Monte Carlo simulation of thermophysical properties of binary Co–Gd liquid alloys

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A B S T R A C T

Monte Carlo method with EAM potential is applied to simulate the thermophysical properties of the liquid Co–6.7, 10.5, 16.8, 22.2, 25.6, and 33.3 at%Gd binary alloys. With the increase of the content of Gd, the simulated surface tension at the melting temperature decreases from 1.422 to 1.293 N/m, whereas the simulated temperature coefficient of surface tension rises from $1.36 \times 10^{-3}$ to $1.84 \times 10^{-3} \text{ N m}^{-1} \text{ K}^{-1}$. Based on the simulated surface tension, the viscosity and diffusion coefficient within the temperature range from 1300 to 2000 K are deduced. The dependence of viscosity on the temperature and the alloy composition has been obtained. The solute diffusion constant changes as a quadratic function of content Gd. The diffusion activation energy varying with the alloy composition is discussed. The calculation results quantitatively indicate that the liquid fluidity increases with the Gd content. Our results might provide the necessary thermophysical parameters which could be used in designing the microstructure and magnetic properties in Co–Gd system.

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1. Introduction

Thermophysical properties in the liquid state are very important parameters for determining the thermodynamic relations during the liquid to solid transition process. Among those thermophysical parameters, surface tension [1–5], viscosity [4–9], and diffusion coefficient [4,5] are three most important ones. The surface tension of alloys is vital for studying the surface segregation effects and the extent of Marangoni flow [8,9], while the viscosity is a kinetic parameter that determines the nucleation and growth rates of crystals in the undercooled liquid. The diffusion coefficient, which decides the atom migration and the characteristic diffusion length ahead of the liquid/solid interface, is a key parameter to the microstructure scaling since most phase transformations are diffusion controlled processes. Although these parameters are crucial to the liquid to solid phase transition, the data are scarce. The measurement of these parameters at high temperatures, however, is difficult since the liquid metals are unstable, easily oxidizable, and fast evaporable. Due to this reason, the molecule simulation methods are developed to solve the problems [3,10–13]. Monte Carlo (MC) method is one of molecule simulation methods, which has been applied to simulate microstructure evolution and magnetic properties of liquid alloys in various conditions, which are difficult to be realized by experimental measurement. In recent years, the MC method has also been used to simulate the thermophysical parameters and been proved to be a valid way to deal with such problems [4,14,15].

Co–Gd alloy is one of the most important systems for the applications in the manufacture of magnetic components at high temperature. Eight intermetallic compounds could form during the liquid to solid transition, which makes the system be developed as a potential magnetic refrigeration material. The study on the properties of bulk Co–xGd alloys has been undertaken in the past due to their interesting ferrimagnetism and anticipated potential in device applications [16,17]. Considerable progress has also been achieved as regard to the properties of the Co–Gd alloys [18–23]. For example, Zhang et al. [21] have prepared the Co–Gd amorphous ribbons with large magnetocaloric effect. Our research results on Co–Gd alloys [22,23] show that, the magnetic properties are related to the phase composition, the grain size, the exchange coupling effect of the soft and the hard magnetic phases, and so on. It is also revealed that the Gd content has drastic effect on the magnetic properties [22]. It can be seen from these results that the strong diffusion of Gd/Co into the intermetallic compounds occurs, which results in the exchange coupling effect of the magnetic phases. Because of the interdiffusion effect between the phases, the grain interface may profoundly influence the properties of such...
magnetic alloys [22]. To analyze the influence of intermetallic compound on the magnetic properties, the thermophysical parameters are necessary but they are in lack for this alloy. Generally, the linear-fitted values from the thermophysical properties of pure metals are used in the calculation [23], which is shown to be not accurate. The shortage of the thermophysical data of Co–Gd liquid obstructs the theoretical description of the relationship between the phase transition process and the magnetic properties.

In this paper, the equilibrium state of Co–Gd liquids with different Gd contents at different temperatures has been determined by MC method with Analytic Modified Embedded-Atomic Method (AMEAM). The surface tension, the viscosity and the diffusion coefficient can then be simulated from the statistical average of equilibrium states. The dependence of these thermophysical properties on the temperature and the alloy composition is examined, which can provide necessary data for the theoretical research of the phase transition and the solidification microstructure.

2. Simulation methods

2.1. Configuration initialization of hcp–hcp system

Different from the fcc–fcc system, the basic unit of the hcp–hcp system used in the simulation includes four atoms locate at (0,0,0), (1/3 a0, ±2/3 a0, 0). Along the directions of x-, y- and z-axes, the unit reproduces (n−1) times, respectively, to form a system of 4n3 atoms with an hcp structure. Here, a0 is the crystal constant derived from the density of liquid alloy. According to the alloy composition, the corresponding atoms in the hcp structure are selected randomly to be changed to the solute atom.

2.2. Energy calculation

One most key point for the MC simulation on the thermophysical parameters of the liquid metals is the right selection of the proper potential function. Due to their hcp structures, we use the EAM potentials with the correction terms for Co [24] and Gd [25] established by Hu et al.

\[ E_i = \sum_j E_{ij} \]  
\[ E_i = F(\rho_i) + \frac{1}{2} \sum_j \phi(r_{ij}) + M(P_i) \]  

Here, M is the correction term to amend the discrepancy of the electron density fitted linearly. \( F(\rho) \) is the embedding energy for placing an atom into that electron density, \( \phi(r_{ij}) \) a short-range pair interaction (core–core repulsion), \( \rho_i \) the total local electron density at atom i computed as a superposition of atomic electron density of the rest atoms in the system. The other parameters are as follows.

\[ F(\rho) = F_0 \left(1 - \ln \left(\frac{\rho}{\rho_0}\right)\right) \left(\frac{\rho}{\rho_0}\right)^{4} \]  
\[ \rho_i = \sum_j r_{ij} \]  
\[ f(r_{ij}) = f_0 \left(\frac{r_{ij}}{r_0}\right)^{\frac{1}{4}} \]  
\[ P_i = \sum_j f(r_{ij}) \left(\frac{a_i - a_j}{a_i^2} + \frac{(y_i - y_j)^2}{a_i^2} + \frac{(z_i - z_j)^2}{a_i^2} \right) \]  

Here, \( f(r_{ij}) \) is the atomic electron density of atom j due to atom i, \( \rho_i \) is equal to 12\( r_{ij} \), \( f_0 \) and \( \beta \) are model parameters. The repulsion between core and core and the correction term for Co atom are as following [24]

\[ \phi(r_{ij}) = k_0 + k_1 \left(\frac{r_{ij}}{r_0}\right)^2 + k_2 \left(\frac{r_{ij}}{r_0}\right)^3 + k_3 \left(\frac{r_{ij}}{r_0}\right)^4 + k_4 \left(\frac{r_{ij}}{r_0}\right)^6 + k_5 \left(\frac{r_{ij}}{r_0}\right)^{12} \]  

And those for Gd atom are [23]

\[ \phi(r_{ij}) = k_0 + k_1 \left(\frac{r_{ij}}{r_0}\right)^2 + k_4 \left(\frac{r_{ij}}{r_0}\right)^3 + k_8 \left(\frac{r_{ij}}{r_0}\right)^4 + k_1 \left(\frac{r_{ij}}{r_0}\right)^6 + k_5 \left(\frac{r_{ij}}{r_0}\right)^{12} \]  

\[ M(P) = 2 \left(1 - \exp \left(-\left(\frac{\ln (P)}{P_0}\right)^4\right)\right) \]  

Here, \( n_i \) is the nearest-neighbor distance for the initial configuration, \( P_i \) the value of \( P \) in the equilibrium position, and \( k \) and \( m \) are model parameters. The repulsion between the different cores is derived from the linearly fitted repulsions of Co and Gd in the light of their molar ratio [10].

2.3. Acquisition method of thermophysical properties

A process for producing two new interfaces from a pure liquid column with unit cross section is designated. For a quasi-static separation process, the work of cohesion equals the work required pulling a column of liquid apart. It is assumed that there exists an interface in the simulation cell, which parallels to x and y axes and perpendicular to the z axis. Then the work of cohesion can be calculated through the statistics of the interaction between pairs of molecules belonging to different sides of the interface, respectively. The surface tension (\( \sigma \)) is the ratio of cohesive work (\( W \)) to the increasing surface area, described in more details elsewhere [26].

\[ \sigma = \frac{W}{A} \]  

Here, S is the area of supposed interface.

Based on the simulated surface tension, the viscosity can be obtained via the well-known empirical models, developed by Egyr, who gives a formula relating the viscosity to the surface tension [27].

\[ \eta = \frac{16 \sqrt{M \pi}}{15 \gamma \pi^{3/2}} \sigma \]  

where, \( \eta \) is the viscosity, \( k \) is Boltzmann constant, \( 1.383 \times 10^{-23} \text{ J K}^{-1} \), and \( M \) is the absolute atomic mass. This relationship is used widely to obtain the viscosity data from the simulated surface energy. Although the viscosity is not calculated directly, its value is more reliable and has been reported previously [3–5]. Furthermore, the solute diffusion coefficient can then be obtained according to the viscosity data by Stokes–Einstein formula [28].

\[ D = \frac{kT}{4\eta r} \]  

where \( r \) is the characteristic particle radius. Though Eq. (14) is not obtained for atomic scale, it is applicable to such a scale and works quite well for liquid metals if \( r \) is taken as ionic radius, which has been proved by Gaskell [28]. The Stokes–Einstein relation was first proposed for describing the diffusion motion of mesoscopic balls in a viscous medium, and has been validated for several molecular solutions at dilute concentrations. However, it fails for dense systems [29]. Considering the range of simulation temperature is not far from the liquidus temperature, the Co–Gd liquid is far from the dense state and does reach the dense state. Therefore, the Co–Gd liquid is treated as a viscous medium here, and each element atom is assumed to be the mesoscopic ball. The diffusion coefficient of each element in the system can be estimated by Eq. (14) based on the viscosity data.

The simulation system starts in an 8 × 8 × 8 cubic box with the hcp configuration, consisting of 2048 atoms. In order to achieve a completely equilibrium liquid state, each simulation runs up to 2 × 10^6 Monte Carlo steps. After the equilibrium in the system is achieved, 50,000 Monte Carlo more steps are applied to calculate the system energy.

Table 1

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<tr>
<th>Parameters of EAM potentials for Co and Gd metals used in the simulation [23–25].</th>
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3. Results and discussion

The calculated results of the surface tensions of liquid Co1-xGdx (x = 6.7, 10.5, 16.8, 22.2, 25.0, and 33.3 at%) alloys at different temperatures are presented in Fig. 1(a). For all alloys, the surface tensions decrease with the increase of temperature. Moreover, if the temperature is fixed at a certain value, the surface tension decreases with Gd content. The relationships between the surface tension and the temperature are fitted linearly in the form of $\sigma = \sigma_0 + \alpha \sigma dT + (T - T_m)$ and the fitted equations are given as:

$$\sigma_{6.7\%Gd} = 1.422 - 0.00136(T - 1673)$$
$$\sigma_{10.5\%Gd} = 1.401 - 0.00142(T - 1658)$$
$$\sigma_{16.8\%Gd} = 1.361 - 0.00148(T - 1635)$$
$$\sigma_{22.2\%Gd} = 1.354 - 0.00158(T - 1597)$$
$$\sigma_{25.0\%Gd} = 1.334 - 0.00164(T - 1574)$$
$$\sigma_{33.3\%Gd} = 1.293 - 0.00184(T - 1499)$$

(15)

For Co–Gd system, the measured data of the surface tension are not available in reported references. In this case, we make a comparison of our calculated data with those of pure Co and Gd. The values of the simulated data of Co–Gd alloys are in between those of pure liquid Co and Gd reported: 1.873–4.90 x 10^{-4}(T - 1766) and 0.810–1.60 x 10^{-4}(T - 1585) N/m, respectively [30], which are also presented in Fig. 1(a).

It shows that with the increase of Gd solute, $\sigma_0$ and $\alpha \sigma dT$ both decrease. The variations in $\sigma_0$ and $\alpha \sigma dT$ with Gd content in Co–Gd system are presented in Fig. 1(b). It can be seen that the surface tension of liquid Co–Gd alloys varies sensitively with the temperature and Gd content, which can be described as:

$$\sigma = (1.45 + 4.71 \times 10^{-3}C_{Gd}) + (-1.33 \times 10^{-3} - 3.50 \times 10^{-6}C_{Gd} - 3.56 \times 10^{-7}C_{Gd}^2)(T - T_m) \text{ mN/m} \quad (16)$$

On the basis of Eq. (13) and the simulated surface tension, the viscosities of Co–Gd liquids at different temperatures are determined, as shown in Fig. 2(a). The viscosity decreases with the increase of temperature. The fitted relationship between viscosity and temperature is as following:

$$\eta_{6.7\%Gd} = 2.98 \times 10^{-4} \text{ exp} \left( \frac{44400}{RT} \right)$$
$$\eta_{10.5\%Gd} = 2.77 \times 10^{-4} \text{ exp} \left( \frac{39533}{RT} \right)$$
$$\eta_{16.8\%Gd} = 2.44 \times 10^{-4} \text{ exp} \left( \frac{32922.44}{RT} \right) \text{ Pa s}$$
$$\eta_{22.2\%Gd} = 2.20 \times 10^{-4} \text{ exp} \left( \frac{36333.31}{RT} \right)$$
$$\eta_{25.0\%Gd} = 2.04 \times 10^{-4} \text{ exp} \left( \frac{37042.25}{RT} \right)$$
$$\eta_{33.3\%Gd} = 1.52 \times 10^{-4} \text{ exp} \left( \frac{30145.34}{RT} \right) \quad (17)$$

The reported temperature-dependent viscosity of pure liquid Co is $2.55 \times 10^{-4} \text{ exp} \left( \frac{44400}{RT} \right) \text{ Pa s}$ and no data is available for pure liquid Gd. It can be seen that the calculated viscosity of Co–Gd liquids is smaller than but close to that of pure liquid Co. The Gd content dependent viscosity coefficient $\eta_0$ and the apparent activation energy of the viscosity for the Co–Gd system can then be deduced and are presented in Fig. 2(b). With the increase of Gd content, $\eta_0$ decreases whereas $Q_g$ increases linearly. From these data, the viscosity of Co–Gd liquids varies with the temperature and the content Gd as the following function.

$$\eta = (3.35 \times 10^{-4} - 5.38 \times 10^{-6}C_{Gd}) \text{ exp} \left( \frac{31485 + 225C_{Gd}}{RT} \right) \text{ Pa s} \quad (18)$$

Fig. 1. (a) Calculated surface tension of liquid Co–Gd alloys versus the temperature and the composition. The liquidus temperatures of the alloys with different compositions are marked by the dashed line. (b) $\sigma_0$ and $\alpha \sigma dT$ versus alloy composition.

Fig. 2. (a) Calculated viscosity of liquid Co–Gd alloys versus the temperature and the composition. The liquidus temperatures of the alloys with different compositions are marked by the dashed line. (b) $\eta_0$ and $Q_g$ versus alloy composition.
The higher content of Gd leads to the smaller bond energy of Co–Gd system than that of Co–Co system, since the bond energy is mainly decided from the atomic radius and the valence electron structure. From this point of view, the atomic interaction between Co–Gd atoms is weaker than that between Co–Co atoms, thus, the average resistance of atomic migration reduces. This indicates that the system atom needs less energy to be activated since the mass and volume of Gd atom are bigger than those of Co atom. The addition of Gd makes the viscosity variation with the temperature more distinct.

The diffusion coefficients of the liquid Co–Gd systems are deduced from the data of the viscosity by the Stokes–Einstein relationship [28] and the results are shown in Fig. 3. Fig. 3(a) presents the diffusion coefficients of Gd in different Co–Gd liquids versus the temperature. It increases with the temperature. The difference between the diffusion coefficients of Gd in different Co–Gd liquids can be seen from the fitted equations.

\[
\begin{align*}
D_{6.7\% Gd} &= 1.66 \times 10^{-7} \exp \left( -\frac{4733.79}{RT} \right) \\
D_{16.8\% Gd} &= 1.76 \times 10^{-7} \exp \left( -\frac{4817.59}{RT} \right) \\
D_{22.2\% Gd} &= 1.97 \times 10^{-7} \exp \left( -\frac{4925.27}{RT} \right) \\
D_{25.0\% Gd} &= 2.14 \times 10^{-7} \exp \left( -\frac{5098.56}{RT} \right) \\
D_{33.3\% Gd} &= 2.91 \times 10^{-7} \exp \left( -\frac{51962.81}{RT} \right) 
\end{align*}
\]

(19)

In order to show the influence of Gd content on the diffusion coefficient, Fig. 3(b) gives the diffusion coefficients in liquid state far from the liquidus temperature, in accordance with the fitted equations in Fig. 3(a). Obviously, at the same temperature above or lower to the liquidus, the diffusion coefficient of Gd in Co–Gd alloy decreases with the addition of Gd content. Based on the fitted equations, the pre-exponential constant \(D_0\) and the diffusion activation energy \(Q\) are also obtained. Both of them increase with the Gd content, as given in Fig. 4. The diffusion activation energy is the energy threshold for atoms to diffuse. The increase of \(Q\) with the addition of Gd indicates that the Gd atom needs more energy to reach the active state. The influence of the temperature and Gd content on the diffusion coefficient can be more apparently observed in Fig. 5, which shows obviously that the influence of temperature on the diffusion coefficient is stronger than that of Gd content. From the simulation data, the following equation can be obtained.

\[
D_{Gd} = \left( 1.67 \times 10^{-7} - 7.13 \times 10^{-10} C_{Gd} + 1.31 \times 10^{-10} C_{Gd}^2 \right) \exp \left( -\frac{46299 + 170C_{Gd}}{RT} \right) \text{m}^2/\text{s}
\]

Fig. 3. (a) Temperature dependence of diffusion coefficients for Gd in Co–Gd liquids. The liquidus temperatures of the alloys with different compositions are marked by the dashed line. (b) The variation of the diffusion coefficients around the liquidus temperatures.

Fig. 4. Calculated diffusion constant and diffusion active energy of Gd in Co–Gd liquids versus the composition.
bution of the alloy composition in the multi-element liquid system, it should be ascribed to the joint of the rare earth element, which could promote the liquid surfactant formation [34] caused by the structure change of the cluster in surface layer. Based on the simulated results, the surface tension of liquid Co–Gd alloys decreases with the increase of the Gd content, suggesting that the increase of Gd atom in the liquid makes clusters in the surface layer vary. The enhancement of Gd content changes not only the liquid structure of the surface layer, but also the species and numbers of clusters in the bulk liquid, which can be tracked from the liquid viscosity and the diffusion coefficients. More and more research found that many short- and mid-range orders, even some of clusters in the bulk liquid, which can be tracked from the liquid structure of the surface layer, but also the species and numbers of clusters in the surface layer. Based on the simulated results, the surface tension of liquid Co–Gd alloys decreases from 1.04 × 10⁻⁸ to 1.2 × 10⁻⁸ N m⁻¹ with the increase of the Gd content.

The thermophysical properties of Co–Gd liquids have been simulated by Monte Carlo method combining with the analytic modified EAM potentials. When the temperature is in the range of 1300–2000 K, and the content Gd is not larger 1/3, the surface tension, the viscosity, and the diffusion coefficient vary with temperature. At the same temperature, with the increase of content Gd, the surface tension and the viscosity decrease, whereas the diffusion coefficients rise. It confirms theoretically that, the addition of Gd to Co–Gd liquids makes the liquid easier to flow. Our results might provide the necessary thermophysical parameters which could be used in designing the microstructure and magnetic properties in Co–Gd system.

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