(t - \tau) \quad (3)$$

The JMA calculations of $\text{Cu}_{56}\text{Zr}_{44}$ alloy were given in Fig.5 (a). Each plot in the crystallization range of $10 < x < 90\%$ gives a nearly straight line with the slope of “ n ” and the intercept of “ k ”. The corresponding values of n and k for the isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy were given on each JMA plot in Fig.5 (a). The Avrami exponents vary from 4.95 to 5.66 for different annealing temperatures. Furthermore, it is generally believed that nucleation and growth mechanism do not remain constant and may change over the whole crystallization process, therefore detailed information on the nucleation and growth is obtained using local Avrami exponent parameter [20], which is defined by

$$n(x) = \frac{\partial \ln[-\ln(1-x)]}{\partial \ln(t - \tau)} \quad (4)$$

The local Avrami exponents, $n(x)$, with crystallized volume fraction, x , for the crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ alloy at different annealing temperatures for $1 < x < 99.9\%$ were plotted in Fig.5 (b). At the early stage of crystallization, n values are starting from 1 where the surface crystallization is dominant which implies that the crystallization is mainly controlled by one dimensional growth with a decreasing nucleation rate [21]. When the crystallization fraction, x , reaches to 5%, the value of n increases up to 4, suggests a three dimensional growth with a constant nucleation rate [21]. During the middle stage of crystallization, n starts to increase up to 5 and 6 for 705 K and the two higher temperatures; 710 and 710 K, respectively. It is widely known that an Avrami exponent value higher than 4 generally indicates discontinuous precipitation, eutectic reactions or any interface controlled growth with an increasing of nucleation rate [21]. However, the Avrami exponent greater than 5 is not expected theoretically. In the final stage of crystallization, where the calculation of the Avrami exponent using JMA equation results in large uncertainties, the value of n for $x > 90$ is not taken consideration [22]. In determining the kinetics of phase transformation involving nucleation and growth, JMA model is significant; however microstructure analysis is required to obtain a full understanding of the relevant mechanism of nucleation and growth.

High energy X-ray diffraction (HEXRD)

In-situ HEXRD analysis was done on $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy under continuous heating rate conditions at 10 K/min in a temperature range starting from 96 to 858 K. The in-situ HEXRD pattern, in Fig.6, indicates the crystallization temperature of 725 K which is also in good agreement with the values of T_x measured from DSC and high-temperature DSC. The HEXRD pattern at 725 K has large amount of amorphous portion therefore,

therefore the Rietveld refinement process was applied starting from the following HEXRD pattern at 728 K. The fitting of interplanar spacing values at 725 K indicates that the amorphous alloy mainly devitrifies into $\text{Cu}_{10}\text{Zr}_7$, however, one of the main peaks corresponding to CuZr_2 is also indexed in Fig. 6. The formation of CuZr_2 phase was further confirmed by the Rietveld modeled HEXRD pattern, in Fig.7 (a), which showed complete crystallization at 728 K. The pattern was very well fitted with orthorhombic $\text{Cu}_{10}\text{Zr}_7$ (with a space group of Cmca) and tetragonal CuZr_2 (with a space group of I4/mmm) with phase fractions of 0.918 and 0.082 (by weight). Based on sequential Rietveld analysis, $\text{Cu}_{10}\text{Zr}_7$ phase was found to stay in equilibrium with CuZr_2 until the precipitation of CuZr (B2) at 1008 K which is in a good agreement with our preliminary observation about the temperature range of CuZr (B2) [14]. The corresponding phase fractions at 1008 K were found as 0.928, 0.062, and 0.011 (by weight) for $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2), respectively. At this point, it should be mentioned that no indications were observed to support the formation of Cu_5Zr_8 phase after the formation of the stable $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases. Fig.7 (d) shows the optimized pattern at 1030 K where CuZr_2 decomposed into $\text{Cu}_{10}\text{Zr}_7$ and CuZr (B2) phases. Further annealing resulted in the growth of CuZr (B2), as seen in Fig.7 (e), before the alloy melts at 1177 K (which obtained from high-temperature DSC).

Transmission Electron Microscopy (TEM)

Microstructural analysis was carried out on isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ ribbons at two different temperatures; 692 and 705 K using TEM in bright field (BF), HRTEM and selected area electron diffraction (SAED) modes. The BF image in Fig.8 (a) shows a core structure (planar-like) surrounded by a morphologically different crystal (cellular-like) embedded in the amorphous matrix for the annealed $\text{Cu}_{56}\text{Zr}_{44}$ sample at 705 K for 7.9 min.

The inset SAED pattern taken from the core structure reveals the primary formation of $\text{Cu}_{10}\text{Zr}_7$ crystal. BF and corresponding SAED further supports that crystallization was initiated by nucleation and growth of $\text{Cu}_{10}\text{Zr}_7$ phase as shown in Fig.8 (b). It is also seen from this BF image that $\text{Cu}_{10}\text{Zr}_7$ embedded in an amorphous matrix and no other crystal was formed in the close neighborhood. Fig. 9 (a) shows the BF image with corresponding SAED pattern taken from the surrounding cellular region around $\text{Cu}_{10}\text{Zr}_7$ core structure. Fig. 9 (b) indicates the three SAED patterns collected by a systematic tilting to three different crystallographic orientations from the cellular region. The results indicate that the structure of surrounding cellular region is $\text{Cu}_{10}\text{Zr}_7$, as well. Therefore, the initially nucleated $\text{Cu}_{10}\text{Zr}_7$ phase tends to change its growth morphology from planar to cellular type after a certain amount of time for an isothermal heating.

Increasing the annealing time up to 9.1 min indicates a further growth of $\text{Cu}_{10}\text{Zr}_7$ crystal, as seen in Fig.10 (a) and (d). The two SAED patterns in Fig.10 (b) and (c) are corresponding to the core and cellular-like $\text{Cu}_{10}\text{Zr}_7$ crystals, respectively. It is clearly seen from the HAADF image in Fig.10 (d) that the morphology is changing into cellular during crystal growth. The elemental quantitative analysis has been carried out on using EDS and shown on the corresponding regions of the image in Fig.10 (d). It should be noted that the EDS values were normalized to composition of the core $\text{Cu}_{10}\text{Zr}_7$ for better understanding in comparison only in Fig.10 (d). It can be seen that there is a slight change in the Cu-concentration from planar to cellular type which may result in the morphological change of $\text{Cu}_{10}\text{Zr}_7$ crystal. At the end of the crystallization where the sample was annealed for 12 min., further growth of cellular $\text{Cu}_{10}\text{Zr}_7$ crystals was observed, as seen in Fig.11. For that specific annealing time, EDS line scan data were collected through the AA' line, scattered in the

STEM image of Cu₅₆Zr₄₄ ribbons in Fig.12 (a). EDS line scan profile, in Fig.12 (b), indicates nearly the similar compositional fluctuation with a little increase in Zr-concentration which confirms that these two different morphologies are corresponding to the Cu-rich phase of Cu₁₀Zr₇.

Raghavan and Cohen [23] proposed to calculate the diffusivity for diffusion controlled growth of spherical crystals, by

$$R^2 = 2D \frac{\bar{C} - C_{\alpha\beta}}{C_{\beta\alpha} - C_{\alpha\beta}} t \quad (5)$$

where R is the particle radius, D is the diffusivity in the amorphous matrix, $\bar{C}$ is the initial concentration of amorphous phase, $C_{\alpha\beta}$ is the concentration of the interface between the crystal and the amorphous matrix, $C_{\beta\alpha}$ is the concentration of the crystal and t is the annealing time. Based on the assumption that Cu₁₀Zr₇ is a spherical and single particle including the planar and circular morphologies together, Eq.5 was used to calculate the diffusivity at 692 K. The BF images in Fig.13 indicate the largest Cu₁₀Zr₇ crystals that were selected for different annealing times and used in the calculations. For the value of R , the largest radius of the particle was taken and the change in the R^2 of the Cu₁₀Zr₇ crystals at different annealing times was plotted in Fig.14 which has a slope of $2D \frac{\bar{C} - C_{\alpha\beta}}{C_{\beta\alpha} - C_{\alpha\beta}}$. With the appropriate values of each term, the diffusivity (D) value in the amorphous matrix at 692 K was found to be 2.07×10^{-12} cm/s².

Discussion

The constant-heating-rate analysis from DSC and high-temperature DSC illustrated single step crystallization for $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy. In addition to the thermal analysis, in-situ HEXRD data were collected to investigate the devitrification sequence during a constant heating at a rate of 10 K/min from 369 to 1131 K. The time-resolved HEXRD patterns were refined using a Rietveld refinement where the phase transition and reaction temperatures; 725, 1008 and 1030 K were identified precisely. The in-situ HEXRD analysis indicated that the crystallization starts at 725 K which is in good agreement with the onset of crystallization values obtained from both DSC and high-temperature DSC for continuously heated amorphous $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 10 K/min. The optimized diffraction pattern at 728 K, where the amorphous sample was completely crystallized, indicates the formation of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 with phase fractions of 0.918 and 0.082 (by weight), respectively. Upon heating from 725 K to 1008 K, $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases stay in equilibrium until the precipitation of CuZr (B2) phase were observed at 1008 K. These three phases coexist together until the dissolution of CuZr_2 at 1030 K and then $\text{Cu}_{10}\text{Zr}_7$ and CuZr (B2) stay in equilibrium where the following in-situ HEXRD patterns indicate the $\text{Cu}_{10}\text{Zr}_7$ and the growth of CuZr (B2) phase with further heating. The phase transitions temperatures were also determined from the high-temperature DSC analysis to compare with HEXRD results. High-temperature DSC thermogram in Fig.3 presents the onset of eutectoid reaction corresponding to the formation of CuZr (B2) as 1004 K. This value is a little lower than that is determined from the fitted HEXRD pattern which gives a phase fraction of CuZr (B2) as 0.011 (by weight). Our previous analysis on HEXRD analysis of constant heating rate devitrification in $\text{Cu}_{50}\text{Zr}_{50}$ amorphous alloy also reveals the precipitation temperature for CuZr (B2) as 1002 K. The

values obtained from both studies are not identical but closed within experimental error. The other crystallization product, Cu_8Zr_3 , which was reported [11] during the devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy, was not observed in our study either during HEXRD or TEM analysis. This is also consistent with our previous study on devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy and the recent findings of Zhou and Napolitano [24]. The difference between the devitrification products may result because of the impurities in the as-quenched alloy where the metallic glassy alloys are very sensitive to any contamination.

The microstructural analysis was performed on isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy for different times at 692 and 705 K using TEM. BF image in Fig.9 (b) reveals that the alloy devitrifies first into $\text{Cu}_{10}\text{Zr}_7$ after incubation. The equiaxed morphology of $\text{Cu}_{10}\text{Zr}_7$ crystals are similar to that we observed during the isothermal annealing of $\text{Cu}_{50}\text{Zr}_{50}$ alloy [25]. However, it is interesting that, in $\text{Cu}_{56}\text{Zr}_{44}$ alloy, the morphology was found to change from planar to cellular during the growth of $\text{Cu}_{10}\text{Zr}_7$, as seen in Fig.10 (a). The cellular-like crystal was analyzed using double-tilt TEM where the SAED diffraction analysis at different orientations, in Fig.10 (b), also confirms that cellular phase is $\text{Cu}_{10}\text{Zr}_7$. The change in morphology from a planar to cellular growth is clearly seen in Fig.10 (b). The EDS analysis in Fig.10 (b) also points out the compositional fluctuation from planar $\text{Cu}_{10}\text{Zr}_7$ crystal to cellular one and to amorphous matrix. The Cu concentration is found to decrease slightly in the cellular part with respect to the core $\text{Cu}_{10}\text{Zr}_7$. The depletion of Cu might be the reason for the morphology change into defected cellular structure. Although we observed the formation of CuZr_2 during the in-situ HEXRD analysis under continuous heating conditions, for the isothermal annealing case; we could not identify the CuZr_2 crystals. The reason for this may be the small amount determined by the Rietveld analysis for the continuous heating

devitrification and also the cellular-like $\text{Cu}_{10}\text{Zr}_7$ crystals may hide tiny CuZr_2 crystals forming near to end of the crystallization period. At the end of crystallization, we could only identify planar and cellular $\text{Cu}_{10}\text{Zr}_7$ as seen in Fig.12. We also reported previously that there was a distinct depletion of Zr at the $\text{Cu}_{10}\text{Zr}_7$ crystal-glass interface and that the composition reaches to that of the CuZr_2 for the isothermally annealed $\text{Cu}_{50}\text{Zr}_{50}$ alloy [25]. This compositional fluctuation facilitates the nucleation of CuZr_2 crystals at the interface, however, the composition of interface is always in Cu- rich and never reaches to that of CuZr_2 . The other interesting point is that, previously we reported the formation metastable CuZr (B2) phase (nucleate for $\text{Cu}_{50}\text{Zr}_{50}$ below the stable temperature of CuZr (B2)) and showed the epitaxial relationship between the CuZr_2 and the CuZr (B2) crystals. Both HEXRD and TEM do not indicate any metastable CuZr (B2) formation in this Cu-rich composition. The reason might be that the composition of $\text{Cu}_{56}\text{Zr}_{44}$ is rich in Cu and away from the CuZr intermetallic in Cu-Zr phase diagram. And also we have very low amount of CuZr_2 compared to that in $\text{Cu}_{50}\text{Zr}_{50}$ alloy, therefore, the driving energy was not enough for CuZr (B2) to create a texture with a specific orientation and preferred CuZr_2 to nucleate on. These may explain why there is no formation of metastable CuZr (B2) observed in the initial devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy. Furthermore, it should be noted that as a difference from the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy, during the devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy, we did not observe the plate-like structures embedded in the amorphous matrix. The findings of these studies also underlie the compositional effect on microstructure. Moreover, EDS line scan profile given for the planar and cellular $\text{Cu}_{10}\text{Zr}_7$ crystal in Fig.13 (a) and (b), confirms that in the cellular part the concentration of Cu is slightly decreasing. It can be concluded that the slight fluctuations in the concentration may induce the modifications on the morphology of

crystals to decrease the energy of system during the growth. The HRTEM analysis of this much defected structure with highly dense stacking faults cellular $\text{Cu}_{10}\text{Zr}_7$ crystals is in progress and remained as a future study. It is already known that Zr has lower diffusion than Cu and it is expected that the growth of $\text{Cu}_{10}\text{Zr}_7$ in the amorphous precursor will be restricted by the Zr concentration. Therefore, the diffusion of Zr at the interface planar-like crystal may result the morphological change during the growth of $\text{Cu}_{10}\text{Zr}_7$. Therefore, it can be concluded that the diffusivity value determined using the equation from Raghavan and Cohen [23] is the diffusivity of Zr in the $\text{Cu}_{56}\text{Zr}_{44}$ glass. The value was found as $2.07 \times 10^{-12} \text{ cm}^2/\text{s}$ at 692K which is larger than the reported value of $5.3 \times 10^{-15} \text{ cm}^2/\text{s}$ for the isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 713 K (where they reported the T_x as 767 K at 10 K/min). The difference may also relate to the selection of different annealing temperatures or any other contamination in the samples. The formation of $\text{Cu}_{10}\text{Zr}_7$ crystals indicates that the growth is diffusion controlled and three dimensional where the local Avrami exponent values at 705 K starts around 1 and reaches to 4 up to 5% percent of crystallization. The average Avrami exponent values were calculated as 4.95 at 705 K was associated to any discontinuous precipitation or any eutectic reactions in Christian's book [21]. The high value of Avrami exponent may reflect the discontinuous growth of $\text{Cu}_{10}\text{Zr}_7$ crystals from planar to cellular. The simultaneous formation of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 were determined from in-situ HEXRD analysis under continuous heating conditions in the eutectic $\text{Cu}_{56}\text{Zr}_{44}$ alloy. Even we could not identify the CuZr_2 crystals with TEM analysis under isothermal annealing conditions; the high number of Avrami exponent value may indicate the formation of eutectic type reaction between $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 . The Kissinger activation energy, E_X , seems to show the energy associated with the crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 .

Conclusions

The devitrification kinetics and phase transformation during the crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy have been investigated in combination of DSC, high-temperature DSC, HEXRD and TEM under continuous heating and isothermal annealing conditions. The evolution of structural hierarchy during the crystallization of $\text{Cu}_{56}\text{Zr}_{44}$ glass under constant heating rate conditions (10K/min) was studied in-situ using HEXRD where each pattern was refined by Rietveld method. The sequence results indicate that the glassy $\text{Cu}_{56}\text{Zr}_{44}$ alloy first devitrifies into a major amount of $\text{Cu}_{10}\text{Zr}_7$ and a minor of CuZr_2 at 725 K and stay in equilibrium until the precipitation of CuZr (B2) phase at 1008 K. The coexistence of these three phases continues until the decomposition of CuZr_2 at 1030 K while $\text{Cu}_{10}\text{Zr}_7$ and CuZr (B2) phases stay in equilibrium. The melting temperature of the alloy was determined as 1177 K from high-temperature DSC analysis. TEM analysis of isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 705 K reveals the initial formation of $\text{Cu}_{10}\text{Zr}_7$. The morphological change from planar to cellular-like during the growth of $\text{Cu}_{10}\text{Zr}_7$ crystal were identified and related to the slight decrease in Cu concentration in the cellular part. The investigations include the HRTEM study of the stacking fault analysis in the defected cellular structure are still in progress and will be an aim of our future study. The other equilibrium phase, CuZr_2 was not observed during the isothermal microstructural studies. The diffusivity of Zr in amorphous precursor was found to be $2.07 \times 10^{-12} \text{ cm}^2/\text{s}$ for the isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 692K. In this study, the stability of Cu_5Zr_8 phase was not observed during the annealing of $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy which supports our previous results for the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy. We also concluded that increasing the Cu content in the Cu-Zr binary system starting from $\text{Cu}_{50}\text{Zr}_{50}$ composition, the metastable CuZr (B2) formation was restricted

related to the decrease in the driving energy for the formation of this phase. The devitrification behavior of the Zr-rich neighbor composition of $\text{Cu}_{50}\text{Zr}_{50}$ in terms of phase selection mechanism is the other topic of ongoing investigation.

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Fig.1. (a) HEXRD diffraction pattern, (b) BF image with (c) corresponding SAED and (d) isochronal DSC plots at 10, 20, 30, 40, 50 and 60 K/min with inset shows the DSC trace at 10 K/min of the as-quenched $\text{Cu}_{56}\text{Zr}_{44}$ ribbons.

Fig.2. Characteristic temperatures determined for melt spun $\text{Cu}_{56}\text{Zr}_{44}$ from DSC traces at different heating rates (ϕ).

Fig.3. Constant-heating high-temperature DSC plot of $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy at 10 K/min.

Fig.4. (a) Isothermal DSC curves and (b) crystallized volume fraction curves at different annealing temperatures of amorphous $\text{Cu}_{56}\text{Zr}_{44}$ alloy.

Fig.5 (a) JMA plots (b) Local Avrami plots for the crystallization of the $\text{Cu}_{56}\text{Zr}_{44}$ amorphous alloy

Fig.6. HEXRD pattern of $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 725 K.

Fig.7. Rietveld refined diffraction patterns for the data collected at (a) 728 K, (b) 1008 K, (c) 1030 K and (d) 1131 K during the continuous heating of $\text{Cu}_{10}\text{Zr}_7$ glassy alloy at 10 K/min.

The vertical marks indicate the reflections for the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases below the HEXRD plots in (a), $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases below the XRD plot in (b), $\text{Cu}_{10}\text{Zr}_7$ and B2 phase below the XRD plot in (c) and (d) from top to bottom, respectively.

Fig.8. BF images of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 705 K for 7.9 min. (a) BF image showing the $\text{Cu}_{10}\text{Zr}_7$ crystals in the core and surrounded with a nodular like structure. Inset shows the corresponding SAED taken from $\text{Cu}_{10}\text{Zr}_7$ crystal at $[112]$ zone axis. (b) BF image showing B2 and corresponding SAED taken from the $\text{Cu}_{10}\text{Zr}_7$ crystals at $[100]$ zone axis.

Fig.9. (a) BF image of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 705 K for 7.9 min. inset shows the corresponding SAED pattern from the cellular-like $\text{Cu}_{10}\text{Zr}_7$ crystal at $[1,0,1]$ zone axis. (b) SAED patterns, at different crystallographic orientations of cellular-like $\text{Cu}_{10}\text{Zr}_7$ crystal, shown on stereographic projection.

Fig.10. (a) BF image of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 705 K for 9.1 min. Corresponding CBED patterns taken from (b) core $\text{Cu}_{10}\text{Zr}_7$ and (c) from the cellular-like $\text{Cu}_{10}\text{Zr}_7$ at $[0,1,0]$ zone axes. (d) High-angle annular dark field (HAADF) image of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 705 K for 9.1 min.

Fig.11. BF image of Cu₅₆Zr₄₄ ribbons isothermally annealed at 705 K for 12 min.

Fig.12. (a) STEM image of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 705 K for 12 min with a line indicating the corresponding EDS analysis (b).

Fig.13. BF images of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons isothermally annealed at 692 K for 31 min. (a), 39 min. (b) and 54 min. (c).

Fig.14. The variation of radius of the largest $\text{Cu}_{10}\text{Zr}_7$ crystallites during the annealing of $\text{Cu}_{56}\text{Zr}_{44}$ ribbons at 692 K with annealing time.

CHAPTER 5: GLASS FORMING ABILITY OF BINARY Cu-Zr AND TERNARY Cu-Zr-Al GLASSY ALLOYS

A paper to be submitted to *Journal of Non-Crystalline Solids*

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Abstract

The thermal stability and glass forming ability (GFA) of Cu-Zr binary and Cu-Zr-Al ternary alloys were investigated using high-temperature differential scanning calorimetry (DSC) under continuous-heating conditions. The reduced glass transition temperature (T_{rg}), γ and supercooled liquid region (ΔT_x) values were obtained from high-temperature DSC analysis for Cu-Zr binary and Cu-Zr-Al ternary alloys. The results have pointed out the best binary Cu-Zr glass former as $\text{Cu}_{64.5}\text{Zr}_{35.5}$ which is then followed by $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$ alloys. It has been observed that the addition of Al as a third impurity element enhances the GFA and thermal stability significantly leading higher ΔT_x , T_{rg} and γ in $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ compared to their parent binary Cu-Zr alloys. Furthermore, analysis of primary devitrification of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glassy alloys at their crystallization temperatures were performed by Rietveld modeling on the in-situ high energy X-ray

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(HEXRD) patterns. The Rietveld fitting indicated simultaneous crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases for both $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys.

Introduction

Metallic glasses have been a promising class of materials due to remarkable chemical, mechanical and physical properties. Afterwards, bulk forms of metallic glassy alloys were produced which allow them to serve as structural materials for future applications and named as bulk metallic glasses (BMG). Since their discovery in 1960s, there have been many efforts given to understand the glass forming ability (GFA) of these alloys and pinpoint the best glass former systems. For example, Turnbull [1] suggested that GFA of the alloys will be favored when the reduced glass transition temperature, T_{rg} ($=T_g/T_l$ where T_g is the glass transition temperature and T_l is the liquidus temperature) is higher than 2/3. Later, Inoue [2-5] proposed three empirical rules which require high negative heats of mixing and large atomic size differences between the constituent elements and the alloy with more than three elements. Inoue also proposed that the wider supercooled liquid region, ΔT_x ($=T_x - T_g$ where T_g is the crystallization temperature), will result in more thermally stable glass and thereby larger GFA. However, there have been many studies reported that the relationship between the ΔT_x and GFA is not proportional and in many systems, low GFA has been reported for relatively large ΔT_x [6-9]. Moreover, Lu and Liu [10] mentioned that ΔT_x is not enough to determine the GFA of the alloys and therefore introduced a new parameter γ ($=T_x/(T_g + T_l)$) which increases with the GFA.

Besides multicomponent BMGs, binary Cu-Zr amorphous alloys were also named as bulk metallic glasses because of their ability to be cast into bulk dimensions [11-16]. Indeed, Cu-Zr binary system is particularly of interest because of their good GFA in wide range of

composition (35-75 at % Cu) [13, 14, 16] which has also been served as basis for many BMGs. Recent investigations showed the enhancement in GFA of binary Cu-Zr alloys with the minor addition of third element, such as Al, Ag and Ti. Regarding to Inoue's and Greer's multicomponent alloy principle, GFA was found to increase more significantly in quaternary and five-component systems. For example, by adding impurity elements into Cu-Zr-Al system, the critical diameters of bulk glass dimensions have been found to increase up to 10, 20 and 30 mm with ΔT_x values of 100, 103 and 99 K for $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ [17], $\text{Cu}_{38}\text{Zr}_{46}\text{Ag}_8\text{Al}_8$ [18] and $\text{Cu}_{34}\text{Zr}_{48}\text{Ag}_8\text{Al}_8\text{Pd}_2$ [19] alloys, respectively. In the present study, we focused on several binary Cu-Zr and ternary Cu-Zr-Al metallic glasses to investigate their GFA using high-temperature differential scanning calorimetry (DSC) under constant heating rate conditions. The effect of Al-addition on the primary crystallization of the parent Cu-Zr binaries were also investigated using high energy X-ray diffraction (HEXRD) technique by applying Rietveld refinement method on the HEXRD patterns. The results were then discussed compared to our previous analysis on the devitrification of Cu-Zr binary alloys.

Experimental Methods

The binary Cu-Zr and ternary Cu-Zr-Al ingots with nominal compositions were prepared from the high purity elements (0.999 Cu, 0.999 Zr, 0.999 Al by weight) by arc melting under an argon atmosphere. Each ingot was remelted and quenched on a water-cooled copper hearth three times for good chemical homogeneity. The amorphous binary Cu-Zr alloys were produced by rapid solidification using a Cu-block single roller free jet melt spinning technique [20, 21] with a tangential wheel velocity of 25 m/s under 1/3 atm He, yielding 1mm wide and 45 μm thick ribbons. Amorphous Cu-Zr-Al rods up to ~2 millimeter in diameter were fabricated by injection casting of the molten alloys in to copper mold. The

analysis of as-prepared alloys were performed using high-temperature differential scanning calorimetry (DSC) and in-situ high energy X-ray diffraction (HEXRD) techniques. High-temperature DSC analysis of the alloys was carried out under continuous heating rate conditions at 20 K/min. The sample pans were preferred as alumina and all the DSC traces were corrected with a baseline prepared using an empty alumina pan at the same conditions with the sample runs. For the HEXRD experiments, synchrotron X-rays of 99.586 keV ($\lambda=0.0124(5)$ nm) were used, and diffraction data were collected in Deby-Scherrer geometry using a charge-coupled device (CCD) with an exposure time of 15 s at a heating rate of 10 K/min. For in-situ HEXRD experiments, rod specimens were first cut into 10 mm lengths and placed into thin walled quartz capillary tubes which were sealed under an Ar atmosphere. The analysis of HEXRD patterns were carried out using Rietveld refinement technique where the lattice parameters, atomic coordinates, occupancies, thermal parameters, phase fractions; background and peak profiles were refined simultaneously during pattern modeling and the details given in elsewhere [22].

Results and Discussion

The amorphous nature of the as-quenched binary $\text{Cu}_x\text{Zr}_{100-x}$ ($x=33.3, 45.5, 50, 56, 64.5$) and ternary $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys were investigated using HEXRD and DSC. HEXRD patterns collected at room temperature, given in Fig.1, show only the broad diffuse scattering peaks which are corresponding to the amorphous structure of each ribbons. The amorphous natures of the as-prepared alloys were further confirmed by the continuous heating high-temperature DSC traces obtained at 20 K/min, as seen in Fig.2. Each DSC trace indicates a distinct glass transition feature followed by an exothermic peak associated with the crystallization and an endothermic peak corresponding to the melting of the alloy. From

each of these DSC traces, glass transition, T_g , onset of crystallization, T_x , peak of crystallization, T_p , and liquidus, T_l temperatures were obtained as indicated in the inset of Fig.2. It is clear that all of these thermal parameters are composition dependent and increasing with the Cu-concentration in the binary Cu-Zr alloys. To investigate the GFA of the alloys, reduced glass transition temperatures, T_{rg} , supercooled liquid region (ΔT_x), and γ parameters were calculated and listed in Table 1. The highest values of T_{rg} and γ were observed for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ and $\text{Cu}_{56}\text{Zr}_{44}$ alloys which are then followed by $\text{Cu}_{50}\text{Zr}_{50}$ binary. It is not surprising that these three alloys have already been known as best Cu-Zr glass former systems, however, it is interesting that $\text{Cu}_{64.5}\text{Zr}_{35.5}$ has the lowest ΔT_x compared to other alloys. This also supports Lu and Liu [10]'s claim about ΔT_x that the glass formation should not be defined by ΔT_x alone and the other parameters should be used to determine the GFA of the alloys. It is also seen that Al-addition decreases the melting temperature, T_m and T_l of the Cu-Zr binary alloys, and thereby, increases the T_{rg} , γ and ΔT_x values of the $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloys compared to that of the parent (closed) binary compositions; $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{56}\text{Zr}_{44}$. It should be noted that $\text{Cu}_{64.5}\text{Zr}_{35.5}$ alloy has comparable high value of T_{rg} with that of the ternary systems even it has lower ΔT_x . As concluded, Al as a third impurity element increases the glass forming ability and the thermal stability of the parent binary Cu-Zr alloys. This also supports the Inoue's empirical rule on multicomponent alloys and Greer's confusion principle [23].

On the other hand, ternary elements do not only affect the GFA but may also change the devitrification pathway of their parent binary alloys. We previously reported the devitrification sequence during the continuous heating of $\text{Cu}_{50}\text{Zr}_{50}$ [22] and $\text{Cu}_{56}\text{Zr}_{44}$ [24] binary alloys using in-situ HEXRD at 10 K/min. We reported the initial formation of

$\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases with weight fractions of 0.399, 0.223 and 0.378, respectively at the crystallization temperature (706 K) of $\text{Cu}_{50}\text{Zr}_{50}$ glass. The interesting result of that study was the precipitation of CuZr (B2) which is only stable above the 1002 K [22, 25]. Furthermore, our previous constant heating in-situ HEXRD analysis on the Cu-rich neighbor composition of $\text{Cu}_{50}\text{Zr}_{50}$ which is $\text{Cu}_{56}\text{Zr}_{44}$ showed the simultaneous crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 with phase fractions of 0.918 and 0.082 (by weight), respectively at 728 K. This analysis indicated the suppression of CuZr (B2) phase by increasing the Cu concentration. In this study, we also investigated the effect of Al addition on initial devitrification mechanism in $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ system compared to $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{56}\text{Zr}_{44}$ alloys. Fig.3 and Fig.4 (a) indicate the in-situ HEXRD patterns collected at the crystallization temperature of the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys under continuous heating conditions at a heating rate of 10 K/min. The Rietveld analysis of the HEXRD pattern in Fig.3, shows that the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloy devitrifies into $\text{Cu}_{10}\text{Zr}_7$ (with a space group of Cmca) and CuZr_2 (with a space group of I4/mmm) phases, simultaneously which may indicate eutectic type transformation. The corresponding weight fractions were measured from the pattern modeling as 0.76 and 0.24 for $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 , respectively. It is an expected result that the composition of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ is rich in Cu-content and the devitrification may similar to that of the Cu-rich binary $\text{Cu}_{56}\text{Zr}_{44}$. Ou et al [26] also reported a simultaneous crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 for $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ glassy alloy which also supports our findings. Fig.4 (a) indicates the HEXRD pattern taken at the crystallization temperature of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glassy alloy. It is not easy to dissolve the primary phase because the pattern has common diffraction and overlapping peaks for $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 crystals. However, it is clear that the crystallization of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ is not as sharp and fast as that of the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloy which

shows eutectic like crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 . It should be also noted that the composition of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ is much closed to that of $\text{Cu}_{50}\text{Zr}_{50}$. Therefore, during the devitrification of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glass, $\text{Cu}_{10}\text{Zr}_7$ may form initially which is then followed by CuZr_2 and CuZr (B2) immediately, based on our previous reports on isothermal crystallization of $\text{Cu}_{50}\text{Zr}_{50}$ alloy. However, this statement requires an additional microstructural investigation. Because of a significant amount of amorphous content, Rietveld modeling was done on the following HEXRD pattern in Fig.4 (b) which confirms the presence of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases with phase fractions of 0.65 and 0.35 (by weight), respectively. The structural parameters refined during Rietveld modeling of HEXRD patterns at T_x of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys were given in Table 2, as well. The other result is that no precipitation of CuZr (B2) phase was observed during the initial devitrification of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glass, even though it has a composition much closer to $\text{Cu}_{50}\text{Zr}_{50}$ alloy. It can be concluded that the minor addition of Al affects the initial phase selection mechanism by suppressing the formation of CuZr (B2). The devitrification of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glass have been investigated previously by Pauly et al [27] who reported the precipitation of martensitic CuZr phase in as-produced $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ ingots. However, in this study, this phase was not observed either in as-quenched (which has fully amorphous structure) or annealed $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ ribbons. This should be related to the quenching rate used during the preparation of amorphous ingots. Moreover, Yamamoto et al [28] using XRD reported the primary precipitation of metastable CuZr (B2) phase during the crystallization of Zr-rich $\text{Zr}_{50}\text{Cu}_{46}\text{Al}_4$ and $\text{Zr}_{50}\text{Cu}_{44}\text{Al}_6$ metallic glass plates. Therefore, increasing the Zr-concentration in the ternary Cu-Zr-Al alloy may favor the precipitation of metastable CuZr (B2) phase.

Conclusions

In the current work, thermal stability and crystallization behavior of several Cu-Zr binary and Cu-Zr-Al ternary alloys were investigated. Thermal analysis of $\text{Cu}_x\text{Zr}_{100-x}$ ($x=35.5, 45.5, 50, 56, 64.5$) indicates that glass transition temperature, T_g and crystallization temperature, T_x are composition dependent and both temperatures are increasing with increasing the Cu-concentration. Thermal data obtained under continuous heating conditions at 20 K/min indicates that $\text{Cu}_{64.5}\text{Zr}_{35.5}$, $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$ binary alloys have higher glass forming ability which is expressed by having high reduced glass transition temperature, $T_{rg} > 0.55$ and γ compared to the other Cu-Zr binaries. The supercooled liquid region, ΔT_x , which is related to the thermal stability of the alloys of Cu-Zr alloys increased significantly by the addition of Al. In our previous studies, we reported the devitrification in $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{56}\text{Zr}_{44}$ glassy alloys under continuous heating conditions using in-situ HEXRD. The initial crystallization was found to start with $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases in $\text{Cu}_{50}\text{Zr}_{50}$ system, while the primary phases were determined as $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 for $\text{Cu}_{56}\text{Zr}_{44}$ alloy. Here, we also investigated the effect of Al on initial devitrification of Cu-Zr binary where the compositions of ternary alloys were selected as $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ which are closer to that of $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$ binaries. In-situ HEXRD analysis under continuous heating conditions at a rate of 10 K/min indicated that the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ amorphous alloys devitrify into $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 simultaneously. Although they have the same initial devitrification, the phase fractions of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases are changing from 0.76 and 0.24 to 0.65 and 0.35 (by weight), respectively with the increase of Zr concentration from $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ glassy alloys to $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$. We did not observe the

formation of CuZr (B2) phase during the crystallization of these glasses even in the $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ which has a similar composition to a parent $\text{Cu}_{50}\text{Zr}_{50}$ binary.

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Fig.1. HEXRD patterns of $\text{Cu}_x\text{Zr}_{100-x}$ ($x=45.5$ (a), 50 (b), 64.5 (c) and 56 (d)), $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ (e) and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (f) alloys at room temperature.

Fig.2. Constant-heating-rate DSC traces of $\text{Cu}_x\text{Zr}_{100-x}$ ($x=33.3$ (a), 45.5 (b), 50 (c), 56 (d), 64.5 (e), $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ (f) and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (g) alloys at 20 K/min. Inset shows the high-temperature DSC trace at 20 K/min of the as-quenched $\text{Cu}_{56}\text{Zr}_{44}$ glass with characteristic temperatures of T_g , T_x , T_p and T_l .

Table 1. Thermal data obtained from high-temperature DSC traces for several binary Cu-Zr and ternary Cu-Zr-Al alloys at 20 K/min.

Alloys	T _g (K)	T _x (K)	T _l (K)	ΔT _x (K)	T _{rg} (T _g /T _l)	γ (T _x /(T _g +T _l))
Cu _{33.3} Zr _{66.6}	620	659	1292	39	0.48	0.35
Cu _{45.5} Zr _{54.5}	651	695	1226	44	0.53	0.37
Cu ₅₀ Zr ₅₀	670	711	1231	41	0.55	0.37
Cu ₅₆ Zr ₄₄	689	731	1191	42	0.58	0.39
Cu _{64.5} Zr _{35.5}	734	774	1240	40	0.59	0.39
Cu _{47.5} Zr _{47.5} Al ₅	682	745	1176	63	0.58	0.40
Cu ₅₀ Zr ₄₅ Al ₅	694	753	1165	59	0.60	0.40

Fig.3. Rietveld refined HEXRD diffraction pattern obtained at the crystallization temperature of continuously heated $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ as-quenched alloys with a heating rate of 10 K/min. The observed and the calculated data are represented by “●” and “—” symbols, respectively. A difference curve and the vertical marks indicate the reflections for the $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases below the XRD plots from top to bottom, respectively. The inset shows the isochronal DSC at a heating rate of 10 K/min leading a T_x of 747 K.

Fig.4. (a) HEXRD diffraction pattern obtained at the at the crystallization temperature of continuously heated Cu_{47.5}Zr_{47.5}Al₅ as-quenched alloys with a heating rate of 10 K/min. Inset shows the isochronal DSC at a heating rate of 10 K/min leading a T_x of 738 K. (b) Rietveld refined HEXRD diffraction pattern collected at 741 K. The observed and the calculated data are represented by “●” and “—” symbols, respectively. A difference curve and the vertical marks indicate the reflections for the Cu₁₀Zr₇ and CuZr₂ phases below the XRD plots from top to bottom, respectively.

Table 2. Structural parameters refined during Rietveld modeling of HEXRD patterns at T_x of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys.

<i>Structure Parameters</i>				<i>$\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$</i>	<i>$\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$</i>
$\text{Cu}_{10}\text{Zr}_7$	<i>Lattice parameters</i>	<i>a</i>		12.7128 [†]	12.724
		<i>b</i>		9.479	9.489
		<i>c</i>		9.484	9.476
	<i>Atomic sites</i>	<i>Atom</i>	<i>Wyckoff</i>	x, y, z	x, y, z
		<i>Cu</i>	16 <i>g</i>	0.145, 0.015, 0.211	0.144, 0.008, 0.194
			16 <i>g</i>	0.358, 0.297, 0.012	0.356, 0.281, 0.005
			8 <i>f</i>	0.000, 0.105, 0.392	0.000, 0.096, 0.389
		<i>Zr</i>	8 <i>f</i>	0.000, 0.310, 0.196	0.000, 0.311, 0.208
			8 <i>e</i>	0.250, 0.259, 0.250	0.250, 0.252, 0.250
			8 <i>d</i>	0.3073, 0.000, 0.000	0.3055, 0.000, 0.000
			4 <i>a</i>	0.000, 0.000, 0.000	0.000, 0.000, 0.000
	<i>Uiso</i>	<i>Cu</i>	16 <i>g</i>	0.018	0.048
			16 <i>g</i>	0.038	0.024
			8 <i>f</i>	0.043	0.038
		<i>Zr</i>	8 <i>f</i>	0.031	0.030
			8 <i>e</i>	0.026	0.037
			8 <i>d</i>	0.026	0.019
CuZr_2	<i>Lattice parameters</i>	<i>a, b</i>		3.2585	3.2491
		<i>c</i>		11.036	11.046
	<i>Atomic sites</i>	<i>Atom</i>	<i>Wyckoff</i>	x, y, z	x, y, z
		<i>Cu</i>	2 <i>a</i>	0.000, 0.000, 0.000	0.000, 0.000, 0.000
		<i>Zr</i>	4 <i>e</i>	0.000, 0.000, 0.347	0.000, 0.000, 0.338
	<i>Uiso</i>	<i>Cu</i>	2 <i>a</i>	0.039	0.070
		<i>Zr</i>	4 <i>e</i>	0.049	0.038

[†] Underlining is used to indicate the inconsistent digit in the number.

CHAPTER 6: STRUCTURAL RELAXATION AND SPECIFIC HEAT IN THE VICINITY OF GLASS TRANSITION IN $\text{Cu}_{50}\text{Zr}_{50}$ METALLIC GLASS

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Abstract

Structural relaxation and specific heat capacity of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy in the vicinity of glass transition temperature were investigated using differential scanning calorimetry (DSC). The relaxation of residual enthalpy frozen in the glass was studied during the isothermal annealing of $\text{Cu}_{50}\text{Zr}_{50}$ glass at 653 K which is well below the glass transition temperature at different annealing times. The results showed the increasing in enthalpy overshoot with increasing the annealing time and which is then saturating around 35 min of annealing. The specific heat capacity analysis under continuous heating at 10 K/min indicated the difference between the glass and the supercooled liquid as 35 J/mol.K.

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Introduction

Bulk metallic glasses have been an interesting branch of materials due to good physical, chemical and structural properties. Since their discovery in 1960s [1], there have been many research devoted to pinpoint the good bulk glass former alloys which can be cast into bulk form that allow them to serve as structural materials. Based on theoretical and experimental studies, several parameters, including reduced glass transition temperature (T_{rg} ($=T_g/T_l$ where T_g is the glass transition temperature and T_l is the liquidus temperature) by Turnbull [2], γ ($=T_x/(T_g+T_l)$ where T_x is the onset of the crystallization temperature) by Lu and Liu [3] and supercooled liquid region (ΔT_x ($=T_x-T_g$) by Inoue, were developed to determine the GFA of bulk metallic glasses. All of these parameters are related to the glass transition temperature and thereby the supercooled liquid region. Therefore, it is important to study the structural changes occur in the vicinity of glass transition zone for better understanding glass formation and thermal stability. The studies in the supercooled liquid region during the annealing of glass below T_g have shown the short range order interactions between the atoms where the atoms in the glassy state gradually approach to their equilibrium sites prior to crystallization. This process is generally named as structural relaxation where the glass reaches to its ideal state and becomes kinetically stable against devitrification at that annealing temperature. Recent advances have shown the importance of structural relaxation studies which allow controlling the structure [4-6] and the physical properties of the glass. For example, Li et al [7] reported that structurally relaxed $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (relaxed by isothermal annealing below the T_g) has higher ductility and strength compared to the unrelaxed one. Recently, Gu et al [8] investigated the effect of structural relaxation on the deformation behavior of $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ bulk metallic glass under

nanoindentation and reported the significant increase in both the hardness and elastic modulus. Therefore, it is essential to investigate the thermal properties of metallic glasses to understand the structural relaxation and glass transition behaviors. The structural relaxation process in amorphous alloys is generally explained by the free volume theory which suggests the existence of excess free volume in the supercooled liquid and equilibrium liquid. During isothermal annealing of the glass below T_g , this excess free volume relaxes into a special thermodynamic state. Therefore, the relaxed sample shows an endothermic enthalpy overshoot which is considered as the recovery of enthalpy lost during the structural relaxation. Connectedly, Wen et al [9] reported the enthalpy overshoot near T_g during the structural relaxation analysis of $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit 4) bulk metallic glass.

As a good glass former with a wide composition range of glass forming ability (35-70 at. % Cu in Cu-Zr alloys), Cu-Zr binary system has attracted much attention as structural materials for future applications. Herein, we studied the thermal relaxation and specific heat of one of the best glass former Cu-Zr alloy: $Cu_{50}Zr_{50}$ amorphous alloy. Previously, we reported the devitrification mechanism in $Cu_{50}Zr_{50}$ metallic glass under both continuous heating and isothermal annealing conditions [10, 11]. These studies have elucidated the phase transformation mechanism and provided information for controlling the microstructure in order to produce amorphous-crystalline composite (ACC) materials with desired structural properties. However, as we mentioned previously, structural relaxation studies affects the properties of glassy structure. At that point, crystallization and structural relaxation can be considered as independent events however the devitrification pathways may relate to the short atomic rearrangements in the supercooled liquid region which can be controlled by structurally relaxing the glass. In the present work, we investigated the effect of annealing time (at a

temperature below T_g) on structural relaxation and measured the specific heat in the vicinity of glass transition in $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass.

Experimental Methods

An ingot with nominal composition of $\text{Cu}_{50}\text{Zr}_{50}$ was prepared from high purity constituents (0.999(9) Cu and 0.999(5) Zr, by weight) by arc melting under an argon atmosphere. The alloy ingot was remelted and quenched on a water-cooled copper hearth three times to obtain good chemical homogeneity. The amorphous alloy was produced by rapid solidification from the liquid by free-jet melt spinning [12, 13] on a copper wheel at a tangential velocity of 25 m/s, under 0.33 atm He using a graphite crucible, yielding ribbons were nominally 1mm wide and 45 μm thick. The glassy structure of the as-quenched $\text{Cu}_{50}\text{Zr}_{50}$ ribbons was confirmed using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The enthalpy relaxation studies were carried out with DSC where the samples with a mass of 10 mg each were initially heated up to 653 K at a heating rate of 100 K/min and annealed at that temperature for 5, 15, 25 and 35 minutes. The samples were then quenched to the room temperature and subsequently heated for an enthalpy recovery experiment with a constant heating rate of 40 K/min until the crystallization was completed. The instrument baseline was performed following a same step with an empty aluminum pan. The specific heat capacity analysis was performed for as-quenched and crystallized specimens in reference to the sapphire standard. The measurements were performed using DSC in “step-scan” mode where the as-quenched and crystal specimens, sapphire standard and an empty pan (serves as a baseline) were heated with a heating rate of 10 K/min and followed by an isothermal step for 1 min in each 10 K intervals up to 808 K until the completion of crystallization. The data for the

crystal was collected after quenching the crystallized specimen using the same heating process. The step-scan method resulted in an enthalpy change (ΔH) which is defined as

$$\frac{dQ}{dt} = \left(\frac{\partial Q}{\partial t} \right)_{\dot{T} \neq 0} - \left(\frac{\partial Q}{\partial t} \right)_{\dot{T} = 0} = C_p m \frac{dT}{dt} \quad (1)$$

where the $(\partial Q/\partial t)_{\dot{T} \neq 0}$ is the power to heat the specimen up to a certain temperature while the $(\partial Q/\partial t)_{\dot{T} = 0}$ is the power to keep the temperature constant in the isothermal interval, C_p is the heat capacity, m is the sample mass. The heat capacity of amorphous, crystalline and supercooled states as functions of temperature were then calculated using the expression below

$$C_{p_{sample}}(T) = \frac{(\Delta H_{sample}(T) - \Delta H_{empty}(T))m_{sapphire}M_{sample}}{(\Delta H_{sapphire}(T) - \Delta H_{empty}(T))m_{sample}M_{sapphire}} C_{p_{sapphire}}(T) \quad (2)$$

where M_{sample} and $M_{sapphire}$ are the molecular weight of sample and sapphire respectively, $C_{p_{sapphire}}$ is the standard specific heat capacity of the sapphire.

Results and Discussion

The thermal behavior of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy was analyzed using DSC, with a heating rate of 40 K/min, as shown in Fig.1. DSC trace exhibits a step-like feature related to the glass transition, T_g , at 672 K and a distinct undercooled liquid region which is followed by an exothermic peak corresponding to a crystallization with an onset, T_x , and peak, T_p , temperatures of 717 and 723 K, respectively. The ΔT_x of 45 K for binary $\text{Cu}_{50}\text{Zr}_{50}$ alloy is not as wide as that of multicomponent BMGs, such as $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ with a ΔT_x of 121 K, $\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}$ with a ΔT_x of 105 K and $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{Pd}_{20}$ with a ΔT_x of 101 K [14] which are generally structural relaxation studies. However, because it serves as a base for many BMGs, it is also important to investigate the structural properties of the parent $\text{Cu}_{50}\text{Zr}_{50}$ glass.

$\text{Cu}_{50}\text{Zr}_{50}$ glass was isothermally annealed at 653 K for different annealing times to investigate the relaxation enthalpy. Fig.2 shows the continuous heating DSC traces at 40 K/min for the pre-annealed samples for 0, 5, 15, 25 and 35 min at 653 K. Each trace shows a strong glass transition signal and an endothermic overshoot in the vicinity of glass transition except for unannealed sample. It is seen that the peak temperature, T_p , of this endothermic overshoot is increasing with the annealing time. The enthalpy of recovery (ΔH) was calculated from the area under this endothermic overshoot peak by taking the difference between the relaxed and unrelaxed samples. This area is equal to the amount of enthalpy loss during relaxation and it is clear that the relaxed samples show obvious endothermic heat recovery while the unrelaxed glass does not show the same effect. The data obtained from the Fig.2 was listed in Table-1 for each annealing time and based on the findings it is clear that the relaxation event is annealing time dependent. On the other hand, it is interesting that the glass transition temperature is also increasing with annealing time which may relate to the differences in the short range atomic rearrangements occur in glass in the supercooled liquid region. Fig. 3 (a) shows the related enthalpy recovery, (ΔH), for different annealing times at 653 K. Generally, glass relaxes to lower states of enthalpy with increasing the annealing time and finally after a longer annealing time approaches to the equilibrium state. Here, the value of ΔH increases sharply and the rate of increase is high in the initial stage of relaxation but then it becomes slower and finally approaches to a saturation point after a certain time of annealing. In this study, it seems that the glass is approaching to a saturation limit at around 35 min of annealing at 653 K. The related enthalpy recovery can also be plotted as a function of logarithmic annealing time, seen in Fig.3 (b) where slope of this linear relationship gives the

average rate of enthalpy relaxation. It is also seen from the plot that the rate is decreasing with an annealing time as the slope is changing.

The glass transition is generally studied by DSC which calculates the specific heat capacity difference between the glassy and supercooled liquid states. Here, the specific heat capacity measurements were carried out using DSC at 10 K/min. Fig.4 shows the specific heat values which were determined experimentally in reference to a sapphire standard for the amorphous, supercooled liquid and crystalline states as functions of temperature. The glass transition and the crystallization temperatures were also indicated on the curves. The jump in the values of specific heat capacity data during the transition from amorphous to supercooled liquid state clearly can be seen. The difference in the specific heat between the glassy and supercooled liquid states was found as 35 J/mol.K near glass transition temperature. This difference is decreasing with the temperature when the glass approaches to crystallization event.

Conclusions

In this study, the thermal properties such as structural relaxation and specific heat capacity of $\text{Cu}_{50}\text{Zr}_{50}$ alloy in the vicinity of glass transition were studied using differential scanning calorimetry (DSC). The enthalpy recovery values were found to increase with increasing the annealing time which then approached to a saturation point where the system reaches its highest stable state in amorphous phase. Based on the analysis, this saturation annealing time was determined as close to 35 min. The specific heat measurements show the difference between the glassy solid and supercooled liquid as 35 J/mol.K near glass transition temperature which is then gradually decreases with decreasing temperature.

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Fig.1. Isochronal DSC plot at 40 K/min

Fig.2. DSC thermographs of Cu₅₀Zr₅₀ annealed at 653 K for 5, 15, 25 and 35 min and then cooled down to R.T and heated at 40 K/min.

Table1. Relaxation data of Cu₅₀Zr₅₀ annealed at 653 K

$t_{annealing}$ (min)	T_g (K)	T_p (overshoot) (K)	$\Delta H_{overshoot}$ (J/g)
5	672	689.66	1.410
15	675	690.94	2.205
25	676.5	690.95	2.538
35	677.5	691.70	2.725

Fig.3. Enthalpy relaxation of $\text{Cu}_{50}\text{Zr}_{50}$ annealed at 653 K as a function of annealing time (a) and log. of annealing time (b).

Fig.4. Specific heat of $\text{Cu}_{50}\text{Zr}_{50}$ alloy continuously heated with 10 K/min.

CHAPTER 7: GENERAL CONCLUSION

Summary

This project focused on the devitrification dynamics in the Cu-Zr binary system to characterize the evolution of structural hierarchy during devitrification, assess the thermal stability of the amorphous structure and quantify the kinetics of devitrification for various heating profiles. In-situ high energy X-ray diffraction (HEXRD), differential scanning calorimetry (DSC), high-temperature DSC and transmission electron microscopy (TEM) were the techniques used during the characterization of the as-quenched and annealed alloys. The following conclusions can be drawn from this study.

The devitrification kinetics of $\text{Cu}_{50}\text{Zr}_{50}$ glass was investigated under constant-heating-rate (10 K/min) conditions over the temperature range of 423 and 1264 K using in-situ HEXRD. The sequential modeling of in-situ HEXRD patterns and quantitative assessment of phase fraction evolution during the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy was performed using a Rietveld refinement method. This analysis revealed that the sequence involves the formation of $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2) phases with phase fractions of 0.399, 0.223 and 0.378 (by weight), respectively, from the amorphous precursor at 706 K, decomposition of CuZr (B2) into more stable $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 with phase fractions of 0.636 and 0.364 (by weight), respectively, upon heat to 789 K, re-precipitation of CuZr (B2) upon heating above 1002 K, accompanied by dissolution of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 until the transformation to CuZr (B2) is complete at 1045 K. In this study, the Cu_5Zr_8 phase which was reported previously by Kneller et al [1] at much lower heating rate of 0.835 K/min, was not observed during the devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy. As conclusion, this study brings out three important

questions; is the difference between Kneller's analysis and ours merged from the different heating conditions used for each study; can the initial rapid multiphase crystallization be distinguished and what are the influences of chemical partitioning, diffusion, strain, and defect accommodation in phase selection and the evolution of structural?

Detailed analysis of isothermal crystallization kinetics and microstructural dynamics associated with devitrification of a $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass were performed at 671 K using in-situ high-energy synchrotron X-ray diffraction (HEXRD), conventional and high resolution transmission electron microscopy (TEM and HRTEM), and DSC. This study revealed the primary formation of $\text{Cu}_{10}\text{Zr}_7$ phase with equiaxed growth morphology. Analysis of further annealing showed the precipitation of a thin layer of the CuZr_2 phase when the size of $\text{Cu}_{10}\text{Zr}_7$ crystals reached to approximately 100 nm. The metastable CuZr (B2) crystal was found to grow epitaxially on the CuZr_2 crystals. This study also showed no stability range for Cu_5Zr_8 phase which supports our previous findings during the constant heating rate devitrification. The other finding is the nucleation of platelike crystals embedded in the amorphous matrix. However, because of their small sizes and common diffraction data, it was not possible to solve these structures.

The further investigation of the crystallization kinetics and phase selection mechanism was studied on one of neighbor compositions of $\text{Cu}_{50}\text{Zr}_{50}$, which is $\text{Cu}_{56}\text{Zr}_{44}$ eutectic alloy. The analysis of the as-quenched and annealed ribbons was done using in-situ HEXRD, TEM and DSC under both isothermal and continuous heating conditions. The devitrification sequence under constant heating rate at 10 K/min was found as; the primary formation of major amount of $\text{Cu}_{10}\text{Zr}_7$ (0.918 by weight) and a minor of CuZr_2 (0.082 by weight) at 725 K, the precipitation of CuZr (B2) phase at 1008 K, coexistence of $\text{Cu}_{10}\text{Zr}_7$, CuZr_2 and CuZr (B2)

phases with fractions of 0.928, 0.062, and 0.011 (by weight) respectively until the decomposition of CuZr_2 in to $\text{Cu}_{10}\text{Zr}_7$ and CuZr (B2) phases at 1030 K. In this study, Cu_5Zr_8 phase was not observed as well during the devitrification sequence of $\text{Cu}_{56}\text{Zr}_{44}$ alloy. The additional microstructural analysis of isothermally annealed $\text{Cu}_{56}\text{Zr}_{44}$ alloy at 705 K revealed the primary formation of $\text{Cu}_{10}\text{Zr}_7$ which grows in generally equiaxed morphology. Further annealing of the alloy resulted in the change of the morphology of $\text{Cu}_{10}\text{Zr}_7$ crystals from planar to cellular-like which was related to the slight decrease in Cu concentration. However, the other equilibrium phase, CuZr_2 could not identified during the isothermal microstructural studies. Different from the initial devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ alloy, metastable CuZr (B2) was not observed during the primary crystallization of $\text{Cu}_{56}\text{Zr}_{44}$. This may be caused because the alloy composition is far from that of CuZr intermetallic. Another interesting result of this study is that we did not observe the nucleation of plate-like structures during the devitrification of $\text{Cu}_{56}\text{Zr}_{44}$ alloy which were observed in more Zr-rich composition; $\text{Cu}_{50}\text{Zr}_{50}$.

The thermal stability and glass forming ability of Cu-Zr binary and Cu-Zr-Al ternary alloys were investigated using high-temperature differential scanning calorimetry (DSC) under constant heating rate conditions. The analysis revealed the three compositions; $\text{Cu}_{64.5}\text{Zr}_{35.5}$, $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$ have the highest GFA with the largest values of reduced glass transition temperature (T_{rg}), γ and supercooled liquid region (ΔT_x). It was found that the addition of Al as a third impurity element increase the ΔT_x , T_{rg} and γ values, leading to a higher GFA and thermal stability. The effect of Al on the initial devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ was also investigated in $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glassy alloys using in-situ high energy X-ray (HEXRD). The Rietveld optimized patterns indicated simultaneous crystallization of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases for both $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloys. However, a more rapid and

eutectic like reaction producing $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 was observed for $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloy compared to that for $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ in which the $\text{Cu}_{10}\text{Zr}_7$ may form initially, followed by CuZr_2 phase. The reaction difference may occur because the compositions of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ are much closed to the eutectic $\text{Cu}_{56}\text{Zr}_{44}$ and $\text{Cu}_{50}\text{Zr}_{50}$, respectively. The other interesting result of this study is the suppression of nucleation of CuZr (B2) by the addition of Al into $\text{Cu}_{50}\text{Zr}_{50}$ alloy.

Structural relaxation of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ alloy in the vicinity of glass transition temperature was investigated during the isothermal annealing of $\text{Cu}_{50}\text{Zr}_{50}$ glass at 653 K, which is well below the glass transition temperature at different annealing times. The result of this study indicated the increase of enthalpy overshoot with increasing the annealing time and then the saturation of overshooting around 35 min of annealing at 653 K. The specific heat capacity analysis in the vicinity of glass formation indicated that the difference between the glass and the supercooled liquid as 35 J/mol.K during the continuous heating at a rate of 10 K/min.

Suggestions for Future Work

In this current project, we focused on the phase selection mechanism with relevant phase competition and the associated dynamics of structural evolution and kinetics of devitrification in Cu-Zr system driven far from equilibrium conditions for various heating profiles. Based on the current results, future suggestions can be given as follows;

- Thermodynamics and kinetic models can be used to predict observed phase sequences and transition rates. Several nucleation and growth models can be tried to model the early crystallization stage in Cu-Zr binary metallic glasses. Kinetics modeling companied with the microstructural investigations will provide better understanding of overall transformation,

including nucleation and growth mechanisms. Thermodynamic models can also be developed to quantify the driving forces for all competing phases over all possible ranges of composition (equilibrium and nonequilibrium).

- In devitrification studies, it is important to study the initial stages of phase decomposition leading into crystal formation as well. The platelike structures formed during the isothermal devitrification of $\text{Cu}_{50}\text{Zr}_{50}$ glassy alloy can be investigated using atom probe tomography (APT) technique. This study will permit to observe variations in the atomic scale compositions with high spatial and chemical resolution. APT allows imaging and identifying an individual atom and is commonly used to select and determine the compositions of small volumes. Atom probe is a combination of field ion microscope and mass spectrometer and the evolution of APT was developed by Müller and Panitz, on 1967 [2] and Müller et. al in 1968 [3]. A schematic sketch of three dimensional atom probe tomography (3DAP) is illustrated in Fig.1. APT has been applied to a wide variety of materials which exhibits electrical conduction. Therefore, metals, semiconductors and some ceramics are the most suitable samples for APT analysis. Sample preparation is the main and significantly important issue to increase the quality of experiments. The sample preparation for APT is much similar to that for TEM. The main sample shape for APT is known as a sharp needle-like shape, illustrated in Fig.2. This technique is useful in obtaining both 3D constructions of small scale structure, and getting quantitative (compositional) information as shown in Fig.3. Therefore, such a study will be helpful in determining the platelike nanocrystals, however, if it is problematic with APT, small angle scattering would be used as an alternative technique.

- The devitrification analysis results can be used in controlling the microstructure to enhance the desired properties of metallic glasses. It has been known that partially crystallized

amorphous/crystalline composites have higher mechanical and physical properties compared to their monolithic amorphous phase. The present study provides the sequence of phases during crystallization under both isothermal and continuous heating conditions. Therefore, using this information, the annealing conditions; such as isothermal or continuous heating, time and temperature can be determined and selected to prepare A/C bulk metallic glasses with desired properties.

- The crystallization pathway is strongly heating rate and alloy composition dependent. For example, we found that formation of metastable CuZr (B2) phase is suppressed at lower heating rates such as 5 K/min, while it is observed for 10 and 20 K/min. Therefore, the light of this information, the time-temperature-transformation (TTT) diagram can be created using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques for several heating profiles.

- Directional devitrification solidification (DDS) technique can be used to investigate the microstructure of alloy samples. This technique provides a high degree of control over the scale and morphology of the crystallizing phase or phases and allow a precisely control the structural hierarchy. In the directional devitrification process, the test sample can be translated through a very small hot zone which is bounded by cold zones on either side. Temperature of the zone and velocity of translation are two critical parameters which control the temperature profile experienced by the specimen. Phase identification and microstructural characterization of DDS samples can be carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), high-temperature DSC and X-ray diffraction (XRD) techniques. The Cu-Zr binaries can be selected as model system

and after achieving control on microstructure other systems can be studied for further experiments.

- The importance of liquid/glass structure in determining the devitrification pathway on subsequent heating can be investigated. If the liquid/glass structure is controllable, then will the pathway mechanism be controllable? This question can be addressed for the future studies.

- The investigation of structural relaxation in the vicinity of glass transition at different annealing temperature and time is significant in determining the relaxation mechanism in glass. The determination of relationship between the structural relaxation and the atomic ordering in the supercooled liquid region will provide the control of glassy structure and thereby the corresponding devitrification mechanism. Therefore, the behavior of structural relaxation by changing the annealing time at different temperatures below the glass transition temperature can be studied in further projects.

- Aluminum as a third impurity element was found to affect the glass forming ability (GFA) and thereby the initial devitrification dynamics of the parent binary Cu-Zr amorphous alloys. As an additional work, the initial phase selection dynamics can be analyzed using TEM on partially annealed ternary samples. Especially, for the $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloy, the formation of CuZr (B2) phase has not been observed even though it has a much close composition to $\text{Cu}_{50}\text{Zr}_{50}$. However, in the literature the metastable formation of CuZr (B2) was reported during the crystallization of $\text{Zr}_{50}\text{Cu}_{46}\text{Al}_4$ and $\text{Zr}_{50}\text{Cu}_{44}\text{Al}_6$ alloys. These high Zr-content compositions may be investigated in terms of understanding the CuZr (B2) phase selection mechanism in Cu-Zr-Al ternaries compared to the binary Cu-Zr alloys.

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Fig. 1. A schematic sketch of 3D atom probe [4].

Fig. 2. Left: Scanning electron microscopy (SEM) image of an electropolished specimen of an aluminum alloy. Right: Microtip specimen of a multilayer Al/SiO₂/Si structure fabricated by ion beam milling with a diamond mask particle [5].

Fig.3. (a) Atom probe image and (b) compositional profile through the precipitate [6].

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