Correlation between Glass Formation and Type of Eutectic Coupled Zone in Eutectic Alloys

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Glass formation is basically to avoid nucleation upon quenching. However, the growth of each nucleus is also important as certain undercooling is needed. Thus the subsequent competition between the growth of crystalline phases and the formation of amorphous phase should be considered. In this paper, we summarized our recent studies in Pd-Ni-Cu-P system and La-Cu-Ni-Al alloy systems. It is concluded that the glass forming ability of a eutectic alloy system depends on the type of the eutectics, i.e. symmetric or asymmetric eutectic coupled zone. For the alloys systems with symmetric eutectic coupled zone, the best glass forming alloys should be at or very close to the eutectic composition. For the alloys with asymmetric eutectic coupled zone, the best glass forming alloys should be at off-eutectic compositions.

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1. Introduction

As bulk metallic glass (BMG) materials have attracted more and more interest nowadays, lots of studies were also made on the glass forming ability (GFA) during the past several decades,¹⁻³ which is of technical importance to the design and development of new BMGs. As a result, several indicators have been proposed to predict the glass forming ability,¹⁻⁶ including the reduced glass transition temperature $T_{rg}$, the critical cooling rate $T_{rg}$ for glass formation. Turnbull’s early work on nucleation of a crystal from the melt showed that $T_{rg}$ is a key parameter to consider in glass formation. Accordingly, the glass former is always associated with deep eutectics, since eutectics is always associated with a minimum liquidus temperature. However, Turnbull’s work is based on the assumption that as long as the nucleation (at a nucleation rate of $\leq 10^{-6} \text{ cm}^3\text{s}^{-1}$) is avoided, the glass will be formed, or that as long as the nucleation rate is higher than $10^{-6} \text{ cm}^3\text{s}^{-1}$, the alloy will be fully crystalline. However, the growth of the nucleus is also important as certain undercooling is needed. Thus the subsequent competition between the growth of crystalline phases and the formation of amorphous phase should be considered. Accordingly, growth kinetics of a crystal may also be a key to determining the condition for the formation of such a glass.

Here, we summarized our recent experimental results on Pd-based and La-based BMG-forming alloy systems and correlated their GFA to the types of eutectic systems in terms of the growth kinetics of individual competitive phases including primary dendrites and eutectic versus glass formation.

2. Experimental Procedure

Pd$_{60-\alpha}$Ni$_{10}$Cu$_{30}$P$_{\alpha}$ (α = 10-20) alloys were prepared by vacuum induction melting of a mixture of pure Pd (99.94%) and a Ni-Cu-P master alloy in quartz tubes followed by water quenching. La$_{100-\gamma}$[Al$_{0.412}$(Cu,Ni)$_{0.588}$]$_{\gamma}$ (γ = 30-56.3) alloys were prepared by arc-melting raw materials (La 99.9%, Al 99.9%, Ni 99.98% and Cu 99.999%) under a Ti-gettered argon atmosphere. Glassy rods with diameters of 1, 1.5 and 2 mm respectively were prepared by chill casting. For La-based alloys, ingots were cast by pouring the molten alloy into the cavity of a copper mold with diameters of 5 to 12 mm and 60 mm long. The corresponding glass transition temperature $T_g$ and crystallization temperature $T_x$, onset melting temperature $T_m$ (solidus) and offset melting temperature (liquidus) $T_l$ were measured by differential scanning calorimetry (DSC) or differential thermal analysis (DTA) at a heating rate of 40 K/min. In addition, ribbon samples for these alloys were obtained by single roller melt-spinning in an argon atmosphere.

3. Results

3.1 Glass formation in Pd-Cu-Ni-P system

Figure 1(a) shows the liquidus temperature $T_l$ and solidus temperature $T_m$ as a function of P content in Pd$_{60-\alpha}$Cu$_{30}$Ni$_{10}$P$_{\alpha}$ alloys. It was found that Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ is very near a eutectic composition.¹¹ As the P content is reduced in the Pd$_{60-\alpha}$Cu$_{30}$Ni$_{10}$P$_{\alpha}$ alloys, the glass forming ability is reduced (the solid line part in Fig. 1(b)). The best glass forming composition is at the eutectic composition. We also observed that the transition from fully amorphous to fully crystalline (eutectic) occurred when the cooling rate is within 0.64 to 1.98 K/s.¹¹ As for the off-eutectic Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{18}$ alloy, the critical cooling rate for fully glass formation is much higher at 250 to 500 K/s.¹¹

3.2 Glass formation in the La-Cu-Ni-Al system

Figure 2(a) shows the liquidus and the solidus temperatures as a function of alloy composition in the quaternary La-Al-(Cu,Ni) alloy system. It shows clearly that La$_{56}$(Cu,Ni)$_{23}$Al$_{11}$ is at the eutectic composition. The critical cooling rate for fully glass formation of this alloy is about 1000 K/s as the critical diameter for fully amorphous formation is only 1.5 mm.¹²
But a composite with a structure of dendrite plus amorphous phase is formed in a 12 mm diameter chill-cast rod and the critical cooling rate for that is 15 K/s. However, in an off-eutectic alloy, La$_{63.1}$Cu$_{21.5}$Ni$_{5.5}$Al$_{15.2}$ alloy a fully amorphous rod with about 10 mm in diameter can be obtained with a critical cooling rate of 9 K/s. This confirms that the optimum glass forming composition is at an off-eutectic composition.

4. Discussion

Two types of eutectic, *i.e.* regular and irregular have been identified in metallic alloy systems. Regular eutectic is of the non-faceted/non-faceted type, in which all the constituent phases possess a low entropy of fusion, such as for Al-CuAl$_2$.\(^7,8\) Irregular eutectic is of the non-faceted/faceted type, in which one of the constituent phases possess a high entropy of fusion, such as Si in Al-Si and C in Fe-C.\(^7,8\) The growth kinetics of regular and irregular eutectics are substantially different, resulting in two types of coupled zone, *i.e.* symmetrical and skewed, where the coupled zone defines the composition and temperature (undercooling) range which leads to entirely eutectic growth.\(^7,8\)

A symmetrical coupled zone is associated with regular eutectic, which always includes the eutectic composition and reflects the similar undercoolings of its constituents when they are primary. A coupled zone is constructed by considering the competitive growth of dendrites and eutectic under steady-state conditions. Each growth morphology, primary dendrites (of both phases) or the eutectic, has its own relationship between growth rate ($V$) and the liquid/solid interface temperature ($T$).\(^7\) The competitive growth criterion is that the morphology having the highest interface temperature for a given growth rate, or the highest growth rate for a given undercooling, will be the one observed.\(^7,8\) A skewed/asymmetrical coupled zone is normally related to irregular eutectic, which is skewed towards the faceted $\beta$ phase due to its growth problems under high undercooling. For such a system, a fully eutectic microstructure may not be obtained when an alloy of eutectic composition is rapidly solidified, instead $\alpha$ plus interdendritic eutectic will be obtained.

For the good glass forming systems, *e.g.* bulk metallic glasses, their glass transition temperature is relatively high compared with their liquidus temperature as shown in the Figs. 3 and 4. Therefore, one can expect that the coupled zone will be limited by the formation of glass at high growth rate.\(^10\) This is to say that for such alloy systems, the amorphous phase is an alternative phase involved in the competition. If we assume that the temperature gradient is constant, we can use cooling rate instead of growth rate.

![Fig. 1](image1.png)  
**Fig. 1** (a) Composition dependence of $T_m$ and $T_l$ and (b) plot showing increase in GFA with increasing P content, showing that the optimum glass formation at the eutectic composition. $\Delta H_{\text{cast}}$ is measured from chill casting 2 mm rod samples, $\Delta H_{\text{ribbon}}$ is measured from its ribbon sample. Dotted lines show the possible trends as the increase of P content.

![Fig. 2](image2.png)  
**Fig. 2** (a) Composition dependence of $T_m$ and $T_l$ and (b) critical diameter for glass formation as a function of Al content in the La$_{100-x}$[(Cu,Ni)$_{0.588}$Al$_{0.412}$]$_x$ alloys, showing that the optimum glass formation at an off-eutectic composition.
4.1 Glass forming region and glass forming ability in eutectic system with symmetric coupled zone

For the symmetric eutectic coupled zone, the glass formation zone will be symmetric around the eutectic composition as shown in Fig. 3. If \( T_g \) has little/small dependence on alloy composition and cooling rate, the glass forming region will be as shown in Fig. 3. From Fig. 3, when the growth temperature of the crystalline constituents is lower than \( T_g \), the glass will be formed. The transition from the fully crystalline (eutectic) to the fully amorphous phase should be very sharp in terms of growth rate as the competition is between the eutectic and the amorphous phase only. As for the off-eutectic composition, the growth temperature of the dendrite is so high that it will always form first. For the remaining liquid, if the growth temperature of the eutectic is high, then eutectic will form. Otherwise, the amorphous phase will be formed, resulting in the formation of a composite, i.e. crystalline dendrite in an amorphous matrix. Furthermore, in order to form fully amorphous for the off-eutectic alloy, the cooling rate has to be high enough so that the growth temperature of the dendrite is lower than \( T_g \). It is evident that the cooling rate required for fully amorphous phase formation for a sufficiently off-eutectic composition is always higher than that for the eutectic alloy. Thus the glass forming ability of the sufficiently off-eutectic alloy in a system with a symmetric eutectic coupled zone is always poorer than that of the eutectic alloy and the best glass former in these systems should always be at or very near the eutectic composition. This is consistent with the results from Pd-Ni-Cu-P system. It is further noticed that composite regions i.e. glass+\( \alpha \) and glass+\( \beta \), are located symmetrically in each side of the glass forming range.

4.2 Glass forming region and glass forming ability in eutectic system with asymmetric skewed coupled zone

For the asymmetric eutectic coupled zone, the glass formation zone will be asymmetric around the eutectic composition as shown in Fig. 4. This is to say that for the eutectic composition, the formation of a dendrite-plus-glass composite will be formed at low cooling rate. Only when the cooling rate is high enough, will a fully amorphous structure form, as \( T_g \) is then higher than that of the dendritic growth temperature. However, for the off-eutectic alloy, the fully glass formation will be achieved at relatively low cooling rate when \( T_g \) is higher than the growth temperature of the dendrite and the \( \alpha \) dendrite. Accordingly, the alloy with eutectic composition always shows a poorer glass forming ability than the off-eutectic alloy for an irregular eutectic system. This indicates that the optimum glass forming ability should be obtained at off-eutectic compositions for eutectic system with skewed eutectic coupled zone. This is consistent with the results from La-Cu-Ni-Al system. It should be further noticed that composite regions i.e. glass+\( \alpha \) and glass+\( \beta \), are located asymmetrically in each side.

5. Summary

We have analyzed the glass forming ability around eutectic composition in terms of the competitive growth of primary dendrites, eutectic and glass. It has been shown that the glass forming ability of a eutectic alloy system depends on the type of the eutectics, i.e. symmetric or asymmetric coupled zone. For the alloy systems with symmetric eutectic coupled zone, which is associated with the regular eutectic, the best glass forming alloys should be at or very close to the eutectic composition. For the alloys with asymmetric eutectic coupled zone, which is associated with the irregular eutectic, the best glass forming alloys should be at off-eutectic compositions, probably towards the side of the faceted phase with a high entropy in the phase diagram.

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