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Effects of refractory elements on the structure and dynamics of molten Ni: An *ab initio* molecular dynamics study

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ABSTRACT

The effects of minor refractory elements (Re, W and Ta) on the structure and dynamics of molten Ni are studied by *ab initio* molecular dynamics simulations. The results show that minor additions of refractory elements would not significantly change the structure of liquid Ni. However, the local structure around Ta is quite different from that around Re or W. In the liquid Ni alloys, the 15lm-type bond pairs dominate. As temperature increases, the numbers of 16lm- and 15lm-type bond pairs would decrease while those of 14lm- and 13lm-type bond pairs would increase. The Ni self-diffusion coefficient of pure Ni shows a temperature dependence described by the Arrhenius law. With the addition of Re and W, the Ni self-diffusion coefficients still exhibit an Arrhenius relationship. However, the self-diffusion of Ni deviates from the Arrhenius law with the addition of Ta.

1. Introduction

As one important kind of high-temperature structural materials, Ni-based single-crystal superalloys are critical to the production of high-performance turbine engines, for both the aircraft and power generation engines [1]. In recent years, with the addition of refractory elements, such as Re, W, Ta to improve the high-temperature strength and resistance, modern superalloy chemistries have become increasingly complex. While such refractory elements have produced a desirable effect of improving the high-temperature performance, they also tend to segregate strongly in the mushy zone (the front of the solidification) during the solidification, which would increase the grain defects during processing [2]. These grain defects, especially the so-called freckle defects (chains of small equiaxed grains), adversely affect the alloys' properties and have been a problem in the solidification of single-crystal Ni-based superalloys [3].

Various studies indicate that freckles are formed due to localized fluid flow resulting from density-driven convection in the mushy zone [4]. During solidification, the dendritic segregation can result in the density variation between the solute and bulk liquid. This density variation would produce the buoyance. When the buoyance becomes large enough compared with the retarding frictional forces, the system would become unstable and prone to the development of the freckle defects [5].

Many different macroscopic criteria have been proposed to predict the formation of freckles. An effective one is that convective instabilities would occur when a Rayleigh number (R) is exceeded. The definition of the Rayleigh number is: [6]

$$\mathrm{Ra}_h = \frac{\frac{\Delta\rho}{\rho_0} ghk}{\alpha v} \tag{1}$$

where $\Delta\rho/\rho_0$ means the density contraction between the solid and liquid phases over the mushy zone; g denotes the gravitational acceleration; K is the average permeability; h is the height of the mushy zone (that is the appropriate length scale of a primary dendrite-arm spacing); and α is the thermal diffusivity; υ is the kinematic viscosity. As the ratio of the driving buoyancy forces to the retarding frictional forces, the Rayleigh number indicates that the formation of freckle defects is most susceptible to the changes of the solute composition and the permeability of the mushy zone.

Considerable progress in elucidating how the freckle is formed during solidification has been made recent years. Mukai et al. [7,8] have measured the densities of several liquid Ni-based alloys. Asta et al. [9,10] used *ab initio* molecular dynamics (AIMD) simulations to develop a model for V(c,T) in superalloys to prove the validity of a mathematical model for freckle formation. However, there are significant open questions concerning the formation of freckles. For example, it is still a big challenge to establish an accurate model to describe the thermosolutal convection. It is also difficult to predict the formation of freckle defects accurately using Rayleigh number because some parameters in Eq. (1) are difficult to acquire currently. Thus further detailed studies on the formation

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of freckles are necessary and important for the development of Ni-based superalloys.

Experimental observations reveal that W and Re promote, and Ta and Mo hinder, the formation of freckles [2,6,11]. During the directional solidification of Ni-based alloys, Re and W segregate preferentially to the solute, which creates a density inversion in the mushy zone. But Ta has the opposite behavior, and can offset the depletion of Re and W, consequentially decreasing the convective instabilities. However, the behavior of the refractory atoms in the liquid superalloys has not yet been analyzed in depth, and theoretical researches are still not sufficient. In this paper, the effects of some refractory element (Re, W, and Ta) on the atomic-scale structure and dynamic properties of liquid Ni were studied by AIMD simulations. The details of the simulations are discussed in Section 2. Then the Section 3 gives and discusses the computational structural and dynamic results. Finally, a summary is presented.

2. Computational methods

All calculations in this paper were performed using the Vienna *ab initio* Simulation Package (VASP), developed at the Institut für Materiaphysik of the Univerität Wien. The approach implemented in VASP is based on the density functional theory (DFT), which has been proved to be powerful and effective in the simulations of liquid metals [12–14]. The ion–electron interaction is described by ultra-soft Vanderbilt pseudopotentials (US-PP) with a generalized-gradient approximation (PW91) for the exchange correlation potential. The simulations were performed in a canonical ensemble with fixed particle number, volume and temperature (NVT) at Γ point. The time step was chosen as 3 fs for solving the Newton's equation. The plane wave cutoff energy is 270 eV, and the energy convergence criterion of self-consistency is 1×10^{-3} meV/atom.

The configurations we used here contain 108 atoms, which have 108 Ni atoms or 106 Ni atoms and 2 refractory atoms (Re, W, Ta). We chose the system of $Ni_{106}X_2$(X = Re, W, Ta) according to the commercial nickel-base superalloys with about 6.0 wt% X, for instance, 3.0 wt% Re, 6.0 wt% W, 6.5 wt% Ta in CMSX-4, and 6.0 wt% Re, 5.0 wt% W, 8.0 wt% Ta in CMSX-10 [15]. That is about 2 atoms of Re, W or Ta in a system with 108 atoms. The initial configuration was constructed with 108 atoms randomly distributed in a cube box, and equilibrated at a temperature well above the melting point. The temperature was controlled at 1723 K, 1823 K and 1923 K, respectively, by the Nosé–Hoover thermostat. To obtain the density of the liquid nickel alloys, the volume of the system was adjusted to keep the condition of zero external pressure at each temperature [9,10,16,17]. The obtained box lengths of the liquid configurations for each system at different temperatures are listed in Table 1. Mukai has proposed an expression to calculate the volume of pure liquid Ni [18]. And the volume predicted by this expression is 7.42, 7.56, 7.70 $cm^3\ mol^{-1}$, respectively, at 1723, 1823 and 1923 K. The discrepancies between our calculation and Mukai's prediction are less than 6%.

In the simulations, the systems were relaxed at each temperature for 10,000 steps, and last 4000 configurations were used for the analysis of the structural and dynamic properties.

3. Results and discussion

3.1. Structural properties

Pair distribution function (PDF) [17,19,20], $g(r)$, is one of the most important and widespread structural quantities. This function denotes the probability of finding the center of an atom at a distance r from the center of another atom compared to a random distribution. In a binary system, the partial pair distribution function is given as follows:

$$g_{AB}(r) = \frac{V}{N_A N_B} \langle \sum_{i=1}^{N_A} \frac{n_{iB}(r, \Delta r)}{4\pi r^2 \Delta r} \rangle \quad (2)$$

where N_A and N_B denote the numbers of A and B atoms in the supercell, respectively, V is the volume of the system, n_{iB} is the number of B atoms in the sphere shell from r to $r + \Delta r$ of the i atom, the symbol $\langle\ \rangle$ here represents the time average.

Fig. 1 shows the total and partial pair distribution functions of three systems of $Ni_{106}X_2$ (X = Re, W, Ta) at three different temperatures. For comparison, the pair distribution function of pure Ni (Ni_{108}) is also shown in the figure. As temperature increases, the intensity of the first peak would decrease for the same system. The positions of the first peaks of $g_{total}(r)$ and $g_{Ni-Ni}(r)$ are all about 2.38–2.42 Å and the intensities are also near the same values for different systems at the same temperature, i.e., the minor doping of refractory elements have not significantly changed the geometric structure of liquid Ni. However, it can be found that the profiles of g_{Ni-X} (see Fig. 1c) show some different behaviors. From $Ni_{106}Re_2$ to $Ni_{106}W_2$ and $Ni_{106}Ta_2$, the position of the first peak moves towards the right, which is about, e.g., at 1723 K, 2.43, 2.46, 2.53 Å, respectively. For g_{Ni-Ni} of pure Ni at 1723 K, the position is about 2.39 Å. Since the position of the first peak is related to the equilibrium bonding distance between ions, it implies that the bonding distance is getting larger in the sequence of Ni–Ni, Ni–Re, Ni–W, Ni–Ta. This obviously is due to the increased atomic radius of the element, which is 135, 188, 193, 200 pm for Ni, Re, W, Ta, respectively. Meanwhile, the intensities of the first peaks of g_{Ni-Re} and g_{Ni-W} are stronger than that of g_{Ni-Ni} of Ni_{108}, while for g_{Ni-Ta}, its intensity of the first peak shows a different behavior as the temperature changes, i.e., weaker than that of g_{Ni-Ni} of Ni_{108} at 1723 K, stronger at 1823 K and almost the same at 1923 K. This demonstrates that the atomic distribution around Ta is quite different from that around Re or W.

From the pair distribution function, we can also get the partial coordination number. The partial coordination number [21,22] can be calculated through the data of partial pair distribution function:

$$N_{AB} = \int_0^{r_{cut}} 4\pi r^2 \rho_B g_{AB}(r) dr \quad (3)$$

where ρ_B is the atomic concentration of element B, r_{cut} is the cutoff distance, i.e., the first-minimum position of $g_{AB}(r)$, here r_{cut} = 3.45 Å. The obtained values of coordination numbers (N_{AB}) at different temperatures for different systems are listed in Table 2.

Table 1
The lengths and volumes of the cube boxes for the systems of Ni_{108}, $Ni_{106}X_2$ (X = Re, W, Ta) at different temperatures.

System	Temperature (K)	Length (Å)	Volume ($cm^3\ mol^{-1}$)	System	Temperature (K)	Length (Å)	Volume ($cm^3\ mol^{-1}$)
Ni_{108}	1723	10.895	7.21	$Ni_{106}W_2$	1723	10.915	7.25
	1823	10.920	7.26		1823	10.945	7.31
	1923	10.935	7.29		1923	10.950	7.32
$Ni_{106}Re_2$	1723	10.913	7.25	$Ni_{106}Ta_2$	1723	10.925	7.27
	1823	10.945	7.31		1823	10.945	7.31
	1923	10.955	7.33		1923	10.955	7.33