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Formation enthalpies of Al–Fe–Zr–Nd system calculated by using geometric and Miedema's models

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ABSTRACT

Formation enthalpy is important for the phase stability and amorphous forming ability of alloys. The formation enthalpies of $Fe_{17}RE_2$ (RE=Ce, Pr, Nd, Gd and Er) obtained by Miedema's theory are in good agreement with those of the experiments. The dependence of formation enthalpy on concentration of Al for intermetallic $(Al_xFe_{1-x})_{17}Nd_2$ have been calculated by Miedema's theory and the geometric model. The solid solubility of Al in $(Al_xFe_{1-x})_{17}Nd_2$ is coincident with the concentration dependence of formation enthalpy. The mixing enthalpies of liquid alloys and formation enthalpies of alloys for Al–Fe–Zr–Nd system have been predicted. The calculated mixing enthalpy indicates that the adding of Fe or Nd decreases monotonously the magnitude of enthalpy. The formation enthalpies of Al–Fe–Zr–Nd system indicate that the shape of the enthalpy contour map changes when the content of Al is less than 50.0 at% and then it remains unchanged except the decrease of magnitude. The formation enthalpy of Al–Fe–Zr–Nd increases with the increase of Fe and/or Nd content. The negative formation enthalpy indicates that Al–Fe–Zr–Nd system has higher amorphous forming ability and wide amorphous forming range. The certain contents of Zr and/or Al are beneficial for the formation of Al–Fe–Zr–Nd intermetallics.

1. Introduction

Al-based bulk metallic glasses and nano-crystalline alloys have attracted considerable attention in recent years due to their outstanding mechanical and physical properties such as high mechanical strength and unique magnetic properties [1–3]. Recently, lots of works have been performed for Al–Fe and Al–Fe–Zr systems [4–13]. Especially, the FeAl alloys offer a combination of attractive properties such as a high specific strength, good strength at intermediate temperature and an excellent corrosion resistance at elevated temperature under oxidizing, carburizing and sulfidizing atmospheres [12]. For Al–Fe–Zr ternary system, Fogagnolo et al. [13] studied $Al_{89}Fe_{10}Zr$ alloys by using mechanical alloying and obtained a nanocrystalline supersaturated solid solution of α-Al.

As we know, formation enthalpy as one of the thermodynamic properties is crucial for multi-component bulk metallic glasses due to the negative formation enthalpy which can be used to estimate the stability of amorphous alloys [3,14,15]. Therefore, many efforts [16–23] have been performed to understand the mechanisms of amorphization and optimization of the glass forming composition by using the formation enthalpy as an important parameter. Furthermore, Al-based bulk metallic glasses, especially with rare earth (RE) elements, provide an important exception from the generality, *i.e.* they do not follow these general rules [24]. However, few of literatures focus on the thermodynamic description for the Al-based bulk metallic glasses with rare earth elements. The thermodynamic data of Al–Fe–Zr–Nd system are still unavailable up till now due to the technical difficulties, constituent complexity, experimental expenses and time consumption.

Thermodynamic properties for alloys can be predicted from theoretical approaches. It was well known that *ab initio* calculations based on density functional theory (DFT) can predict accurate formation enthalpies for intermetallic compounds [25], but require an enormous amount of computational time and the knowledge of crystalline structure in details. Miedema's model [26,27] has been extended to calculate the standard formation enthalpies of intermetallics [28,29] and liquid alloys [30], phase-diagram thermodynamics [31,32], phase stability of alloys by mechanical alloying [33,34].

In generally, Miedema's theory can predict the formation enthalpies of binary system directly. For the ternary and/or multinary system, formation enthalpies should be estimated by extrapolation from their constituent binaries. Bakker [35] has proposed a method, in which the mole fraction of each element of the ternary

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system is extensively expressed as similarly as that in the binary system. Hereafter, for ternary and/or multinary systems, more extrapolation methods such as extended Miedema's model [36], and asymmetric geometric extrapolation methods (for example, those based on Toop's model [37]) have been proposed. Among those models, some of them do not consider the effect of an additive element on the properties of binary alloys, and the asymmetric method has inaccuracies due to the individual experience-based choice of the asymmetric constituent. Then, the modified asymmetric geometric model, which is independent on the choice of the asymmetric elements, has been proposed [38,39].

Due to the high glass forming ability, Al–Fe–Zr system has been widely studied [40]. In general, rare earth elements can be used to improve some physical properties of a material, then, as one of the rare earth elements, whether Nd additive can affect the thermodynamic properties of the Al–Fe–Zr system or not? The aim of this work is to calculate the mixing enthalpies of liquid and formation enthalpies of Al–Fe–Zr–Nd alloys, with the modified asymmetric geometric model and Miedema's theory. The remainder of this paper is organized as follows. In Section 2, the method and calculation details are described. In Section 3, the thermodynamic properties are presented and discussed. Finally, some conclusions are drawn in Section 4.

2. Computational method

de Boer et al. [27] used a so-called macroscopic-atom-method to predict formation enthalpies of binary systems. The formation enthalpy of the binary *i–j* alloy can be expressed as follows:

$$\Delta H_{ij}^{C}(y_i, y_j) = y_i y_j \left(f_j^i \Delta H_{i\ in\ j}^{C} + f_i^j \Delta H_{j\ in\ i}^{C} \right) \tag{1}$$

$$f_j^i = y_j^s \left[1 + \gamma \left(y_i^s y_j^s \right)^2 \right] \tag{2}$$

$$y_i^s = \frac{y_i V_i^{2/3}}{y_i V_i^{2/3} + y_j V_j^{2/3}} \tag{3}$$

$$\Delta H_{i\ in\ j}^{C} = \frac{P V_i^{2/3}}{(1/2)\left((1/n_i^{1/3}) + (1/n_j^{1/3}) \right)} \left[-(\Delta\varphi)^2 + \frac{Q}{P}(\Delta n^{1/3})^2 - \alpha \frac{R}{P} \right] \tag{4}$$

$$V_i^{2/3}(\text{alloy}) = V_i^{2/3}(\text{pure}) \left[1 + a_i f_j^i (\varphi_i - \varphi_j) \right] \tag{5}$$

where V, ϕ, n is mole volume, electron chemical potential, and electronic density at the Wigner–Seitz cell boundary, respectively. P, Q, R, α, γ and a are empirical parameters, in which $Q/P=9.4$, $\alpha=0.73$ for a liquid alloy, $\alpha=1$ for a solid alloy if one component is a transition metal, or $\alpha=0$ otherwise. $\gamma=0$ for a random solution or $\gamma=8$ for a long-range ordered alloy. The description of all above parameters can be referred to Ref. [27].

According to Ouyang's model [38,39], the formation enthalpies of quaternary alloy can be calculated as follow:

$$\begin{aligned} \Delta H_{ijkl} = {} & \frac{x_i x_j}{y_{ij}^i y_{ij}^j} \Delta H_{ij}\left(y_{ij}^i, y_{ij}^j \right) + \frac{x_i x_k}{y_{ik}^i y_{ik}^k} \Delta H_{ik}\left(y_{ik}^i, y_{ik}^k \right) + \frac{x_j x_k}{y_{jk}^j y_{jk}^k} \Delta H_{jk}\left(y_{jk}^j, y_{jk}^k \right) \\ & + \frac{x_i x_l}{y_{il}^i y_{il}^l} \Delta H_{il}\left(y_{il}^i, y_{il}^l \right) + \frac{x_j x_l}{y_{jl}^j y_{jl}^l} \Delta H_{jl}\left(y_{jl}^j, y_{jl}^l \right) \\ & + \frac{x_k x_l}{y_{kl}^k y_{kl}^l} \Delta H_{kl}\left(y_{kl}^k, y_{kl}^l \right) \end{aligned} \tag{6}$$

where ΔH_{ijkl} is the formation enthalpy of quaternary alloy. ΔH_{ij}, ΔH_{ik}, ΔH_{jk}, ΔH_{il}, ΔH_{jl} and ΔH_{kl} are formation enthalpies of the six constituent binaries systems, correspondingly. x_i, x_j, x_k and x_l are the mole fractions of four constituents in the quaternary system, y_{ij}^i and y_{ij}^j are the mole fractions of the constituents i and j extrapolated to binary system i–j from the quaternary system. They are expressed as follows:

$$\begin{aligned} y_{ij}^i &= x_i + \delta_{ij}^i (x_k + x_l) \\ y_{ij}^j &= x_j + \delta_{ij}^j (x_k + x_l) \\ y_{ik}^i &= x_i + \delta_{ik}^i \left(x_j + x_l \right) \\ y_{ik}^k &= x_k + \delta_{ik}^k \left(x_j + x_l \right) \\ y_{jk}^j &= x_j + \delta_{jk}^j (x_i + x_l) \\ y_{jk}^k &= x_k + \delta_{jk}^k (x_i + x_l) \\ y_{il}^i &= x_i + \delta_{il}^i \left(x_j + x_k \right) \\ y_{il}^l &= x_l + \delta_{il}^l \left(x_j + x_k \right) \\ y_{jl}^j &= x_j + \delta_{jl}^j (x_i + x_k) \\ y_{jl}^l &= x_l + \delta_{jl}^l (x_i + x_k) \\ y_{kl}^k &= x_k + \delta_{kl}^k \left(x_i + x_j \right) \\ y_{kl}^l &= x_l + \delta_{kl}^l \left(x_i + x_j \right) \end{aligned} \tag{7}$$

with

$$\begin{aligned} \delta_{ij}^i &= \frac{\lambda_i}{\lambda_i + \lambda_j}; \\ \delta_{ij}^j &= \frac{\lambda_j}{\lambda_i + \lambda_j}; \\ \delta_{ik}^i &= \frac{\lambda_i}{\lambda_i + \lambda_k}; \\ \delta_{ik}^j &= \frac{\lambda_k}{\lambda_i + \lambda_k}; \\ \delta_{jk}^j &= \frac{\lambda_j}{\lambda_j + \lambda_k}; \\ \delta_{jk}^k &= \frac{\lambda_k}{\lambda_j + \lambda_k}; \\ \delta_{il}^i &= \frac{\lambda_i}{\lambda_i + \lambda_l}; \\ \delta_{il}^l &= \frac{\lambda_l}{\lambda_i + \lambda_l}; \\ \delta_{jl}^j &= \frac{\lambda_j}{\lambda_j + \lambda_l}; \\ \delta_{jl}^l &= \frac{\lambda_l}{\lambda_j + \lambda_l}; \\ \delta_{kl}^k &= \frac{\lambda_k}{\lambda_k + \lambda_l}; \\ \delta_{kl}^l &= \frac{\lambda_l}{\lambda_k + \lambda_l} \end{aligned} \tag{8}$$

and