Prediction of Critical Compositions for Bulk Glass Formation in La-Based, Cu-Based and Zr-Based Ternary Alloys

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Using a quasi-chemical method coupled with Miedema’s semi-empirical method, we have estimated critical glass-forming compositions for bulk metallic glasses of metal-metal type alloys such as La–Ni–Al, Cu–Zr–Ti and Zr–Ni–Al that exhibit maximum temperature spans of their supercooled liquid region, \( \Delta T_a = T_a - T_f \), reaching 37–77 K. We applied Cowley’s chemical short-range order (CSRO) parameters \( \eta_{ij} \) for specific constituent \( i-j \) atomic pairs calculated by the quasi-chemical method to obtain the short-range order parameter \( \gamma \) of the amorphous phase, which is used as a constant in the calculation of formation enthalpies by Miedema’s method. In this study, the constant \( \gamma \) is treated as a function of the composition of atomic pairs such as \( \eta_{ij}(\gamma) \). From the calculated results, it appears that the most negative value of \( \eta_{ij} \) corresponds to a highly stable liquid state because of the occurrence of chemical short-range order, implying that bulk metallic glasses can be produced. Stability and instability of the liquid phase have been discussed in terms of the compositional dependence of Cowley’s CSRO parameters and enthalpy difference parameters. The calculated results predict fairly well the critical glass-forming compositions for the various bulk metallic glasses, even predicting the asymmetrical composition dependence of the glass-forming composition ranges. Furthermore, the relation of \( \eta_{ij} (= \eta_{ji}) \) with interaction parameters \( \varepsilon_{ij} \) yields the characteristics of interaction between dissimilar solutes in 0-1-2 ternary metallic solutions.

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1. Introduction

In a previous article,1) we applied Miedema’s semi-empirical method2) to make accurate predictions of the glass-forming composition ranges (hereafter referred to as GFR) of Zr–Ni–Al ternary alloys. In making theoretical estimates of formation enthalpies for various competing phases of the alloy system including amorphous, solid solution and intermetallic compound phases, we extensively investigated the dominant factors that influence the GFR and glass-forming abilities (hereafter referred to as GFA) of the metallic glasses. Based on these theoretical assessments, we found that large negative enthalpies of mixing, atomic size differences among the constituent elements, and short-range order existing in the liquid phase strongly stabilize the glassy phase, leading to a high GFA for an alloy system. In contrast, stable intermetallic compounds with high melting temperatures tend to constrain any extension of the GFR. Based on our findings, we feel certain that bulk metallic glasses (hereafter referred as BMG) that exhibit extremely wide temperature span of their supercooled liquid region, indicating the stabilization of liquid phase, can be produced when those essential conditions are substantially satisfied. Nevertheless, we have not yet achieved pinpoint accuracy in predicting the critical compositions required for the formation of bulk metallic glass. The principal reason for this uncertainty may be a rather simplified approximation introduced in Miedema’s formalism with respect to atomic-interaction behavior, in which there exist only “pair-interactions” between individual atoms, i.e., A-B, B-C and C-A pairs, among individual constituent elements in A-B-C ternary alloys.

In order to make a more accurate prediction of the critical compositions for BMGs, a potential “many-body interactions” among the constituent element atoms should be effectively introduced in the model. For this purpose, we have used the following two methods. First one is the quasi-chemical method3) by which Desrè4) has recently predicted the degree of chemical short-range order (hereafter referred as CSRO) in a typical liquid phase of the bulk glass forming Zr–Ni–Al alloy system. In this model, interactions among individual atoms in a liquid phase are consistently treated in the framework of the quasi-lattice model with nearest neighbor pair-interaction approximation in thermal equilibrium, and also treated with statistical mechanics as a canonical ensemble of condensed matter. Desrè calculated Cowley’s CSRO parameter5) which is defined by the probability of finding another atom \( j \) around an atom \( i \) at the center of the first shell. The calculated Cowley’s CSRO parameters suggest compositional variations of the stability of the liquid phase that imply the critical composition for the most stable liquid. Second, we used another model to consider the degree of interactions between solute-1 and solute-2 in solvent-0 which may represent effective “many-body interactions” in a pseudo-potential formalism coupled with a hard-sphere model (hereafter referred to as PS-HS model). The model was proposed by Ueno and Waseda6) for theoretical evaluation of interaction parameters \( \varepsilon_{ij}^2 \) in 0-1-2 ternary metallic solutions. From the sign and numerical values of the parameter \( \varepsilon_{ij}^2 \), we can recognize whether the interactive force between solute-1 and solute-2 in solvent-0 is a repulsive or attractive one, and the degree of interaction between them. Specific understanding of the stability of the

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liquid phase in dilute or low-alloy compositions would be possible based on a relationship between the interaction parameters $\varepsilon^2_{ij}$ derived by the PS-HS model and the corresponding Cowley’s CSRO parameters derived by the quasi-chemical method.

In the present study, we have used the quasi-chemical method coupled with Miedema’s semi-empirical method to predict critical compositions of the most stable liquid phase of glassy alloys in systems such as La–Ni–Al, Cu–Zr–Ti and Zr–Ni–Al, as shown by the maximum temperature span of the supercooled liquid region, $\Delta T_c = (T_s - T_g)$, reaching about 37–77 K. Furthermore, we have explored the mechanisms for bulk glass formation from the standpoint of pair interactions between individual constituent elements including the effect of surrounding atoms in those glassy alloys.

2. Fundamental Calculations

2.1 Miedema’s semi-empirical method

The mathematical formalisms of Miedema’s semi-empirical method are precisely described elsewhere. Here we briefly describe their essence. In Miedema’s model, the mixing enthalpy for an infinite dilution of two transition metals A and B, which is considered to be the interfacial enthalpy of atomic cells, is formulated as

$$
\Delta H^\infty_A (in\ B) = \Delta H^\text{m} (A in B) = \frac{2V_A^2}{\left(n_{\text{at}}^A \right)^{1/3} + \left(n_{\text{at}}^B \right)^{1/3}} \times [-P(\Delta \varphi)^2 + Q(\Delta n_{\text{at}}^A)^2 - R^*],
$$

where $V_A$ is the molar volume of an A atom, $n_{\text{at}}^A$ and $n_{\text{at}}^B$ are the electron density of atomic cells, $\Delta \varphi$, the difference between the modified electronegativities of dissimilar atomic cells of A and B atoms. $P$ and $Q$ are constants to be determined empirically; $R^*$ is a correction value for an alloy of a transition metal with one of the polyvalent non-transition metals such as Al. Equation (1) shows explicitly that a large $\Delta \varphi$ implies an attractive bonding and a large $\Delta n_{\text{at}}$ a repulsive one. On the basis of these mixing enthalpy values for binary alloys, the compositional dependence of the formation enthalpies of the amorphous phase $\Delta H^\text{Chem}_{ABC} (Amo)$ and a solid solution phase $\Delta H^\text{Chem}_{ABC} (SS)$ of A–B–C ternary system can be calculated as described in the previous article. In this case, the $\Delta H^\text{Chem}_{ABC} (Amo)$ is expressed as

$$
\Delta H^\text{Chem}_{ABC} (Amo) = \Delta H^\text{Chem}_{ABC} (Amo) + \Delta H^\text{topological}_{ABC},
$$

where $\Delta H^\text{Chem}_{ABC} (Amo)$ is an enthalpy of chemical mixing and $\Delta H^\text{topological}_{ABC}$ is a topological enthalpy. When the formation enthalpy of the amorphous phase, $\Delta H^\text{Chem}_{ABC} (Amo)$, is more negative than that of the solid solution phase, $\Delta H^\text{Chem}_{ABC} (SS)$, the amorphous phase is likely to be stable. In other words, the formation of the amorphous phase is preferred in the composition range where the condition $\Delta H^\text{Chem}_{ABC} (SS) - \Delta H^\text{Chem}_{ABC} (Amo) \geq 0$ is satisfied. The theoretical GFR can be predicted by estimating the parameters of the formation enthalpy difference. A parameter, $\gamma (= 0$ for the CSRO free case; $= 5$ for the usual CSRO case) is also introduced to describe CSRO in the amorphous phase. The factor $[1 + \gamma (c^2_{i,j} c^3_j)^2]$ needs to be multiplied to an enthalpy of chemical mixing $\Delta H^\text{Chem}_{ABC} (Amo)$ in case that the CSRO exists in the amorphous phase, where the $c^3_j$ is the surface fraction of the cell of i-th element.

2.2 Quasi-chemical method

As described in section 1, Desre’s has recently predicted the compositional dependence of the degree of CSRO in a liquid phase of the Zr–Ni–Al alloy system using the quasi-chemical method. In this method, interactions among individual atoms in a liquid phase are consistently treated in the framework of the quasi-lattice model with nearest neighbor pair-interaction approximation in thermal equilibrium, and also treated as a many-particle problem of the statistical mechanics of a canonical ensemble of condensed matter. The quasi-chemical method is a very promising method in spite of its rather simple mathematical formulation. It can be shown to be fundamentally equivalent to the Bragg-Williams approximation or Bethe’s approximation, which were successively developed for solving the problem of order-disorder transitions in crystalline solids. The configuration partition function $Q$ of the ternary Zr–Ni–Al alloy system is expressed in terms of the pair-interaction energy (designated by $\varepsilon_{\text{NN}}$, $\varepsilon_{\text{NAl}}$, $\varepsilon_{\text{NAl}}$, $\varepsilon_{\text{NN}}$, $\varepsilon_{\text{ZZ}}$, $\varepsilon_{\text{ZZ}}$, $\varepsilon_{\text{Zn}}$, $\varepsilon_{\text{Zn}}$, $\varepsilon_{\text{Zn}}$, $\varepsilon_{\text{Zn}}$), the number of dissimilar atomic pairs denoted by $zm$, $zn$ and $zp$ for Ni–Zr, Al–Zr and Al–Ni respectively and the mole fraction of Ni and Al, denoted $x$ and $y$ respectively. Here $z$ is the coordination number of the first shell ($z = 10$ is applied in this case). Maximization of the partition function $Q$ versus $m, n$ and $p$ leads to an equilibrium condition. The corresponding values of $m^*$, $n^*$ and $p^*$ are given by eqs. (3) to (5):

$$
\frac{p^2}{(y - p^* - n^*)(y - m^* - p^*)} = \exp \left(-\frac{2\lambda}{RT}\right),
$$

$$
\frac{n^2}{(x - p^* - n^*)(1 - x - y - m^* - n^*)} = \exp \left(-\frac{2\mu}{RT}\right),
$$

$$
\frac{m^2}{(x - m^* - n^*)(1 - x - y - m^* - n^*)} = \exp \left(-\frac{2\nu}{RT}\right),
$$

where $T$ is temperature (K), $R$ the gas-constant and $\lambda, \mu$ and $\nu$ are interaction parameters given as

$$
\lambda = z \left( \varepsilon_{\text{NN}} - \frac{\varepsilon_{\text{NAl}} + \varepsilon_{\text{NAl}}}{2} \right),
$$

$$
\mu = z \left( \varepsilon_{\text{NN}} - \frac{\varepsilon_{\text{NAl}} + \varepsilon_{\text{NAl}}}{2} \right),
$$

$$
\nu = z \left( \varepsilon_{\text{NAl}} - \frac{\varepsilon_{\text{NAl}} + \varepsilon_{\text{NAl}}}{2} \right),
$$

From Miedema’s tables, $\lambda = -88.5$ KJ, $\mu = -207$ KJ, $\nu = -182$ KJ are used. From the calculated $m^*$, $n^*$ and $p^*$ in the whole range of concentration of the ternary alloy, it is possible to deduce the corresponding Cowley’s order parameters $\eta_{ij}$ which measure the CSRO and are defined as

$$
\eta_{ij} = 1 - \frac{z_{ij}}{z_{ij}},
$$

where $z_{ij}$ is the partial coordination number of $j$ atoms around an atom $i$ located at the center of the first shell of coordination. $x_{ij}$ is the average mole fraction of component
j in the liquid. Clearly, negative values of $\eta_j$ correspond to the development of CSRO and zero to complete randomness. In the present application the $\eta_j$ are related to the average number of pairs (per atom) $z^p_j$, $zn^*_j$ and $zn^*$ through the simple relations:

$$\eta_{AIni} = 1 - \frac{P^{x}_{AIni}}{xy},$$

$$\eta_{NiZr} = 1 - \frac{\eta_{NiZr}}{y(1-x-y)},$$

$$\eta_{AlZr} = 1 - \frac{P^{x}_{AlZr}}{x(1-x-y)}.$$  \hfill (8)

From the numerical solutions of eqs. (3) to (5), order parameters $\eta_{NiZr}$, $\eta_{AlZr}$ and $\eta_{AIni}$ are calculated. The method has been applied to La–Ni–Al and Zr–Cu–Ti alloys for the first time in this study. The compositional dependence of Cowley’s parameters for Zr–Ni–Al alloys is also calculated, and a novel trial is performed in which the obtained Cowley’s parameters are transformed to the CSRO parameter $\gamma$ in Miedema’s model to derive $\Delta H(SS) - \Delta H(Amo)$ with high accuracy.

3. Results and Discussion

3.1 Prediction of GFR and CSRO parameters in glassy alloys

3.1.1 La–Ni–Al alloys

It is well recognized that ternary La–Ni–Al alloys show high GFA in a wide glass-forming compositional range. Furthermore, a bulk metallic glass\(^{10)}\) with a diameter of 3 mm can be formed by copper mold casting at a critical composition of La\(_{55}Ni_{20}Al_{25}\) which corresponds to a supercooled liquid region of temperature span ($\Delta T_{x\ max} = 69$ K).\(^{11)}\) Similarly, a large maximum value of the reduced glass transition temperature ($T_g/T_m = 0.71$) at a composition of La\(_{50}Ni_{25}Al_{25}\) is also reported. Those extremely large values of $\Delta T_c$ and $T_g/T_m$ indicate that the supercooled liquid of the corresponding compositions in La–Ni–Al alloys has a high stability against nucleation and growth of crystalline phases. In fact, a minimum value of the critical cooling rate $R_c$ of La\(_{55}Ni_{20}Al_{25}\) alloy is 87 K/s\(^{12)}\) which is an extremely small value corresponding to a low growth velocity of 4.5 mm/s\(^{13)}\) for the crystalline phase. In addition, from a theoretical standpoint, this alloy system is particularly attractive in that it contains only three elements and yet displays high GFA. Bearing the above in mind, this alloy system was considered to be well suited to the aim of the present study: to predict the critical composition of bulk metallic glass and to understand the precise mechanism involved.

Figure 1 shows experimentally determined GFR\(^{14)}\) in La–Ni–Al alloys compiled in a database for rapidly quenched (RQ: melt-spin) ternary amorphous alloys and also their GFR as calculated using Miedema’s method. The theoretical GFR is determined by a condition of $\Delta H(SS) - \Delta H(Amo) > 0$ as described in the previous paper,\(^{11)}\) in which CSRO in the amorphous phase is not assumed ($i.e.$ $\gamma = 0$). Fairly good agreement between experimental GFR and theoretical GFR is observed in this case, although some discrepancy exists in the Al-rich region. However, the theoretical GFR does not indicate the critical composition which may correspond to the most stable liquid phase or the supercooled liquid phase.

Figure 2 shows the composition dependence of the calculated Cowley’s order parameter $\eta_{AIna}$, $\eta_{NiLa}$ and $\eta_{AIni}$ in the liquid phase of La\(_{50}Ni_{25}Al_{25}\) alloys. It is clear in Fig. 2 that the parameter $\eta_{AIna}$ and $\eta_{NiLa}$ show respective negative maximum values ($\eta_{AIna\ max} \approx -0.7$, $\eta_{NiLa\ max} \approx -0.54$) in the vicinity of La\(_{50}Ni_{25}Al_{25}\) which corresponds to a maximum value of the reduced glass transition temperature ($T_g/T_m = 0.71$). The parameter $\eta_{AIna}$ goes to extremely large positive values in the lower Ni fraction (La-rich) composition ranges, and then decreases to small negative values at higher Ni fractions. This suggests that the Al–Ni atomic pair seems to be destabilized, implying that Al and Ni atoms become repulsive to each other in the liquid phase in La-based, Cu-based and Zr-based ternary alloys.
On the other hand, the Ni fraction at the boundaries of the experimental GFR is ~0.0 and ~0.6; the calculated values of $\eta_{\text{AlLa}}$ and $\eta_{\text{NiLa}}$ at these compositions are rather small negative values ($\eta_{\text{AlLa}} = -0.2 \sim -0.3$, $\eta_{\text{NiLa}} = -0.1 \sim 0.0$). These results suggest that the boundaries of experimental GFR are determined by a competition between a less-ordered liquid (amorphous) phase and primary solid solution phases. This idea is consistent with the fact that the experimental values of $\Delta T_g$ and $T_g/T_m$ in the vicinity of those boundaries become small compared to their maximum values. We therefore suggest that the theoretical GFR, assuming complete randomness ($\gamma = 0$) in the amorphous phase, predicts the experimental GFR rather well, as shown in Fig. 1.

### 3.1.2 Cu–Zr–Ti alloys

Inoue et al.\textsuperscript{15} have recently reported that bulk glassy alloys with a thickness of 4 mm can be formed in the Cu–Zr–Ti ternary system by copper mold casting. The maximum $T_g/T_m$ of the system reaches 0.62–0.63 at critical compositions of $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$. We have examined this alloy system to determine whether or not similar theoretical results can be obtained in the La–Ni–Al system described in section 3.1.1.

Figure 3 shows experimentally determined GFR\textsuperscript{14) in Cu–Zr–Ti alloys compiled in a database for rapidly quenched (RQ: melt-spun) ternary amorphous alloys and whose GFR is calculated using Miedema’s method. The theoretical GFR is determined using the condition $\Delta H(\text{SS}) - \Delta H(\text{Amo}) > 0$, in which CSRO in the amorphous phase is not assumed ($i.e.$ $\gamma = 0$). An agreement between the experimental GFR and the theoretical GFR is not good in this case. However, as for a middle domain of the theoretical GFR, it agrees rather well with the middle domain of the experimental GFR that roughly corresponds to the critical compositions of $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$.

Figure 4 shows the composition dependence of the calculated Cowley’s order parameters $\eta_{\text{CuZr}}$, $\eta_{\text{TiCu}}$ and $\eta_{\text{TiZr}}$ at 1000 K in the liquid phase of $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$ and $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$ alloys. It is clear in Fig. 4 that the parameter $\eta_{\text{CuZr}}$ shows a negative maximum value ($\eta_{\text{CuZr}} \text{max} = -0.5$) in the vicinity of $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$ which corresponds to a maximum of the reduced glass transition temperature $T_g/T_m$ of the system. The parameter $\eta_{\text{TiCu}}$ also shows a shallow negative peak ($\eta_{\text{TiCu}} \text{max} = -0.25$) at $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$. The range of rather deep negative values of $\eta_{\text{CuZr}}$ and $\eta_{\text{TiCu}}$ agrees with the experimental GFR for $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10}$ alloys which include Cu fractions in the range 0.4–0.6. The values of $\eta_{\text{TiZr}}$ at low Cu content ($\text{Cu} < 0.4$) are nearly zero and increase to positive values, reaching almost 0.5 at $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ with increasing Cu content. This suggests that the Cu–Zr–Ti–Cu atomic pairs prefer to be highly ordered and hence enhance the stability of the liquid phase at those critical compositions of $\text{Cu}_{60}\text{Zr}_{20-30}\text{Ti}_{10-20}$. The Ti–Zr atomic pair seems to be destabilized, implying that Ti and Zr atoms become repulsive to each other in the liquid phase in Cu-rich compositional ranges.

### 3.1.3 Zr–Ni–Al alloys

Zhan et al.\textsuperscript{9} have reported that ternary Zr–Ni–Al alloys show high GFA in a wide glass-forming compositional range.\textsuperscript{16) A bulk metallic glass with a diameter of 1.4 mm can be formed by water quenching at a composition of $\text{Zr}_{60}\text{Ni}_{30}\text{Al}_{20}$.\textsuperscript{17)} A wide and stable supercooled liquid region of temperature span $\Delta T_g = 77$ K\textsuperscript{16} is obtained at $\text{Zr}_{60}\text{Ni}_{25}\text{Al}_{15}$. Similarly, a maximum value of reduced glass transition temperature $T_g/T_m (= 0.64)$ at a composition of $\text{Zr}_{60}\text{Ni}_{30}\text{Al}_{20}$\textsuperscript{16} is also reported. These extremely large values of $\Delta T_g$ and $T_g/T_m$ indicate that the supercooled liquid of the corresponding compositions in Zr–Ni–Al alloys has a high stability against nucleation and growth of crystalline phases.

The experimentally determined GFR of Zr–Ni–Al alloys was presented in a previous report.\textsuperscript{1} The GFR of the alloys is quite wide and can be divided into Zr-rich and Al-rich regions. The theoretical GFR obtained with Miedema’s method predicts well the wide GFR and non-GFR observed in the vicinity of the pure Zr-phase.\textsuperscript{1} We also found that the glassy phase is formed preferentially in the regions where the intermetallic compounds are not stabilized.\textsuperscript{1} However, we did not produce satisfactory predictions of critical compositions for bulk metallic glass.

Figure 5 shows the composition dependence of calculated Cowley’s order parameters $\eta_{\text{NiZr}}$, $\eta_{\text{AlZr}}$ and $\eta_{\text{AlNi}}$ at 1000 K in
the vicinity of Zr\(_{50}\)/Ni\(_{30}\)/Al\(_{20}\) alloys. It is clear in Fig. 5 that both parameter of \(\eta_{NiZr}\) and \(\eta_{AlZr}\) show large negative maximum values (\(\eta_{NiZr, max} \sim -0.8\), \(\eta_{AlZr, max} \sim -0.75\)) in the vicinity of Zr\(_{50}\)/Ni\(_{30}\)/Al\(_{20}\) which corresponds to a maximum value of the reduced glass transition temperature \(T_g/T_m\). The range of rather deep negative values of \(\eta_{NiZr}\) and \(\eta_{AlZr}\) agrees with the experimental GFR for Zr\(_{60}\)/Ni\(_{30}\)/Al\(_{10}\) alloys which covers the Ni fraction range of 0.05–0.55. The parameter \(\eta_{AlNi}\) goes to extremely large positive values in the lower Ni fraction (Zr-rich) composition ranges, and then decreases to small negative values at higher Ni fractions. This suggests that the Al–Ni atomic pair seems to be destabilized, implying that Al and Ni atoms become repulsive to each other in the liquid phase in Zr-rich compositional ranges, and in contrast stabilized (attractive to each other) in Ni-rich compositional ranges. Thus the composition dependence of these Cowley’s CSRO parameters clearly indicates the interactive effect of the solvent constitutions on the stabilization of specific atomic pairs.

In the present study, we have for the first time applied a composition dependent function of Cowley’s CSRO parameters \(\eta_{ij}\) for the specific constituent i-j atomic pairs (calculated by the quasi-chemical method) to the CSRO parameter \(\gamma\) of the amorphous phase utilized in the calculations of formation enthalpies by Miedema’s method. That is, the constant \(\gamma\) is treated as a function of the composition of certain atomic pairs: \(\gamma_i(\eta_{ij})\). In the calculations, the following novel empirical relation is introduced for this alloy system:

\[
\gamma_i(X_{Al}, X_{Ni}) = -6.25\eta_{ij}(X_{Al}, X_{Ni})
\]

where \(X_{Al}\) and \(X_{Ni}\) are fraction of Al and Ni, respectively. In eq. (9), \(\gamma_i(X_{Al}, X_{Ni})\) varies between 0 and 5 with the corresponding values of \(\eta_{ij}\) such as 0 to \(-0.80\), for example. Figure 6 shows the composition dependence of the calculated enthalpy difference parameter of \(\Delta H(SS) - \Delta H(Amo)\) using eq. (9) which we call the “Quasi-Chemical model + Miedema’s model”. The calculated enthalpy difference parameters of \(\Delta H(SS) - \Delta H(Amo)\) based on the conventional Miedema’s model are shown in the figure for comparison. The experimentally determined GFR and critical composition range for a maximum \(\Delta T_x (>70\,K)\) are also shown in the figure. The predicted critical composition range of Ni that corresponds to the maximum value of \(\Delta H(SS) - \Delta H(Amo)\) in the “Quasi-chemical model + Miedema’s model” agrees surprisingly well with the experimentally determined critical composition range for a maximum \(\Delta T_x (>70\,K)\). The agreement of the model’s prediction with experimentally determined GFR is surprisingly good, extending even to an asymmetrical compositional dependence on the Ni fraction. Thus the calculated enthalphy difference parameter of \(\Delta H(SS) - \Delta H(Amo)\), taking into account Cowley’s CSRO parameter, predicts the critical composition of the most stabilized liquid state of the alloy system with a high accuracy. The fact that intermetallic compounds are preferably stabilized at higher fractions of Ni (more than about 0.50–0.60\(^{1}\)) is well explained by those considerations.

Furthermore, we have tried to estimate the temperature dependence of CSRO parameters \(\eta_{AlZr}\) in the same alloys as shown in Fig. 7. The compositional dependence of the \(\eta_{AlZr}\) at 1000 K and 1500 K are both shown in the figure. At 1500 K the most negative value of \(\eta_{AlZr}\) tends to be less negative by about 0.20 than at 1000 K. On the other hand, positive
values of $\eta_{\text{AlNi}}$ at 1000 K in higher Ni fraction ranges decrease by about 0.20 compared with that at 1500 K. These estimates of $\eta_{\text{AlNi}}$ suggest that CSRO tends to be weakened when the temperature is raised substantially. In other words, with a decrease of liquid phase temperature, the CSRO may be enhanced, inducing a stable supercooled liquid state. Such an “effect of melting liquid temperature” in CSRO has been shown experimentally in a Zr–Al–Cu–Pd alloy by small-angle X-ray scattering (SAXS) measurements at 1273–1573 K by Fan et al.\(^{18}\) They called the atomic clusters caused by CSRO of Zr–Pd pairs in the liquid phase “quenched-in nuclei”. Thus the validity of the theoretical estimate shown in Fig. 7 is confirmed by experimental evidence in this case.

### 3.2 Estimation of interaction parameters of $e_i^2$

Here we discuss the repulsive interactions of dissimilar solute atoms dispersed among substantial numbers of solvent atoms. As described in section 3.1.3, the parameter $\eta_{\text{AlNi}}$ in the composition ranges of lower Ni fractions (Zr-rich) goes to extremely large positive values. This suggests that the Al–Ni atomic pair is destabilized, and Al and Ni atoms become repulsive to each other in the liquid phase in Zr-rich mixture. We now discuss the degree of interaction between solute-1 and solute-2 in solvent-0 which may represent the “many-body interactions” in a pseudo-potential formalism coupled with a hard-sphere model (hereafter referred to PS-HS model).\(^7\) The parameter $e_i^2$ is expressed as,

$$e_i^2 = e_i^2(\text{hs}) + e_i^2(\text{ps})$$

where $e_i^2(\text{hs})$ and $e_i^2(\text{ps})$ are the interaction parameters based on the hard-sphere model and the pseudo-potential model, respectively. It may be noticed that the former mainly corresponds to the contribution from the hard-core repulsive part in the pair potential and the latter should be attributed to the contribution from the soft part in the pair potential. Based on the hard sphere description for the free energy of the hard sphere system\(^19\) and the pseudo-potential theory of metals,\(^20\) the respective terms may be given by:\(^7\)

$$e_i^2(\text{hs}) = (1 - m)(1 - n) + tE_1 + t^2E_2 + 3t^3E_3 + 9t^4E_4,$$

$$e_i^2(\text{ps}) \approx \frac{1}{8\pi T} \left[ \left( \frac{V_1}{V_0} \right) \Delta H_2^\text{HS} \left( \text{in1} \right) - \left( \frac{V_2}{V_0} \right) \Delta H_2^\text{HS} \left( \text{in0} \right) - \left( \frac{V_1}{V_0} \right) \Delta H_2^\text{HS} \left( \text{in0} \right) \right],$$

$$E_1 = (1 - n)(\alpha_3^2 - m) + (1 - m)(\alpha_3^2 - n) + 3(\alpha_2^2 - m)(\alpha_1 - n) + 3(\alpha_2 - m)(\alpha_1^2 - n),$$

$$E_2 = (\alpha_2^2 - m)(\alpha_1^2 - n) + 9(\alpha_2^2 - m)(\alpha_1^2 - n),$$

$$E_3 = (\alpha_2 - m)(\alpha_3^2 - n) + 3(\alpha_2^2 - m)(\alpha_1^2 - n) + 3(\alpha_2^2 - m)(\alpha_1^2 - n),$$

$$E_4 = (\alpha_3^2 - m)(\alpha_1^2 - m),$$

$$\alpha_1 = \frac{\sigma_1}{\sigma_0}, \quad \alpha_2 = \frac{\sigma_2}{\sigma_0}, \quad n = \frac{V_1}{V_0}, \quad m = \frac{V_2}{V_0},$$

$$t = \frac{\eta_0}{(1 - \eta_0)}.$$
that the mechanisms for bulk glass formation must be discussed with specific reference to mutually related essential factors such as,

1) development of CSRO in the liquid state (cohesion with atomic clustering),
2) stabilization of the liquid state (inducing decreased melting temperature),
3) realization of wide temperature span of supercooled liquid region,
4) high stability against nucleation and growth of crystalline phase (transformation kinetics),
5) appearance of high glass-forming ability,
6) evidence of formation of bulk metallic glasses.

In the present study, we have intensely examined items 1) and 2). From the results obtained, we can say that CSRO clustering in the liquid state of a critical composition would strongly stabilize the liquid phase. This may induce a decrease of melting temperature \(T_m\), and \(T_g\) may increase with increasing \(\Delta H(\text{SS}) - \Delta H(\text{Amo})\) as described previously.\(^1\) That is, the reduced glass transition temperature \(T_g/T_m\) may be increased. On the other hand, experimental evidences of 3), 5), 6) at the critical compositions of bulk glasses in La–Ni–Al, Cu–Zr–Ti and Zr–Ni–Al alloys are well recognized as discussed in section 3.1, although factor 4) remains insufficiently investigated. With those discussions in mind, 3), 4), 5) and 6) would be achieved through maximizing the stabilization of the liquid phase. We are convinced that this stabilization is brought about only by the development of CSRO clustering in the liquid state.

4. Conclusions

Critical compositions for the most stable liquid phase which exhibits maximum temperature span of the supercooled liquid region, \(\Delta T_s (= T_s - T_g)\), reaching 37–77 K have been predicted using the quasi-chemical method coupled with Miedema’s semi-empirical method, in glassy alloys such as La–Ni–Al, Cu–Zr–Ti and Zr–Ni–Al systems. Furthermore, we explored the mechanisms for bulk glass formation from the standpoint of pair interactions between individual constituent elements in those glassy alloys. The results are summarized as follows:

1) The most negative-maximum values of Cowley’s chemical short-range order parameters \(\eta_{ij}\) in the liquid phase of La–Ni–Al, Cu–Zr–Ti and Zr–Ni–Al alloys can predict the critical compositions for the most stable liquid phase which exhibits maximum temperature span of supercooled liquid regions.

2) The boundaries of experimentally determined glass-forming composition ranges are associated with a rather small negative value of \(\eta_{ij}\) which implies near randomness of local atomic configurations.

3) The calculated enthalpy difference parameter \(\Delta H(\text{SS}) - \Delta H(\text{Amo})\), taking \(\eta_{ij}\) into account, predicts the critical composition of the most stabilized liquid state of the alloy system better than that without \(\eta_{ij}\).

4) The predicted values of the interaction parameters \(\eta_{ij}\) in an 0-1-2 solid solution which includes the effect of environmental solvent atoms are consistent with the values of \(\eta_{ij}\).

5) The critical glass-forming compositions for bulk metallic glasses can be predicted by the calculation of \(\eta_{ij}\) and \(\Delta H(\text{SS}) - \Delta H(\text{Amo})\).

REFERENCES