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Activity coefficient and solubility of yttrium in Fe-Y dilute solid solution

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Abstract: The density functional theory (DFT) and density functional perturbation theory (DFPT) within the quasi-harmonic approximation were employed to investigate the activity coefficient of Y in dilute Fe-Y solid solution. The ground states of Fe-Y compounds and the thermodynamic properties of bcc Fe were calculated, and the stable and metastable structures of Fe-Y compounds were predicted as well. With the temperature increasing, the Y activity coefficient in bcc Fe matrix increased rapidly, and the interaction between Y and Fe became more favorable. Based on the calculated thermodynamic properties, the solubility of Y in bcc Fe matrix as a function of temperature was predicted, and compared with the experimental data.

Keywords: density functional theory; activity coefficient; solubility; Fe-Y; rare earths

In the past years, the addition of rare earth (RE) elements has been regarded promising in steels. It has been proved that La, Ce and Y are important addition elements in improving the mechanical and corrosion resistance properties[1,2]. Additionally, the previous studies reveal that RE elements can affect the properties of steels in terms of the solidification, phase transformations, and recrystallization behavior as well[3–5].

In spite of the progress in RE application so far, it is apparent that many questions still remain rather controversial. For the prediction and understanding of RE related phenomena in steels, the knowledge of thermodynamic properties is indispensable[6]. However, the experimental and theoretical information about thermodynamic properties of Fe-RE binary are far from satisfactory. By electromotive force (EMF) measurements, Subramania et al.[7] investigated the Gibbs free energies, enthalpies and entropies of phase formation of Fe-Y alloys. Wu and Wang et al.[8,9] reported the interaction coefficients of rare earth elements with carbon, nitrogen, niobium, and other common elements in liquid iron. Su et al.[10] evaluated the Ce-Fe binary system using the calculation of phase diagram method (CALPHAD). Meanwhile, for the case of RE alloying steel, there are relatively few previous investigations on the solubility of RE elements in Fe, which is essential for designing of RE containing steels. Actually, due to their relatively small solubility limit in Fe, it is difficult to determine the precise value by experimental method[11].

To describe accurately the thermodynamic parameters of binary solid solutions, it is necessary to investigate the activity coefficients of the species in solution[12]. Consequently, the solubility of the solute elements in Fe matrix can be calculated on the basis of regular solution model. In this respect, the density functional theory (DFT) has been dedicated to the study of some binary and ternary solutions, and has been proved to be an effective approach in thermodynamic study[13–15]. To our knowledge, few studies have tried to estimate the thermodynamic properties of Fe-RE solutions using this theoretical method.

The yttrium containing ferritic steels have attracted significant interest due to their high resistance to irradiation-induced damage and enhanced high temperature mechanical properties, as the consequence of the Y-Ti-O enriched nanoclusters[16,17]. In this case, the thermodynamic parameter and solubility of yttrium are fundamental to understanding the involved phase transition process. In the present work, we presented a method for predicting activity coefficient of Y in dilute Fe-Y solid solution using the first-principles calculations. Furthermore, we applied it to calculate the interaction parameters of Y with Fe, and the solubility of Y in Fe matrix.

1 Methodology

For the solid solution of Fe-Y system, the relation between activity a and chemical potential μ of Y can be expressed as follows[18]:

$$\ln a_{\mathrm{Y}}(T,x)=\frac{\mu_{\mathrm{Y}}(T,x)-\mu_{\mathrm{Y}}^{0}(T,x)}{k_{\mathrm{B}}T} \tag{1}$$

where μ_{Y}^{0} and μ_{Y} represent the chemical potential of Y in pure bulk and in solution $Fe_{1-x}Y_x$, respectively, k_{B} is the

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Boltzmann constant, T is the absolute temperature. According to the regular solution model, the Y activity coefficient can be calculated in terms of the activity and the corresponding atomic fraction x:

$$\gamma_{\mathrm{Y}}\left(T,x\right)=\frac{a_{\mathrm{Y}}(T,x)}{x} \tag{2}$$

In the dilute solution where Henry's law is satisfied, the activity coefficient of Y is independent of its atomic fractions at a certain temperature.

The chemical potential difference in Eq. (1) can be calculated in terms of the differences in enthalpy (ΔH) and entropy (ΔS) for the Y atoms in the Fe solution and the pure Y bulk, respectively:

$$\mu_{\mathrm{Y}}(T,x)-\mu_{\mathrm{Y}}^{0}(T,x)=\Delta H(T)-T\Delta S(T) \tag{3}$$

By combination of Eqs. (1), (2), (3) and the configurational entropy difference of Y, $\Delta S_{\mathrm{conf}}=-k_{\mathrm{B}}$, the activity coefficient can be deduced as follows:

$$\gamma_{\mathrm{Y}}=\exp\left[\frac{\Delta H(T)-T\Delta S_{\mathrm{nc}}(T)}{k_{\mathrm{B}}T}\right] \tag{4}$$

where $\Delta S_{\mathrm{nc}}(T)$ is the non-configurational entropy of the system per Y atom, and is expressed as follows:

$$\Delta S_{\mathrm{nc}}(T)=S_{\mathrm{FeY}}(T)-N_{\mathrm{Fe}}S_{\mathrm{Fe}}^{0}(T)-S_{\mathrm{Y}}^{0}(T) \tag{5}$$

where $\Delta S_{\mathrm{FeY}}(T)$ is the entropy of the supercell containing N Fe atoms and one Y atom, $S_{\mathrm{Fe}}^{0}(T)$ and $S_{\mathrm{Fe}}^{0}(T)$ are the entropies of one Fe and Y atom, respectively, in their pure bulk state. The solution enthalpy $\Delta H(T)$ can be obtained following the similar process.

In combination with quasi-harmonic approach, the Helmholtz free energy $F(V, T)$ as a function of volume V and temperature T, can be depicted in terms of the first-principles calculations[19]:

$$F(V,T)=E(V)+F_{\mathrm{vib}}(V,T)+F_{\mathrm{el}}(V,T) \tag{6}$$

where $E(V)$ is the static energy at 0 K and volume V. $F_{\mathrm{vib}}(V,T)$ is the lattice vibrational contribution to the Helmholtz free energy, and under the quasi-harmonic approximation it can be expressed as[20]:

$$F_{\mathrm{vib}}(V,T)=k_{\mathrm{B}}T\int_{0}^{\infty}\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\right]g(\omega)d\omega \tag{7}$$

where $\hbar$ is the Planck's constant, $g(\omega)$ is the phonon DOS of the structure. $F_{\mathrm{el}}(V,T)$ denotes the thermal electronic contribution to the free energy, which cannot be ignored due to the non zero electronic density for metal system at the Fermi level, and can be determined through the one-dimensional integration of the electronic density of states (DOS) following the Fermi-Dirac distribution[21]. As the first-principles calculations are carried out at zero pressure, the Helmholtz free energy is equal to the Gibbs energy.

Once the activity coefficient of Y is available, the interaction parameter between Fe and Y can be obtained by[12]:

$$I_{\mathrm{FeY}}=k_{\mathrm{B}}T\ln\gamma_{\mathrm{Y}} \tag{8}$$

The calculations were performed using the Vienna *ab initio* simulation program (VASP) with projector-augmented-wave (PAW)[22–24], based on the density functional theory (DFT). The exchange-correlation energy is described by spin-polarized Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA)[25]. The cutoff energy of the plane waves is 350 eV. The Brillouin zone k-points are selected using 5×5×5 Monkhorst-Pack grids. The energy convergence tolerance is 1.0×10^{-5} eV/atom and the forces converge to lower than 0.001 eV/nm.

The vibrational thermodynamic properties are evaluated from the phonon density of state calculated using the supercell approach within the framework of force-constants method. The density functional perturbation theory (DFPT) implemented in VASP was employed to calculate the real-space force constants of supercells, and the phonon frequencies were calculated from the force constants with PHONOPY package[26]. We used the supercells containing 2×2×2 (104 atoms) unit cells for $Fe_{12}Y$ phase, and 3×3×3 supercell for the pure Fe and Y. For the pure bcc Fe and the dilute solution Fe_nY (n=127), 4×4×4 (128 atoms) supercell is used, in which a Fe atom on the central site is substituted with a Y atom.

2 Results and discussion

2.1 Ground states

In order to determine the equilibrium structural parameters of the bcc Fe and Fe-Y compounds, the total energy of each was calculated by variation of the cell volume. And the equilibrium lattice constants were obtained by fitting the volume vs. energy data points to the Vinet equation of state (EOS)[27]. The calculated lattice parameter of bcc Fe is a=0.2866 nm, which is in good agreement with the experimental value[28].

For the stability of Fe-Y compounds in different crystal structures, we calculated the formation enthalpy of Fe_pY_q by the following expression:

$$\Delta H_{f}^{\mathrm{Fe-Y}}=H_{\mathrm{atom}}^{\mathrm{Fe-Y}}+\frac{p}{p+q}H_{\mathrm{atom}}^{\mathrm{Fe}}-\frac{q}{p+q}H_{\mathrm{atom}}^{\mathrm{Y}} \tag{9}$$

where $H_{\mathrm{atom}}^{\mathrm{Fe-Y}}$, $H_{\mathrm{atom}}^{\mathrm{Fe}}$ and $H_{\mathrm{atom}}^{\mathrm{Y}}$ are the energy per atom of Fe_pY_q, pure bcc Fe and Y, respectively. The calculated formation enthalpies are plotted in the form of convex hull plots in Fig. 1 to evaluate the phase stability at 0 K. The vertices of the convex hull of a scatter plot of formation enthalpy vs. atomic fraction identify stable structures, and the points above the convex hull denote the metastable or unstable structures at 0 K. The calculations of the formation enthalpies confirm that the stable structures of Fe-Y compounds are $Fe_{12}Y$.tI26, $Fe_{17}Y_2$.hP38, Fe_3Y.hR12 and Fe_2Y.cF24, which is consistent with the previous studies[29,30]. The calculated lattice parameters and formation enthalpies of the stable structures are listed in Table 1.