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A New Parameter for Glass–Forming Ability of Binary Bulk Metallic Glasses

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Summary

We proposed a parameter $\varphi = (\Delta H_m^c - R\Delta T_e^{mix})/\Delta H_m^c$ as a criterion for glass–forming ability (GFA) of binary alloys near eutectic composition using the thermodynamic data of the equilibrium phase diagram by considering the relative thermodynamic stability of the liquid phase. The larger φ is, the larger GFA is in different binary alloy systems. A linear fit of $R_c=7.73\times10^{23}\exp(-65.26\varphi)$ is obtained, where R_c denotes the critical cooling rate to form glass from liquid. Since φ is determined directly from thermodynamic data of elements and well known equilibrium phase diagram, GFA of binary alloys can be easily estimated without any thermal measurement after fabrication of BMGs.

Keywords; bulk metallic glasses (BMGs); glass–forming ability (GFA); binary phase diagram; eutectic composition; critical cooling rate;

1. Introduction

Bulk metallic glasses (BMGs) have been extensively developed due to their excellent physical and mechanical properties, which leads to the foundation of many new BMGs experimentally [1, 2]. Correspondingly, theoretical progress for finding new BMGs has also been made, which is related to the evaluation on the glass forming ability (GFA) of alloys.

To do that, many criteria have been established. The earliest criterion is the reduced glass transition temperature $T_{rg}=T_g/T_m$ or improved $T_{rg}=T_g/T_l$, where T_g, T_m and T_l are the glass transition temperature, melting temperature and liquidus temperature, respectively [3, 4].

This criterion directly relates GFA to the relative value of T_g from T_m or T_l. Note that the liquidus temperature denotes a temperature in an alloy phase diagram, above which the phase is fully liquid. Thus, the improved criterion has clarified the actual definition of T_m. Let T_x denote the crystallization temperature for a heated glass with a certain heating rate, $K=(T_x-T_g)/(T_l-T_x)$ [5] characterizes the relative stability of the liquid in terms of the corresponding T_l. $\gamma=T_x/(T_g+T_l)$ is another more complicated consideration [6], where the importance of both T_g and T_l characterizing the stability of liquid is emphasized. These models are widely used as indicators of GFA for BMGs although there are some differences in their sense of GFA when the alloy system changes from one to another, or alloy composition changes for a given alloy system [7].

Since these temperatures need to be determined after a thermal analysis for BMGs, these parameters can hardly supply a composition–design principle to find a new BMG or a suitable composition for alloying design with the best GFA.

The above models only consider some related characterized temperatures. Other models suggest the close relationship between GFA and the thermodynamic data of alloys, $\gamma^* = H^{amor}/(H^{inter} - H^{amor})$ is defined where H^{amor} and H^{inter} are the glass formation enthalpy and intermetallic compound formation enthalpy, respectively [8]. This parameter reveals that GFA is achieved against crystallization. Another criterion is $\varepsilon = -\Delta S^{mix}/\Delta H^{mix}$ with S_{mix} and H_{mix} being the mixing entropy and the mixing enthalpy, respectively [9]. This criterion reflects the atomic rearrangement–inhibiting ability (ARIA) of the alloys. Both parameters describe GFA of metallic glasses as a competition of disordering (amorphization) against ordering (crystallization) from two aspects. The problem of the above two criteria is that these thermodynamic data need to be calculated with many assumptions.

In light of the above models, one can see there is a need to find a criterion for GFA of alloys, which is only based on well–known elemental thermodynamic data and phase diagram. It is clear that all elements and binary phase diagrams are well studied. Thus, once a model is based on the two sources, a best GFA of an alloy with a certain composition can be determined.

In this contribution, a parameter φ as criterion for GFA of binary alloys is developed in light of the stability of liquid phase. This criterion can be determined by well–known thermodynamic data of elements and phase diagram without any data from an obtained BMG. Usefulness of is confirmed from result that φ is related to logR_c linearly.

2. Model

It is well known that the stability of a liquid phase decides GFA of alloys. This could be reflected by drop of T_l induced by alloying compared with the corresponding i–th element melting temperature $T_{m, i}$. Since the minimum of T_l is the eutectic temperature of a given alloy T_e, we define $\Delta T_e^{mix} = T_m^{mix} - T_e$ as a scale reflecting the big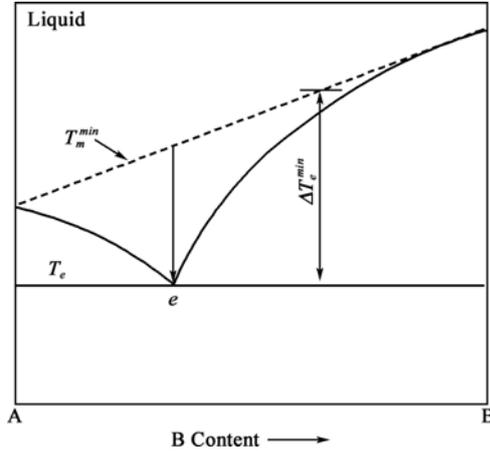gest stability ability of alloying for a liquid phase, where $T_m^{mix} = \sum_i^n x_i T_{m,i}$ is the ideal melting temperature for a mechanically mixed alloy with x_i being molar fraction of i–th component in an n–component alloy. Fig.1 shows such a schematic binary eutectic–phase diagram for the above definition. The ΔT_e^{mix} represents the stable degree of liquid phase and how deep the eutectic is at the eutectic composition in given alloy system.

On the other hand, as well–known, the Gibbs free energy difference, ΔG^{l-s}, between liquid(denote, l) and corresponding crystal(denote, s) has also played an important role in predicting the GFA of a glass former. At melting temperature, the Gibbs free energy difference, $\Delta G_m^{l-s} = \Delta H_m - T_m\Delta S_m$, where ΔH_m is the molar melting enthalpy and ΔS_m is the molar melting entropy.

At any temperature T below T_m, ΔG can be expressed as follows [10]:

$$\Delta G = \Delta H_m \left(\frac{T_m - T}{T_m} \right) \qquad (1)$$

As shown in the Eq. (1), $\Delta H_m \propto \Delta G$ and thus is related to the driving force for crystallization and reversely to GFA. In addition, one can simply consider that the ΔH_m at T_m is the driving force for crystallization, and then, the larger ΔH_m is, the more facile crystallization is, consequently, the more difficult the glass formation is.

Figure 1. Schematic definition of ΔT_e^{mix} in binary eutectic phase

diagram.

As mentioned above, metallic glass formation is a competing process of amorphous against crystallization and a destroying process of the stability of liquid phase. Therefore, we can here introduce a measure, $\Delta T_e^{mix} / \Delta H_m$, reflecting the decreasing degree of the drive force for the crystallization against the stability of liquid phase, and then;

$$\text{GFA} \propto \frac{\Delta T_e^{mix}}{\Delta H_m} \qquad (2)$$

In the light of Ziman liquid theory, supposing that the melt is an ideal solution, ΔH_m can be calculated by following expression [11]:

Table 1. Related parameters in Eq. (4). H_m^c is the melting enthalpy of the alloy, T_m^{mix} the ideal melting temperature of the alloy. D_{max} is the typical thickness (or diameter), from references reported previously, and $\log R_c$ is the critical cooling rate, calculated by using approximate formula $R_c = 10/D^2$ (D in unit of cm) from [14]

Alloy	H_m^c, kJ/mol	T_m^{mix}, K	T_e, K	$R\Delta T_e^{mix}$, kJ/mol	φ	D_{max}, mm	$\log R_c$, , K/s	Ref.
$Cu_{46}Zr_{54}$	17.49	1 773.61	1 201	4.76	0.73	2.0	2.4	[14]
$Cu_{50}Zr_{50}$	17.18	1 742.81	1 196*	4.54	0.74	2.0	2.4	[15]
$Cu_{60}Zr_{40}$	16.39	1 665.80	1 158	4.22	0.74	1.5	2.6	[16]
$Cu_{64}Zr_{36}$	16.08	1 635.00	1 158	4.00	0.75	2.0	2.4	[17]
$Cu_{64.5}Zr_{35.5}$	16.04	1 631.15	1 158	3.93	0.76	2.0	2.4	[18]
$Cu_{55}Hf_{45}$	19.53	1 874.47	1 253	5.16	0.73	1.5	2.6	[16]
$Cu_{65}Hf_{35}$	18.14	1 759.65	1 243	4.29	0.76	2.0	2.4	[20]
$Cu_{66}Hf_{34}$	18.00	1 748.17	1 243	4.20	0.77	2.0	2.4	[21]
$Ni_{60}Nb_{40}$	22.48	2 137.00	1 451	5.70	0.75	1.0	3	[22]
$Ni_{61.5}Nb_{38.5}$	22.30	2 121.65	1 451	5.57	0.75	1.5	2.6	[23]
$Ni_{62}Nb_{38}$	22.24	2 116.55	1 451	5.53	0.75	2.0	2.4	[8]
$Ni_{62.4}Nb_{37.6}$	22.18	2 112.46	1 451	5.50	0.75	2.0	2.4	[24]
$Ni_{80}P_{20}$	14.12	1 446.10	1 143	5.47	0.61	–	6	[25]
$Pd_{81}Si_{19}$	23.10	1 801.21	1 137	5.52	0.76	6.0	1.4**	[26]
$Pd_{82}Si_{18}$	22.76	1 802.62	1 093	6.02	0.73	–	3.4	[24]
$Zr_{62}Ni_{38}$	19.72	1 976.02	1 283	5.76	0.71	–	4	[8]
$Zr_{65}Be_{35}$	16.52	1 929.10	1 238	6.91	0.58	–	7	[27]
$Zr_{70}Fe_{30}$	18.91	2 032.80	1 201	6.91	0.63	–	5.7	[25]
$Zr_{70}Cu_{30}$	18.75	1 896.83	1 268	5.23	0.72	–	4.9	[28]
$Zr_{70}Pd_{30}$	19.80	2 037.90	1 303	6.11	0.69	–	6	[29]
$Zr_{80}Ni_{20}$	20.37	2 047.94	1 233	6.77	0.67	–	5.9	[25]

*: For $Cu_{50}Zr_{50}$ at the line compound composition, because of the absence of eutectic line, the melting point of the compound CuZr is introduced by using its binary phase diagram instead of T_e.

**: For $Pd_{81}Si_{19}$, in order to unify, using its D_{max} value, R_c is estimated though its R_c is reported to 8K/s.

$$\Delta H_m^c = \sum_{i=1}^{n} (x_i \Delta H_{m,i}) \qquad (3)$$

, where x_i is the mole percent of $i-th$ component, n is

component number, $\Delta H_{m,I}$ is molar melting enthalpy of $i-th$ component and subscript c denotes a calculated value, but not an experimental one.

On the other hand, $H_{m,i} = T_{m,i}S_{m,i}$ where $T_{m,i}$ and $S_{m,i}$ are melting temperature and the molar melting entropy of $i-th$

component of the system [12].

Now we can define the parameter φ for the estimate of GFA as follows:

$$\varphi = \frac{\Delta H_m^c - R\Delta T_e^{mix}}{\Delta H_m^c} = 1 - \frac{R\left(\sum_{i=1}^{n} x_i T_{m,i} - T_e\right)}{\sum_{i=1}^{n} \left(x_i T_{m,i} \Delta S_{m,i}\right)} \quad (4)$$

where R is the gas constant to convert parameter φ to dimensionless measure.

3. Results and Discussion

As seen in Eq. (4), the values of φ will be changed from 0 to 1.0. As parameter φ reflects the relative decreasing degree of the drive force for crystallization near eutectic composition, the larger φ is, the better GFA will be.

In terms of Eq. (4), values of φ of some binary alloys and BMGs are calculated and shown in Tab.1 where the calculated T_m^{mix} are also given, where T_e is cited value [12] and the related elemental data are shown in Tab. 2.

In the calculations, for $Cu_{50}Zr_{50}$ BMG, the composition is just a line compound. Its T_m here is used instead of T_e. Tab.1 also includes experimental data of the typical thickness (or diameter) D_{max} of BMGs under the critical cooling rates R_c where $R_c = 10/D_{max}^2$ is assumed [13]. For $Pd_{81}Si_{19}$ BMG, although $R_c = 8K/s$ [27], R_c is still estimated by its D_{max} value in order to unify the method.

Table 2. For some individual elements, its number Z, structure, melting temperature $T_{m,i}$, molar melting entropy $\Delta S_{m,i}$, molar melting enthalpy $\Delta H_{m,i}$, calculated by Eq. (4). The data for $T_{m,i}$ and $\Delta S_{m,i}$ cited from Ref. [12]

Z	element	structure	$T_{m,i}$, K	$S_{m,I}$, J/(mol·K)	$H_{m,I}$, kJ/mol
4	Be	hcp	1 560.00	5.061	8.00
14	Si	fcc	1 687.00	29.762	50.21
15	P	monocl.	317.30	2.077	0.66
26	Fe	bcc	1 811.00	7.623	13.81
28	Ni	fcc	1 728.30	10.114	17.48
29	Cu	fcc	1 357.77	9.768	13.26
40	Zr	hcp	2 127.85	9.868	21.10
41	Nb	bcc	2 750.00	10.909	30.00
46	Pd	fcc	1 828.00	9.155	16.73
60	Nd	hcp	1 289.00	5.541	7.14
72	Hf	hcp	2 506.00	10.852	27.20
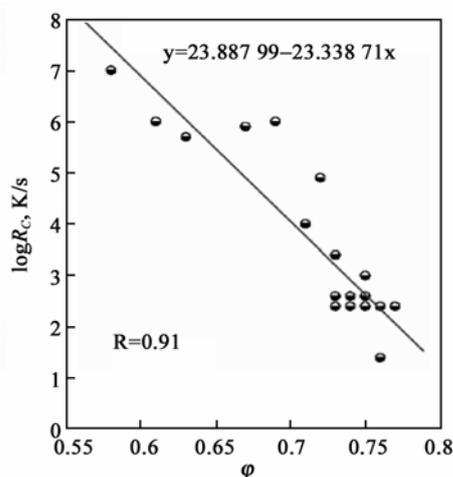
Figure 2. $\log R_c(\varphi)$ function for binary BMGs where the data cited from Tab.1.

Based on the data shown in Tab.1, $\log R_c(\varphi)$ is plotted, which is shown in Fig.2 where $\log R_c$ in terms of Fig.2 has been fitted as a linear function.

$$\log R_c = (23.88 \pm 2.12) - (28.34 \pm 2.94)\varphi \quad (5.a)$$

or

$$R_c = 7.73 \times 10^{23} \exp(-65.26\varphi) \quad (5.b)$$

As shown in Fig.2, $\varphi \propto 1/\log R_c$ is found. The result suggests that $\varphi \geq 0.73$ is the condition to form BMGs.

The parameter φ is sensitive to the alloy composition. For example, the composition difference of $Pd_{82}Si_{18}$ and $Pd_{81}Si_{19}$ alloys is only 1at%, the corresponding φ values however are 0.73 and 0.76, respectively. In our knowledge, no any criterion for GFA could show a so large change with this small composition difference.

On the other hand, there are a few eutectics and intermetallic compounds in binary phase diagrams with better glass formers; for example, Cu–Zr, typical glass–forming binary alloy system, has five eutectics and six intermetallic compounds are found. The influences of such eutectics and intermetallic compounds on the GFA of binary alloys should be taken into consideration over the wide range of composition.

No glass formers have been found at eutectic composition of various binary systems with unsolved puzzle so far, better glass former (i.e., bulk glass formers) can be found within the narrow range of off–eutectic composition in the binary alloy systems with metallic elements [18]. In lights of these results, the present work suggests the way to research composition with the better GFA within the near eutectic.

Wang et al. suggested that, for Cu–Zr alloy system, $Cu_{50}Zr_{50}$(at%) alloy, which is corresponding to composition of line–type compound CuZr, can be cast fully amorphous into a copper model in rod up to 2 mm in diameter and its formation can be explained by using deep metastable eutectic phase diagram, consisting of compound $Cu_{51}Zr_{14}$, the highest melting point among compounds in the system and terminal solid solution α–Zr, and the glass can be formed in the wide range of the metastable eutectic composition[19]. In their results, great interest is that for bulk glass former $Cu_{50}Zr_{50}$ alloy, the main competitor crystalline phase is in the primary compound phase $Cu_{51}Zr_{14}$ of copper–rich side in metastable eutectic system. This is in good accordance with the fact that primary crystalline phase competing glass–forming phase in simple binary eutectic system such as Au–Si, in which the first metallic glass was found.

Nevertheless, in our current study, primary phase was considered as the compound CuZr, corresponding to the composition of amorphous phase, and its melting point and GFA of the alloy were evaluated using phase diagram and ideal mixing enthalpy, respectively. In other words, on the basis of the earlier results that the glass–forming process of binary alloys is the competitive process between crystallization and amorphization process, the primary phase disturbing the glass–forming at the melting point was considered to be a crystalline phase with the same composition as the corresponding glass alloy. This is based on the fact that Gibbs free energy difference of liquid and solid phase is related to the GFA, no matter whether the crystalline phase is solid solution

or compound as seen in Eq. (2) and Eq. (3). The parameter φ defined in the current study cannot identify the primary phase of solidification as seen in Ref. [19]. If a crystalline phase competing with a glass former is known and the thermodynamic data were added to the parameter φ, the reliability and accuracy will be higher. But the glass forming process is very complicated and the study on the physical property of the melt and its metallurgy of solidification is still under development, so our assumptions suggested in the definition of parameter φ do not seem to be too unreasonable. Though parameter φ is yet theoretically derived and not experimentally proved, it is confirmed that φ involves practical and potential utilities in terms of its effectiveness in the reliability and availability as seen in Fig.2.

The use of this criterion is simple relatively to compare with the previous criteria because it can be determined by well–known elemental thermodynamic data and the equilibrium phase diagram without any additional measurement. Since all of the above consideration has not limited the component numbers of alloy systems although the present results concerned with only binary systems, it could be extended to ternary or multi–component systems when the corresponding phase diagrams are available.

4. Conclusions

φ as a criterion for GFA of BMGs has been proposed in the present study, which reflects the decreasing degree of the drive force for the crystallization in light of the stability of liquid phase. It is found that GFA characterized by $\log R_c$ could be a positive linear function of $1/\varphi$. Evident advantages of the criterion are that φ reflects well the change of GFA when alloy composition varies a little in the same alloy system and the criterion only needs well–known elemental data and phase diagram.

Acknowledgements

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