Available online at www.sciencedirect.com
SCIENCE DIRECT
Trans. Nonferrous Met. Soc. China 19(2009) 199−204
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Thermodynamic investigation of Fe-Ti-Y ternary system

GONG Wei-ping(龚伟平), CHEN Teng-fei(陈腾飞), LI Da-jian(李大建), LIU Yong(刘 咏)
State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China

Received 5 March 2008; accepted 9 September 2008

Abstract: An extensive investigation on the Fe-Ti-Y system was performed via experimental measurement and thermodynamic calculation. The Fe-Ti-Y ternary couples at 1 273 K were prepared with a desire to provide accurate phase relationships needed for the refinement of this ternary phase diagram. And a tentative isothermal section of Fe-Ti-Y at 1 273 K was built based on the experimental information. In the thermodynamic modeling, the thermodynamic parameters for the Ti-Y binary system and the ternary phase in the Fe-Ti-Y system were evaluated. Those for the Fe-Ti and Fe-Y systems from literature were slightly modified for the compatibility. The isothermal sections of Fe-Ti-Y ternary system at 873 K and 1 273 K were calculated. The ternary compound $Fe_{11}TiY$ and $Fe_2(Ti, Y)$ solid solution formed from Fe_2Ti and Fe_2Y are detected, which is in good agreement with the literature information.

Key words: Fe-Ti-Y; thermodynamic calculation; $Fe_{11}TiY$; diffusion couple

1 Introduction

A promising approach for achieving high creep strength and radiation damage resistant alloys is to create a very high density of fine-scale features that act as dislocation obstacles, serve as the dominant nucleation site for small helium bubbles and can promote vacancy-interstitial recombination. A high density of coherent nanometer-scale Y-O-Ti nanoclusters(NCs) are produced by mechanical alloying (MA) Fe-Cr-Ti powders with Y_2O_3 followed by hot consolidation[1−8]. Its high-temperature strength, radiation response, lattice Monte Carlo simulations of nanocluster formation in nanostructured ferritic alloys were studied[5−7].

In the targeted technological application, basic knowledge is required for process development and optimization, in particular the thermodynamic and transport properties of Fe-Cr-Ti powders and their mixtures with Y_2O_3 as well as in the addition of elements. However, these data are scarce and not easily accessible in literatures. As a consequence, intensive efforts are made both on research and development aspects and on data development.

The Fe-Ti-Y system is investigated in this work because it is the subsystem of the Fe-Cr-Ti-Y-O steel and it has not been thermodynamically evaluated up till now.

2 Evaluation of data from literatures

The information on phase diagram for the binary sub-systems of Fe-Ti-Y is available in Refs.[9−14]. MURRARY[9−10], KUBASCHEQSKI[11] and HARI KUMAR et al[12] evaluated the Fe-Ti system respectively and indicated that there are two stable intermediate phases, FeTi and Fe_2Ti. The Fe-Y system has been studied quite thoroughly by various investigators and the latest assessment was carried out by ZHANG et al[13]. In the work of ZHANG et al[13], four intermediate compounds $Fe_{17}Y_2$, $Fe_{23}Y_6$, Fe_3Y and Fe_2Y were detected. According to Ref.[14], the Ti-Y system is a simple eutectic-type phase diagram with limited mutual solubility of components. This work adopted the thermodynamic data from Refs.[10, 13] for Fe-Ti, Fe-Y system, respectively, but made a thermodynamic assessment on the Ti-Y system with the available information.

For Fe-Ti-Y system, a ternary compound $Fe_{10.8}Ti_{1.2}Y$ was observed by DE MOOIJ and BUSCHOW[15] in the alloys with composition of $Fe_{12-x}Ti_xY$ homogenized and equilibrated at 1 123 K for 14−21 d. In the work of LIU et al[16], the compound

Foundation item: Project(50634060) supported by the National Natural Science Foundation of China; Project(50721003) supported by the Creative Research Group of National Natural Science Foundation of China
Corresponding author: CHEN Teng-fei, Tel: +86-731-8830067; E-mail: tengfei@mail.csu.edu.cn
DOI: 10.1016/S1003-6326(08)60252-6

$Fe_{10.8}Ti_{1.2}Y$ was confirmed.

3 Experimental

3.1 Experimental procedure

Prior to the present experiment, a preliminary thermodynamic calculation for the Fe-Ti-Y system is performed by using the available thermodynamic database. The computed Fe-Ti-Y phase diagram is used to guide the choice of the experimental temperatures. Another reason to conduct the experiment is that even the most detailed measurement[15−16] failed to obtain accurate data on the ternary phases.

Iron (99.95%, mass fraction), titanium (99.5%, mass fraction) and yttrium (99.5%, mass fraction) were used as the starting materials. The binary Fe-Ti couples were first prepared by diffusion welding the elemental bars in a silica capsule back-filled with high purity argon at 1 273 K for 72 h. One of the Fe-Ti couples and a Y block were ground, polished, cleaned, and then swathed together with Mo wires to make a Fe-Ti-Y diffusion couple, which was wrapped in Mo foil. The Fe-Ti-Y diffusion couples as shown schematically in Fig.1 were annealed in a diffusion furnace at (1 273±1) K for 1200 h and subsequently quenched in water.

After standard metallographic preparation, all of the Fe-Ti-Y couples were examined by optical microscopy and scanning electron microscopy (SEM).

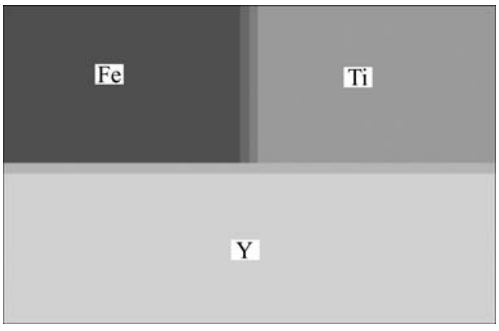


Fig.1 Construction of Fe-Ti-Y diffusion couple

3.2 Experimental results

The microstructure of a Fe-Ti-Y couple annealed at 1 273 K for 1 200 h is shown in Fig.2. The backscattered electron images (BSE) of the Fe-Ti, Fe-Y and Fe-Ti-Y couple annealed at 1 273 K for 1 200 h are given in Figs.3−5, respectively. The isothermal section of Fe-Ti-Y system at 1 273 K is constructed in Fig.6 according to the experimental data.

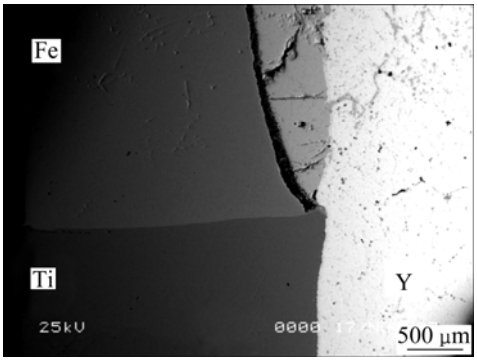
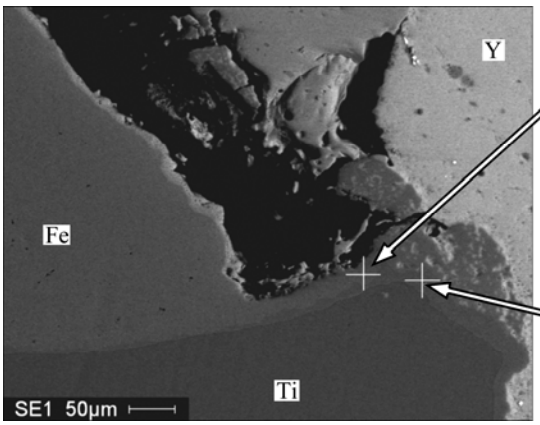


Fig.2 Microstructure of ternary couple annealed at 1 273 K for 1 200 h

As shown in Figs.3 and 4, the data close to the boundary binary systems are in accord with the literature ones and the reported binary compounds Fe_2Ti, FeTi in the Fe-Ti system, Fe_2Y, Fe_3Y, $Fe_{23}Y_6$, $Fe_{17}Y_2$ in the Fe-Y system are confirmed by the present experiments. The experimental results show that Fe_2Ti and Fe_2Y form a continuous solid solution, namely Fe_2(Y, Ti). In the ternary triple, a ternary phase with the composition of approximate Fe_9TiY is detected. Several works have reported the ternary phase $Fe_{12-x}Ti_xY$, so in this work the detected ternary compound is treated as $Fe_{12-x}Ti_xY$. More experimental measurements are required.

4 Thermodynamic models

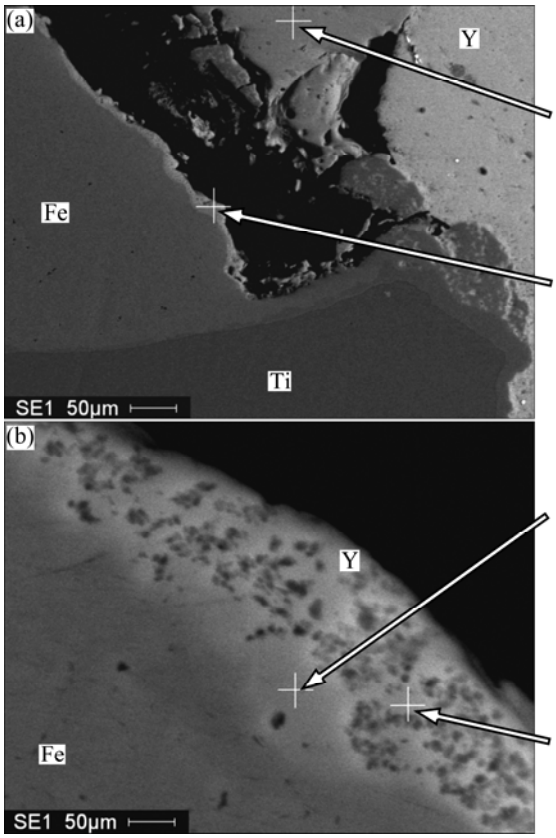
In the present modeling, thermodynamic assessments on Ti-Y and Fe-Ti-Y system are carried out.



Element	w/%	x/%
Ti K	29.03	32.29
Fe K	70.97	67.71

Element	w/%	x/%
Ti K	46.32	50.15
Fe K	53.68	49.85

Fig.3 Backscattered electron image (BSE) of Fe-Ti binary couple annealed at 1 273 K for 1 200 h



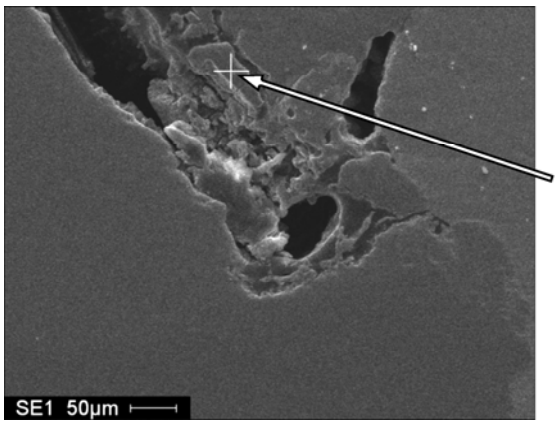
Element	w/%	x/%
Y L	42.85	31.98
Ti K	0.57	0.79
Fe K	56.58	67.23

Element	w/%	x/%
Y L	31.74	22.58
Ti K	0.69	0.91
Fe K	67.58	76.52

Element	w/%	x/%
Y L	25.01	17.28
Ti K	1.46	1.87
Fe K	73.53	80.86

Element	w/%	x/%
Y L	21.26	14.46
Ti K	1.50	1.90
Fe K	77.24	83.64

Fig.4 Backscattered electron images (BSE) of Fe-Y binary couple annealed at 1 273 K for 1 200 h



Element	w/%	x/%
Y L	17.76	11.66
Ti K	13.96	17.01
Fe K	68.27	71.33

Fig.5 Backscattered electron image (BSE) of Fe-Ti-Y ternary couple annealed at 1 273 K for 1 200 h

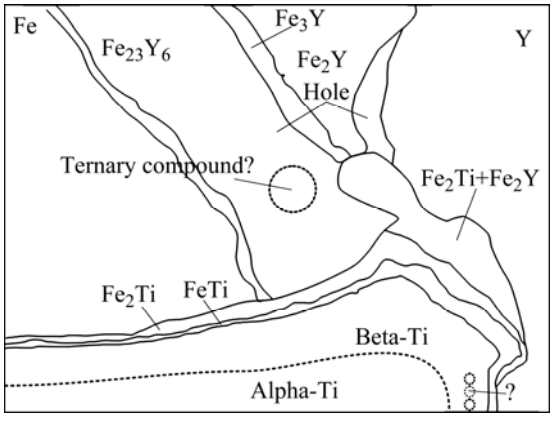


Fig.6 Scheme of Fe-Ti-Y diffusion triple at 1 273 K

The thermodynamic parameters in the Fe-Ti and Fe-Y systems are taken from Refs.[10, 13], respectively. In this work, only the analytical expressions for Gibbs energies of the ternary phases are briefly presented.

4.1 Liquid phase

The Gibbs energy of the ternary liquid phase is described by the Redlich–Kister polynomial[17]:

$$^{\Theta}G^{\mathrm{L}}(\mathrm{m}) = x^0(\mathrm{Fe})G^{\mathrm{L}}(\mathrm{Fe}) + x^0(\mathrm{Ti})G^{\mathrm{L}}(\mathrm{Ti}) + x^0(\mathrm{Y})G^{\mathrm{L}}(\mathrm{Y}) + RT(x(\mathrm{Fe})\ln x(\mathrm{Fe}) + x(\mathrm{Ti})\ln x(\mathrm{Ti}) + x(\mathrm{Y})\ln x(\mathrm{Y})) + x(\mathrm{Fe})x(\mathrm{Ti})L^{\mathrm{L}}(\mathrm{Fe},\mathrm{Ti}) + x(\mathrm{Fe})x(\mathrm{Y})L^{\mathrm{L}}(\mathrm{Fe},\mathrm{Y}) + x(\mathrm{Ti})x(\mathrm{Y})L^{\mathrm{L}}(\mathrm{Ti},\mathrm{Y}) + {}^{\mathrm{ex}}G^{\mathrm{L}}(\mathrm{Fe},\mathrm{Ti},\mathrm{Y}) \quad (1)$$

where R is the gas constant, x(Fe), x(Ti) and x(Y) are the mole fractions of Fe, Ti and Y, respectively. The standard element reference(SER) state[18], i.e. the stable structure of the element at 298 K and 10^5 Pa, is used as the reference state of the Gibbs energy. The parameters denoted as $L^L_{i,j}$ (i, j=Fe, Ti, Y) are the interaction parameters from the binary systems.

The excessive Gibbs energy ${}^{ex}G^{L}(\mathrm{Fe,Ti,Y})$ is expressed as

$$ {}^{ex}G^{L}(\mathrm{Fe,Ti,Y}) = x(\mathrm{Fe})x(\mathrm{Ti})x(\mathrm{Y})[x(\mathrm{Fe})L^{L}(\mathrm{Fe}) + x(\mathrm{Ti})L^{L}(\mathrm{Ti}) + x(\mathrm{Y})L^{L}(\mathrm{Y})] \quad (2) $$

where L^{L}(Fe), L^{L}(Ti) and L^{L}(Y) are the ternary interactive parameters to be optimized.

4.2 Model used for ternary compound

Due to the very few experimental data, the ternary phase $Fe_{12-x}Ti_xY$ is treated as a stoichiometric compound with the formula $Fe_{11}TiY$. The Gibbs energy for $Fe_{11}TiY$ relative to the pure elements is expressed by

$$ {}^{\Theta}G^{S}(\mathrm{Fe_{11}TiY}) = (11/13){}^{\Theta}G^{\mathrm{BCC}}(\mathrm{Fe}) + (1/13){}^{\Theta}G^{\mathrm{HCP}}(\mathrm{Ti}) + (1/13){}^{\Theta}G^{\mathrm{HCP}}(\mathrm{Y}) + A + BT \quad (3) $$

where the coefficients A and B are to be evaluated in the present work. The parameters ${}^{\Theta}G^{\mathrm{BCC}}(\mathrm{Fe})$, ${}^{\Theta}G^{\mathrm{HCP}}(\mathrm{Ti})$ and ${}^{\Theta}G^{\mathrm{HCP}}(\mathrm{Y})$ are the Gibbs energies of BCC-Fe, HCP-Ti and HCP-Y, respectively.

Through taking into account of crystal structure and experimental homogeneities, sublattice models are employed to describe the solid solution phase Fe_2(Ti, Y). In accordance with the formula for the sublattice model, the molar Gibbs enrgy of Fe_2(Ti, Y) can be expressed as

$$ {}^{\Theta}G_{\mathrm{m}}[\mathrm{Fe_2(Ti,Y)}] = x''(\mathrm{Ti}){}^{\Theta}G_{\mathrm{Fe:Ti}}[\mathrm{Fe_2(Ti,Y)}] + x''(\mathrm{Y}){}^{\Theta}G_{\mathrm{Fe:Y}}[\mathrm{Fe_2(Ti,Y)}] + x''(\mathrm{Ti})x''(\mathrm{Y})\cdot\{L^{0}_{\mathrm{Fe:Ti,\,Y}} + [x''(\mathrm{Ti}) - x(\mathrm{Y})]L^{1}_{\mathrm{Fe:Ti,Y}}\} \quad (4) $$

where x''(Ti) and x''(Y) are the site fractions of Ti and Y in the second sublattice. The two parameters denoted as ${}^{\Theta}G_{\mathrm{Fe:Ti}}[\mathrm{Fe_2(Ti,Y)}]$ and ${}^{\Theta}G_{\mathrm{Fe:Y}}[\mathrm{Fe_2(Ti,Y)}]$ are relative to the Gibbs energies of BCC-Fe, HCP-Ti and HCP-Y, respectively, at the same temperature. $L^{i}_{\mathrm{Fe:Ti,Y}}$ (i=0, 1) is ternary parameters to be evaluated.

5 Parameter evaluation

The optimization was conducted using the Thermo-calc software package[19]. The critically selected experimental data were processed with a specific weight factor reflecting the experimental uncertainty. The optimization process consists of five steps.

In the first step, the Gibbs energies of the phases in the Ti-Y system were evaluated by reproducing the experimental phase diagram information. In the next step, the thermodynamic parameters for Fe-Ti and Fe-Y systems were slightly modified from Refs.[10, 13], for the compatibility. In the third step, the Gibbs energy of liquid Fe-Ti-Y mixtures as well as the ternary solid solution phases was calculated, to reproduce the experimental information. An excellent agreement between calculations and experimental data from Refs.[15−16] and this work is obtained. In the fourth step, the Gibbs energy functions of ternary compound $Fe_{11}TiY$ were constructed by using the present measurement as well as the literature information. In the last step, all model parameters were assessed simultaneously in a least square optimization to represent the key experimental data within experimental uncertainty.

6 Results and discussion

By adopting the thermodynamic parameters in Refs.[10, 13] for the Fe-Ti and Fe-Y binary systems, and combining the present optimized parameters for Ti-Y system and Fe-Ti-Y ternary phases, the thermodynamic properties and phase diagram of Fe-Ti-Y ternary system can be calculated. Figs.7−9 show the calculated phase diagrams for Fe-Ti, Fe-Y and Ti-Y systems, respectively. Fig.10 and Fig.11 show the present calculated isothermal sections of Fe-Ti-Y system at 873 K and 1 273 K, respectively. Compared with the experimental phase diagram at 1 273 K (Fig.6), the good agreement between the experiments and thermodynamic calculation is obtained. Moreover, the present calculation indicates that the ternary compound $Fe_{11}TiY$ can exist at temperature between 873 K and 1 273 K.

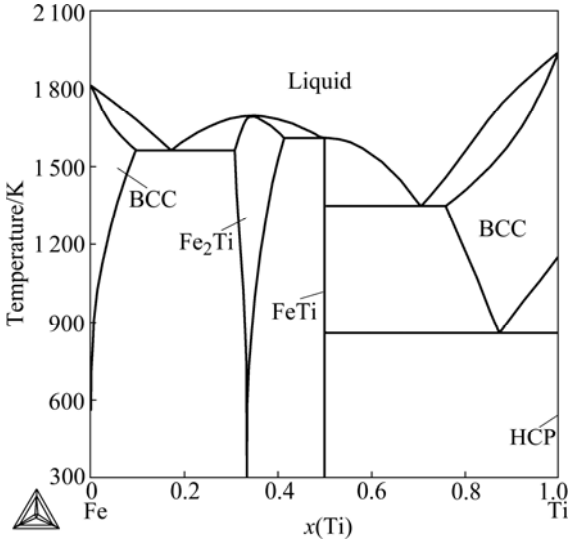


Fig.7 Calculated Fe-Ti phase diagram with thermodynamic parameters from Ref.[6]

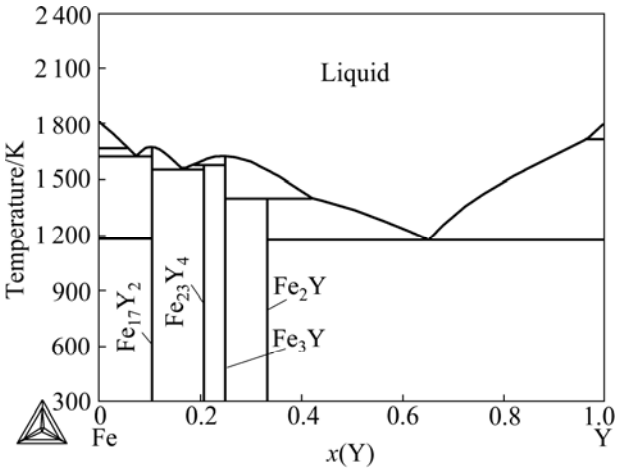


Fig.8 Calculated Fe-Y phase diagram with thermodynamic parameters from Ref.[9]

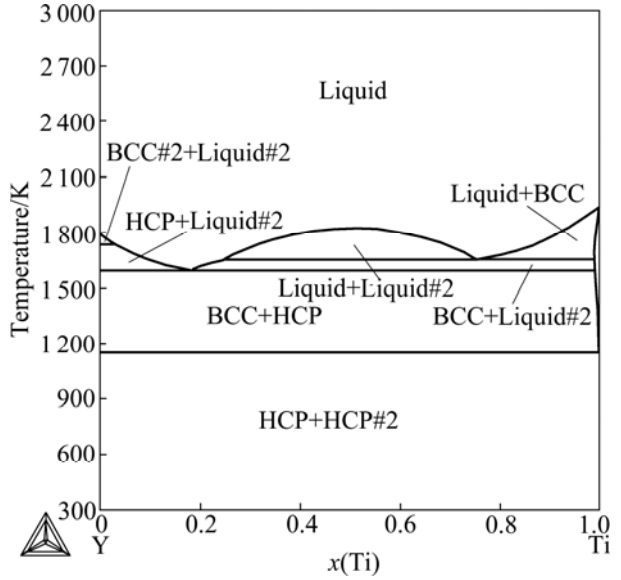


Fig.9 Calculated Ti-Y phase diagram

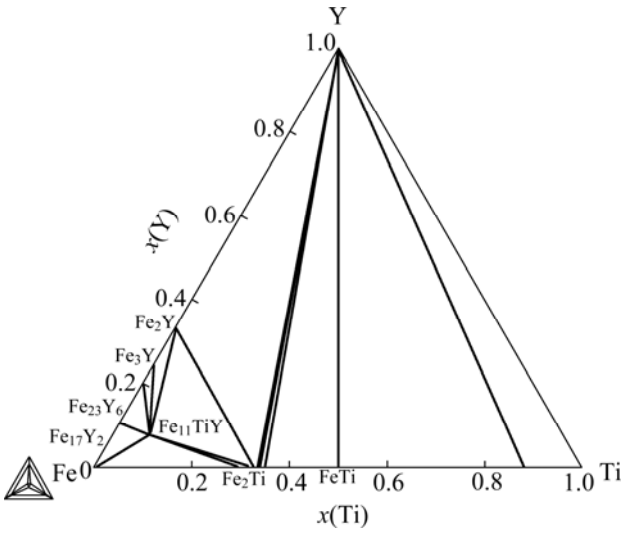


Fig.10 Calculated isothermal section of Fe-Ti-Y at 873 K

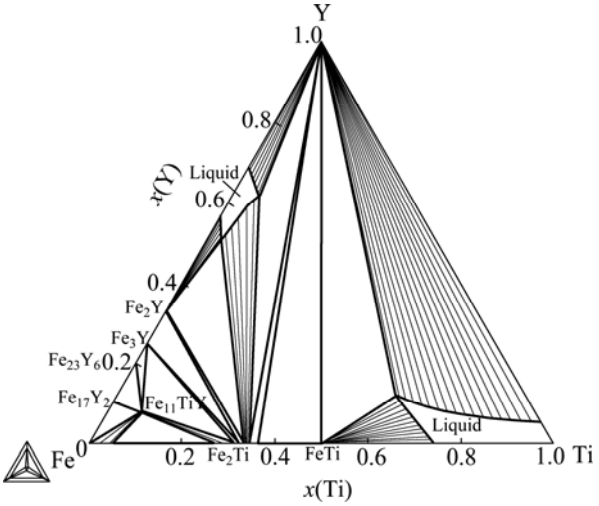


Fig.11 Calculated isothermal section of Fe-Ti-Y at 1 273 K

7 Conclusions

On the basis of the literature information, the thermodynamic parameters for the Ti-Y binary system are optimized. On the basis of the thermodynamic parameters for the Fe-Ti and Fe-Y binary systems, a slight modification is made for compatibility. The Fe-Ti-Y ternary diffusion couples at 1 273 K are prepared and analyzed by optical metallurgy and SEM. The thermodynamic optimization and calculation on the Fe-Ti-Y system are carried out to reproduce the information. The ternary phases $Fe_2(Ti, Y)$ and $Fe_{11}TiY$ are detected by both the present experiments and thermodynamic calculation and the good agreement between the calculation and experiments is obtained.

References

[1] ALINGER M J, ODETTE G R, HOELZER D T. The development and stability of Y-Ti-O nanoclusters in mechanically alloyed Fe-Cr based ferritic alloys [J] J Nulc Mater, 2004, 329/333: 382−386.

[2] UKAI S, NISHIDA T, OKUDA T, YOSHITAKE T. R & D of oxide dispersion strengthened ferritic martensitic steels for FBR [J] J Nucl Mater, 1998, 258/263: 1745−1749.

[3] DEGUELDRE C, CONRADSON S, HOFFELNER W. Characterisation of oxide dispersion-strengthened steel by extended X-ray absorption spectroscopy for its use under irradiation [J]. Computational Mater Sci, 2005, 33: 3−12.

[4] MILLER M K, KENIK E A, RUSSELL K F, HEATHERLY L, HOELZER D T, MAZIASZ P J. Atom probe tomography of nanoscale particles in ODS ferritic alloys [J]. Mater Sci Eng A, 2003, A353: 140−145.

[5] ALLEN T R, GAN J, COLE J I, MILLER M K, BUSBY J T, SHUTTHANANDAN S, THEVUTHASAN S. Radiation response of a 9 chromium oxide dispersion strengthened steel to heavy ion irradiation [J]. Journal of Nuclear Materials, 2008, 375(1): 26-37.

[6] ALINGER M J, WIRTH B D, LEE H J, ODETTE G R. Lattice Monte Carlo simulations of nanocluster formation in nanostructured ferritic alloys [J]. Journal of Nuclear Materials, 2007, 367/370(1):

153−159.

[7] HOELZER D T, BENTLEY J, SOKOLOV M A, MILLER M K, ODETTE G R, ALINGER M J. Influence of particle dispersions on the high-temperature strength of ferritic alloys [J]. Journal of Nuclear Materials, 2007, 367/370(1): 166−172.

[8] PAREIGE P, MILLER M K, STOLLER R E, HOELZER D T, CADEL E, RADIGUET B. Stability of nanometer-sized oxide clusters in mechanically-alloyed steel under ion-induced displacement cascade damage conditions [J]. Journal of Nuclear Materials, 2007, 360(2): 136−142.

[9] MURRY J L. Bull alloy phase diagrams [M]. OH: ASM International, Metals Park, 1981: 320.

[10] MURRY J L. Phase diagram of binary titanium alloys [M]. MURRY J L, ed. OH: ASM International, Metals Park, 1987: 99.

[11] KUBASCHEQSKI O. Iron-binary phase diagram [M]. Berlin: Springer-Verlag, 1982: 152.

[12] HARI KUMAR K C, WOLLANTS P, DELAEY L. Thermodynamic reassessments and calculation of Fe-Ti phase diagram [J]. Calphad, 1994, 18(2): 223−235.

[13] ZHANG W, LIU G, HAN K. The Fe-Y (iron-yttrium) system [J]. J Phase Equilibria, 1988, 13: 304−308.

[14] ELLIOTT R P. Constitution of binary alloys [M]. First Supplement, New York: McGraw-Hill, 1965: 865.

[15] DE MOOIJ D B, BUSCHOW K H J. Some novel ternary ThMn12-type compounds [J]. J Less-Common Metals, 1988, 136: 207−215.

[16] LIU Zhong-yi, JIN Zhan-peng, XIA Chang-sha. 873 K isothermal section of phase diagram for Y-Fe-Ti ternary system [J]. Scripta Mater, 1997, 37(8): 1129−1134.

[17] REDLICH O, KISTER A T. Algebraic representation of thermodynamic properties and the classification of solution [J]. Ind Eng Chem, 1948, 40: 345−348.

[18] DINSDALE A T. SGTE data for pure elements [J]. Calphad, 1991, 15: 317−425.

[19] SUNDMAN B, JANSSON B, ANDERSSON J O. The Thermo-Calc databank system [J]. Calphad, 1985, 9: 153−190.

(Edited by YANG Bing)