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A New Model in Glass Forming Range of Binary Alloys

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ABSTRACT

Glassy metals have been prepared by various techniques such as rapid cooling of liquid or vapor phase, atom by atom deposition, particle bombardment and solid state reactions such as mechanical alloying. It is well known that glassy metal cannot be produced in every binary composition, thus determination of the range of composition in which the glass is produced, is very important. There are several models to predict the possibility and extent of amorphization in binary alloy systems. Most of them are designed based on microstructural properties such as Egami or Miracel model, thermodynamical phenomena such as enthalpy in Miedema or Bakker Model and statistical analysis of existing experimental data such as analyzing enthalpy vs. atomic radios ratio in Zhang model. In these models, the production process is not considered, while the experimental data shows that glass forming range is process dependent. In the present research, by considering the conditions of mechanical alloying process, a new microstructural model based in atomic arrangement changes during process was developed. Using this model the difference of glass forming range in the processes of mechanical alloying and rapid solidification of liquid was justifiable and the supposed model was more adaptive to mechanical alloying produced glasses than another models.

Key words: Glassy metals, modeling, mechanical alloying, glass forming range

INTRODUCTION

Although, crystalline structure is introduced as a main structure of metallic alloys, since 1960, discovering of glassy metals by clement changed the materials science and engineering (Clement *et al*., 1960). Glassy metals have attracted wide interests (Helal, 2006) because of their unique properties, such as high mechanical ductility and strength, excellent soft magnetic behavior, and temperature independent electrical conductivity (Chaudhari *et al*., 1980). For the last three decades, glassy metals have been mainly prepared by rapid solidification with very high cooling rates (10^5-10^{12} K sec^{-1}). The large value of cooling rate was limiting the production process. Additionally, recent development regarding to corrosion rate of metals have led to improve corrosion behavior using glassy metals (Ekuma *et al*., 2007) whereas, because of quenched in-lattice defects, the corrosion resistance of mechanical alloyed is higher than rapid solidified glassy metals (Rana *et al*., 2001).

Until 1983, glassy metals have been successfully synthesized using various techniques by solid-state reactions, Ni_3Nb_2 by Mechanical Alloying (MA), Zr_3Rh by hydrogen absorption and thin films of Au-La by interdiffusion (Gaskell, 1983). In the experiment of annealing of Au-La multilayers to form an amorphous phase, Schwarz suggested that the unusual fast diffusion of one

species in the other and the large negative heat of mixing are necessary to form glassy metals from crystalline phases (Schwarz, 1988). Finally, in multilayer structures, the optimum thickness of amorphous layer growth by low ion energy implantation has been calculated using mathematical model (Boubetra and Bouafia, 2008).

MA is the process of frequently fracturing and welding of the blend of powders in a highly energetic environment to produce a controlled, extremely fine microstructure. This process has been mainly used for producing metal matrix composite reinforced by oxide particles, nanostructure alloys (Khosroshahi *et al*., 2008) and non-stoichiometric compounds with various atomic ratios (Song and Lee, 2006). In addition to ease of MA to rapid solidification, the MA process could generate a fine scale mixing of the liquid immiscible system (Cu-Pb) or the solid immiscible system (Cu-Fe) which have the troubles of heavy segregation during rapid solidification from the liquid phase and despite the very large variation between the melting points of Nb and Sn, the homogeneous Nb3Sn compound, be provided by MA. Glassy metals can be obtained either from the mixtures of pure elements or from the intermetallic compounds (Lu and Lai, 1995). The flowing and pressing properties of the amorphous powders produced by MA are excellent and thus at adequate pressures and temperatures well below the crystallization temperature of the amorphous alloy, it can be consolidated into fully dense bulk by hot pressing. So, the amorphization by MA offers a low-priced method and a promising approach to the synthesis of bulk objects from glassy metals (Suryanarayana, 2001). On the other hand, MA processing has some disadvantages for instance $Mn_{0.8}Zn_{0.2}Fe_2O_4$ catalyst compound, synthesized by the self combustion method has better mechanical and magnetic properties compared to conventional ball milling method (Puspitasari *et al*., 2011).

Glassy metals were experimentally confirmed to present a glass transition by Turnbull and Cohen (1970). Also through a successful preparation of continuous long length of ribbons, a large scale production of glassy metals was achieved. And also recently, using copper mold casting, full glassy rod of La Alloy with 12 mm diameter was synthesized (Zhang, 2006).

The intention of this study was to understand the range of composition in which glassy metals formation is possible in the other word GFR (Glass Forming Range) prediction in MA process. To satisfy this goal, the amorphization conditions of simple alloy by mechanical milling will be discussed. Finally, from the view point of thermodynamics of microstructure, the possible amorphization composition of MA will be described.

MATERIALS AND METHODS

For three decades, glassy metals production was limited to the rapid solidification process so, the amorphous structure was defined as a maintaining a random structure of the liquid by suppressing the nucleation and growth of the long-range ordered crystal structure during solidification. There are some models to describe the structure of glassy metals, which the cluster model is the most practical of them (Bakai, 1994) in this model short-range order in metallic glasses consisting of a lot of atomic clusters that are interconnected with weak bonds is assumed. Because of particular arrangement of atomic clusters, the local density in some area is large enough to stabilize the glass structure. For example, the four atoms of the same size as a compact cluster provide a tetrahedron filling 78% by volume of space locally. This value is even more than packing factor of closed packed crystal structures (FCC and HCP). This improved packing factor cannot be extended to the global scale of the glass structure as the lack of translational symmetry necessarily produces gaps among clusters.

Inoue has proposed a set of empirical rules for metallic glass design, to produce these densely packed clusters: (1) The alloy must be composed of three or more different elements (2) The atomic size between constituent elements must vary by a specified value (~12% or more) and (3) The mixing enthalpy of the constituent elements must be less than zero (Inoue, 1998). Miracle has shown that the highly dense clusters can be made by elements of varying atomic sizes, where the solute elements act as the center of solvent element coordination shells. Higher coordination number structures and higher packing density occur by increasingly different atomic sizes between elements (Miracle, 2004). For example, cluster with a coordination number of 24 is result of a radius ratio of solute to solvent atom of 1.659. This ratio was achieved in metallic glass design in the case of Fe-based glass with Er is a solute element. As indicated by Inoue's first empirical rule and explained in detail by Miracle's structural model, the glass forming ability can be increased by the addition of a third or fourth elemental species. Miracle has shown that smaller solutes can occupy interstitial sites between the high coordination number clusters formed between the solvent and large solute atoms. Also, the cluster model can explain the structure of liquids (Egami, 2006).

Accordingly, by considering the liquid curve in Gibbs free energy diagram as an amorphous phase Gibbs free energy diagram and extrapolating of this curve to room temperature, the stability range of composition of metastable amorphous phase in binary alloy system can be determined. Due to this model, T_C (Critical Temperature) is defined as the equal temperature of interception of liquid phase and the crystalline phase Gibbs free energy curves. Figure 1 schematically shows the Gibbs free energy (G) versus composition (x) curves of one liquid phase and two solid solution phases at 500 K for A-B binary system. T_C (x = 0.4) = 500 K solid-I and liquid, and T_C (x = 0.7) = 500 K for solid-II and liquid were determined from the intersections of the curves. Also, it is possible to get the T_C versus x curve by scanning the whole temperature and composition domains; The typical T_C curves for A-B binary system with a single eutectic point, is revealed in Fig. 2.

It should be noted that this model has been designed supposing impossibility of the terminal solid solution decomposition.

In this research, using Thermo-Calc software Ver. 2010, by considering the T_C is equal to room temperature, the glass forming ranges of some binary alloys were calculated and the results were compared with the experimental and another model data.

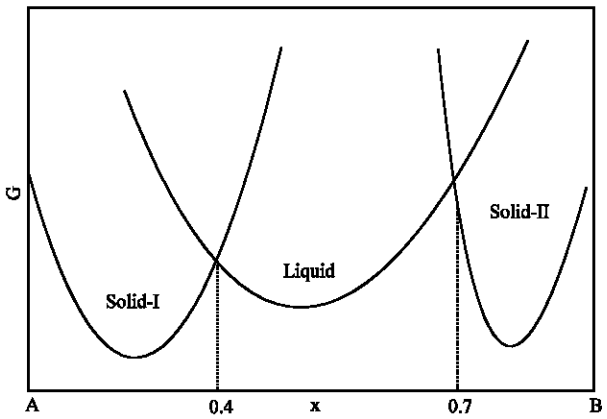

Fig. 1: Schematic diagram of Gibbs free energy curves of solid and liquid phases for A-B binary system at a fixed temperature T. The intersection of the curves presents the compositions of x = 0.4 and x = 0.7 corresponding to this critical temperature

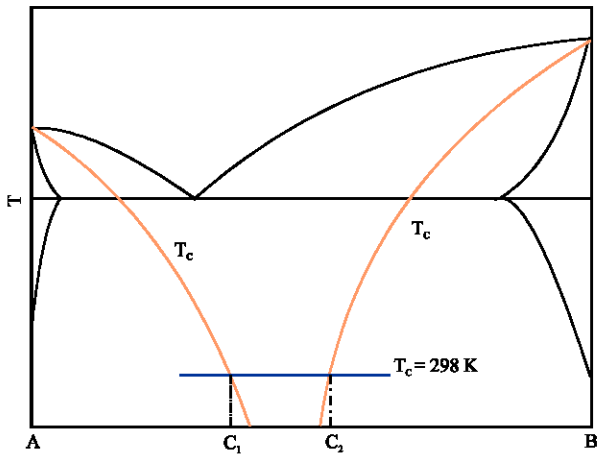

Fig. 2: Schematic diagram of the simple eutectic phase diagram of A-B binary alloys with T_C curves

Table 1: The minimum concentrations of solute atom necessary to fabricate glassy metal for 17 binary alloy systems as a result of suggested model using Thermo-Calc software at T_C = 298 K and P = 105 Pa

Solvent	Co	Co	Co	Fe	Fe	Hf	Mn	Ni	Ni
Solute	B	Ti	Zr	C	Zr	Ni	Hf	P	Ta
C_{min}^{SM} (Minimum concentration as a result of suggested model)	0.17	0.24	0.07	0.16	0.11	0.08	0.08	0.17	0.18
Solvent		Ni	Pd	Ti	Ti	Zr	Zr	Zr	Zr
Solute		Zr	Si	Ni	Si	Al	Co	Fe	Ni
C_{min}^{SM} (Minimum concentration as a result of suggested model)		0.10	0.14	0.22	0.15	0.18	0.14	0.19	0.21

RESULTS AND DISCUSSION

The minimum concentrations of solute atom necessary to fabricate glassy metal for 17 binary alloy systems as a result of suggested model using Thermo-Calc software at T_C = 298 K and P = 10^5 Pa were calculated. The calculated data using supposed model is shown in Table 1.

The experimental data of minimum concentration of glass formation in MA process collected by Suryanarayana (2001) the experimental data of minimum concentration of glass formation in rapid solidification process collected by Egami and Waseda (1984) and the calculated minimum concentration for glass formation predicted by Egami model in comparison to the suggested model calculated data has been drawn in Fig. 3. Interesting results obtained from the comparison of these data, as a first and most important, the calculated data from the suggested model has more acceptable similarity to MA process data than rapid solidification process records. The main reason of this similarity is the critical temperature in the proposed model is more comparable to MA process temperature than freezing temperature in rapid solidification process.

As a one another result of Fig. 3 the proposed model calculated data is lower than MA process records. Two major reasons can be attributed to this event, at first the increasing of local temperature of grinding medium in MA and secondly the limitation of experiments.

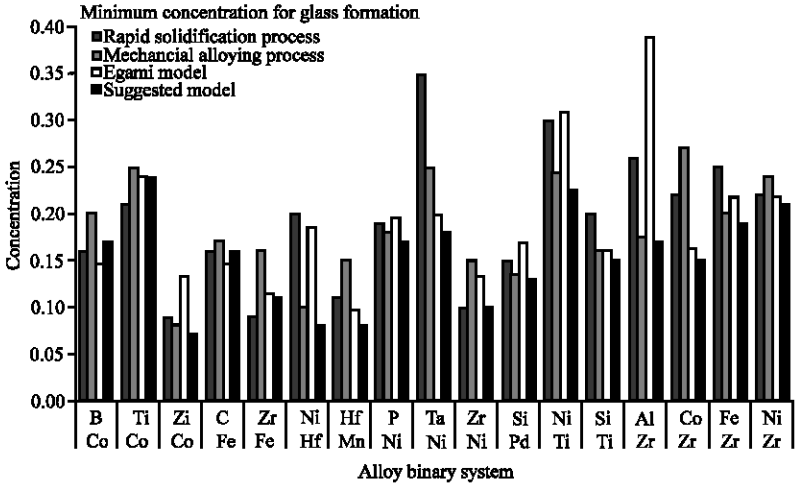

Fig. 3: A comparison between minimum concentrations of solute necessary to provide glassy metals using rapid solidification process, MA process, Egami model and the proposed model

CONCLUSION

Due to extraordinary properties of glassy metals, production of this category of materials from is very essential. Production of glassy metals is limited to specific compositions of binary alloys and because of expensive cost of experiments the modeling and calculation of the glass forming range is very vital. In the existent models, the influence of producing process is unnoticed, while the producing process is a very important factor that affecting the glass forming range (Fig. 3) the proposed model that is based on microstructure of glassy metals and process temperature has a successful adaptation to MA results. So, the glass forming range in MA process can be justified by the suggestive model, even more than the known Egami model.

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