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Gibbs energy calculation of liquid Zr–Al–Ni and Zr–Al–Cu–Ni alloys with clusters

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Abstract The Gibbs energies of liquid Zr–Al–Ni and Zr–Al–Ni–Cu alloys with multi-clusters are calculated based on the statistical mechanism in this paper. The results show that the quantity of clusters depends mainly on the temperature and the concentration of the melt. It increases gradually with the decrease of temperature or with the increase of x_{Ni} in liquid $(\mathrm{Zr}_{80}\mathrm{Al}_{20})_{1-x}\mathrm{Ni}_x$ alloys; the quantity of $\mathrm{Zr}_2\mathrm{Ni}$ clusters reaches its maximum of 0.061 mole at $x_{\mathrm{Ni}} = 0.336$. In $(\mathrm{Zr}_{80}\mathrm{Al}_{20})_{1-x}\mathrm{Ni}_x$ liquid alloy the existence of clusters causes the falling of the Gibbs energy. The Gibbs energy drops about 4000 J/mol at $x_{\mathrm{Ni}} = 0.35$ if the effect of cluster of $\mathrm{Zr}_2\mathrm{Ni}$ is considered or about 8000 J/mol at $x_{\mathrm{Ni}} = 0.40$ if both of clusters of $\mathrm{Zr}_2\mathrm{Ni}$ and ZrNi are taken into account.

Introduction

A great number of clusters will form spontaneously in supercooled liquid of bulk metallic glass [1, 2], which results in lower Gibbs energy and more stable supercooled liquid [3, 4]. Hamada and Fujita [5] proposed that the metallic glass was composed of clusters in 1982. Later Serebryakov [6] assumed that the metallic glass was composed of clusters which had the composition close to the steady or unsteady state compound in the phase diagram and intercluster layers which were solid solution similar to liquid. Chen and Hui [7] developed the multicomponent short-range-order (MCSRO) model in which the MCSRO domains were considered to distribute randomly among the free atoms. Desre [8–10] treated the cluster with the ensemble theory and gave the probability of clusters by Gauss distribution as follows:

$$a_l = \frac{1}{Q_f} \exp\left(-\frac{n}{RT} \Delta G_f(C, C_0)\right) \tag{1}$$

where Q_f is the partition function, $\Delta G_f(C, C_0)$ is the isothermal Gibbs energy of formation of one mole of clusters in melt of C_0 (n, atoms in the cluster; C, composition of the cluster) and R is the gas constant. The difficulty of this method is to obtain the partition function in the calculation of the probability of the cluster.

Recently, many methods of modeling and simulation have been used to investigate the structure, formation and evolvement of the clusters, such as First Principle [11, 12], Mont Carlo method [13] and Molecular Dynamics [14, 15]. However, the calculations are limited in the small system with 500–1000 atoms due to the capability of computing processing. Up to date, very little has been reported on the effect of the cluster on the Gibbs energy of the metallic glass alloys, especially to the Zr-based alloys. This may be a new method to quantitatively analyze the glass-forming ability of the metallic glass alloy.

This paper calculates the Gibbs energy of liquid Zr–Al–Ni and Zr–Al–Ni–Cu alloys with multi-clusters with the statistical mechanism in order to explain the mechanism of formation of bulk metallic glass.

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Mathematical model

Quantity calculation of clusters

The multicomponent liquid is assumed to consist of v components, and the average composition of the liquid, C_0, is defined by a set of (v–1) molar fractions: $c_{1,0}$, $c_{2,0}$,...$c_{v-1,0}$. The composition of cluster, C, is defined as c_1, c_2,... c_{v-1}.

Other assumptions are proposed in order to calculate the quantity of clusters as follows: (1) The liquid is assumed to be composed of clusters; (2) Interaction between the clusters is assumed to be weak and can be ignored, so the liquid alloy is regarded as an approximation independent particle (cluster) system; (3) Every cluster has its unique microstate which is described by n (atoms in the cluster) and C (composition of the cluster); and (4) The number of clusters with the same microstate is unlimited. So, the liquid alloy is regarded as the Boltzmann system which is described as

$$a_l = \omega \exp\left(-\frac{E_i}{kT}\right) \tag{2}$$

where a_l is the probability of the particle with energy level of E_i, ω is a constant determined by the normalizing condition and k is the Boltzmann constant.

The Boltzmann distribution can be written as

$$a_l = \omega_l \exp(-\alpha) \exp\left(-\frac{n}{RT}\Delta G_f(C, C_0)\right) \tag{3}$$

where α is a constant, $\Delta G_f(C,C_0)$ is the isothermal Gibbs energy of formation of one mole of clusters in the melt of C_0 and ω_l is the microscopic state of the cluster.

The cluster is determined by its composition, C, atom number, n, and the position, x, y, z.

$$h = \Delta C \times \Delta n \times \Delta x \times \Delta y \times \Delta z \tag{4}$$

Then the microscopic states of clusters in the bulk liquid with volume of V in the range of dCdn, can be written as

$$\omega_l = \frac{V}{h}\mathrm{d}C\mathrm{d}n \tag{5}$$

So the cluster number in the bulk liquid with volume of V in the range of dCdn is:

$$m = \frac{V}{h} \mathrm{e}^{-\alpha} \mathrm{e}^{-n\frac{\Delta G_f(C,C_0)}{RT}} \mathrm{d}n\mathrm{d}C \tag{6}$$

If the atom number in the whole system is N, from the normalizing condition:

$$N = \iint n\frac{V}{h} \mathrm{e}^{-\alpha} \mathrm{e}^{-n\frac{\Delta G_f(C,C_0)}{RT}} \mathrm{d}n\mathrm{d}C \tag{7}$$

If

$$\iint n \mathrm{e}^{-n\frac{\Delta G_f(C,C_0)}{RT}} \mathrm{d}n\mathrm{d}C = Z \tag{8}$$

The cluster number can be obtained by combining Eq. 6 with $\mathrm{e}^{-\alpha} = \frac{Nh}{VZ}$ derived from Eq. 7:

$$m = \frac{N}{Z} \mathrm{e}^{-n\frac{\Delta G_f(C,C_0)}{RT}} \mathrm{d}n\mathrm{d}C \tag{9}$$

If N_0 represents the Avogadro constant, the cluster number with the composition of C in 1 mole liquid with C_0 is:

$$m_0 = \frac{N_0}{Z} \mathrm{e}^{-n\frac{\Delta G_f(C,C_0)}{RT}} \mathrm{d}n \tag{10}$$

Then the quantity (unit: mole) of clusters in 1 mole liquid alloy is:

$$f = \int n m_0 / N_0 \mathrm{d}n \tag{11}$$

ΔG_f can be represented approximately by a free energy-composition diagram based on Ref. [8] as shown in Fig. 1. The point J is the intersection of the tangent to the Gibbs energy curve for C_0 and the vertical line at C.

Gibbs energy of melt with clusters

The Gibbs energy of liquid alloy is expressed as the sum of two contributions for convenience of calculation, according to Serebryakov's assumption [6], one from the clusters and the other from the bulk melt. The interaction between the bulk melt and the clusters is weak and can be ignored, which is illustratively shown in Fig. 2.

If there are n_i kinds of clusters in a multicomponent liquid alloy, the Gibbs energy of the system, G, is written as

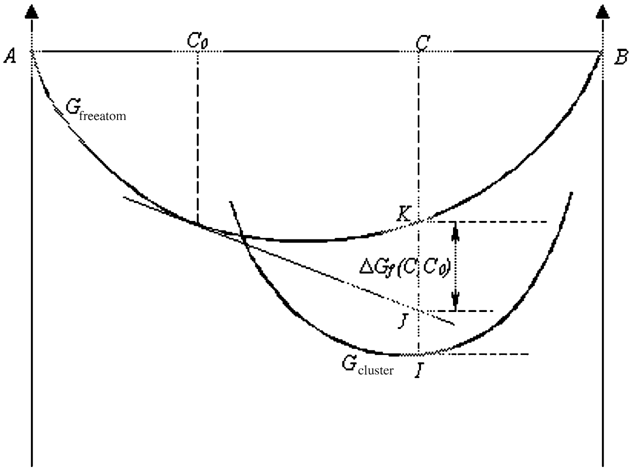

Fig. 1 The schematic graph of ΔG_f. (G_{freeatom} is the molar Gibbs energy of liquid composed of free atoms, and G_{cluster} is the molar Gibbs energy of a cluster)

Table 1 Parameters used in computation

Alloy system	i	A_i	B_i	Ref.
Al–Zr	0	–82055	–25	[16]
	1	–3311	–2.5	[16]
	2	10000	0	[16]
Cu–Ni	0	32238.7	–11.109	[17]
	1	–619.65	–1.0881	[17]
	2	–213.49	0.97309	[17]
Al–Cu	0	–39801	–5.6591	[18]
	1	21762.8	–2.3533	[18]
	2	6367.8	–12.069	[18]
Cu–Zr	0	–67500	5.49	[19]
	1	–2500	1.98	[19]
	2	0	0	[19]
Zr–Ni	0	–10695	–1.823	[19]
	1	–4274.5	3.044	[19]
	2	670.7	–0.46	[19]

Note: for an a–b–c ternary alloy,
$G^{\text{ex}} = x_a x_b \sum_{i=0}^{i=2}(x_a - x_b)^i(A_i + B_i T) + x_a x_c \sum_{i=0}^{i=2}(x_a - x_c)^i(A_i + B_i T) + x_b x_c \sum_{i=0}^{i=2}(x_b - x_c)^i(A_i + B_i T)$
$G = G^{\text{ex}} + RT(x_a \ln x_a + x_b \ln x_b + x_c \ln x_c)$

Table 2 Parameters used in computation [20]

Alloy system		Parameter (300 K < T < 2000 K)
Ni–Al	A_{Ni}	$4.18 \times (-48608 - 33.02\,T + 3.328 \times 10^{-2}\,T^2 - 6.528 \times 10^{-6}\,T^3)$
	B_{Al}	$4.18 \times (-22008 - 31.12\,T + 3.328 \times 10^{-2}\,T^2 - 6.528 \times 10^{-6}\,T^3)$

Note: $G^{ex} = x_{\text{Ni}} x_{\text{Al}}(x_{\text{Ni}} A_{\text{Ni}} + x_{\text{Al}} B_{\text{Al}})$

$$G = \sum_{i=1}^{n_i} f_i G_i + (1 - \sum_{i=1}^{n_i} f_i) G_l + RT\left[\sum_{i=1}^{n_i} f_i \ln f_i + (1 - \sum_{i=1}^{n_i} f_i) \ln(1 - \sum_{i=1}^{n_i} f_i)\right] \tag{12}$$

where f_i is the quantity of the *ith* kind clusters, G_i is the molar Gibbs energy of the clusters and G_l is the molar Gibbs energy of the rest bulk liquid.

The calculation procedures are as follows: (1) The Gibbs energy curves are computed with parameters in Tables 1 and 2, then ΔG_f is obtained from the geometric relationship in Fig. 1, and then the quantity of the *ith* kind clusters f_i is computed based on Eq. 6 to Eq. 11; (2) The molar Gibbs energy of cluster G_i is calculated according to Fig. 1; (3) The composition of the rest bulk liquid is determined by mass conservation, and G_l is obtained with the parameters in Tables 1 and 2; and (4) the Gibbs energy of liquid with clusters is computed according to Eq. 12.

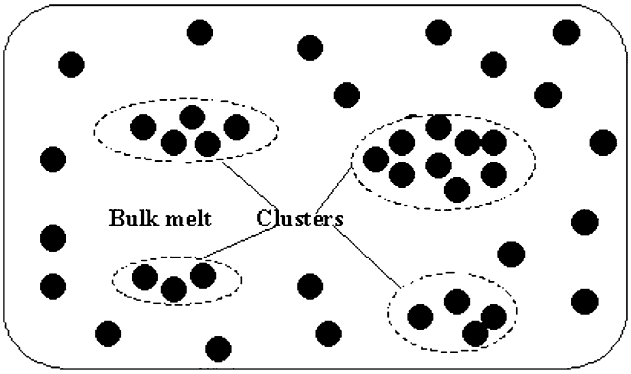

Fig. 2 The multicomponent liquid with clusters

Results and analysis

Liquid Zr–Al–Cu–Ni alloy with Zr_2Ni, Zr_2Cu and Zr_6NiAl_2 clusters and liquid Zr–Al–Ni alloy with Zr_2Ni, ZrNi, Zr_6NiAl_2 and Zr_5Ni_4Al clusters are investigated. As the fist approach only two kinds of clusters (Zr_2Ni and ZrNi) are considered in calculation of the Gibbs energy of the melt with clusters.

Effect of temperature on the quantity of cluster

Figure 3 shows the quantity of clusters in 1 mole the liquid alloys. It can be clearly seen that the quantity of cluster increases with the decrease of temperature. The quantity of clusters rises from 0.036 to 0.048 mole for $Zr_{60}Al_{15}Ni_{25}$, or from 0.025mole to 0.033mole for $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ if the temperature drops from

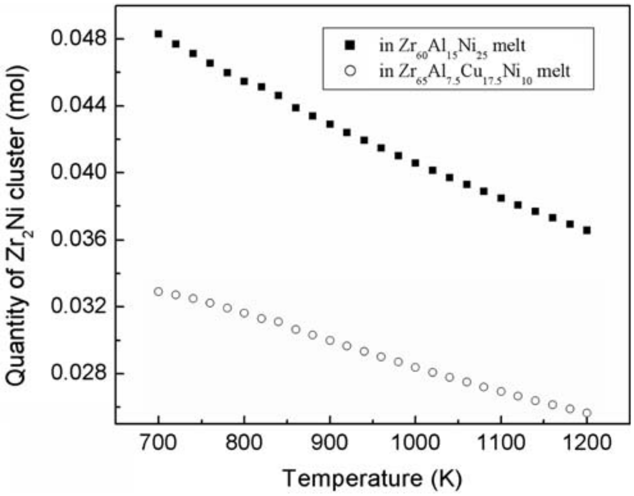

Fig. 3 The quantity of clusters in 1 mole liquid alloy

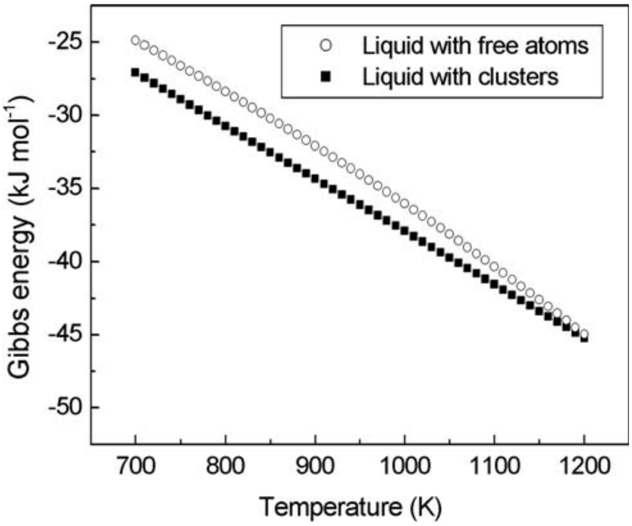

Fig. 4 The Gibbs energy of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$

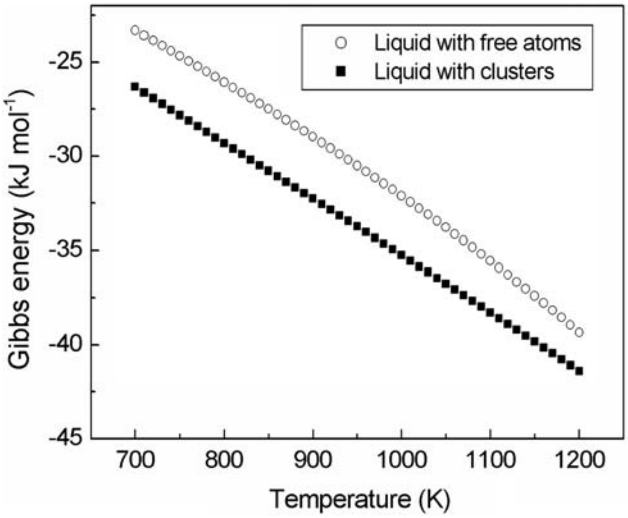

Fig. 5 The Gibbs energy of $Zr_{60}Al_{15}Ni_{25}$

1200 to 700 K. The formation of clusters is determined both by the Gibbs energy difference between the clusters and the liquid, which is the driving force for cluster formation, and by the mobility of atoms. At lower temperature, the Gibbs energy difference is larger and the driving force for cluster formation is higher. As temperature decreases, the Gibbs energy difference increases so that the cluster quantity rises. On the other hand, based on the statistical mechanics, the mobility of atoms will decrease at lower temperature, which makes atoms diffusion more difficult and the probability of cluster formation decrease.

Another result shown in Fig. 3 is that the quantity of clusters in liquid $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy is lower than that in liquid $Zr_{60}Al_{15}Ni_{25}$ alloy. Compared with $Zr_{60}Al_{15}Ni_{25}$, the Gibbs energy of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ is lower and closer to that of Zr_2Ni cluster. So the driving force to form Zr_2Ni cluster is smaller and this results in a smaller quantity of Zr_2Ni clusters in liquid $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy. In addition, the molar fractions of Zr and Ni are decreased comparatively due to the introduction of the Cu element, which results in a smaller probability of Zr_2Ni cluster formation.

The Gibbs energies of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ and $Zr_{60}Al_{15}Ni_{25}$ with Zr_2Ni clusters and with free atoms are shown in Figs. 4 and 5, respectively. Obviously, both the liquids with clusters have lower Gibbs energy than that with free atoms, which is more distinct at lower temperature. The Gibbs energy of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy will drop about 2000–3000 J/mol according to the results of the existence of clusters (Fig. 4). Since the precipitated crystalline phase is Zr_2Cu in $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ [21], the Gibbs energy difference between the liquid alloy and the crystalline phase, i.e., the nucleation driving force, will then be smaller. These may be the reason of the higher glass-forming ability of the Zr-based bulk metallic glass alloy.

The relationship between the quantity of clusters and the atom number in 1mole liquid $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy is shown in Fig. 6. The quantity of clusters drops sharply with the increase of the atom number to about 10, then it varies unnotably. The quantity of clusters is 1.32×10^{-4}mole when the atom number is 10, it drops to 2.71×10^{-8}mole when the atom number increases to 20. This shows that smaller clusters are more favored in the liquid alloys.

Effect of composition on the quantity of cluster

Figure 7 shows the computed results of the quantity of Zr_2Ni clusters in liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloys. The

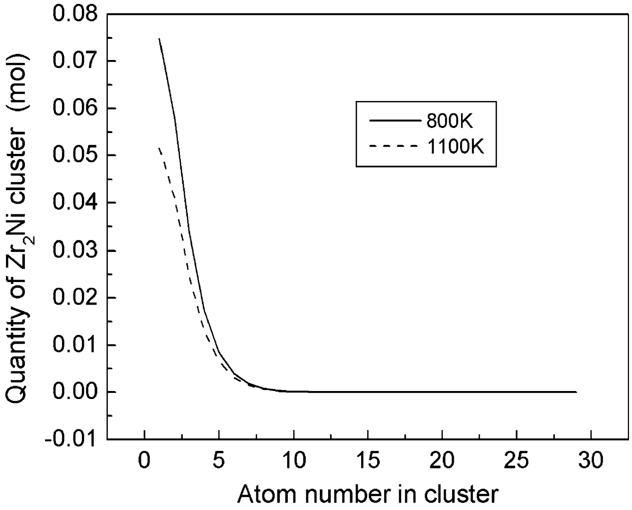

Fig. 6 Relationship between the quantity of clusters and atom number in 1 mole liquid $Zr_{60}Al_{15}Ni_{25}$ alloy

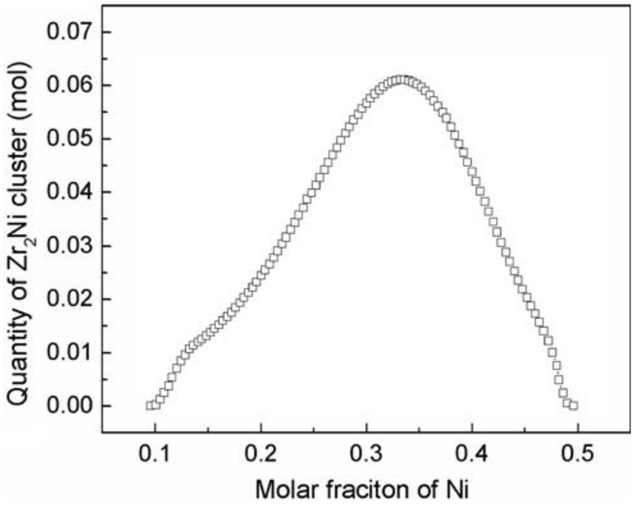

Fig.7 Quantity of clusters in 1mole liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloy at 1000 K

quantity of Zr_2Ni clusters rises with the increase of molar fraction of x_{Ni}, it reaches the highest value of 0.061 mole when the molar fraction of x_{Ni} rises to 0.336. If the fraction of Ni is further increased, the molar faction of Zr is decreased, which makes the formation of cluster difficult.

The computed Gibbs energies of liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloys with various clusters at 1000 K are shown in Fig. 8. It can be seen that three Gibbs energy values all drop firstly to the lowest points at $x_{Ni} = 0.35–0.40$ and then rise with the increase of x_{Ni}. Compared with the melt with free atoms, the Gibbs energy of the melt with Zr_2Ni clusters will drop about 4000 J/mol at $x_{Ni} = 0.35$ due to the existence of Zr_2Ni clusters. When both Zr_2Ni and ZrNi exist in the melt, the Gibbs energy will drop further, for example, about 8000 J/mol at $x_{Ni} = 0.40$. Therefore, the existence of clusters lowers the Gibbs energy of the melt significantly, which results in a lower driving force to the nucleation of the crystalline phase.

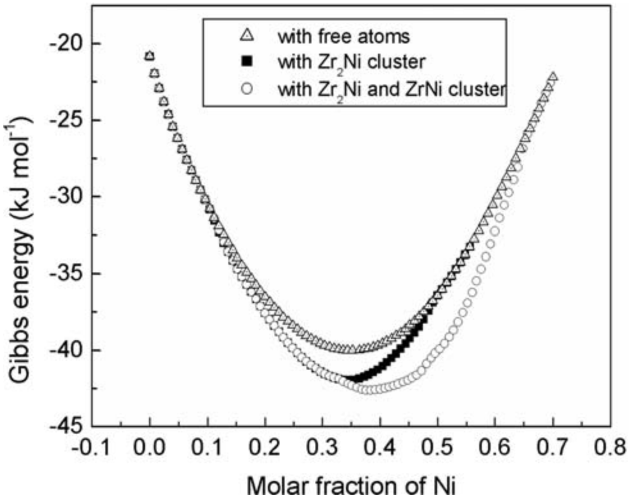

Fig. 8 The Gibbs energy of liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloys with different clusters at 1000 K

Additionally, when the mole fraction of x_{Ni} is lower than 0.34, the Gibbs energy curves with Zr_2Ni cluster and with ZrNi and Zr_2Ni clusters are nearly overlapped. This means that the ZrNi cluster can hardly be formed in this composition region. Because the formation of the cluster depends on the melt composition, the quantity and the kind of clusters can be maximized to favor the formation of the metallic glass by selecting appropriate alloy composition.

Conclusions

(1) The Gibbs energies of liquid Zr–Al–Ni and Zr–Al–Ni–Cu alloys with multi-clusters are calculated based on the statistical mechanism.

(2) The quantity of clusters depends mainly on the temperature and the concentration of melt. The quantity of clusters increases gradually with the decrease of temperature. With the increase of x_{Ni} in liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloys, the quantity of clusters rises and reaches the maximum value of 0.061 mole with the x_{Ni} of 0.336. The quantity of clusters in liquid $Zr_{60}Al_{15}Ni_{25}$ alloy is higher than that in liquid $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy.

(3) The existence of clusters leads to the drop of the Gibbs energy for liquid $(Zr_{80}Al_{20})_{1-x}Ni_x$ alloys. The Gibbs energy drops about 4000 J/mol at

$x_{\mathrm{Ni}} = 0.35$ if only Zr_2Ni is considered; the Gibbs energy drops about 8000 J/mol at $x_{\mathrm{Ni}} = 0.40$ when both Zr_2Ni and ZrNi clusters are taken into account.

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