CHANGE IN THE SYSTEM FREE ENERGY OF HIGH Cr HEAT RESISTANT STEELS WITH ANNEALING AT ELEVATED TEMPERATURES

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ABSTRACT

Advanced high Cr heat resistant steels have complex microstructures, which contain intermetallic compounds such as the Laves phase together with carbonitrides. The microstructure evolution leads to the change of the system free energy. This energy is based on the idea that the morphological evolution occurs with the change of the total free energy, i.e., the system free energy (G_{sys}), which is given by the summation of the chemical free energy (G_0), the interfacial energy (E_{surf}) and the elastic strain energy (E_{str}) between the matrix and precipitates. In this study, morphological changes of two kinds of ferritic steels (0.1C-10Cr-3W-3Co-Mo-Nb-V-N steel and 0.1C-12Cr-2W-3Co-Mo-Nb-V-N steel) are estimated on the basis of the system free energy. The results lead to the following findings: (i) The coherent fine Laves phase is unstable in the 2W steel even in the early stage of annealing at 873K and 923K. (ii) The coherent Laves phase is stable in the 3W steel in the early stage of annealing at 873K and 923K, but the incoherent one becomes stable in the later stage of annealing (e.g. a few hours at 923K). These findings obtained from the calculation are consistent with the experimental results of the two steels.

KEYWORDS

Laves phase, microstructure evolution, high Cr steel, heat resistant steel, ferritic steel, system free energy, interfacial energy, elastic strain energy

INTRODUCTION

Advanced high Cr heat resistant ferritic steels developed recently contain a large amount of refractory elements such as Mo and W in order to increase their creep strength at elevated temperatures [1-6]. Its microstructure becomes quite complicated, namely, it consists of the martensite phase, $M_{23}C_6$ carbide, MX carbonitrides and intermetallic compounds such as the Laves phase. It is well known that the evolution of the complex microstructure is related closely to the long-term creep strength of the steels, although the creep strength depends on a variety of factors, e.g., the stability of the martensite phase, the diffusivity of alloying elements, the coalescence rate of precipitates in the steels, etc. Therefore, a quantitative estimation of the microstructure evolution of the steels is necessary for predicting the long-term creep strength of high Cr ferritic steels.

Here, the issue is how to make a quantitative estimation of the microstructure evolution in these steels. We have proposed that the system free energy concept is one of the best ideas for quantifying the microstructure evolution. This concept is based on total energy change associated with the microstructural change [7]. In the previous work, we reported that the microstructure change of the Laves phase in Fe-Cr-W-C quaternary steels was predictable with the aid of the system free energy concept and that the fine coherent Laves phase could precipitate in high Cr ferritic steels containing more than 3mass%W [8]. However, the volume fractions of both $M_{23}C_6$ carbide and the Laves phase were supposed to be constants in the previous calculation. The purpose of this study is to evaluate quantitatively the free energy change associated with the microstructural change, in particular, morphological change of the Laves phase in high Cr heat resistant ferritic steels on the basis of the system free energy concept, in consideration of the change of volume fractions of both $M_{23}C_6$ carbide and the Laves phase.

1. THEORY OF THE SYSTEM FREE ENERGY FOR FERRITIC STEELS

The system free energy is defined by the sum of a chemical free energy, G_0, an elastic strain energy, E_{str}, an interfacial energy in the unit volume of the microstructure, E_{surf}, and an elastic interaction energy, E_{int}. Here, E_{surf} is called simply as “interfacial energy” in this paper. The total free energy is denoted as system free energy, G_{sys} ($=G_0+E_{str}+E_{surf}+E_{int}$) [7].

Following the previous report [8], the concept of system free energy is explained in Fig.1 as follows. When the Laves phase precipitates from supersaturated steel, it has usually been considered that the free energy becomes the chemical free energy at A in Fig.1, i.e., G_0. However, since the coherent precipitation of the Laves phase inevitably causes additional free energies such as elastic strain energy, E_{str}, and the interfacial energy E_{surf}. Thus the free energy increases from the point A to B and X_0 (G_{sys}) in Fig.1, i.e., the free energy of the microstructure is not G_0 but G_{sys}. G_{sys}-G_0 gradually decreases during the microstructure evolution such as the coarsening of the precipitates. Therefore it is expected that the evaluation of G_{sys} make it possible to predict the microstructure evolution.

The existence of $M_{23}C_6$ carbide is also being considered in this simulation. But this carbide precipitates incoherently even in the as-tempered state in high Cr ferritic steel, and the morphological change of $M_{23}C_6$ carbide is smaller than that of the Laves phase. Therefore, the contribution of both elastic strain energy and interfacial energy generated from this carbide to the change of system free energy is disregarded in this study. Also, volume fractions of both $M_{23}C_6$ carbide and the Laves phase are small, and hence the interaction energy E_{int} in G_{sys} is set to be zero in this simulation. Furthermore, MX type carbonitrides are not considered to influence the microstructure evolution of the Laves phase, because the volume fraction of the carbonitrides scarcely change during aging at about 1000K due to their high stability in the ferritic steels. As a result, the system free energy is estimated by the sum of chemical free energy, G_0, elastic strain energy, E_{str}, and interfacial energy, E_{surf}.

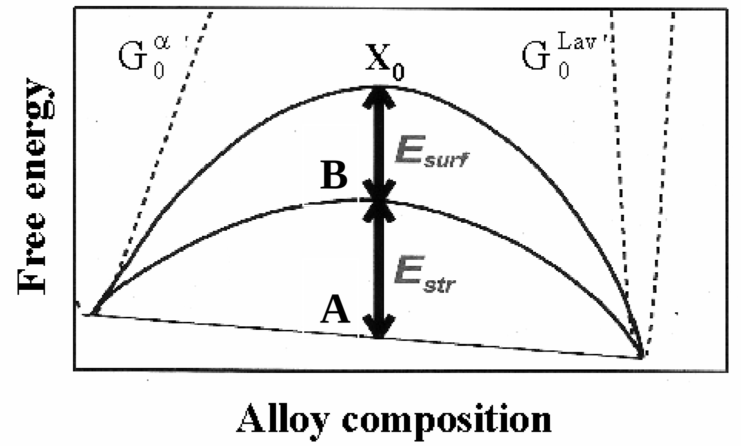

Fig.1 A schematic drawing of the free energy changes with microstructure evolution in high Cr ferritic steels.

In this study, the chemical free energy was calculated by assuming that the experimental steel consisted of the eight elements which were main elements of high Cr ferritic steels. The chemical free energies of the α phase, Laves phase and $M_{23}C_6$ carbide were calculated according to the sub-lattice model. The molar Gibbs energy and the molar interaction energy are given in the Thermo-Calc database. Temperature dependence of the excess free energy associated with magnetic ordering is being considered using the formula proposed by Hillert and Jarl [9].

The elastic strain energy generated from the coherent fine Laves phase is considered according to Fe-Cr-W-C quaternary steels [8]. Then the elastic strain energy is given by

$$E_{str}=\beta\frac{E}{1-\nu}\left(c_{Laves}-c_{\alpha}\right)^2\eta^2 V_f f\left(1-f\right) \quad . \tag{1}$$

Here, β is a constant, and f is the volume fraction of the precipitate. It is assumed that the

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elastic strain energy E_{str} for the fine Laves phase is about 20% of the value for the coherent precipitate in Fe-W binary system [8]. Then β is set to be 0.2 in this simulation. c_{Laves} and c_{α} are chemical compositions of the Laves phase and the ferrite phase, respectively. $\eta(c_{Laves} - c_{\alpha})$ is the eigen strain between the ferrite phase and the Laves phase in the coherent plane [4,5]. E and ν are the Young's modulus and the Poisson's ratio, respectively, and the values of pure iron as shown below are used in this study.

E : 1.9×10^{11} Pa ,
ν : 0.185 .

Interfacial energy in the unit volume of the microstructure E_{surf} between the Laves phase and the matrix is evaluated in both the coherent and incoherent states by using the following equation.

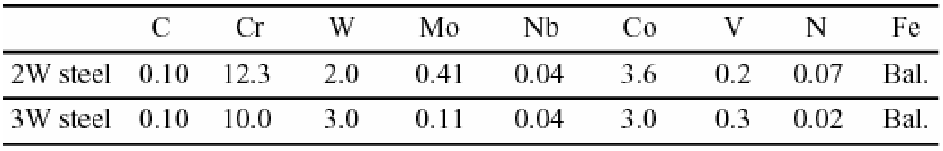
$$E_{surf} = A\gamma_S V_f \,, \qquad (2)$$

where A is interfacial area per unit volume and V_f is the molar volume. The coherent and incoherent interfacial energy densities were set to be $0.15 J/m^2$ and $0.468 J/m^2$, respectively, in this study [8]. Also, $M_{23}C_6$ carbide is known to precipitate incoherently in the ferritic steels, and hence energy density for this carbide/matrix interface was assumed to be $2.5 J/m^2$ in this study according to an average value reported on some carbides [10].

2 EXPERIMENTAL PROCEDURES

In order to simulate the system free energy against real annealing times, the volume fractions of both the Laves phase and $M_{23}C_6$ carbide in an annealing time are needed, and some experiments were carried out using two kinds of steels.

Table 1 Chemical compositions of steels investigated in this study, in mass%.



	C	Cr	W	Mo	Nb	Co	V	N	Fe
2W steel	0.10	12.3	2.0	0.41	0.04	3.6	0.2	0.07	Bal.
3W steel	0.10	10.0	3.0	0.11	0.04	3.0	0.3	0.02	Bal.

2.1 STEEL PREPARATION

For a series of experiments, two kinds of steels were prepared. Their chemical compositions are listed in Table 1. W content of the two experimental steels are 2 mass% and 3 mass%, respectively, for evaluating the morphological change of the Laves phase depending on the W content. The ingots of these steels were prepared by vacuum induction melting and the processed by hot-forging in a conventional way. In order to control the grain size, they were normalized at 1373K for 5h, followed by tempering at 993K for 20h. Subsequently, they were cut into plates with the size of 20×10×5mm. The plates were austenitized at 1323K for 1h followed by

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quenching into water. After this quenching treatment, the plates were annealed at 873K, 923K and 973K for 50, 100, 250, 500, 1000 and 2500 h, respectively.

2. 2 MEASUREMENTS OF SIZE AND VOLUME FRACTION OF PRECIPITATES

The average particle size of the Laves phase as well as the area fractions of both the Laves phase and $M_{23}C_6$ carbide were measured using the STEM/EDX microstructures. Extraction replicas for STEM/EDX observation were prepared from the annealed specimens, and the microstructures and EDX spectra were taken using a conventional TEM/STEM operated at 200kV.

Extracted residues from the experimental steels were also prepared electrically using an 1% acetyl-acetone-10% tetra-methyl-ammonium-chloride-ethanol solution. The mass fractions of both the Laves phase and $M_{23}C_6$ carbide were calculated using the total mass fraction measured from the extracted residues as well as the area fractions of the Laves phase and $M_{23}C_6$ carbide by the following equations,

$$m_f^{M_{23}C_6} = \frac{A_{M_{23}C_6} \times M_{mass}^{M_{23}C_6} \times M_{mol}^{Lav}}{A_{M_{23}C_6} \times M_{mass}^{M_{23}C_6} \times M_{mol}^{Lav} + A_{Lav} \times M_{mass}^{Lav} \times M_{mol}^{M_{23}C_6}} \times m_f \, , \tag{3}$$

$$m_f^{Lav} = 1 - m_f^{M_{23}C_6} - m_f^{MX} \, , \tag{4}$$

where, m^i_f is the mass fraction of *i* phase, A_i is the volume fraction of *i* phase obtained from the area analysis measured by the STEM/EDX images, M^i_{mass} and M^i_{mol} are the saturated mass fraction and mole fraction, respectively, calculated by the Thermo-Calc. m_f is the total mass fraction of the precipitates obtained from the experiments. The amount of MX carbonitride is very small, so it is assumed that the volume fraction of the MX carbonitride was a constant calculated by the Thermo-Calc irrespective of the annealing time.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 MICROSTRUCTURE OBSERVATION

Figure 2 shows typical STEM/EDX microstructures taken from the 3W steel annealed at 873K for 100h. W rich precipitates were identified as the Laves phase, Cr-rich ones as $M_{23}C_6$ carbides, and V- or Nb-rich ones as the MX carbonitrides. On the basis of these microstructure observations, the average particle size of the Laves phase was measured by an image analyzing method. The change in the average particle size of the Laves phase is shown in Fig.3, (a) for the 2W steel and (b) for the 3W steel. The growth rate of the size was nearly equal to $t^{1/3}$ irrespective

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of neither annealing temperature nor W content, although the initial size showed the temperature dependence, i.e., the size became large with increasing the annealing temperatures.

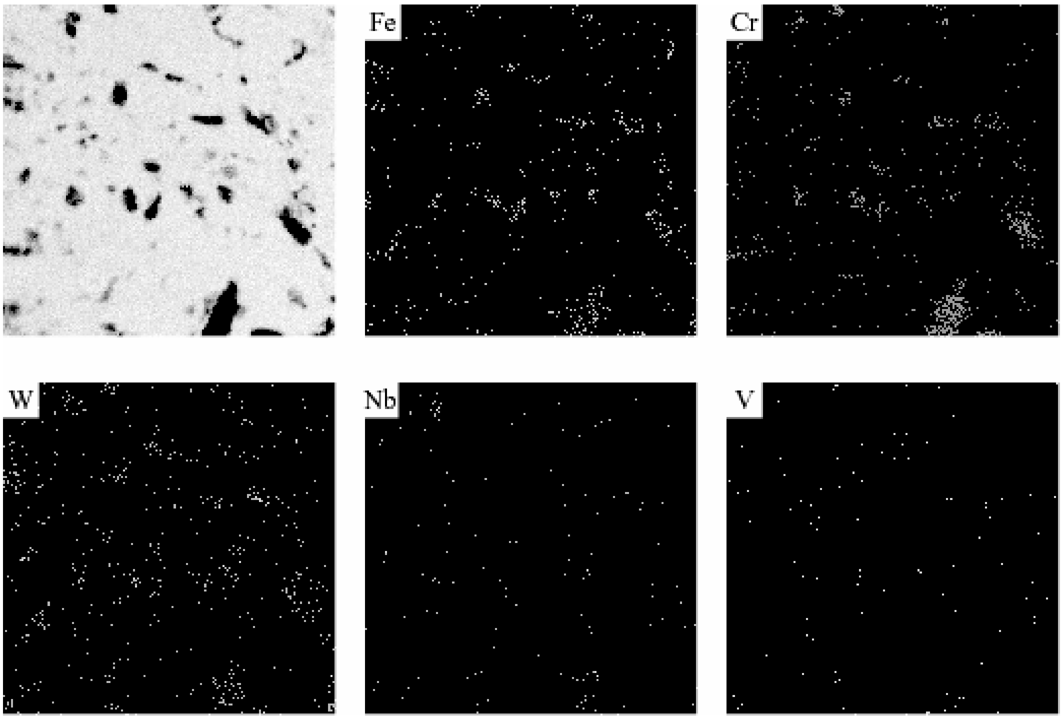

Fig.2 STEM/EDX microstructures of the 3W steel annealed at 873K for 100h.

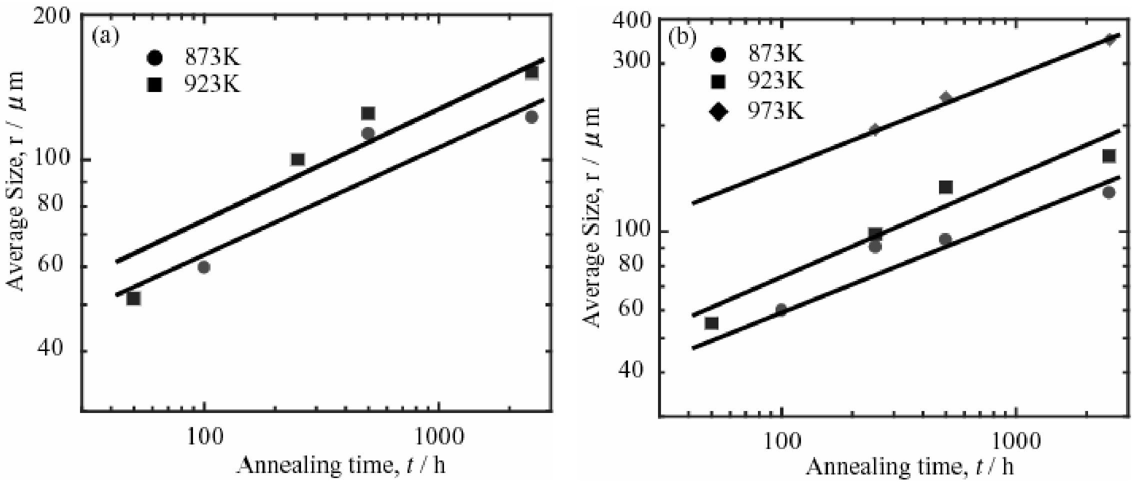

Fig. 3 Change in the average size of the Laves phase, (a) in the 2W steel and (b) in the 3W steel, with annealing time.

3.2 MEASUREMENT OF THE VOLUME FRACTION

The mass fractions of the total precipitates obtained by the extracted residues taken from the 2W and 3W steels are shown in Table 2. The total mass fraction was separated to each fraction of the

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Laves phase, $M_{23}C_6$ carbide and MX carbonitride by the calculation as mentioned in section 2.2.

Table 2 Total mass fractions of the precipitates in 2W and 3W steels.

Steel	Annealing temperature	mass fraciton 250h	500h	2500h
2W steel	873	3.24	3.69	4.66
	923	3.53	3.82	4.31
3W steel	873	4.00	4.43	4.98
	923	4.28	4.47	5.00

The changes in the mass fraction of both $M_{23}C_6$ carbide and the Laves phase with annealing time are shown in Fig.4, (a) for the 2W steel and (b) for the 3W steel. It is generally known that the volume change of a precipitate with time, t, obeys the Johnson-Mehl-Avrami equation expressed as

$$V_f = A\left\{1 - \exp(-kt^n)\right\}. \qquad (5)$$

Here, A is the saturated value of the precipitate, and this can be calculated using the data base of the Thermo-Calc. The constants, k and n, are determined by the least square fitting of Eq.(5) to the experimental data. The fitting result is shown in Fig.4 as the solid lines. These results were utilized for calculating the system free energy.

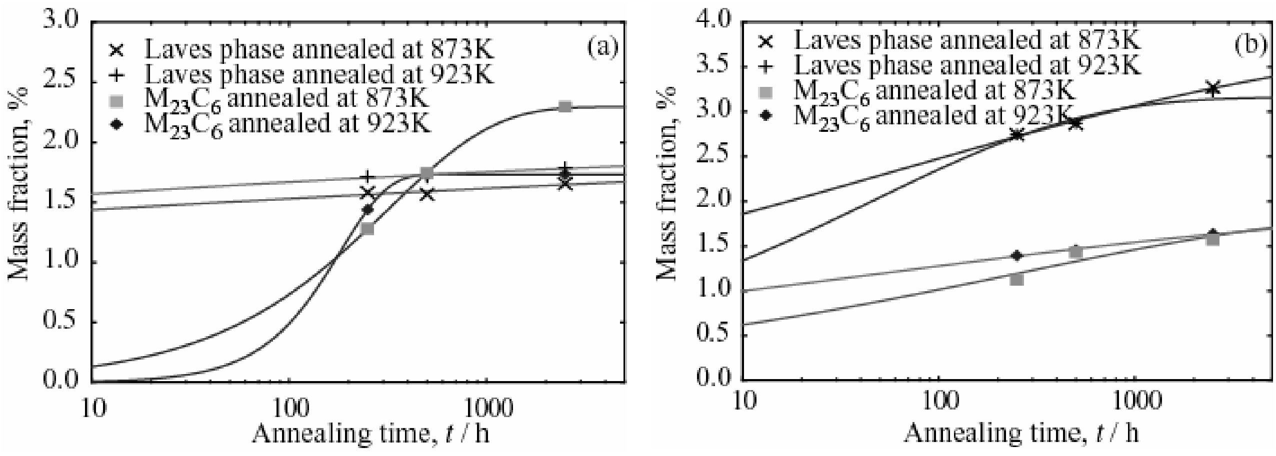

Fig.4 The Changes in the mass fractions of the precipitates with annealing time, (a) 2W steel and (b) 3W steel.

3.3 CALCULATION OF THE SYSTEM FREE ENERGY

In order to obtain the free energy change associated with the microstructure evolution of the Laves phase, the system free energy was calculated as the following three cases: (i) precipitating $M_{23}C_6$

carbide but no Laves phase (denoted as supersaturated solid solution), (ii) precipitating the coherent Laves phase, and (iii) precipitating the incoherent Laves phase. Here, the volume fraction of the MX carbonitride was set to be a constant value calculated by the Thermo-Cal using the steel composition, because this carbonitride is quite stable compared with $M_{23}C_6$ carbide and precipitates fully in very early stage of the annealing.

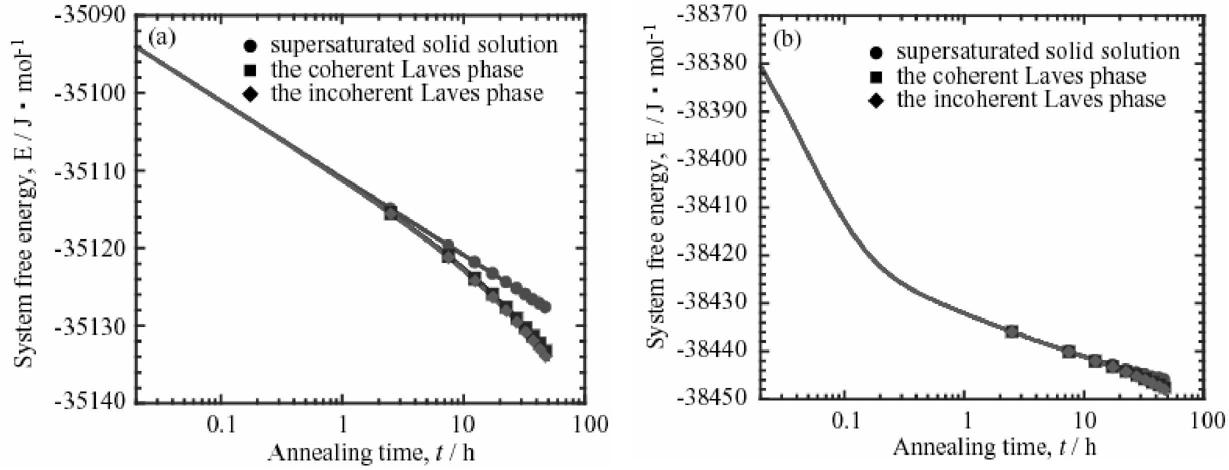

Fig.5 Changes in the system free energy of 2W steel annealed at (a) 873K and (b) 923K

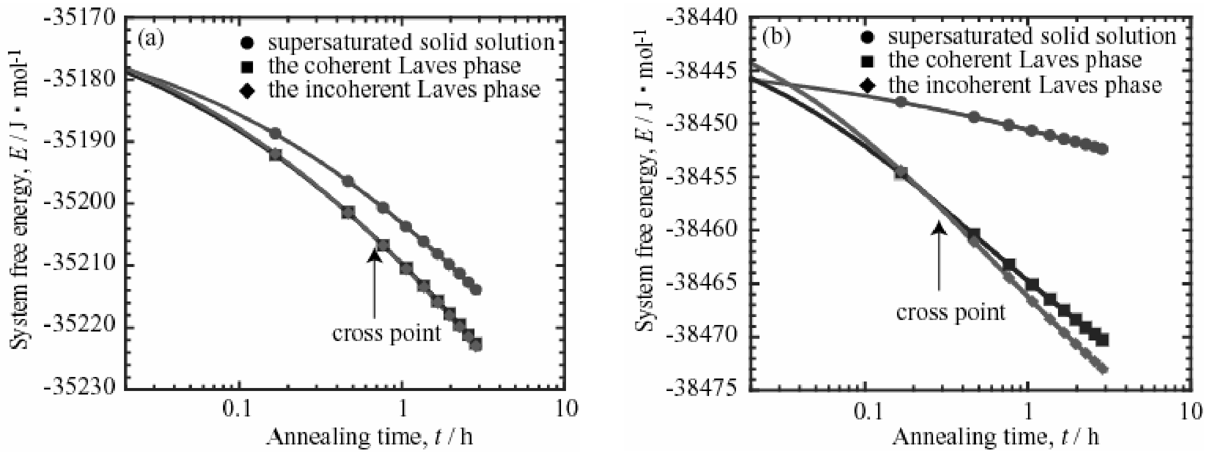

Fig.6 Changes in the system free energy of 3W steel annealed at (a) 873K and (b) 923K

The calculated results on the three cases of the system free energy of the 2W steel are shown in Fig.5, (a) at 873K and (b) at 923K. When the incoherent Laves phase precipitated in this steel (case (iii)), the system free energy exhibited the lowest value in whole annealing time at both 873K and 923K. Then it is possible to precipitate the incoherent Laves phase during annealing but not the coherent one. But the energy difference between the microstructure precipitating the incoherent Laves phase (case (iii)) and precipitating only $M_{23}C_6$ carbide (case (i)) was very small and it was about 2J/mol at 923K.

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On the other hand, the calculated results on the 3W steel are shown in Fig.6, (a) at 873K and (b) at 923K. At both annealing temperatures, the system free energy for precipitating the coherent Laves phase (case (ii)) exhibited the lowest value in the initial stage of annealing. But the system free energy for precipitating the incoherent Laves phase (case (iii)) became lower at an annealing time indicated by an arrow as the cross point in each figure. These results indicate that the coherent Laves phase can precipitate in the initial stage of annealing but the incoherent one becomes more stable during annealing than the coherent one. Then it is possible to transform the coherent Laves phase to the incoherent one after the annealing time at the cross point (Fig.6).

As shown in Figs. 5 and 6, the incoherent Laves phase was stable in the 2W steel even in the initial stage of annealing, whereas the coherent Laves phase was stable in the 3W steel in the early stage of annealing. These results are consistent with our previous work that the critical W content for the Laves phase formation is nearly 2W and that for the coherent one is about 3W in Fe-Cr-W-C quaternary steels [8]. In the previous study, the volume fractions of both $M_{23}C_6$ carbide and the Laves phase were set to be constants, but these fractional changes were considered in this work. Then it was found that the change of the volume fractions of both $M_{23}C_6$ carbide and the Laves phase did not affect inherently the critical W content to the morphological change from the coherent phase to the incoherent one. This is probably because all calculations in the three cases take account of the energy change with respect to $M_{23}C_6$ carbide and hence the effect of $M_{23}C_6$ carbide on the change of the system free energy is similar in the three cases, so that the position of the cross point of the energy curves (Fig.6) does not change, although each energy value in the three cases will change by the precipitation of $M_{23}C_6$ carbide.

From this works, it is considered that the Laves phase precipitated in steels containing less than 3W does not strengthen directly the long-term creep strength, because the coherent Laves phase changes quickly to the incoherent one in these steels. The analysis of change in the system free energy with annealing time is useful to predict the microstructure evolution in high Cr ferritic steels.

4. SUMMARY

The change in the system free energy associated with the microstructure evolution in high Cr heat resistant ferritic steels was investigated in consideration of volume changes of both $M_{23}C_6$ carbide and the Laves phase. The obtained results are summarized as follows;

(1) The formation of only the incoherent Laves phase was predicted in 2W steel annealed at both 873K and 923K, whereas it was suggested that the coherent Laves phase was able to precipitate in 3W steel in the initial stage of annealing at the two temperatures.

(2) The results in this study were consistent with the previous work in Fe-Cr-C-W quaternary system. It was found that the change of the volume fractions of both $M_{23}C_6$ carbide and the Laves phase did not affect inherently the critical W content to the morphological change of the Laves phase.

(3) The system free energy concept was useful to predict the morphological changes in high Cr heat resistant steels.

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