Calculations of Amorphous-Forming Composition Range for Ternary Alloy Systems and Analyses of Stabilization of Amorphous Phase and Amorphous-Forming Ability

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The amorphous-forming composition range (AFCR) was calculated for 338 ternary amorphous alloy systems on the basis of the database given by Miedema's model in order to examine the applicability of the model, to analyze the stability of the amorphous phase, and to determine the dominant factors influencing the ability to form an amorphous phase. The mixing enthalpies of amorphous and solid solution phases were expressed as a function of alloy compositions on the basis of chemical enthalpy. Based on the Eshelby and Friedel model, an elastic enthalpy term was added to the model for the solid solution. Furthermore, an average melting temperature of the constituent elements was added to the model as the topological enthalpy in an amorphous phase. An amorphous phase was assumed to have been formed at the composition where the enthalpy of an amorphous phase was smaller than that of a solid solution. The AFCR was calculated for 335 systems except for the Al-Cu-Fe, Al-Mo-Si and Au-Ge-Si systems. The calculated results are in agreement with the experimental data for Cu-Ni- and Al-Ti-based systems. For typical amorphous alloy systems exemplified by the Zr-, La-, Fe- and Mg-based systems, it was recognized that the calculated AFCR had been overestimated as a result of the model being simplified. We have also shown that the elastic enthalpy term arising in a solid solution phase stabilizes the amorphous phase, and the stabilization mechanism is particularly notable in Mg-based amorphous alloy systems. Short-range order plays an important role in the formation of Al-, Fe- and Pd-metalloid based systems. The following factors have a great influence on amorphous-forming ability: (1) three empirical rules for the achievement of high AFA, (2) melting temperature and viscosity at the melting temperature, (3) elastic enthalpy arising in a solid solution, and (4) short-range order observed in an amorphous phase. The importance of the latter two factors was only identified as a result of the present study.

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1. Introduction

In the early 1990's, Inoue *et al.* proposed three empirical rules for the achievement of high glass-forming ability:¹⁾ (1) multicomponent alloy systems consisting of more than three elements, (2) significant difference in atomic size ratios, above about 12%, among the main three constituent elements, and (3) negative mixing heats among their elements. These rules have acted as a guiding principle for the fabrication of new metallic glasses, and a great number of trials based on the principle have enabled us to fabricate many bulk metallic glasses.¹⁾

Recently, we proposed a model for the estimation of amorphous-forming compositions by deducing thermodynamical functions from the three empirical rules. In this model, mismatch entropy (S_σ) and mixing enthalpy (ΔH) corresponding to the second and the third term of the rules, respectively, were defined as a function of composition in a multicomponent system satisfying the first term. The following two results were derived by applying this model to amorphous alloys: critical cooling rate²⁾ for forming typical multicomponent metallic glasses, and the statistical values³⁾ of S_σ and ΔH for 351 ternary amorphous alloy systems.⁴⁾ These results indicate the possibility of creating a general model for analyzing the features of amorphous alloys.

It is well known that Miedema's model⁵⁾ is one of the general models, and is applicable to a number of alloy systems. For instance, it was reported that the model was applied to amorphous alloys to calculate amorphous-forming composition ranges (AFCR) in Zr-Co,⁶⁾ Nb-Au,⁶⁾ V-Ni,⁶⁾ Ni-Ti⁷⁾

and Ni-Cu⁷⁾ binary systems and the Ti-Ni-Cu ternary system.⁷⁾ In this model, mixing and elastic enthalpies have been incorporated as some of the parameters in the analysis of AFCR. Since the elastic enthalpy results from an atomic size mismatch corresponding to the second term of the rules, calculated AFCR by Miedema's model in ternary systems reflects numerical expression of the three empirical rules which are used to analyze the amorphous-forming ability.

The purpose of this paper is to calculate amorphous-forming composition ranges for ternary systems on the basis of the database given by Miedema's model to examine the applicability of the model, to analyze the stability of the resulting amorphous phase, and to study dominant factors influencing amorphous-forming ability.

2. Calculation Method

Basic concepts for the calculation of AFCR were followed in previous studies.⁶⁻⁸⁾ In the present study, five kinds of enthalpy terms were taken into account: enthalpies for chemical mixing ΔH^{chem} , amorphous state ΔH^{amor} , solid solutions $\Delta H^{\text{s.s.}}$, topology $\Delta H^{\text{topological}}$ and elastic $\Delta H^{\text{elastic}}$. The definition formulae for ΔH^{amor} , $\Delta H^{\text{s.s.}}$ and $\Delta H^{\text{topological}}$ were given as eqs. (1) to (3).⁶⁻⁸⁾

$$\Delta H^{\text{amor}} = \Delta H^{\text{chem}}(\text{amor}) + \Delta H^{\text{topological}} \quad (1)$$

$$\Delta H^{\text{s.s.}} = \Delta H^{\text{chem}}(\text{s.s.}) + \Delta H^{\text{elastic}} \quad (2)$$

$$\Delta H^{\text{topological}} = 3.5 \sum_{i=1}^3 c_i T_m^1 \quad (3)$$

Here, c_i is the composition of the i -th element and T_m^i is its melting temperature. In eqs. (1) and (2), ΔH^{chem} was defined as eq. (4): the sum of the mixing enthalpy of the constituent binary subsystem $\Delta H_{ij}^{\text{chem}}$ with respect to the composition of the constituent elements based on the regular solution model. For a solid solution and an amorphous phase, $\Delta H_{ij}^{\text{chem}}$ was defined by eqs. (5) and (6), respectively, using interfacial enthalpy ΔH^{int} .⁷⁾

$$\Delta H^{\text{chem}} \equiv \sum_{\substack{i=1 \\ i \neq j}}^3 \Delta H_{ij}^{\text{chem}} c_i c_j \quad (4)$$

$$\Delta H_{ij}^{\text{chem}}(\text{s.s.}) = x_j^s \Delta H_{i \text{ in } j}^{\text{int}} + x_i^s \Delta H_{j \text{ in } i}^{\text{int}} \quad (5)$$

$$\Delta H_{ij}^{\text{chem}}(\text{amor}) = f_i^s \Delta H_{i \text{ in } j}^{\text{int}} + f_j^s \Delta H_{j \text{ in } i}^{\text{int}} \quad (6)$$

$$x_i^s = \frac{c_i V_i^{2/3}}{c_i V_i^{2/3} + c_j V_j^{2/3}}, \quad x_j^s = 1 - x_i^s \quad (7)$$

$$f_i^s = x_i^s \left[1 + 5 \left(x_i^s x_j^s \right)^2 \right] \quad (8)$$

Here, x_i^s is the surface fraction and defined by eq. (7)⁶⁻⁸⁾ with a molar volume of i -th atom V_i , which is taken from a previous study.⁸⁾ The f_i^s defined by eq. (8) is the degree to which i -th atoms are in contact with j -th atoms,^{6,8)} and the multiplying factor $[1 + 5(x_i^s x_j^s)^2]$ is due to the short-range order observed in the amorphous phase.⁹⁾

Equations (9) to (11) show the method of calculating $\Delta H^{\text{elastic}}$ on the basis of a continuous elastic model, widely known as the sphere and hole model, proposed by Eshelby¹⁰⁾ and Friedel.^{11,12)} The elastic enthalpy term of a constituent binary subsystem $\Delta H_{ij}^{\text{elastic}}$ was defined as eq. (10)^{7,8)} with elastic enthalpy of i -th element in j -th in the dilution limit $\Delta H_{i \text{ in } j}^{\text{elastic}}$ expressed by eq. (11). In eq. (11), bulk modulus K and shear modulus G were taken from a previous study,⁸⁾ and modified volumes W_i and W_j of a sphere (i) and a hole (j) due

to internal stress were calculated on the basis of their definition formulae.⁸⁾ In accordance with the definition shown in eq. (2), $\Delta H^{\text{elastic}}$ was taken into account only for a solid solution.^{7,8)}

$$\Delta H^{\text{elastic}} \equiv \sum_{\substack{i=1 \\ i \neq j}}^3 \Delta H_{ij}^{\text{elastic}} c_i c_j \quad (9)$$

$$\Delta H_{ij}^{\text{elastic}} = c_j \Delta H_{i \text{ in } j}^{\text{elastic}} + c_i \Delta H_{j \text{ in } i}^{\text{elastic}} \quad (10)$$

$$\Delta H_{i \text{ in } j}^{\text{elastic}} = \frac{2K_i G_j (W_i - W_j)^2}{4G_j W_i + 3K_i W_j} \quad (11)$$

Finally, taking the difference in enthalpy terms between an amorphous state and a solid solution:^{7,8)} Subtraction of eq. (2) from eq. (1) gives eq. (12).

$$\Delta H^{\text{amor}} - \Delta H^{\text{s.s.}} = (\Delta H^{\text{chem}}(\text{amor}) - \Delta H^{\text{chem}}(\text{s.s.})) + \Delta H^{\text{topological}} - \Delta H^{\text{elastic}} \quad (12)$$

An amorphous phase was assumed to be formed at a composition with a negative value for eq. (12).⁷⁾ Equation (12) has three terms on the right side, giving a different contribution to stability for an amorphous phase and a solid solution. The first and the third terms, $(\Delta H^{\text{chem}}(\text{amor}) - \Delta H^{\text{chem}}(\text{s.s.}))$ and $-\Delta H^{\text{elastic}}$, give negative values, which stabilize the amorphous phase. In contrast, the second term $\Delta H^{\text{topological}}$ with the positive sign stabilizes the solid solution. AFCR was calculated for 338 ternary alloy systems in the database⁴⁾ except for 14 systems containing D (Dysprosium), H, Mm (Mish Metal), O, and Te on account of the lack of a V_i value.^{5,8)} Some of the values for $\Delta H_{ij}^{\text{int}}$ and $\Delta H_{i \text{ in } j}^{\text{elastic}}$ have been summarized in Table 1. These values were used for the systems that will be shown in section 3. In the case of a system having more than one references regarding amorphous-forming composition (AFC) in the database,⁴⁾ all the AFCs of each reference were traced in the present study in order to define one AFC corresponding to the alloy system.

Table 1 Interfacial enthalpy ΔH^{int} and elastic enthalpy $\Delta H^{\text{elastic}}$ for typical alloy systems calculated in the present study.

System	$\Delta H_{i \text{ in } j}^{\text{int}}/\text{kJmol}^{-1}$						$\Delta H_{i \text{ in } j}^{\text{elastic}}/\text{kJmol}^{-1}$					
	A in B	B in A	B in C	C in B	C in A	A in C	A in B	B in A	B in C	C in B	C in A	A in C
Al-Cu-Fe	-34	-29	48	53	-42	-49	16	12	0	0	17	13
Al-Mo-Si	-21	-21	-76	-72	-9	-10	0	2	2	2	3	3
Au-Ge-Si	-47	-41	11	10	-48	-58	0	1	3	3	4	5
Al-La-Ni	-126	-187	-145	-81	-83	-98	65	61	71	130	24	17
B-Co-Mn	-88	-109	-21	-21	-146	-118	21	39	3	1	24	36
B-Fe-Ni	-95	-120	-6	-6	-106	-85	30	51	1	1	35	19
Be-Ti-Zr	-105	-148	-1	-1	-227	-140	63	136	15	15	211	119
Cu-Ni-Ti	13	14	-125	-154	-40	-34	0	2	38	39	33	21
Cu-Ni-Zr	13	14	-165	-236	-110	-83	0	2	92	90	96	62
Cu-Hf-Ni	-62	-81	-204	-145	14	13	76	99	104	115	2	0
Al-Mg-Ti	-6	-7	68	59	-119	-119	14	8	7	11	1	0
Al-Nb-Ti	-73	-75	8	8	-119	-119	1	1	0	0	1	0
Al-Ni-Ti	-98	-83	-125	-154	-119	-119	17	24	38	39	1	0
Al-Cu-Ti	-34	-29	-34	-40	-119	-119	16	12	21	33	1	0
Al-Ni-Zr	-98	-83	-165	-236	-190	-165	17	24	92	90	22	16
B-Fe-Zr	-95	-120	-84	-118	-386	-227	30	51	80	76	208	138
La-Mg-Ni	-32	-24	-16	-12	-81	-145	26	23	15	64	130	71
Ni-P-Pd	-124	-152	-146	-148	0	0	2	4	0	0	0	16

3. Results

First, AFCR was calculated for the 338 ternary systems. As a result, it was found that 335 systems, except for Al–Cu–Fe, Al–Mo–Si and Au–Ge–Si, have AFCR. A reason for the absence of AFCR for these three systems is attributed to the values of $\Delta H_{ij}^{\text{int}}$ and $\Delta H_{i \text{ in } j}^{\text{elastic}}$ in Table 1. In accordance with eq. (12), the following characteristics of the values are considered to destabilize the amorphous phase: a positive value for ΔH^{mix} as well as a small $\Delta H^{\text{elastic}}$ value for Cu–Fe in the Al–Cu–Fe system and small $\Delta H_{i \text{ in } j}^{\text{elastic}}$ values for the Al–Mo–Si and Au–Ge–Si systems.

Secondly, the systems with a large number of AFCs in the database⁴⁾ were focused on. Table 2 summarizes the 10 largest number of AFCs for which the numbers are greater than 100. The systems underlined in Table 2 were selected on account of the homogeneous distribution of AFCs in the composition triangle. Figure 1 shows calculated AFCR and experimentally determined AFCs for the four systems underlined in Table 2. The results for Al–Ni–Zr will be shown in section 3.3. It is seen in Fig. 1 that the calculated AFCR tends to be greater than that experimentally determined for all of the systems. The other tendency is that the location of AFCR

Table 2 The number of amorphous-forming compositions (AFCs) in the systems selected for having the 10 largest number of AFCs in the database.³⁾ The systems underlined exhibit homogeneous distribution of the amorphous-forming composition range in the composition triangle.

System	The number of AFCs
<u>Al–La–Ni</u>	337
B–Fe–Si	268
B–Fe–Zr	225
<u>Al–Ni–Zr</u>	171
<u>B–Co–Mn</u>	168
<u>B–Fe–Ni</u>	156
B–Ni–Si	120
Cu–Pd–Si	114
B–Cu–Fe	112
<u>Be–Ti–Zr</u>	104

was slightly shifted to that of AFCs in the composition triangle for B–Co–Mn and B–Fe–Ni systems. These tendencies are thought to be based in the following three reasons: (1) limitation of the number of experimental results, (2) simplification inherent in the present model, and (3) lack of information about equilibrium phase diagrams. The first reason indicates that all of the compositions have not been studied systemati-

Fig. 1 Calculated amorphous-forming composition ranges (AFCR) and experimentally determined amorphous-forming compositions (AFCs).

Fig. 2 Experimental and calculated amorphous-forming composition ranges for Cu–Ni–Ti, Cu–Ni–Zr and Cu–Hf–Ni systems.

cally because of either scientific or engineering interests. The second and the third reasons are due to two calculation conditions wherein no kinetical factors were taken into account for the formation of the amorphous phase in the present study, and that all of the crystalline phases except a solid solution were not considered in the present study.

Details of AFCR will be shown below for the following alloy systems: (1) Cu–Ni based system, (2) Al–Ti based system and (3) typical amorphous-forming systems classified by Inoue.¹⁾

3.1 Cu–Ni base systems

Figure 2 shows the calculated and the experimental results for Cu–Ni–Ti, Cu–Ni–Zr and Cu–Hf–Ni systems. The calculated AFCR agrees with ACRs obtained by experimental data⁴⁾ for the Cu–Ni–Ti system, and also coincides with those for the Cu–Ni–Zr and Cu–Hf–Ni systems. This consistency is due to the three systems having relatively simple AFCs in the composition triangle. Considering the simplification inherent in the present calculation model, agreement of the AFCR with the experimental data is fairly good in these systems. A feature of AFCs for these systems is that AFCs tend to contact two binary subsystems. This tendency is due to two constituent elements, Cu and Ni, having nearly the same melting temperature and the mechanical modulus. In addition to

these systems, the B–Co–Mn, B–Fe–Ni and Be–Ti–Zr systems shown in Fig. 1 belong to this type.

3.2 Al–Ti base systems

Figure 3 shows calculated AFCR and experimental AFCs for the Al–Mg–Ti, Al–Nb–Ti, Al–Ni–Ti and Al–Cu–Ti systems. It is seen in Fig. 3 that the calculated AFCR tends to contact one binary subsystem for the Al–Mg–Ti and Al–Nb–Ti systems, and three subsystems for the other two systems. The calculated AFCR agrees with the experimental AFCs for the Al–Mg–Ti and Al–Ni–Ti systems. The ACRs coinciding with and close to the Al–Ti binary subsystem of the Al–Mg–Ti and Al–Ni–Ti systems are at variance with those of Al–Nb–Ti and Al–Cu–Ti in the original references of the database.⁴⁾ This variance is due to the difference in fabrication methods among these ternary systems, and the Al–Nb–Ti and Al–Cu–Ti systems are expected to have ACRs coinciding with or close to the Al–Ti binary subsystem when an appropriate experimental technique is employed. A number of AFCs located near the Al–Ti binary subsystem for the Al–Mg–Ti and Al–Ni–Ti systems support the presence of an amorphous phase in a composition range from 25 to 69 at%Ti in the calculated AFCR. It is thus considered that the AFCR agrees with the AFCs for the Al–Ti base systems.

Fig. 3 Experimental and calculated amorphous-forming composition ranges for Al-Mg-Ti, Al-Nb-Ti, Al-Ni-Ti and Al-Cu-Ti systems.

3.3 Typical amorphous-forming system

Figure 4 shows the calculated and the experimental results for the Al-Ni-Zr, B-Fe-Zr, La-Mg-Ni and Ni-P-Pd systems. These four systems were selected in the previous study³⁾ as representative examples of each group in accordance with the classification of the typical amorphous alloys. In Fig. 4, the Al-Ni-Zr, B-Fe-Zr and La-Mg-Ni were calculated to have AFCR over the whole composition range except the corners in the composition triangle, indicating that the calculated AFCR for these systems was overestimated. Contrary to this overestimation of AFCR for the above systems, the AFCR for the Ni-P-Pd system was calculated in a smaller range than that for the other systems, and shifted to the P-rich corner in the composition triangle. The difference in the range of AFCR between Ni-P-Pd and the other three systems comes from the difference in stability for the amorphous phase. The details will be discussed in the next section.

4. Discussion

We will first discuss the factors controlling AFCR for the alloy systems shown in Figs. 1 to 4. It is considered that the factors which influence AFCR are ΔH^{int} , T_m , $\Delta H^{\text{elastic}}$, viscosity, diffusion, intermediate phases and so on. Among the factors ΔH^{int} , T_m and $\Delta H^{\text{elastic}}$ are selected in the present

study as the dominant factors influencing the calculation of AFCR.

The calculated and experimental results tend to agree for the systems shown in Figs. 2 (Cu-Ni-Ti, Cu-Ni-Zr and Cu-Hf-Ni) and 3 (Al-Mg-Ti, Al-Nb-Ti, Al-Ni-Ti and Al-Cu-Ti). On the other hand, AFCR for the alloy system in Figs. 1 (Al-La-Ni, B-Co-Mn, B-Fe-Ni and Be-Ti-Zr) and 4 (Al-Ni-Zr, B-Fe-Zr, La-Mg-Ni and Ni-P-Pd) has been overestimated. In order to clarify the reason for the overestimation, the relations between average values for ΔH^{int} and $\Delta H^{\text{elastic}}$, some of which are calculated by the values listed in Table 1, are shown in Fig. 5. The fifteen systems mentioned above are plotted in an aggregate area in Fig. 5, indicating these systems have been adequately selected as representative amorphous systems. Broken lines surround the areas containing the systems shown in Figs. 2 and 3, and Figs. 1 and 4, respectively. Although the two areas surrounded by the broken lines overlapped, the average value of ΔH^{int} and $\Delta H^{\text{elastic}}$ for the systems shown in Figs. 2 and 3 are plotted at the right-lower side in Fig. 5 for those in Figs. 1 and 4. This implies a tendency that calculated AFCR with an average value of small and negative ΔH^{int} as well as a small $\Delta H^{\text{elastic}}$ value agrees with the experimental result. The disagreement between the calculated and the experimental results for the system shown in Figs. 1 and 4, which has large and negative ΔH^{int} and large

Fig. 4 Experimental and calculated amorphous-forming composition ranges for Al-La-Ni, B-Fe-Zr, La-Mg-Ni and Ni-P-Pd systems.

Fig. 5 Relation between average values of $\Delta H_{\text{ave}}^{\text{int}}$ and $\Delta H_{\text{ave}}^{\text{elastic}}$ for the ternary amorphous systems. The values of $\Delta H_{\text{ave}}^{\text{int}}$ and $\Delta H_{\text{ave}}^{\text{elastic}}$ for the fifteen alloy systems in the figure are calculated using the values in Table 1.

Fig. 6 Elastic enthalpy $\Delta H^{\text{elastic}}$ for Zr-, La-, Fe-, Mg-, Pd- and Pt-based binary systems. The $\Delta H^{\text{elastic}}$ was calculated at an equiatomic composition, and is plotted against the atomic number corresponding to the constituent elements in the above-described systems.

$\Delta H^{\text{elastic}}$, is presumably because other factors except apart from the three dominant factors strongly influence AFCR. For instance, it is reported that the systems with large and negative ΔH^{int} values have a high possibility of having an intermediate phase,⁵⁾ and have extremely high viscosity.¹³⁾ These reports support the contention that an amorphous single phase is difficult to obtain experimentally in a wide composition area. Because the intermediate phases and viscosity are not treated in the present study, the calculated results tend to be greater than the experimental results.

The discussion now focuses on the factors which bring about the stabilization of an amorphous phase. The following three effects for typical amorphous systems are discussed: $\Delta H^{\text{elastic}}$, short-range order, and the relation among ΔH^{chem} , $\Delta H^{\text{elastic}}$ and short-range order. Furthermore, another effect of short-range order for amorphous systems is also analyzed.

First, the effect of $\Delta H^{\text{elastic}}$ for the stabilization of an amorphous phase is discussed for typical amorphous systems. Figure 6 plots $\Delta H^{\text{elastic}}$, calculated at an equiatomic composition in a binary system, against the atomic number of the constituent elements. From Fig. 6, the Zr-, La- and Fe-based systems have large $\Delta H^{\text{elastic}}$ most of which are in the range of 20 to 125 kJ/mol, followed by Mg-based systems with relatively high $\Delta H^{\text{elastic}}$ among the Mg-, Pd- and Pt-based systems with small atomic numbers. The Mg-based systems have the highest $\Delta H^{\text{elastic}}$ value of nearly 40 kJ/mol with the constituent elements of which the atomic number is around the 20's. Since $\Delta H^{\text{elastic}}$ stabilizes the amorphous phase in accordance with eq. (12), the Mg-Ni and Mg-Cu based systems may possibly have high amorphous-forming ability. This possibility agrees with the experimental data that Ni or Cu is an essential element for the formation of an amorphous phase in

the Mg-based amorphous alloy systems.¹⁾

On the other hand, the Pd-based systems have rather small values of $\Delta H^{\text{elastic}}$ less than 15 kJ/mol with the other constituent elements except Be, B, C, Y, Sn, Sb, Ln (lanthanide metals), Pb, Bi, Th and U. Among the Pd-based alloy systems, Pd-Ln systems have a high probability of forming an amorphous phase for two reasons. The first is that high $\Delta H^{\text{elastic}}$ values of nearly 20 kJ/mol are obtained with Ln, and secondly that ΔH^{chem} at an equiatomic composition for Pd-Ln is as large as -30 kJ/mol.⁵⁾ In accordance with the database,⁴⁾ however, no amorphous phase was reported in the Pd-Ln system. It is therefore reasonable that the amorphous-forming ability for Pd-based systems is attributable to factors other than the three empirical rules and elastic enthalpy term. The assumed factors for the Pd-based amorphous systems are low melting temperature and high viscosity at the melting temperature, which have already been discussed in previous studies.^{2,3)}

Secondly, in order to discuss the effect of the short-range order on the stabilization of the amorphous phase, AFCR was calculated under the condition where the short-range order factor $[1 + 5(x_i^s x_j^s)^2]$ expressed in eq. (8) was ignored. This calculation condition implies that $\Delta H^{\text{chem}}(\text{amor})$ is equal to $\Delta H^{\text{chem}}(\text{s.s.})$, and that eq. (13) is used instead of eq. (12).

$$\begin{aligned} \Delta H^{\text{amor}} &= \Delta H^{\text{chem}}(\text{s.s.}) + \Delta H^{\text{topological}} \\ -\Delta H^{\text{s.s.}} &= \Delta H^{\text{topological}} - \Delta H^{\text{elastic}} \end{aligned} \quad (13)$$

Figure 7 shows the calculated and experimental results in typical amorphous-forming alloy systems. Comparing Figs. 4 and 7, little change in AFCR is seen in the B-Fe-Zr and La-Mg-Ni systems, indicating that the $\Delta H^{\text{elastic}}$ controls the AFCR for these systems. The AFCRs in the Al-Ni-Zr sys-

Fig. 7 Experimental and calculated amorphous-forming composition range for Al–La–Ni, B–Fe–Zr, La–Mg–Ni and Ni–P–Pd systems under the condition where the short-range order is ignored.

tem are almost equal, although Fig. 7 shows a slight decrease in the AFCR range for the compositions near the Al-rich corner and the Al–Zr binary subsystem. In strong contrast to the above-described three systems, the AFCR in the Ni–P–Pd system disappears in Fig. 7. The absence in the AFCR for the Ni–P–Pd system implies that its stability in the amorphous phase is low, and this low stability results in the smaller AFCR area as compared with the other alloy systems shown in Fig. 4. The difference of AFCRs in the Ni–P–Pd system shown in Figs. 4 and 7 indicates the possibility that the short-range order plays a role in the stabilization of the amorphous phase.

Thirdly, the relation among ΔH^{chem} , $\Delta H^{\text{elastic}}$ and short-range order for typical amorphous systems is analyzed. Figure 8 shows enthalpies-composition diagrams in pseudo-binary systems for Zr–AlNi, Fe–BZr, Mg–LaNi and Pd–NiP. In Fig. 8, ΔH^{amor} , $\Delta H^{\text{s.s.}}$, ΔH^{chem} , $\Delta H^{\text{topological}}$ and $\Delta H^{\text{elastic}}$ were plotted against equiatomic solute compositions of AlNi, BZr, LaNi and NiP. The ΔH^{amor} and $\Delta H^{\text{s.s.}}$ crosses at the composition corresponding to the boundary of AFCR in Fig. 4. The difference between $\Delta H^{\text{chem}}(\text{amor})$ and $\Delta H^{\text{chem}}(\text{s.s.})$ results from the short-range order factor expressed by the multiplying factor $[1 + 5(x_i^s x_j^s)^2]$ in eq. (8). The $\Delta H^{\text{chem}}(\text{amor})$ coincides with $\Delta H^{\text{chem}}(\text{s.s.})$ under the

condition where the short-range order is ignored, and this condition replaces ΔH^{amor} with $\Delta H^{\text{amor}} (= \Delta H^{\text{amor}}(\text{s.s.}) + \Delta H^{\text{topological}})$. The boundaries of AFCR accordingly shift slightly toward the center of the composition triangle shown in Fig. 7. An exception to the change in the AFCR boundary was observed in the Pd–NiP pseudo-binary systems. No cross point was seen between $\Delta H^{\text{amor}} (= \Delta H^{\text{amor}}(\text{s.s.}) + \Delta H^{\text{topological}})$ and $\Delta H^{\text{s.s.}}$ in the Pd–NiP pseudo-binary system shown in Fig. 8. The absence of AFCR of the Pd–NiP system is due to a considerably small $\Delta H^{\text{elastic}}$ value compared with that of short-range order. The characteristics of $\Delta H^{\text{elastic}}$ and ΔH^{chem} in the pseudo-binary systems are summarized as follows: The $\Delta H^{\text{elastic}}$ decreases in the order of Fe–BZr > Zr–AlNi > Mg–LaNi > Pd–NiP and the ΔH^{chem} increases in the order of Zr–AlNi and Fe–BZr < Pd–NiP < Mg–LaNi.

Thus, the stabilization mechanisms for an amorphous phase in the typical alloy systems can be summarized as follows. The Al–Ni–Zr and B–Fe–Zr systems having relatively large and negative ΔH^{amor} as well as large $\Delta H^{\text{elastic}}$ have a similar stabilization mechanism. The large $\Delta H^{\text{elastic}}$ of the B–Fe–Zr system stabilizes an amorphous phase, while the medium $\Delta H^{\text{elastic}}$ of the Al–Ni–Zr system stabilizes an amorphous phase. The difference can be seen at the composition of the AFCR boundary in Zr and Fe corners. The B–Fe–Zr

Fig. 8 Enthalpies versus composition diagrams in pseudo-binary systems of Zr-AlNi, Fe-BZr, Mg-LaNi and Pd-NiP.

Table 3 Ternary amorphous alloy systems in which no amorphous-forming composition range was calculated under the condition that the short-range order is ignored.

Ag-Al-Mg	Al-Mn-Si	Cu-Pd-Si	Mn-P-Si	Si-Ti-V
Ag-Pd-Si	Al-Mo-Si	Cu-P-Pd	Mo-Nb-Si	
Al-Cr-Ge	Al-Nb-Ti	Fe-Mn-P	Mo-P-Rh	
Al-Cr-Si	As-P-Pd	Fe-Mo-P	Mo-P-Ru	
Al-Cu-Fe	Au-Ge-Si	Fe-Ni-P	Nb-Si-Ta	
Al-Cu-Mn	Au-Pd-Si	Fe-Pd-Si	Nb-Si-Ti	
Al-Cu-V	B-C-N	Fe-P-Pd	Nb-Si-V	
Al-Fe-Ge	Co-Cr-P	Fe-P-Si	Nb-Si-W	
Al-Fe-P	Co-Ni-P	Fe-P-V	Ni-Pd-Si	
Al-Fe-Si	Co-Pd-Si	Ge-Mn-Pd	Ni-P-Pd	
Al-Ga-Mg	Cr-Fe-P	Ge-Nb-Si	Ni-P-Pt	
Al-Ge-Mn	Cr-Ge-Pd	Ge-Pd-Si	Pd-Rh-Si	
Al-Ge-V	Cr-Ni-P	Ir-P-Pd	P-Pd-Ti	
Al-Mg-Pd	Cr-Pd-Si	Mn-Pd-Si	P-Ru-W	
Al-Mg-Ti	Cu-Ni-P	Mn-P-Pd	Si-Ta-Ti	

system has a lower solute composition than that for the Al-Ni-Zr system, and the difference agrees with the location of the experimental AFCs in the composition triangle. For the Mg-LaNi system, the much lower $\Delta H^{\text{elastic}}$ sufficiently stabilizes a solid solution on account of the small absolute value of ΔH^{amor} in the system. Although the Pd-NiP system has approximately zero $\Delta H^{\text{elastic}}$, the short-range order observed in the amorphous phase plays a role in the stabilization of the amorphous phase.

Finally, in order to clarify the effect of the short-range order on the stabilization of an amorphous phase shown in eq. (8), the AFCR was again calculated for 338 ternary systems using eq. (13). Table 3 summarizes the ternary systems in which

no AFCR was calculated. Most of the ternary alloy systems listed in Table 3 contain Si, P, Pd, Al, Fe or Ge, and a number of binary subsystems of Al-, Fe- and Pd-metalloid were seen accordingly. It is thus considered that in the Al-, Fe- and Pd-metalloid base systems an amorphous phase can be formed on account of the of short-range order effect. The possibility of this being so for the Al-based amorphous alloys was supported by the detection of a prepeak in a coherent intensity profile in a previous study.¹⁴⁾ The prepeak, which is rarely observed in other metallic amorphous alloys, has frequently been observed in Al-based amorphous alloys¹⁴⁾ of Al-Mn,¹⁵⁾ Al-Mn-Si,¹⁵⁾ Al-Ge-Ni¹⁶⁾ systems. It is generally understood that the prepeak is attributed to the presence of a short-range order.¹³⁾ In addition to the Al-based amorphous alloy systems, Pd- and Fe-metalloid systems were reported to have a short-range order in their amorphous phase from radial distribution function data.¹⁷⁾

5. Conclusions

Amorphous-forming composition ranges (AFCR) were calculated for 338 amorphous-forming ternary systems on the basis of the database given by Miedema's model, and were compared to the experimental data of the amorphous-forming compositions (AFCs). Furthermore, the stabilization of an amorphous phase and the amorphous-forming ability (AFA) were analyzed from the viewpoint of the elastic enthalpy term arising in a solid solution and short-range order observed in an amorphous phase. The main results obtained can be summarized as follows.

- (1) AFCR is calculated in 335 ternary alloy systems except for Al-Cu-Fe, Al-Mo-Si and Au-Ge-Si.
- (2) The calculated results are in agreement with the ex-

perimental results for Cu–Ni- and Al–Ti-based systems.

(3) In the typical amorphous systems with high AFA exemplified by the Zr-, La-, Fe- and Mg-based systems, the calculated AFCR is overestimated as a result of a simplification inherent in the present model.

(4) The elastic enthalpy arising in the solid solution stabilizes the amorphous phase, and the stabilization mechanism is particularly notable in Mg-based amorphous systems.

(5) The Short-range order observed in amorphous alloys plays an important role in the formation of Al-, Fe- and Pd-metalloid based amorphous alloys.

(6) The following factors are of great importance for the estimation of AFA: (1) three empirical rules for the achievement of high AFA, (2) melting temperature and viscosity at the melting temperature, (3) elastic enthalpy arising in a solid solution, and (4) short-range order observed in the amorphous phase.

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