

Estimation of Relative Glass Forming Abilities of Multicomponent Alloy Systems

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A thermodynamic calculation scheme based on a CALPHAD method has been studied to evaluate the relative glass forming abilities (GFAs) of multicomponent alloy systems. The concept of the normalized driving force has been developed for estimation of the relative GFAs of different alloy systems. Driving forces of formation of crystalline phases under metastable supercooled liquid state have been calculated for different alloy systems to predict the possible crystalline phases and the maximum driving forces normalized by the respective melting temperatures are correlated with the experimentally obtained GFAs of the alloys. It shows that the estimated relative GFAs of different alloy systems based on the normalized driving forces agree well with the experimental results. [doi:10.2320/matertrans.MJ200718]

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1. Introduction

Since bulk amorphous alloys can have ultra-high strength and good corrosion resistance,¹⁻⁴ which are quite attractive for structural applications, there is a continuing interest in finding new bulk amorphous alloy systems having high glass forming abilities (GFAs).

Several approaches have been suggested to develop the bulk amorphous alloys with high GFAs. The most well known ones are three empirical component rules;⁵ *i.e.*, 1) multicomponent systems consisting of more than three elements, 2) significant difference in atomic size above 12% among the main constituent elements, and 3) large negative heats of mixing among the constituent elements. Besides these, there have been several attempts using the thermodynamic approach to predict the compositions of alloys having high GFAs for several alloy systems.^{6,7} This approach is based on the concept of local melting minimum criterion, which suggests that the compositions exhibiting the local melting minimum points favor amorphous phase formation. More sophisticated theoretical approaches have also been performed considering nucleation kinetics and other physicochemical properties, in order to predict composition dependencies of GFA.⁸⁻¹¹ The difficulty in the above sophisticated works is that it is not always easy to find good input parameters (physicochemical property values).

Recently, it has been shown that driving force criterion based on a simple thermodynamic approach can effectively predict the compositions of alloys having high GFAs.^{12,13} The driving force criterion is based on the assumption that the phase having the highest driving force among all possible crystalline phases is most likely to form first. Considering that the formation of an amorphous phase would be favored when the nucleation and growth of crystalline phases are retarded, then the composition with the highest GFA can be the one with the lowest driving force of formation of crystalline phases. Although the driving force criterion or local melting minimum criterion based on the thermodynamic approach can predict the composition having high

GFA in a given alloy system, there is no method which can predict the relative GFAs of different alloy systems.

In the present paper, we apply the driving force criterion to predict the relative GFAs of various alloy systems by comparing the maximum calculated driving forces. Comparisons have been made with experimental results on the same alloys.

2. Experimental Procedure

Three different kinds of Fe-base amorphous alloys, Fe₆₂Zr₈B₁₅Mo₁₅ (F1), Fe₆₂Zr₈B₁₅Mo₈Co₇ (F2), and Fe₆₃-Zr₈B₁₅Mo₇Co₆Al₁ (P0) were prepared by induction melting of pure elements and pre-alloys. The melt spun ribbon of about 100 μm in thickness and the rod shaped samples of various diameters were prepared by melt spinning and injection copper mold casting, respectively. The amorphous nature of the samples was analyzed by X-ray diffraction (XRD) analysis. In order to analyze the atomic arrangements of the alloys in as-cast state, extended X-ray absorption fine structure (EXAFS) analyses of the melt spun ribbon samples were performed at 7C1 beam line of Pohang Accelerator Laboratory at POSTECH.

3. Thermodynamic Calculation

All thermodynamic calculations in the present study are performed using the critically assessed thermodynamic parameters, based on the CALPHAD method.¹⁴ Here, the Gibbs energies of individual phases are described using thermodynamic models. Then, the model parameters are optimized considering relevant experimental information on phase equilibria or the other thermodynamic properties. The calculation of phase equilibrium is performed based on the minimum-Gibbs-energy-criterion, *i.e.*, the Hillert's equilibrium condition.¹⁵ The input parameters for calculation are optimized so that the experimental information on the phase diagram and other thermodynamic quantities of the corresponding binary systems is reproduced by calculation, considering no ternary phase except FeMoB phase. The present study for the Fe-base amorphous alloy systems are based on the critically assessed binary descriptions of Fe-Zr

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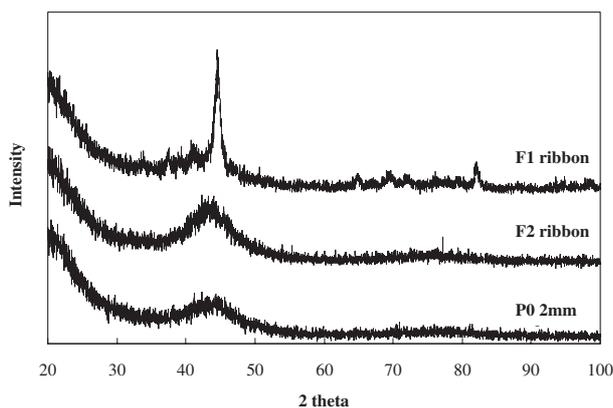


Fig. 1 XRD peaks of the alloys.

by Servant *et al.*,¹⁶ Zr-B by Rogl *et al.*,¹⁷ Fe-B by Rompaey *et al.*,¹⁸ Mo-B by Pan,¹⁹ etc. Determination of ternary or higher interaction parameter was not attempted since the experimental information could be reproduced well by the calculation with only binary descriptions. The driving forces of possible crystalline phases in each alloy were calculated at the supercooled state, 300 K below their calculated melting temperature, to determine the types of possible crystalline phases. The degree of supercooling was set at 300 K based on our previous research on Zr- and Cu-base alloys.²⁰ It showed that at the critical cooling rates, the degree of supercooling needed for the formation of amorphous structure is around 300 K. The maximum value among the driving forces of crystalline phases in each alloy was divided by its calculated melting temperature for normalization. All the basic thermodynamic calculations and their assumptions are described in the previous studies.^{12,13}

4. Results and Discussion

Figure 1 shows the XRD results of the alloys. The maximum thickness that can be amorphized is less than 100 μm for F1 alloy, about 100 μm for F2 alloy, and 2 mm for P0 alloy. F2 alloy can be an amorphous only when it is melt spun. The strong crystalline peaks were found even in a melt spun ribbon sample of F1 alloy.

Figure 2(a) shows the driving forces of crystalline phases along the composition line $\text{Fe}_{63}\text{Zr}_x\text{B}_{23-x}\text{Mo}_7\text{Co}_6\text{Al}_1$ (P0) with varying Zr content. According to the present driving force diagram, at 8% Zr, ZrB_2 phase has the highest possibility to form during solidification of the alloy, followed by MoB phase. Same result has been obtained for the other alloys using the same approach (Fig. 2(b) and 2(c)).

Figure 3 shows the Fourier transformed plot of (a) Zr K-edge and (b) Mo K-edge EXAFS spectra of the alloys. As shown in Fig. 3(a), ZrB_2 phase exists (indicated by a dashed line) in all alloys except F1 alloy. On the other hand, Mo K-edge EXAFS spectrum shows the presence of MoB phase in P0 and F1 alloys, but not in F2 alloy. The analyses of driving force diagrams and EXAFS spectra indicate that the major crystalline phases that can form in the alloys are ZrB_2 and MoB. However, careful analyses of phase diagrams constructed in the present study show that ZrB_2 pre-exists with the melt at the melting temperatures of the alloys. Therefore,

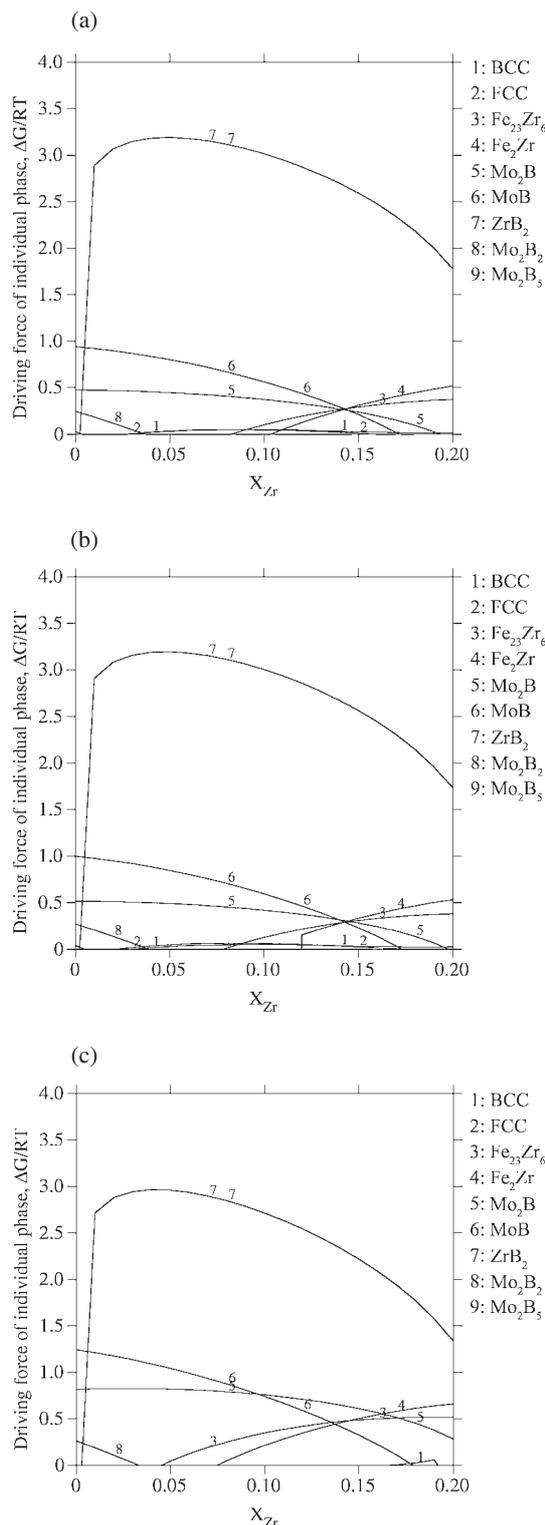


Fig. 2 The driving forces of crystalline phases; (a) F1 alloy, (b) F2 alloy, and (c) P0 alloy.

it is assumed that the crystalline phase that forms during solidification is MoB and the value of maximum driving force was obtained for MoB phase.

Table 1 shows the calculated melting temperature, the value of maximum driving force, and the value of normalized driving force (*i.e.*, the value of maximum driving force divided by melting temperature). Since ZrB_2 pre-exists in the melts ($\sim 5 \text{ V\%}$) of the F2 and P2 alloys, the actual

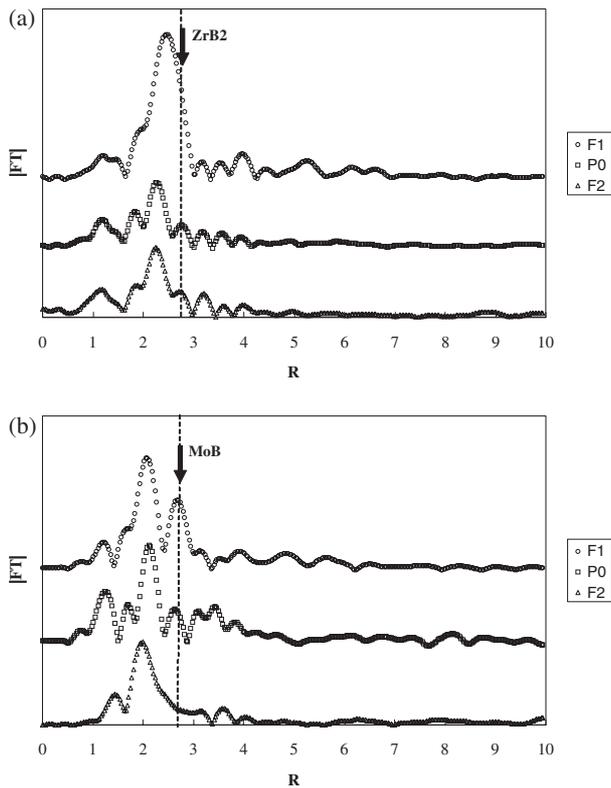


Fig. 3 Fourier transformed plots of (a) Zr K-edge and (b) Mo K-edge EXAFS spectra of the alloys.

Table 1 The calculated melting temperature, the maximum driving force, and the normalized driving force of the alloys. The values calculated considering the pre-existence of ZrB₂ in the melts are shown in square brackets.

Composition	Calculated Tm (K)	Maximum DF (kJ/mol)	Relative DF (J/mol*K)
Fe ₆₂ Zr ₈ B ₁₅ Mo ₁₅ (F1)	1644	9.764	5.939
Fe ₆₂ Zr ₈ B ₁₅ Mo ₈ Co ₇ (F2)	1696	8.228	4.851
[Fe ₆₃ Zr _{7.6} B _{14.2} Mo _{8.1} Co _{7.1}]		[7.974]	[4.702]
Fe ₆₃ Zr ₈ B ₁₅ Mo ₇ Co ₆ Al ₁ (P0)	1703	7.813	4.588
[Fe ₆₄ Zr _{7.6} B _{14.2} Mo _{7.1} Co _{6.1} Al ₁]		[7.582]	[4.452]

compositions of the remaining melts will be different from the original compositions. Considering the amounts of Zr and B in ZrB₂, the compositions of the remaining melts were calculated and the corresponding values of melting temperatures, maximum and normalized driving forces are indicated in square brackets. Since a smaller value of normalized driving force indicates a higher GFA in driving force criterion concept, it can be said that P0 alloy has the highest GFA followed by F2 and F1 alloys.

Table 2 shows the values of N obtained by EXAFS experiments. The value of N represents the coordination number around a certain atom when it is multiplied by 12. Since the value of N can represent the coordination number, it can be said that the alloy with a lower value of N has a more amorphized atomic arrangement and also higher GFA than the ones with a higher value of N. Comparison of N values of the alloys indicates that P0 alloy has the highest GFA

Table 2 The values of N obtained by EXAFS analyses.

Composition	N
Fe ₆₂ Zr ₈ B ₁₅ Mo ₁₅ (F1)	0.6248
Fe ₆₂ Zr ₈ B ₁₅ Mo ₈ Co ₇ (F2)	0.5428
Fe ₆₃ Zr ₈ B ₁₅ Mo ₇ Co ₆ Al ₁ (P0)	0.4473

followed by F2 and F1 alloys, which agrees with the estimation based on the normalized driving force shown in Table 1.

As shown in the previous studies,^{12,13)} thermodynamic calculations of driving forces of crystalline phases can be a useful guide for the prediction of alloy compositions with high GFAs in multicomponent bulk amorphous alloy systems. Since the amorphization is inversely related to the driving forces of crystalline phases involved, we can predict not only the compositions having high GFAs but also the first forming crystalline phase which has the highest value of driving force in a given composition. Through the simple manipulation of database for the elements involved, we can construct the representative database for each alloy. By setting the same degree of undercooling for all the alloy systems during calculation and normalizing the maximum driving forces of crystalline phases by the respective melting temperatures of the alloy systems to obtain the normalized driving force, we can extend the concept of driving force criterion from the prediction of alloy composition with the highest GFA in a given alloy system to the estimation of relative GFAs of different alloy systems. The present results show that the prediction of the most possible crystalline phases based on driving force criterion is in agreement with the experimental results. Moreover, the estimated order of GFAs for the studied alloy systems based the normalized driving force is in agreement with the experimental results.

The order of GFAs mentioned above indicates that partial substitution of Mo with Co and Al improves the GFA of the alloy. It has been suggested that the co-addition of alloying elements can effectively increase the degree of the satisfaction of the empirical rules, which means the more sequential size mismatch among the elements and the increase in number of cases for the atomic arrangement.²¹⁾ Also the newly made atomic pairs with the added alloying elements have negative heat of mixing, which are helpful for the improvement of GFA. For example, the values of heat of mixing for Co-B and Co-Zr are -57 kJ/mol and -35 kJ/mol, respectively.²²⁾ It is also noticed that even the small addition of Al can be very helpful for the improvement of GFA. This might be due to the generation of extremely strong Al-B atomic pairs in the amorphous structure, which prevents the atomic rearrangement required for the precipitation of the primary crystalline phases including boron atom.²³⁾

5. Conclusion

In this study, the concept of the normalized driving force has been developed for the comparison of the relative GFAs of different alloy systems. The degree of undercooling was kept same for the calculations of driving forces of crystalline phases and such calculated values of maximum driving force

were divided by the respective melting temperatures of the alloys for normalization. The order of GFAs expected by the normalized driving forces agrees well with the experimental results. This normalized driving force concept might be helpful for the development of bulk amorphous alloys having high GFAs.

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