Prediction of σ Phase Formation in Fe–Cr–Ni–Mo–N Alloys

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The formation of σ phase was investigated in Fe–Cr–Ni–Mo–N alloys with high nitrogen content. The amounts of the σ phase are correlated with the calculated δ-Fe values. The Md-PHACOMP (Phase Computation) method, which takes into consideration the effect of nitrogen and carbon content as well as microsegregation at the interdendritic region, can predict the σ precipitations. The numerical methodology for a multi-phase-field model can be also applied to σ phase formation by δ to (γ + σ) transformation.

KEY WORDS: solidification; segregation; phase transformation; phase-field model; stainless steel.

1. Introduction

In harsh corrosive environments where conventional general purpose stainless steels such as SUS304 and SUS316 lack durability, austenitic stainless steels with high molybdenum and nitrogen concentrations are used. However, Fe–Cr–Ni–Mo–N alloys have a problem in that the material quality deteriorates as a result of σ phase formation. Especially in weld application, where the alloy is used with a solidification microstructure as it is, material characteristics such as toughness and corrosion resistance are affected to a large extent by the formation of the σ phase.1–4) However, the amount of the σ phase cannot currently be predicted for Fe–Cr–Ni–Mo–N alloys.

Cieslak et al.5) explained the precipitation of the TCP (Topologically Close Packed) phase in Ni-base alloys during weld solidification by the Md-PHACOMP (Phase Computation) method.6,7) They applied the average Md value to the composition of the interdendritic region after solidification, and proved a correlation between the Md value and TCP phase precipitation. Koseki and Ogawa8) calculated the average Md value from the composition of the interdendritic region with microsegregation taken into consideration, and showed a correlation between the average Md value and the precipitation of intermetallic phases in Cr–Ni–Fe–Mo alloys. However, they stated that the correlation did not hold in a high nitrogen content, which the Md value does not cover.

The phase-field model has been recently developed as a method for simulating interfacial pattern formation in the solidification process.9–12) Moreover, the phase-field model has been extended to multiphase and multicomponent systems.13–17) The multi-phase-field model is a useful tool for microstructure simulation of industrial materials. However, applications for σ phase formation in stainless steels have not been reported yet. We conducted phase-field simulations in Fe–Cr–Ni–Mo–N alloy in order to evaluate the behavior of σ phase formation during solidification and solid-state phase transformation.

In this study, the microstructure and segregation of Fe–Cr–Ni–Mo alloys with high nitrogen content were examined to clarify the influence of the components on σ phase formation, and then the prediction of σ phase formation is discussed.

2. Experimental Procedure

Table 1 shows the compositions of the alloys used in this work. The materials are based on Fe–25%Cr–Ni–2%Mo alloy with the concentrations of the austenite stabilizing elements (Ni, Mn and N) varied. All the test samples are cast ingots produced in a small vacuum induction furnace. The microstructures of the specimens were observed by optical microscope after electrolytical etching in 10% oxalic acid. The samples were then subjected to electrolytic etching in a 10% KOH aqueous solution to measure the amount of the σ phase using an image analyzer. The No. 1 sample, in which almost no σ phase was observed, was further ana-

Table 1. Chemical composition of the materials used.

| No. | C  | Si  | Mn  | P  | S  | Ni  | Cr  | Mo  | Cu  | N  |
|-----|----|-----|-----|----|----|-----|-----|-----|-----|----|
| 1   | 0.024 | 0.49 | 0.49 | 0.021 | 0.0033 | 16.34 | 25.81 | 2.11 | 0.31 | 0.324 |
| 2   | 0.025 | 0.50 | 3.00 | 0.019 | 0.0005 | 14.98 | 25.22 | 2.10 | 0.32 | 0.312 |
| 3   | 0.019 | 0.49 | 0.49 | 0.022 | 0.0004 | 17.81 | 25.87 | 2.52 | 0.31 | 0.245 |
| 4   | 0.021 | 0.26 | 0.49 | 0.022 | 0.0003 | 18.91 | 25.28 | 2.78 | 0.31 | 0.184 |
| 5   | 0.019 | 0.49 | 2.99 | 0.019 | 0.0006 | 18.40 | 25.29 | 2.52 | 0.32 | 0.235 |

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analyzed by electron probe micro-analyzer (EPMA) to measure the microsegregation of each element. The measurement was conducted at the 20-mm surface layer of the cast samples, as this layer was comparatively rough in microstructure, and suitable for accurate analysis of the solute concentrations at the interdendritic region.

3. Results and Discussion

3.1. Microstructure and \( \sigma \) Phase Formation

The primary \( \gamma \)-austenite dendritic structures were observed in all the samples. Although formation of the \( \sigma \) phase was clearly observed in the interdendritic regions of samples Nos. 2 through 5, the \( \sigma \) phase observed in sample No. 1 was extremely limited. Figure 1 shows the microstructures in the 20-mm surface layer of samples No. 1 and No. 5. The cooling rates at the 2-mm, 10-mm, and 20-mm surface layers, estimated on the basis of the equation proposed by Suzuki and Nagaoka\(^{18}\) for type 310 stainless steel with a primary \( \gamma \) solidification mode, were approximately 40 K/s, 2 K/s, and 0.7 K/s, respectively. The relation between the secondary dendrite arm spacing (\( \lambda \)) and the cooling rate (\( \varepsilon \)) is expressed by Eq. (1).

\[
\lambda = 44\varepsilon^{-0.38}
\]

The solidification behavior of the alloy system related to this work corresponds to the austenitic-ferritic (AF) solidification mode of austenitic stainless steels. In other words, as the concentration levels of Cr and Mo increased in the primary \( \gamma \) solidification, an \( \delta \) phase forms during the terminal stage of solidification at the interdendritic region, resulting in a dual-phase structure of \( \gamma \) and \( \delta \). It is known that the \( \delta \) phase transforms into an intermetallic phase such as \( \sigma \) phase during cooling after solidification, especially in the case of high-Mo content alloys.\(^{8,19}\) Magnetic ferrite scope examination did not detect \( \delta \)-Fe; thus the \( \delta \) phase can be assumed to have transformed into \( \sigma \) phase.

Figure 2 shows the relation between the precipitation of the \( \sigma \) phase in the 2-mm, 10-mm, and 20-mm surface layers of the cast samples, and the \( \delta \)-Fe values calculated by Eq. (2). The area fractions of the \( \sigma \) phase increase along with the increase in the calculated \( \delta \)-Fe values.\(^{20}\)

\[
\delta \text{-Fe}=2.9\times([Cr]+[Mo]+0.3[Si])-2.6\times([Ni]+0.3[Mn])
+0.25[Cu]+35[C]+20[N])-18
\]

The amount of the \( \sigma \) phase in the 2-mm surface layer of the cast sample is smaller than those at deeper levels, which suggests a dependency on the cooling rate. It is known that the amount of \( \delta \)-Fe is reduced as a result of an increase in the solidification cooling rate in electron beam welding of Fe–Cr–Ni alloys with an AF solidification mode.\(^{21}\) When the cooling rate is high, the microstructure is fine and the microsegregation of Cr and Mo decreases as the result of shorter diffusion length, and the amount of \( \delta \)-Fe, which transforms to \( \sigma \) phase, is also reduced. The amounts of the \( \sigma \) phase are correlated with the calculated \( \delta \)-Fe values. The calculated \( \delta \)-Fe value can be usually applied to the primary \( \delta \) solidification mode. However, this value was used as a parameter for secondary \( \delta \) precipitation in this work. Thus, another quantitative method for the prediction of \( \sigma \) phase formation may be required.

3.2. Md-PHACOMP Method

Md-PHACOMP is a method to predict the precipitation of detrimental TCP phases, such as the \( \sigma \) phase, in heat-resistant alloys. Morinaga \textit{et al.}\(^{5,7,22}\) proposed the Md-PHACOMP method, which uses the d-orbital energy level “Md” for the evaluation of phase stability. The Md values of the
The components listed in Table 2 are determined by the DV-Xα (Discrete Variational) cluster method for γ-Fe. The Md values of C and N determined by phase diagram estimation for δ+γ/γ boundary was used in this work. The average Md value of the alloy system is defined by Eq. (3).

$$\text{Md} = \sum X_i (\text{Md})_i$$ .............................(3)

where $X_i$ is the atomic fraction of each element, and $(\text{Md})_i$ is the Md value of the element $i$. The precipitation of the $\sigma$ phase can be predicted by the critical Md value, which is considered to be around 0.92 in the case of the $\sigma$ phase of Cr–Ni–Fe–Mo alloys. This study, which focuses on Fe–Cr–Ni–Mo–N alloys, also evaluated the critical Md value using the concentration of the interdendritic region.

Figure 3 shows the microsegregation of Mo in sample No. 1 at the 20-mm surface layer. From the microsegregation measurement shown in this figure, the composition of the interdendritic region (Cb) in the $\gamma$ phase was determined, and the segregation ratio was defined on the basis of the ratio of Cb to the initial composition (Co). Table 3 shows the microsegregation ratios of each element. The segregation ratios of Si, Mn and Mo are large, while that of N is small as the diffusion rate becomes large.

Figure 4 shows the relation between the amounts of the $\sigma$ phase and the average Md values. The figure shows a close correlation between them; the critical Md value stands at 0.92. The segregation ratio of carbon was assumed to be equal to that of nitrogen. Ezaki et al. proposed the relation between the critical value of average Md and temperature for $\sigma$ phase formation in Fe–Cr–Ni–Mo–N alloys as shown in Eq. (4). The average Md of 0.92 corresponds to $\sigma$ phase formation at 1376 K.

$$\text{Md}_c = 7 \times 6.25 \times 10^{-5} + 0.834$$ .............................(4)

It is believed that the prediction of critical phase formation in Fe–Cr–Ni–Mo–N alloys is possible by using the Md-PHACOMP method that takes the effect of nitrogen into consideration.

### 3.3. Multi-phase-field Model

Calculation of a multi-phase-field model in Fe–Cr–Ni–Mo–N alloys was performed in association with the CALPHAD software package, Thermo-Calc, in conjunction with the Fe-DATA ver.6 database. The details of multi-phase-field model are described in Refs. 26), 27). Phase-field equations and diffusion equations were solved by the finite difference method using MICRESS software. The data used in the simulation are listed in Table 4. The calculation were performed on a square measuring $2.5 \times 10^{-3}$ mm$^2$ using 200×200 grid points. The numerical interface thickness was set to 4 grids and the cooling rate was set to 2 K/s, corresponding to a 10-mm surface layer.

The numerical procedure for nucleation model is briefly explained as follows: At first, the seeds of $\delta$ and $\sigma$, which

| Table 2. Md values for the elements in Fe–Ni alloy with austenite structure. |
|------------------|---|---|---|---|---|---|---|---|
|                | C  | Si | Mn | Ni | Cr | Mo | Cu | N  | Fe |
|                | −0.230 | 1.900 | 0.957 | 0.717 | 1.142 | 1.550 | 0.615 | −0.400 | 0.858 |

| Table 3. Measured segregation ratio in alloy No. 1. |
|-----------|---|---|---|---|---|
|          | Si | Mn | Ni | Cr | Mo |
|          | 1.20 | 1.18 | 1.01 | 1.05 | 1.24 |
|          | 1.14 | 1.06 |

| Table 4. Data used in the simulation. |
|------------------|---|---|---|---|---|---|---|
| Parameter | Value | Ref. |
| L−γ | $3 \times 10^{-3}$ J/cm$^2$ | 28) |
| L−δ | $2 \times 10^{-3}$ J/cm$^2$ | 28) |
| γ−γ | $4 \times 10^{-3}$ J/cm$^2$ | 27) |
| γ−δ | $7 \times 10^{-3}$ J/cm$^2$ | 29) |
| δ−δ | $1 \times 10^{-4}$ J/cm$^2$ | 27) |
| γ−σ | $5 \times 10^{-2}$ cm$^3$/J/s | 27) |
| δ−σ | $3 \times 10^{-2}$ cm$^3$/J/s | 27) |
| γ−σ | $1 \times 10^{-6}$ cm$^3$/J/s | 27) |
| δ−σ | $3 \times 10^{-6}$ cm$^3$/J/s | 27) |

Fig. 3. Microsegregation of Mo in No. 1 alloy at the 20-mm surface layer.

Fig. 4. Relationship between the amounts of $\sigma$ phase and the average Md values taking the effect of N into consideration.
have capability to nucleate, are virtually distributed on the liquid/γ interface and in the δ phase region, respectively, according to the parameters defined in Table 5. At this stage, no nucleation occurs. Then, during the cooling process, at intervals of the time as shown in Table 5, it is checked whether each virtually distributed seed can nucleate by comparing the temperature at its position with the amount of undercooling estimated by classical nucleation theory. Finally, the newly formed δ and σ region are taken into account in the phase field calculation procedures.

The simulation results for Fe–25.3%Cr–16.4%Ni–2.5%Mo–0.24%N alloy are presented in Figs. 5 through 7. This composition is related to alloy No. 1 in Table 1. The effects of C, Si, Mn and Cu were added to Cr and Ni equivalent values by Eq. (1). As the temperature decreases under the liquidus, the primary γ-dendrite grows from the melt (Fig. 5(a)). The δ-Fe nucleates at the interdendritic region during the final stage of solidification, followed by a growth of the δ phase at the liquid/γ interface (Fig. 5(b)). As the temperature falls below 1 350 K, the σ phase nucleates at the γ/δ interface, and δ-to-σ phase transformation proceeds (Fig. 5(c)). “Boundary” in this figure means the mixing region of two or three phases. Figure 8 shows the change in the molar fraction of phases. After solidification, the simulation results for Fe–25.3%Cr–16.4%Ni–2.5%Mo–0.24%N alloy are presented in Figs. 5 through 7. This composition is related to alloy No. 1 in Table 1. The effects of C, Si, Mn and Cu were added to Cr and Ni equivalent values by Eq. (1). As the temperature decreases under the liquidus, the primary γ-dendrite grows from the melt (Fig. 5(a)). The δ-Fe nucleates at the interdendritic region during the final stage of solidification, followed by a growth of the δ phase at the liquid/γ interface (Fig. 5(b)). As the temperature falls below 1 350 K, the σ phase nucleates at the γ/δ interface, and δ-to-σ phase transformation proceeds (Fig. 5(c)). “Boundary” in this figure means the mixing region of two or three phases. Figure 8 shows the change in the molar fraction of phases. After solidification,
The amount of the molar fraction of the s phase at 1200 K was about 0.030. Grid points under the condition of 20 K/s cooling. The possible by using the average Md value, Md-PHACOMP
dendritic region during primary solidification. The calculated δ-Fe values proved to correspond with the γ phase formation in Fe–Cr–Ni–Mo–N alloys.

Another calculation in the same composition was carried out on a square measuring 6.25 × 10^-4 mm^2 using 200 × 200 grid points under the condition of 20 K/s cooling. The molar fraction of the s phase at 1200 K was about 0.030. The amount of the σ phase was reduced by an increase in the cooling rate (i.e., fine microstructure) as compared with Fig. 8. The same tendency as with Fig. 2 was obtained by the multi-phase-field simulations. It is thought that further adjustment of calculating conditions and the thermodynamic database for a multi-component alloy system permit a more quantitative discussion on the microsegregation analysis and the σ phase formation.

4. Conclusion

The authors studied the prediction of σ phase formation in Fe–Cr–Ni–Mo–N alloys. σ precipitation is considered as a phase transformation of the δ-Fe formed at the interdendritic region during primary γ solidification. The calculated δ-Fe values proved to correspond with the σ precipitations. The prediction of σ phase formation in these alloys was possible by using the average Md value, Md-PHACOMP method, with solute concentration in the interdendritic region taken into consideration. The critical Md value for σ phase formation stands at 0.92. Moreover, the calculation of a multi-phase-field model in Fe–Cr–Ni–Mo–N alloys was performed in association with the calculation of phase diagram. It will be a useful tool in analyzing the microstructure and σ phase formation in Fe–Cr–Ni–Mo–N alloys.

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