Rare Metal Materials and Engineering
Volume 46, Issue 11, November 2017
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(11): 3188-3192.

ARTICLE

First-Principles Study of Phase Stability and Solubility in Fe-RE (Y, La, Ce) Alloys

Gao Xueyun[1,2], **Ren Huiping**[1], **Li Yiming**[1], **Wang Haiyan**[1]

[1] Inner Mongolia University of Science and Technology, Baotou 014010, China; [2] Beris Engineering and Research Corporation, Baotou 014010, China

Abstract: The solubility limit of elements plays a crucial role in alloy designing, as well as in the understanding of kinetic processes in alloys. Using first-principles calculations, we calculated the ground states of Fe-RE compound, and predicted the stable and metastable structures of Fe-Y and Fe-Ce. The results indicate that the stable structures for Fe-Y compounds are $Fe_{12}Y$.tI26, $Fe_{17}Y_2$.hP38 and Fe_2Y.cF24, and those for Fe-Ce binary are $Fe_{17}Ce_2$.hP38, $Fe_{19}Ce_5$.hR24 and Fe_2Ce.cF24. Based on the statistical-thermodynamic theory of dilute lattice gas, we presented a systematic series of calculations of the solubility limits of RE in α-Fe as a function of temperature. It is found that the solubilities are sorted in the following order: $S_{La}>S_{Ce}>S_Y$, corresponding to the trend in the solubility formation enthalpies: $H_{sol}(La)< H_{sol}(Ce)< H_{sol}(Y)$.

Key words: solubility; Fe-RE; stable structure; first-principles

The addition of RE elements has been investigated recently owing to their effect of purification and modification of inclusion, improvement of phase transformations, recrystallization behavior, as well as the high-temperature oxidation resistance and the corrosion resistance of steels[1-5]. Moreover, dilute addition of Y or La to ferritic Fe alloys gives the high resistance of irradiation-induced damage and enhances high temperature mechanical properties to oxide dispersion strengthened (ODS) alloys, due to the formation of RE-Ti-O-enriched nanoclusters[6,7]. In spite of the progress in RE application so far, it is apparent that many questions still remain rather controversial.

In the case of RE alloyed steels, some properties of the alloy were observed to be opposite in the change trend with the increasing of RE content[8]. The knowledge of solubility is essential for designing an alloy with particular physical, chemical and mechanical properties. However, to the best of our knowledge, there are relatively few previous experimental or theoretical investigations on the solubility of RE elements in Fe. Actually, due to their relatively small solubility limit (at ambient temperature, the solubility of RE is on the order of ppm) in Fe, bigger atomic size, as well as the active physicochemical properties, it is difficult to determine the precise value by experimental method [9].

It was recently demonstrated that the first-principles calculation can predict the solubility in binary alloys accurately. By employing density functional theory (DFT), Ozolins and Ravi et al.[10-12] studied the solubility curves for Al based binary alloys (Al-Sc, Al-Cu, and Al-RE etc.), Chepulskii et al.[13] developed an “high-throughput” approach to calculate the solubility in Ti-based binary alloys. Furthermore, Zhang et al. [14] calculated the phase stability of Mg-La and Mg-Nd binary alloy, and discussed the solubility based on regular solution model.

In the present work, we study the stability of intermetallic compound in Fe-RE binary alloy system by DFT, and then carry out a systematic first-principles calculation to predict the solubilities of Y, La and Ce in α-Fe based on the statistical-thermodynamic theory of dilute lattice gas.

1 Computational Methodology

The calculations were performed using the Vienna *ab* initio simulation program (VASP) with projector-augmented-wave (PAW)[15-17], based on the density functional theory (DFT).

Received date: October 14, 2016
Foundation item: National Natural Science Foundation of China (51101083)

Corresponding author: Ren Huiping, Professor, School of Material and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, P. R. China, Tel: 0086-472-6958984, E-mail: renhuiping@sina.com

The exchange-correlation energy was described by spin-polarized Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA)[18]. The cutoff energy of the plane waves was 350 eV. The computations performed within a 4×4×4 supercell including 128 atoms, and the Brillouin zone k-points were selected using 5×5×5 Monkhorst-Pack grids. The energy convergence tolerance was 1.0×10^{-4} eV/atom and the forces converge to lower than 0.1 eV/nm. Within these criteria, the calculated lattice constant for α-Fe is 0.2858 nm, in good agreement with the previous reported value of 0.2866 nm[19].

2 Results and Discussion

2.1 Ground states of Fe-RE intermetallics

The study began with the exploration of the possible ground states of Fe-RE by calculating the formation enthalpy of Fe-RE compounds[14]. We do not consider Fe-La system in this section, because Fe-La compounds have not been observed experimentally[20]. The formation enthalpy (H_f) of Fe_mRE_n is calculated by the following expression[21]:

$$\Delta H_{\mathrm{f}}^{\mathrm{Fe\text{-}RE}} = H_{\mathrm{atom}}^{\mathrm{Fe\text{-}RE}} - \frac{m}{m+n} H_{\mathrm{Fe}}^{\mathrm{atom}} - \frac{n}{m+n} H_{\mathrm{RE}}^{\mathrm{atom}} \tag{1}$$

where, $H_{\mathrm{atom}}^{\mathrm{Fe\text{-}RE}}$, $H_{\mathrm{Fe}}^{\mathrm{atom}}$ and $H_{\mathrm{RE}}^{\mathrm{atom}}$ are the energy per atom of Fe_mRE_n, pure α-Fe and RE (Y and Ce), respectively. The results of formation enthalpy are presented in Fig.1. The phase stability is evaluated by a convex hull plot which connect the pure Fe, pure RE and ground states by straight line, in which a phase with a certain component located right at the line is stable and that above the line is metastable.

The calculated ground state properties (formation enthalpy and lattice constants) are summarized in Table 1, along with the reported results. It can be seen that the formation enthalpy of several intermetallic compounds and lattice constants are in good agreement with the previous experimental and calculated data.

For Fe-Y compounds, the calculated stable structures are $Fe_{12}Y$.tI26, $Fe_{17}Y_2$.hP38 and Fe_2Y.cF24, and the results indicate that $Fe_{29}Y_3$.mS64, Fe_5Y.hP6, $Fe_{23}Y_6$.cF116, Fe_7Y_2.hR18 and Fe_3Y.hR12 are metastable. For Fe-Ce compounds, the stable structures are $Fe_{17}Ce_2$.hP38, $Fe_{19}Ce_5$.hR24 and Fe_2Ce.cF24, and the metastable structures are $Fe_{13}Ce$.cF112, Fe_5Ce.hP6 and Fe_3Ce.hR12.

In the case of $Fe_{17}RE_2$, consistent with the previous studies[22,23], the formation enthalpies of $Ni_{17}Th_2$-type (hP38) structure are lower than that of $Zn_{17}Th_2$-type (hR19) structure, which indicates that the former structure is stable for both Fe-Y and Fe-Ce compounds. The formation enthalpy of $Fe_{12}Y$.tI26 ($ThMn_{12}$-type structure) is –0.968 eV, comparable to the reported value [24]. In the case of $Fe_{12}Ce$.tI26, the formation enthalpy (0.083eV) is in good agreement with reported value of 0.11 eV [25], and this positive value indicates that $Fe_{12}Ce$ is unstable and cannot be formed under normal conditions. It is noteworthy that from the calculations, $Fe_{19}Ce_5$.hR24 has the lowest formation enthalpy (–0.729 eV) compared with all other compounds in Fe-Ce system, implying strong stability in this hR24 structure.

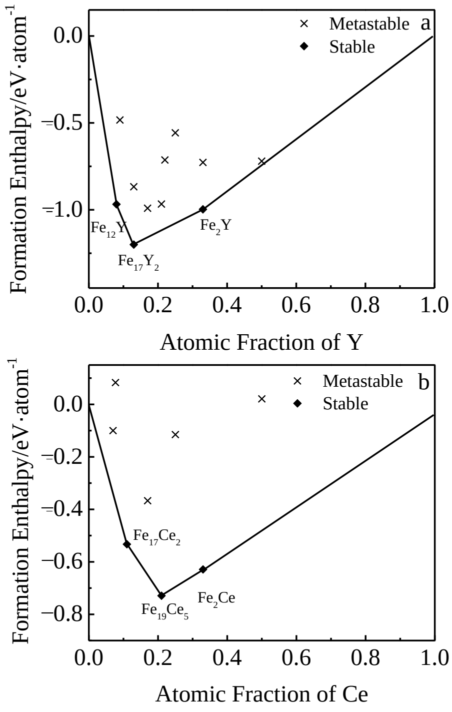

Fig.1 Formation enthalpies of intermetallic compounds in Fe-Y (a) and Fe-Ce (b) binary

Table 1 Calculated ground state results of stable phase in Fe-Y and Fe-Ce binary alloys

Phase	Space group	Pearson symbol	Lattice constant/nm	$\Delta H_{\mathrm{f}}^{\mathrm{Fe\text{-}RE}}$/ eV·atom^{-1}
$Fe_{12}Y$	I4/mmm	tI26	a=0.8611, c =0.4693 a=0.8338, c=0.4707[24]	–0.968 –0.973[24]
$Fe_{17}Y_2$	P63/mmm	hP38	a=0.8370, c =0.8140 a=0.8471, c=0.8309[23]	–1.209
Fe_2Y	Fd-3m	cF24	a=0.7523 a=0.7386 [26]	–0.997
$Fe_{17}Ce_2$	P63/mmm	hP38	a=0.8377, c=0.8138 a=0.8490, c=0.8281[27]	–0.533
$Fe_{19}Ce_5$	R-3mH	hR24	a=0.5083	–0.729
Fe_2Ce	Fd-3m	cF24	a=0.7544 a=0.7302[27]	–0.629

2.2 Solubility

In the case of a disordered dilute solution of solute atoms (B) and vacancies (V) in a solid solvent (A), neglecting the interactions of solute-solute, solute-vacancy and vacancy-vacancy [28], the enthalpy of solid solution can be expressed as:

$$H = H_{\mathrm{A}}^{\mathrm{atom}} N + \Delta H_{\mathrm{B,A}} N_{\mathrm{B}} + \Delta H_{\mathrm{V,A}} N_{\mathrm{V}} \tag{2}$$

where $H_{\mathrm{A}}^{\mathrm{atom}}$ denotes the enthalpy per atom of the pure solvent solid, $\Delta H_{\mathrm{B,A}}$ and $\Delta H_{\mathrm{V,A}}$ are the enthalpy change of the solid upon inducing of one substitutional atom B and one vacancy, respectively, N is atom numbers of pure solvent A matrix, N_B and N_V are the numbers of solute atom (B) and vacancy (V), respectively.

The enthalpy of each atom in solid solution can be obtained from Eq. (3):H

$$H_{\text{atom}} = H/(N_{\text{B}}+N_{\text{A}}) = H_{\text{A}}^{\text{atom}} + \Delta H_{\text{B,A}} x_{\text{A}} + (\Delta H_{\text{V,A}} + H_{\text{A}}^{\text{atom}}) x_{\text{V}} \quad (3)$$

where x_α (α=A, B, V) are the atom concentration of solvent, solute and vacancy, respectively, and can be expressed as:

$$x_\alpha = N_\alpha/(N_{\text{A}}+N_{\text{B}}) \quad (4)$$

The formation enthalpy of solid solution system is:

$$\Delta H_{\text{atom}} = H_{\text{atom}} - x_{\text{A}} H_{\text{A}}^{\text{atom}} - (1-x_{\text{A}}) H_{\text{B}}^{\text{atom}} \quad (5)$$

By combining Eqs. (3) and (5), we have

$$\Delta H_{\text{atom}} = H_{\text{f}}^{\text{B}} x_{\text{B}} + H_{\text{f}}^{\text{V}} x_{\text{V}} \quad (6)$$

where H_{f}^{B} and H_{f}^{V} are the formation enthalpies for a defect of solute atom and vacancy, respectively:

$$H_{\text{f}}^{\text{B}} = \Delta H_{\text{B,A}} - H_{\text{B}}^{\text{atom}} + H_{\text{A}}^{\text{atom}} \quad (7)$$

$$H_{\text{f}}^{\text{V}} = \Delta H_{\text{V,A}} + H_{\text{A}}^{\text{atom}} \quad (8)$$

According to the regular solution approximation, the formation Gibbs free energy of a dilute solution is defined as:

$$\Delta G_{\text{atom}} = \Delta H_{\text{atom}} - T\Delta S_{\text{atom}} \quad (9)$$

where ΔH_{atom} can be obtained from Eq. (6), T denotes the temperature. ΔS_{atom} is the formation entropy, and can be calculated within the mean-field approximation[29]:

$$\Delta S_{\text{atom}} = -\frac{k_{\text{B}} N}{N_{\text{A}} + N_{\text{B}}} \sum_{\alpha=\text{A,B,V}} c_\alpha \ln c_\alpha \quad (10)$$

where k_B is the Boltzmann constant, c_α denotes the site concentrations of solvent, solute atom and vacancy:

$$c_\alpha = N_\alpha / N \quad (11)$$

By combining Eqs.(4), (9), (10) and (11), the formation Gibbs free energy is written as follows:

$$\Delta G_{\text{atom}} = \Delta G_{\text{atom}}^{\text{B}} + \Delta G_{\text{atom}}^{\text{V}} \quad (12)$$

where

$$\Delta G_{\text{atom}}^{\text{B}} = H_{\text{f}}^{\text{B}} x_{\text{B}} + k_{\text{B}} T \left[x_{\text{B}} \ln x_{\text{B}} + (1-x_{\text{B}}) \ln(1-x_{\text{B}}) \right] \quad (13)$$

$$\Delta G_{\text{atom}}^{\text{V}} = H_{\text{f}}^{\text{V}} x_{\text{V}} + k_{\text{B}} T \left[x_{\text{V}} \ln x_{\text{V}} + (1-x_{\text{V}}) \ln(1-x_{\text{V}}) \right] \quad (14)$$

In the case of a solid solution with fixed atomic composition x_B, the equilibrium vacancy concentration x_V^{eq} is obtained by calculating the minimization of the formation Gibbs free energy:

$$\frac{\partial \Delta G_{\text{atom}}^{\text{V}}}{\partial \Delta x_{\text{V}}} = 0 \quad (15)$$

Then the equilibrium concentration and formation Gibbs free energy of vacancy can be obtained by manipulating Eqs. (14) and (15):

$$x_{\text{V}}^{\text{eq}} = \left[\exp\left(\frac{H_{\text{f}}^{\text{V}}}{k_{\text{B}} T} \right) - 1 \right]^{-1} \quad (16)$$

$$\Delta G_{\text{atom}}^{\text{V}} \left(x_{\text{V}}^{\text{eq}} \right) = k_{\text{B}} T \ln \left[1 - \exp\left(-\frac{H_{\text{f}}^{\text{V}}}{k_{\text{B}} T} \right) \right] \quad (17)$$

Eq. (16) indicates that the equilibrium concentration of vacancy is determined by the vacancy formation enthalpy and temperature [21].

At a given temperature, the solubility of solute B in solvent solid A, is the achievable maximum concentration of B in the solution solid without precipitation of second phase. The formation Gibbs free energy for the mixture of the disordered dilute solution and the ground state phase at composition x_B , is given by:

$$\Delta G_{\text{atom}}^{\text{mix}}(x) = \frac{x_{\text{B,gs}} - x}{x_{\text{B,gs}} - x_{\text{B,A}}} \Delta G_{\text{atom}}(x_{\text{B,A}}) + \frac{x - x_{\text{B,A}}}{x_{\text{B,gs}} - x_{\text{B,A}}} \Delta G_{\text{atom}}^{\text{gs}}(x_{\text{B,gs}}) \quad (18)$$

where $x_{\text{B,gs}}$ and $\Delta G_{\text{atom}}(x_{\text{B,gs}})$ are the atomic concentration and formation Gibbs energy of ground state, respectively. The manipulation of Eqs. (13) and (18) leads to:

$$x_{\text{B,A}} = \left[\exp(H_{\text{sol}} / k_{\text{B}} T) + 1 \right]^{-1} \quad (19)$$

In the case of the low-solubility limit, the solubility formation enthalpy is expressed as:

$$H_{\text{sol}} = H_{\text{f}}^{\text{B}} - \Delta H_{\text{atom}}^{\text{gs}} / x_{\text{B,gs}}^{0} + \Delta G_{\text{atom}}^{\text{V}} \left(x_{\text{V}}^{\text{eq}} \right) / x_{\text{B,gs}}^{0} \quad (20)$$

Therefore, for the calculation of low-solubility of disordered dilute solution, we need the knowledge of formation enthalpy $\Delta H_{\text{atom}}^{\text{gs}}$ and composition $x_{\text{B,gs}}^{0}$ of the ground state, as well as the formation enthalpies of solute atom and vacancy, i.e. H_{f}^{B} and H_{f}^{V} [13]. In the case of a binary without intermediate ground states, e.g. Fe-La system, the ground state is B, and the second term of Eq. (20) is zero, therefore H_{sol} is determined by the formation enthalpy of solute atom defect H_{f}^{B} and formation Gibbs free energy of vacancy $\Delta G_{\text{atom}}^{\text{V}} \left(x_{\text{V}}^{\text{eq}} \right)$.

The calculated vacancy formation enthalpy H_{f}^{V} is 2.45 eV, comparable to the reported value of 2.23 eV [30]. The solubility formation enthalpy H_{sol} for Y, La and Ce are calculated to be 0.85, 0.69, 0.79 eV, respectively. Fig. 2 shows the calculated solubility of Y, La and Ce. As indicated in Fig. 2, the solubilities of these three RE elements have a clear trend: $S_{\text{La}} > S_{\text{Ce}} > S_{\text{Y}}$, corresponds to the trend in the solubility formation enthalpies: $H_{\text{sol}}(\text{La}) < H_{\text{sol}}(\text{Ce}) < H_{\text{sol}}(\text{Y})$. The discrepancy of the solubilities of these three solutes is bigger with temperature

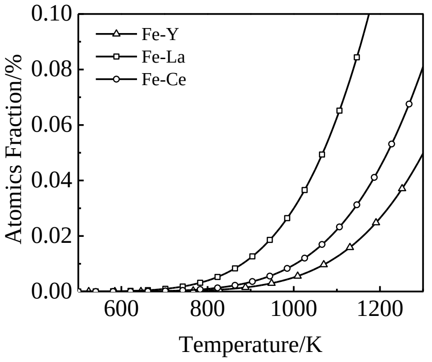

Fig.2 Calculated solubilities of Y, La and Ce in α-Fe as function of temperature

rising, and this trend is apparently above 700 K. The solubilities of Y and Ce at 973 K obtained here are 0.0038 at% and 0.0074 at%, respectively, lower than the experimentally measured values of 0.025 at%Y and 0.033 at%Ce [31] reported by Li et al. While Ref. [32] reported an experimental investigation of Fe-Ce binary system, and the Ce solubility was determined to be less than 0.04at.% in the temperature range of 1123~1173 K, which is below but close to the computed value in the present work. For the Fe-La binary at 1053 K, the predicted solubility of La is 0.045 at%, which is lower than the upper limit of 0.1 at% reported in Ref. [27].

In the case of experimental measurements, part of metastable or unstable compounds will remain in the matrix with the non-equilibrium freezing, and RE solute atoms tend to segregate at grain boundary of the polycrystalline metals[33,34]. Additionally, due to the relatively small solubility of RE, the measurement results may be influenced in a relatively large degree by the defects and grain boundary in the species. For the theoretical calculations, the study is based on the assumption that the solute is placed in the pure matrix, and the interactions between the solute with vacancy, and between these two defects themselves, are neglected. Therefore, the measured solubilities tend to be overestimated compared to the calculation results.

3 Conclusions

1) We have presented calculations of the ground states and solubility limits of Fe-RE (Y, La and Ce) binary by density functional theory. The stable structures for Fe-Y compounds are $Fe_{12}Y$.tI26, $Fe_{17}Y_2$.hP38 and Fe_2Y.cF24, and those for Fe-Ce binary are $Fe_{17}Ce_2$.hP38, $Fe_{19}Ce_5$.hR24 and Fe_2Ce.cF24. And the results of the ground state are comparable with the available experimental and theoretical data.

2) According to the formation enthalpy of the ground state, we investigated the solubilities of RE (Y, La and Ce) in α-Fe on the basis of the statistical-thermodynamic theory of dilute lattice gas. It is found that the solubility of La is higher than that of Y, and Ce has a solubility in α-Fe intermediate between La and Y. Finally, we discussed the quantitative differences between our theoretical results and the reported experimental data.

References

1 Yan M F, Zhang C S, Sun Z. *Applied Surface Science*[J], 2014, 289: 370

2 Hao W, Geng W T. *Nuclear Instruments and Methods in Physics Research Section B*[J], 2012, 280: 22

3 Yoo Y H, Choi Y S, Kim J G *et al*. *Corrosion Science*[J], 2010, 52: 1123

4 Samanta S K, Mitra S K, Pal T K. *Materials Science and Engineering A*[J], 2006, 430: 242

5 Thanneeru R, Patil S, Deshpande S *et al*. *Acta Materialia*[J], 2007, 55: 3457

6 Miller M K, Kenik E A, Russell K F *et al*. *Materials Science and Engineering A*[J], 2003, 353: 140

7 Helean K B, Ushakov S V, Brown C E *et al*. *Journal of Solid State Chemistry*[J], 2004, 177: 1858

8 Liu H, Liu C, Jiang M. *Materials and Design*[J], 2012, 33: 306

9 Zandbergen H W, Andersen S J, Jansen J. *Science*[J], 1997, 277: 1221

10 Ozolins V, Asta M. *Physical Review Letters*[J], 2001, 86: 448

11 Ravi C, Wolverton C, Ozolins V. *Europhysics Letters*[J], 2006, 73: 719

12 Zhang X D, Wang S Q. *Computational Materials Science*[J], 2014, 90: 56

13 Chepulskii R V, Curtarolo S. *Acta Materialia*[J], 2009, 57: 5314

14 Zhang Hui, Wang Shaoqing. *Acta Metallurgica Sinica*[J], 2012, 48(7): 889 (in Chinese)

15 Kresse G, Hafner J. *Physical Review B*[J], 1993, 47: 558

16 Kresse G, Furthmüller J. *Physical Review B*[J], 1996, 54: 11 169

17 Blochl P E. *Physical Review B*[J], 1994, 50: 17 953

18 Perdew J P, Burke K, Ernzerhof M. *Physical Review Letters*[J], 1996, 77: 3865

19 Jiang D E, Emily A. *Physical Review B*[J], 2003, 67: 214 103

20 Meschel S V, Nash P, Gao Q N *et al*. *Journal of Alloys and Compounds*[J], 2013, 554: 232

21 Korzhavyi P A, Ruban A V, Lozovoi A Y *et al*. *Physical Review B* [J], 2000, 61: 6003

22 Imai Y, Watanabe A, Amagai Y A *et al*. *Journal of Alloys and Compounds*[J], 2005, 389: 220

23 Wang Y G, Yang F M, Chen C P *et al*. *Journal of Alloys and Compounds*[J], 1996, 242: 66

24 Ma H F, Huang Z, Chen B *et al*. *Science China, Physics, Mechanics & Astronomy*[J], 2010, 53: 1239

25 Zhou C, Pinkerton F E, Herbst J F. *Journal of Alloys and Compounds*[J], 2013, 569: 6

26 Tsvyashchenko A V, Fomicheva L N. *Journal of Magnetism and Magnetic Materials*[J], 1991, 98: 285

27 Kubaschewski O. *Iron-Binary Phase Diagrams*[M]. Berlin: Springer-Verlag,1982

28 Tucker J D, Najafabadi R, Allen T R *et al*. *Journal of Nuclear Materials*[J], 2010, 405: 216

29 Clouet E, Sanchez J M. *Physical Review B*[J], 2002, 95: 094 105

30 Huang S Y, Worthington D L, Asta M *et al*. *Acta Materialia*[J], 2010, 58: 1982

31 Li Laifeng, Xing Zhongshu. *Acta Metallurgica Sinica*[J], 1993, 29(3): 40 (in Chinese)

32 Chuang Y C, Wu C H, Shao Z B. *Journal of the Less Common Metals*[J], 1987, 136: 147

33 Wang Haiyan, Gao Xueyun, Ren Huiping *et al*. *Rare Metal Materials and Engineering*[J], 2014, 43(12): 2739 (in Chinese)

34 Wang Haiyan, Gao Xueyun, Ren Huiping *et al*. *Acta Physica Sinica*[J], 2014, 63: 148 101 (in Chinese)

Fe-RE (Y La, Ce)合金中相稳定性和固溶度的第一性原理研究

高雪云 [1, 2]，任慧平 [1]，李一鸣 [1]，王海燕 [1]

(1. 内蒙古科技大学，内蒙古 包头 014010)

(2. 中冶东方工程技术有限公司，内蒙古 包头 014010)

摘　要：合金元素的固溶度对于新型合金的设计和合金动力学过程的研究具有重要的作用。利用密度泛函理论，计算了 Fe-RE 二元化合物的基态，确定了 Fe-Y 和 Fe-Ce 体系的稳态和亚稳态结构。计算结果表明，Fe-Y 的稳定结构为 $Fe_{12}Y$.tI26、$Fe_{17}Y_2$.hP38 和 Fe_2Y.cF24，Fe-Ce 的稳定结构为 $Fe_{17}Ce_2$.hP38、$Fe_{19}Ce_5$.hR24 和 Fe_2Ce.cF24。基于稀格子气统计热力学理论，利用第一性原理计算得到了稀土元素在 α-Fe 中随温度变化的固溶度曲线。结果显示，稀土 Y、La 和 Ce 元素在 α-Fe 中的固溶度为 $S_{La}>S_{Ce}>S_{Y}$，这一趋势对应于三者在 α-Fe 中的溶解形成焓关系：$H_{sol}(La)< H_{sol}(Ce)< H_{sol}(Y)$.

关键词：固溶度；Fe-RE；稳定结构；第一性原理

作者简介：高雪云，男，1980 年生，博士生，内蒙古科技大学材料与冶金学院，内蒙古 包头 014010，电话：0472-6958984，E-mail: gaoxueyun126@163.com