PHASE DIAGRAMS AND σ- PHASE PRECIPITATION IN SOME STAINLESS STEELS①

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ABSTRACT Phase diagrams of the Fe-Cr-Ni system have been calculated in order to examine the sigma(σ) phase composition range and its stability. Calculation indicates that σ phase starts to precipitate at 977 ℃ and then disappears after the invariant reaction $\gamma + \sigma \rightarrow \alpha_1 + \alpha_2$ occurs at 464 ℃. Here α_1 and α_2 represent Fe-rich and Cr-rich ferrites respectively. Particularly, effect of Cr and Ni contents on the σ precipitation in the 18-8 type stainless steels was formulated by the present calculation. The σ precipitation was also examined in a super duplex stainless steel Fe-25 Cr-7. 2 Ni-3. 6 Mo-0. 25 N(wt. -%), and calculated phase diagram shows that the σ precipitation takes place only when annealing this steel at temperature below 920 ℃. The addition of nitrogen content up to 0. 6 wt. -% can not prevent the σ precipitation in such steel.

Key words: Fe-Cr-Ni phase diagram σ- phase precipitation

1 INTRODUCTION

Most stainless steels are based on the Fe-Cr-Ni system with additions of other alloying elements. A serious problem encountered in practice is the precipitation of the intermetallic σ phase, which can result in a strong deleterious effect on mechanical properties of the steels. A lot of experimental works[1-11] have been carried to investigate the σ phase region and its precipitation in stainless steels. Most of the experimental results have been discussed by Rivlin and Raynor[12] in a comprehensive review on the Cr-Fe-Ni system. Nevertheless, due to the sensitivity of σ formation to the presence of impurities and the sluggishness of equilibria involving σ phase, it is not enough from experiments to know very well the temperature and composition ranges over which σ phase remains stable. On the other hand, thermodynamic calculation can provide detailed information on the phase composition and stability range as long as there is reasonable thermodynamic descriptions of the phases in the system.

Recently, Hillert and Qiu[13] reassessed the Fe-Cr-Ni system by thermodynamic methods, and their calculation also shows good agreement with experimental data regarding the σ phase. Unfortunately, only a few phase diagrams concerning σ phase were presented in their publication. The purpose of the present work is to examine the σ phase stability range through phase diagram calculation using the thermodynamic description presented by Hillert and Qiu[13]. Particular attention will be paid to certain stainless steels including a super duplex stainless steel with small additions of Mo and N.

The phase diagram calculation method applied in this study makes use of thermodynamic models for the molar Gibbs energy of the individual phases in the Fe-Cr-Ni-Mo-N system. The main phase involved here are the σ phase, solid solution phase ferrite $\alpha(bcc)$ and austenite $\gamma(fcc)$, and some nitrides. All of them have been described using thermodynamic models in previous works[13-15], and Gibbs energy for each phase has also been presented on the basis of its model. In this report we shall give a brief discussion of the models for these phases.

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2 THERMODYNAMIC MODELS

The σ phase with tetragonal structure originates from the binary Fe-Cr and Fe-Mo systems, and it exhibits certain range of homogeneity[16, 17]. It is also found that Ni can be dissolved in the σ phase[12]. After taking into account its structure and atom arrangement. Fernandez Guillermet[17] described the σ phase in the Fe-Mo system using a three-sublattice model, i. e. $Fe_8(Fe, Mo)_8Mo_4$, where Fe and Mo atoms on the second sublattice can be substituted for each other. Similarly, the σ phase in the Fe-Cr system was treated as $Fe_8(Cr, Fe)_8Cr_4$ by Andersson and Sundman[16]. The solubility of Ni in the σ phase is then described by allowing Ni atoms enter into the first and second sublattices, as Hillert and Qiu did in the Fe-Cr-Ni system[13] and Frisk in the Fe-Mo-Ni system[15]. Therefore, the σ phase in the Fe-Cr-Mo-Ni system is modelled as $(Fe, Ni)_8(Cr, Fe, Mo, Ni)_8(Cr, Mo)_4$. No nitrogen solubility in the σ phase was considered. Thermodynamic descriptions of the σ phase in the four ternary systems are already evaluated in previous studies[13-15]. These descriptions will be combined for the present calculation.

Since nitrogen is dissolved as an interstitial solute in ferrite α and austenite γ, the solution phases α and γ were treated as interstitial solutions with two sublattices $(Cr, Fe, Mo, Ni)_1(N, Va)_c$, where the metallic atoms (Cr, Fe, Mo, and Ni) were assumed to substitute for each other on the first sublattice, and interstitial nitrogen and vacancies (Va) substitute for each other on the second one. The subscript c represents the number of interstitial sites per metallic atom. According to the atom arrangement it is known that for the *bcc* structure $c = 3$ and for the *fcc* structure $c = 1$. Thermodynamic descriptions of the two phases were taken from ref. [15].

The nitrides and other intermetallic phases formed in the Fe-Cr-Ni-Mo-N system are also dealt with sublattice models in previous evaluations[14, 15], and they will not be discussed further in this report.

3 CALCULATION AND DISCUSSION

3.1 Fe-Cr-Ni *System*

An isothermal section of the Fe-Cr-Ni system was calculated at 1 000 ℃, as given in Fig. 1. It shows there are only two phases (α and γ) at this temperature. Usually, the composition of austenitic stainless steels fall into the γ phase region, whereas duplex stainless steels are located in the two-phase region (α + γ). With decreasing temperature the σ phase will precipitate from austenite or the mixture of austenite and ferrite. This can be seen from the calculated isothermal sections at lower temperatures, as shown in Fig. 2 through Fig. 5. These diagrams indicate the σ phase composition and region. As a summary, we present in Fig. 6 the projection of the γ solvus together with isotherms calculated by Hillert and Qiu[13] where the arrows indicate temperture decreasing. It shows the composition and temperature of γ in equilibrium with σ or α. In Fig. 6 there are two critical points marked with asterisks. The first one represents the start point of the σ precipitation at 977 ℃, and the second one represents the invariant reaction $\gamma + \sigma \rightarrow \alpha_1 + \alpha_2$ at 464 ℃ after which σ will be no longer stable. Here α_1 and α_2 represent Fe-rich and Cr-rich ferrites, respectively. It should be noticed that although the σ single phase region is not very extensive, it can coexist with other phases in a very wide composition region covering most stainless steels. This could have significant implications for the stability of steels annealed at moderate temperatures over long periods.

In order to examine the occurrence of the σ phase with temperature, two vertical sections were calculated for the basic composition of the 18-8 type austenitic stainless steels, as presented in Fig. 7(a) and (b). These two diagrams show effect of Cr and Ni contents on the σ precipitation in such steels. From Fig. 7, it can be seen that σ phase can directly precipitate from austenite in the 18-8 steels during cooling, and then disappear on further cooling.

3.2 Fe-Cr-Ni-Mo-N *System*

Li and co-workers[18] recently investigated the precipitation of the σ phase and its effect on hot ductility in the Fe-25Cr-7.2Ni-3.6Mo-0.25N (in wt.-%) super duplex stainless steel after undergoing thermal treatments at temperatures between 600 and 1 100 ℃. Some of their results are closely related to thermodynamic properties and phase diagram of the steel system, thus provides an important experimental base for examing the phase diagram. On the other hand, the thermodynamic properties of the Fe-Cr-Ni-Mo-N system have been assessed by Frisk[15] using thermodynamic models. Such assessment is based on the evaluations of lower order systems in which relevant experimental information was taken into account, and thus phase diagrams of the Fe-Cr-Ni-Mo-N system can be calculated with

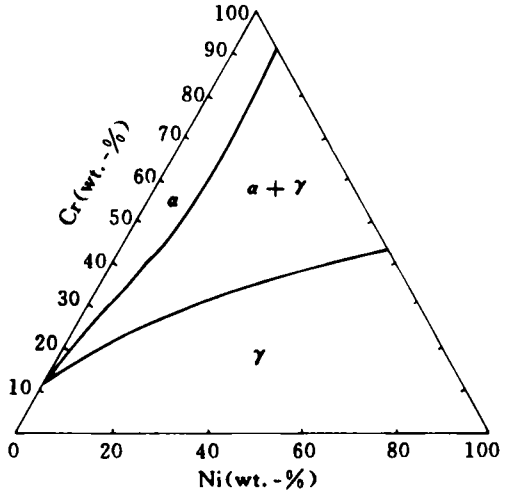

Fig. 1 Calculated isothermal section of the Fe-Cr-Ni system at 1 000 ℃

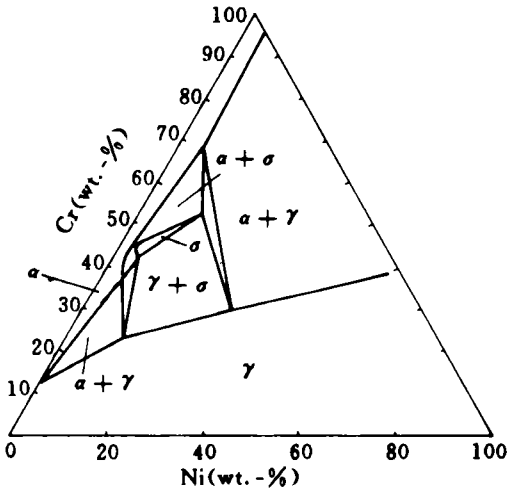

Fig. 2 Calculated isothermal section of the Fe-Cr-Ni system at 900 ℃

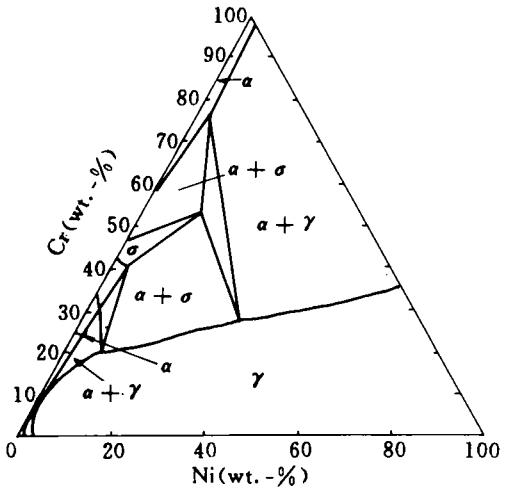

Fig. 3 Calculated isothermal section of the Fe-Cr-Ni system at 800 ℃

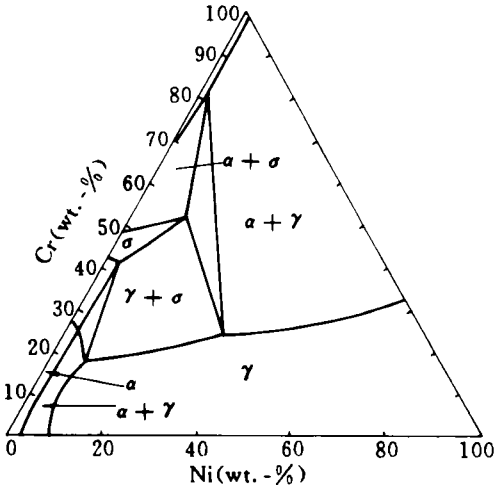

Fig. 4 Calculated isothermal section of the Fe-Cr-Ni system at 700 ℃

certain confidence. Therefore, it is particularly interesting to compare the experimental results with thermodynamic calculation. The steel sample used by Li and co-workers[18] also contains very small amounts of other elements (e.g. Si, Mn, Cu, W) in addition to the main elements, but for simplicity only the main elements will be considered in the present calculation.

A phase diagram was calculated for the Fe-25 Cr-7.2 Ni-3.6 Mo-N alloys in Fig. 8, where the dashed line represents the steel with 0.25 wt.-% N. The diagram shows phase relations and stability range of various phases. It is clear that the steel consists of ferrite α and austenite γ after solution treatment at temper-

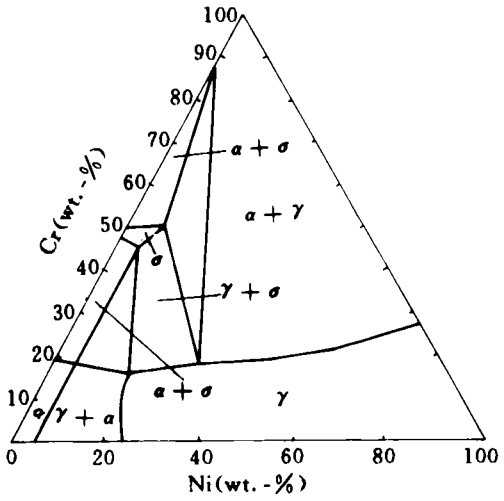

Fig. 5 Calculated isothermal section of the Fe-Cr-Ni system at 550 ℃

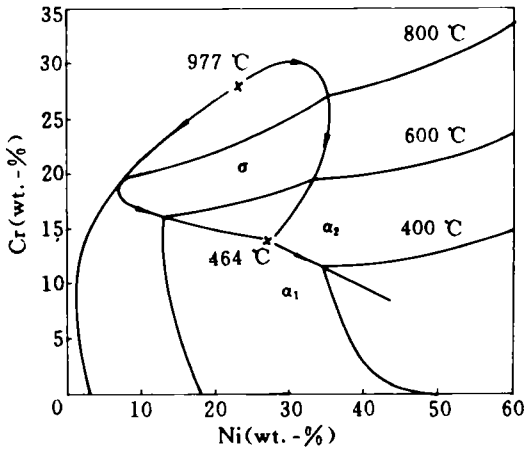

Fig. 6 Projection of the γ solvus in the Fe-Cr-Ni system together with isotherms at 400, 600, and 800 ℃ calculated by Hillert and Qiu[13]

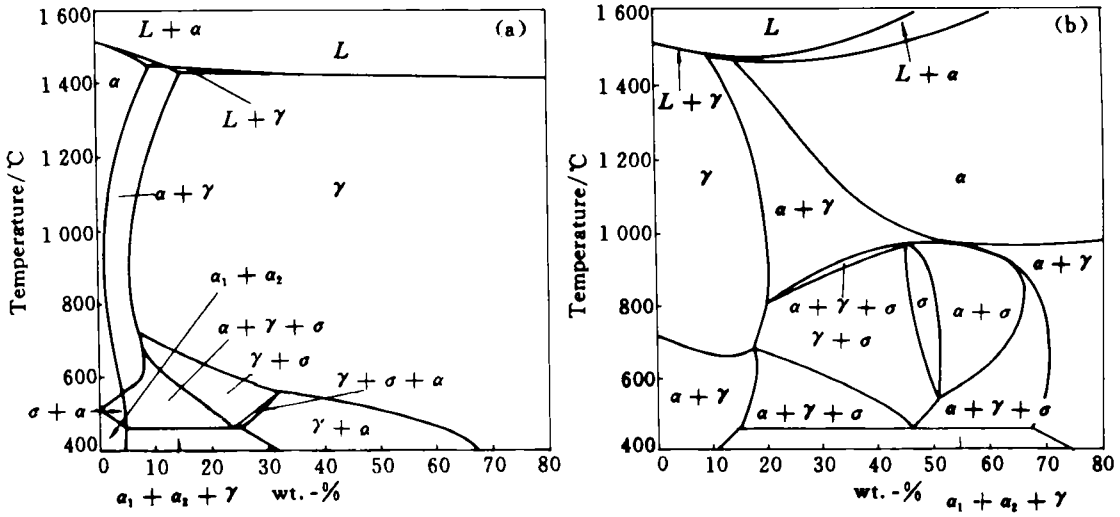

Fig. 7 Vertical sections of the Fe-Cr-Ni system calculated for the 18-8 type stainless steels
(a)—Fe-18Cr-Ni; (b)—Fe-Cr-8Ni

atures above 1 000 ℃. The calculated compositions of σ and γ at 1 100 ℃ are very close to corresponding values determined by energy-dispersive X-ray spectroscopy (EDXS) in ref. [8]. The σ phase can start to precipitate only when annealing the steel at temperatures below 920 ℃. This agrees very well with the experimental observation[18] which led to the conclusion that the effect of σ phase precipitation on the mechanical properties of the steel disappears at 1 000 ℃. At temperatures below 725 ℃ an intermetallic compound λ phase can precipitate from the steel, but its precipitation may not be observed in practice due to kinetic reason. In the calculation the λ phase is approximately treated as stoichiometric compound with the formula $(Cr,Fe)_2Mo$. Besides, there is another intermetallic compound named chi phase in Fig. 8, which can precipitate from austenite at higher nitrogen content. Chi phase is treated with three sublattice model $(Cr,Fe)_{24}(Cr,Mo)_{10}(Cr,Fe,Mo)_{24}$.

Experiment work[19] has shown that the addition of N can prevent the σ precipitation in austenitic stainless steels and this has been illustrated by Qiu[20] through thermodynamic calculation of phase diagrams. However, from Fig. 8 it is noticed that this is not the case in the duplex stainless steels. In other words, the duplex stainless steels are always saturated with σ phase below 900 ℃ and the addition of N up to 0.6 wt.-% can not give rise to preventing σ precipitation.

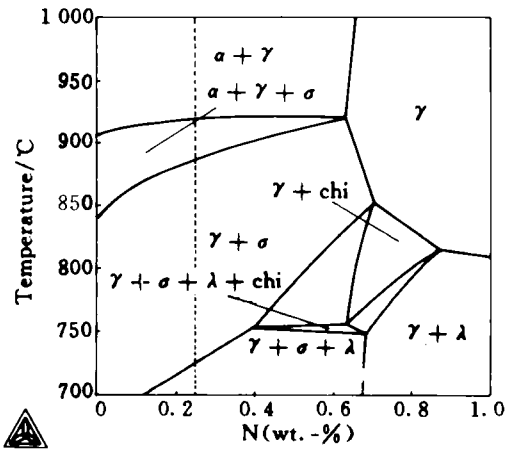

Fig. 8 Vertical section calculated for the Fe-25 Cr-7.2 Ni-3.6 Mo-N alloys, where the dashed line represents the super duplex stainless steel with 0.25 wt.-% N

The calculated Ni and Mo contents in σ phase at 800 ℃ are close to the reported values[18] from chemical analysis, but the calculated Cr content is somewhat higher by 20% than the experiment one. The σ phase fraction was determined to be 30% (in volume) based on X-ray diffraction analysis (XRA) after the sample was annealed at 800 ℃ for 60 min, whereas the calculation gives only 10.6% at the same temperature. These differences may be taken as an indication that the properties of σ phase have not been described very well in the Fe-Cr-Mo-Ni-N system, and further evaluation should be made in the future.

4 SUMMARY AND CONCLUSION

Phase diagrams have been calculated for the σ phase in the Fe-Cr-Ni system using its recent thermodynamic description assessed by Hillert and Qiu[13]. A series of isothermal and vertical sections of the ternary phase diagrams were presented, and they demonstrate the composition and temperature ranges over which σ phase remains stable. According to the calculation, σ phase starts to precipitate at 977 ℃ and finally disappears after the invariant reaction $\gamma + \sigma \rightarrow \alpha_1 + \alpha_2$ occurs at 464 ℃. Particularly, effect of Cr and Ni contents on the σ precipitation in the 18-8 type stainless steels was formulated by the present calculation.

Finally, the σ precipitation was examined in the super duplex stainless steel Fe-25 Cr-7.2 Ni-3.6 Mo-0.25 N. Calculated phase diagram indicates that the addition of nitrogen content up to 0.6 wt.-% can not prevent the σ precipitation in such steel. The σ precipitation starts only when annealing this steel at temperature below 920 ℃ which agrees very well

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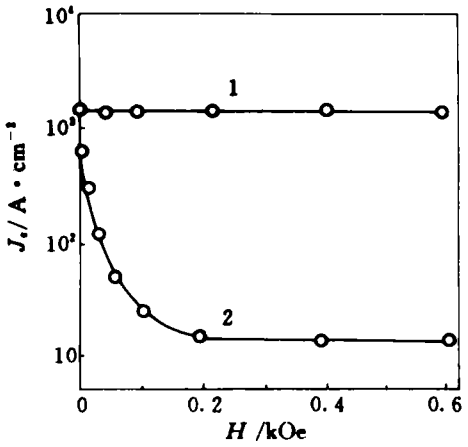

Fig. 5 The dependence of the J_c (77 K) of Y-Ba-Cu-O superconductor on magnetic field

(1)— P_{O_2} -alternatively treated; (2)—sintered

polycrystalline after P_{O_2} -alternative treatment show that the oxyen pressure can be controlled to decrease the temperature of melt-texture growth and improve the properties of $YBa_2Cu_3O_{7-\delta}$ superconductor.

4 CONCLUSION

The melting temperature of $YBa_2Cu_3O_{7-\delta}$ can be decreased by controlling P_{O_2} in the atmosphere. The P_{O_2} -alternative treatment would result in melt- growth of $YBa_2Cu_3O_{7-\delta}$ at a temperature lower than 920 ℃, and improve the field dependence of J_c.

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with experimental observation. However, the calculation shows certain difference with experimental data on the σ phase fraction at 800 ℃.

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