Modelling of Sigma Phase Dissolution by Solution Treatment in Super Duplex Stainless Steel

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The modelling of the dissolution behavior of the sigma phase by solution treatment in duplex stainless steel was investigated to clarify the condition of heating temperature and time necessary to finish dissolving the harmful phase into the matrix. To determine that dissolution condition of the sigma phase experimentally, the heat treatment test at various temperatures and durations was conducted after pre-aging to form an amount of sigma phase using the super duplex stainless steels with 25%Cr-6/7%Ni-3/4%Mo-0/2%W-0.3%N. Using the experimental results, the model which considering the effect of initial situation of sigma phase on the condition of solution treatment to achieve the dissolution condition, was suggested. The solution treatment at higher temperature and for longer heating time was necessary to dissolve the retained sigma phase in the initial microstructure consisting of two phases of austenite and sigma without ferrite compared to that with ferrite phase. The critical condition by the experimental results was described as a linear function of the inverse of solution temperature and the logarithm of holding time. The effect of the chemical composition of the steel on that critical condition was reflected in a parameter in that function proposed.

KEY WORDS: duplex stainless steel; sigma phase; modelling; solution treatment; dissolution of sigma phase; kinetics.

1. Introduction

Duplex stainless steels are widely applied to the various structures because they exhibit high cost-effectiveness. These steels have the potential to obtain a high corrosion resistance, high strength and high toughness economically because they have lower nickel content in comparison with that in austenitic stainless steels. In later years, super duplex stainless steels, improved the corrosion resistance by increasing the amount of chromium, molybdenum, tungsten and nitrogen, have been developed.1–10) However, the increase in the amount of these elements promotes the harmful intermetallic such as sigma phase. Therefore the prevention of this phase formation is an important subject in the welding, fabrication, and manufacturing process for practical use.

Many research works11–28) have focused on sigma phase precipitation in duplex stainless steel applicable to the heat treatment, hot work or welding process. Although the sigma phase is extremely harmful for the practical performance of duplex stainless, that phase can be dissolved into the matrix by the proper solution treatment even though the precipitation occurs by manufacturing process or welding process. The critical condition of heating temperature and time necessary to finish dissolving the phase depends on the condition of initial sigma phase precipitation before solution treatment. However, the effect of that initial condition has not always been clarified systematically.

The aim of this work is to investigate the effect of initial situation of sigma phase before solution treatment on the dissolution condition of retained sigma phase into matrix using the specimens with various pre-aging conditions. On the basis of those experimental results, a model was proposed, which represents the critical condition of the heating temperature and time necessary to finish dissolving the sigma phase.

2. Experimental

Duplex stainless steels consisting of 25%Cr-Ni-Mo-W-0.3%N are shown in Table 1 including 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel provided as UNS S39274 used, which were melt with a laboratory electric furnace. Those steels were worked by using the 15 mm thick plates manufacturing by hot forging and hot rolling followed by solu-
tion treatment. Solution treatment is performed at 1323 K for 1,800 s and quenched by water. Those plates were machined to the specimens of 11 × 11 × 60 mm size and the specimens were pre-aged at 1,173 K for 1 ks or 360 ks. The specimens pre-aged in the two conditions were solution treated at various constant temperatures at 1,350 to 1,573 K during various time followed by quenching to room temperature with helium gas shower. After the heat treatment the specimens were polished in the cross section and electrochemically etched in 10% oxalic acid and 10N KOH aqueous solution in cross section for microstructure observation. Employing those etched specimens, the dissolution of sigma phase in to the matrix was detected with the microscope of 500 magnification. Precipitates were observed and analyzed with transmission electron microscope (TEM) using extraction replica.

3. Experimental Result

3.1. Initial Situation of Sigma Phase Precipitation after Pre-aging

The precipitation properties of sigma phase during the pre-aging process were investigated to clarify the initial situation of sigma phase precipitation before the solution treatment. Two pre-aging conditions were performed. One is at 1,173 K for 1 ks defined as the pre-aging condition A and the other is at 1,173 K for 360 ks as the pre-aging condition B. The precipitates were confirmed as sigma phase as shown in Fig. 1 as an example in the 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel pre-aged at 1,173 K for 1000 s.

Figures 4 and 5 show the microstructure change during the solution treatment in the 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel with the pre-aging condition A and B. The initial microstructure in the pre-aging condition A consisted of three phases of ferrite, austenite and sigma phase. After the solution treatment at 1,343 K for 60 s, the sigma phase still retained though it was partially dissolved and after solution treatment for 240 s, the sigma phase was completely dissolved into the matrix. From the result, it was clarified that the time to dissolve the sigma phase completely could be between 60 s and 240 s. The initial microstructure in the pre-aging condition B consisted of two phases of austenite and sigma phase without ferrite, which means the equilibrium microstructure after all of the ferrite phase was completely transformed into sigma and austenite phase. After solution

| Table 1. Chemical compositions of steels employed (mass%). |
|-----------------|------|------|------|------|------|------|------|------|
|                | C    | Si   | Mn   | Ni   | Cr   | Mo   | W    | N    | α (%) | T_{eq} (K) |
| W1             | 0.020| 0.30 | 0.51 | 7.0  | 25.2 | 2.97 | 2.16 | 0.31 | 44    | 1339      |
| WN1            | 0.021| 0.30 | 0.50 | 5.9  | 24.9 | 2.93 | 2.15 | 0.28 | 52    | 1320      |
| M3             | 0.018| 0.31 | 0.51 | 7.0  | 25.1 | 3.91 | –    | 0.29 | 52    | 1314      |

\[ X = \frac{V(t)}{V_{eq}} = 1 - \exp\left[ -(k_{p}t)^{m}\right] \quad (1) \]

, where X is the ratio of sigma phase fraction at a time in the equilibrium condition at 1,173 K and k_{p} is the growth rate constant already obtained for the each steel in the previous work.\(^{24}\) The growth of sigma phase was subject to the above equation with the value m of 2.5 within the heating time of 600 s. Using that equation, the growth properties during heating were calculated. The result is shown in Fig. 3. Precipitation was on the way to the equilibrium stage in the pre-aging condition A and precipitation reached the equilibrium stage in the pre-aging condition B. The value m of 2.5 means that the nucleation occurs with constant rate. In the pre-aging condition A in the aging time excess 600 s, therefore the growth deviated from the equation.

Fig. 1. TEM micrograph of precipitates identified as sigma phase in 25Cr-7Ni-3Mo-2W-0.3N steel pre-aged at 1,173 K for 1,000 s.

Fig. 2. Growth property of sigma phase in 25Cr-Ni-Mo-W-0.3N steel during pre-aging at 1,173 K.
treatment at $1373\,\text{K}$ for 3 ks, the sigma phase was retained in spite of the much longer heating time than the time to achieve the complete dissolution of the sigma phase in the pre-aging condition A. In that microstructure, the sigma phase surrounded by just austenite phase was observed. After the solution treatment for 10 ks, the sigma phase was completely dissolved into matrix.

The complete dissolution condition of the sigma phase was investigated using the specimens which are solution treated in various temperature and heating time. The result in the pre-aging condition A is shown in Fig. 6. After solution treatment at $1333\,\text{K}$, all the specimens had the retained sigma phase. The equilibrium solvus temperature of the sigma phase obtained using thermodynamic data base\(^{30}\) was approximately $1340\,\text{K}$, therefore it was considered that the sigma phase could retain by the solution treatment at $1333\,\text{K}$ even for the longer heating time. From those experimental results, it was clarified that the heating time excess 100 s at $1343\,\text{K}$ and 60 s at $1353\,\text{K}$ respectively are necessary for the complete dissolution of the sigma phase. The result in the pre-aging condition B is shown in Fig. 7. After the solution treatment even at the higher temperature of $1373\,\text{K}$ for the longer time of 3 ks, the retained sigma phase was not dissolved. However, that retained sigma phase was completely dissolved into the matrix after the solution treatment for 10 ks at $1373\,\text{K}$ or for 500 s at $1573\,\text{K}$. The solution treatment at the higher temperature and for the longer heating time was necessary for the complete dissolution of the retained sigma phase formed in the pre-aging condition B compared with that formed in the pre-aging condition A. In the microstructure consisting of three phases of ferrite, austenite and sigma phase in the pre-aging condition A, the dissolution of the sigma phase is promoted by the diffusion.

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**Fig. 3.** Growth of sigma phase in $25\text{Cr}-3\text{Ni}-2\text{W}-0.3\text{N}$ steel during pre-aging at $173\,\text{K}$.

**Fig. 4.** Example of dissolving process of sigma phase at $1343\,\text{K}$ in $25\text{Cr}-7\text{Ni}-3\text{Mo}-2\text{W}-0.3\text{N}$ steel pre-aged at $173\,\text{K}$ for 1 kss (Pre-aging condition A). (Online version in color.)

**Fig. 5.** Example of dissolving process of sigma phase at $1373\,\text{K}$ in $25\text{Cr}-7\text{Ni}-3\text{Mo}-2\text{W}-0.3\text{N}$ steel pre-aged at $173\,\text{K}$ for 360 ks (Pre-aging condition B). (Online version in color.)
of Cr atom in ferrite phase. However, there was no ferrite phase in the microstructure in the pre-aging condition B, which implies that the dissolution of the sigma phase is promoted by the diffusion in austenite phases which has relatively much smaller diffusion rate. For example, the diffusion coefficients of Cr atom in ferrite and austenite phase at 1373 K are $1.9 \times 10^{-13}$ and $1.5 \times 10^{-15}$ m$^2$/s, respectively. This is considered to be a reason of the large difference of the dissolution condition between the two pre-aging conditions.

The critical conditions for the complete dissolution of the sigma phase was drawn as solid line in Figs. 6 and 7, which are corresponding to the following Eqs. (2) and (3), respectively.

$$\frac{1}{T} = 8.01 \times 10^{-5} \cdot \log \left( \frac{t_d}{3.23 \times 10^{-8}} \right)$$

$$\frac{1}{T} = 7.25 \times 10^{-5} \cdot \log \left( \frac{t_d}{4.93 \times 10^{-7}} \right)$$

As the results, it was confirmed that the critical condition of the sigma phase dissolution is described as the above linear function of the inverse of temperature and the logarithm of time where the constant values are determined from the experimental data of solution treatment at higher temperatures excess the equilibrium solvus temperature of the sigma phase in that steel.

### 3.3. Sigma Phase Dissolution in Steels Consisting of Various Chemical Composition

In the steels consisting of various chemical composition, the dissolution behavior was investigated by the solution treatment at various temperatures for the constant heating time of 100 s. The result is shown in Fig. 8. In the steels tested, the retained sigma phase formed in the pre-aging condition A was completely dissolved into the matrix by the solution treatment at the higher temperatures than the equilibrium solvus temperatures of the sigma phase in each steel.

### 4. Discussion

#### 4.1. Model of Sigma Phase Dissolution by Solution Treatment

Generally, the amount of reduction of the radius and the volume of a spheroidal particle at a time $t$ during solution treatment are described as $(2D\omega t)^{1/2}$ and as $4\pi/3 (2D\omega t)^{3/2}$ in the diffusion control condition, where $D$ is a diffusion coefficient and $\omega$ is the supersaturation. The parameter of $\omega$ is defined as $X_1 - X_0 - X$ where $X_1$, $X_0$, and $X$ are concentrations of Cr at phase interface, in matrix and in sigma phase, respectively as shown in Fig. 9. When the value of $(2D\omega t)^{1/2}$ reaches the value equal to the initial radius of precipitates, that particle finishes dissolving into the matrix by solution treatment. In that model in the pre-aging condition A, the ferrite phase is considered as the matrix phase because the Cr diffusion in the ferrite phase dominates the critical condition of dissolution of sigma phase. On contrary in the pre-aging condition B, the austenite phase is always considered as the matrix phase. Because the critical condition of the complete dissolution of sigma phase is always determined by the sigma phase surrounded just by the austenite phase even when the ferrite phase forms in the immediate stage as an example shown in Fig. 5.

Actually, there are dispersed a large number of sigma phase particles in the pre-aged microstructure. It is consid-
The critical condition of the sigma phase dissolution was considered to correspond to the dissolution of the maximum size of sigma phase means that it is completely dissolved into matrix. The size of sigma phase can be according to some statistic distribution, but it is not easy to specify that maximum size. In this work using precipitation model of sigma phase in the pre-aging process shown as Eq. (1), the initial size of sigma phase was investigated. Generally, in the pre-aged microstructure, much number of sigma phase with each radius of \( r_{oi} \) is considered to distribute in a volume of \( V_0 \). Statistically that distribution is considered as the sigma phase with an average radius of \( r_{om} \) exists in a density of \( N_{pin} \). The both cases shall be equivalent, therefore the volume fraction of sigma phase corresponding to \( 4\pi / 3 \sum r_{oi}^3 / V_0 \) is considered to be equal to that of \( 4\pi / 3 \cdot N_{pin} r_{om}^3 \). Hence, the following equation is obtained.

\[
N_{pin} r_{om}^3 = \frac{\sum r_{oi}^3}{V_0} \tag{4}
\]

The average radius of sigma phase \( r_{om} \) in a time of \( t \) is describes as \( \sqrt{\frac{r_{om}^2}{2D_0 \tau}} \), so that

\[
V(t) / V_0 = N_{pin} \cdot 4\pi / 3 \cdot \left[ r_{om}^3 - 2D_0 \omega t \right]^{3/2} \tag{5}
\]

where \( V(t) \) is total volume of sigma phase equal to \( 4\pi / 3 \sum r_{oi}^3 \).

The critical condition of the sigma phase dissolution corresponds to the case with the right side of that equation equal to 0. Therefore, the solution treatment time \( \tau_0 \) for finishing to dissolve the sigma phase with the initial radius of \( r_{om} \) into the matrix, is described as the following,

\[
r_{om}^3 = 2D_0 \omega \tau_0 \tag{6}
\]

From Eq. (6)

\[
\tau_0 = \frac{r_{om}^2}{2D_0 \omega} / \left( D_0 \exp(-Q / RT) \right) \tag{7}
\]

where \( Q \) and \( D_0 \) are an activation energy and a temperature independent constant term in the diffusion coefficient of Cr respectively in the description of \( D = D_0 \exp(-Q / RT) \), and \( R \) is gas constant. Rearranging the above equation, the following linear function of the inverse of temperature and the logarithm of time to finish to dissolve the sigma phase is obtained.

\[
1 / T = 2.303R / Q \cdot \log \left( \frac{\tau_0}{ \tau_0} \right) \tag{8}
\]

where \( \tau_0 \) is \( r_{om}^3 / (2D_0 \omega) \), which is non dimensional constant.

The inclination of this linear relation is the constant value of 2.303R/Q. The values of inclination obtained as Eqs. (2) and (3) from the data in Figs. 6 and 7 were approximately matched the values of 2.303R/Q for ferrite and austenite phase, respectively. The value of \( 1 / \tau_0 \) corresponds to the constants obtained experimentally as a coefficient of \( t \) in Eqs. (2) and (3). From the above results, the critical condition of the complete dissolution of the retained sigma phase is determined by Eq. (8), and that equation is uniquely determined by the value of parameter of \( \tau_0 \) equal to \( \tau_{om}^3 / (2D_0 \omega) \). Then, the effect of chemical composition of steels is included in the term of \( \omega \).

### 4.2. Consideration of Critical Condition

It was confirmed that the experimental results of the critical condition of sigma phase complete dissolution were described by Eq. (8) with \( \tau_0 \) as a fitting parameter. Therefore, that dissolution phenomena was clarified to be controlled by the Cr atom diffusion. The initial condition of sigma phase precipitation is considered to be reflected to the parameter of \( \tau_0 \). In the following the relation between the parameter of \( \tau_0 \) and the initial condition of sigma phase, that precipitation behavior was considered.

At the initial stage of solution treatment \( t = 0 \), the following is obtained from the above Eq. (5).

\[
\frac{V(0)}{V_0} = N_{pin} \cdot 4\pi / 3 \cdot \tau_{om}^3 \tag{9}
\]

When the value of sigma phase fraction of \( V(0)/V_0 \) and the value of \( r_{om} \) are known, the value of \( N_{pin} \) is determined from the above equation. Assuming the number density of nucleation site of sigma phase follows the Boltzmann’s distribution, which is described as the following,

\[
N_{pin} = N_\sigma \cdot \exp \left[ -\Theta \left( T_{eq} / \Delta T \right)^2 / RT \right] \tag{10}
\]

where \( \Delta T = T_{eq} - T \) and \( N_\sigma \) and \( \Theta \) are the number of nucleation site in a unit volume and the parameter regarding the dependence of temperature on nucleation, respectively reported in the previous work. From Eqs. (9) and (10), the following is obtained.

\[
\tau_{om}^3 = 3 / 4 \cdot \pi \cdot \frac{V(0)}{V_0} / N_{pin} \tag{11}
\]

When the nucleation site is the vertex of grain boundary in the grain with the size of \( R_G \), the number of nucleation site in a unit volume \( N_\sigma \) is obtained as the following.

\[
N_\sigma = 12 / R_G^3 \tag{12}
\]

The value of \( \omega \) in various steels was calculated as shown in Fig. 10 according to the above definition using thermodynamic data base. In the calculation, the equilibrium Cr contents in ferrite and austenite phase and metastable equilibrium Cr content in sigma phase from thermodynamic data base were applied to the values of \( X^t \), \( X^M \) and, \( X^\sigma \), respectively. The value of \( \omega \) in the vicinity of 1 400 K in the 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel was approximately 1.5. The critical condition of the sigma phase dissolution was obtained as experimental result with \( \tau_0 \) of 3.23 × 10^{-8} in that steel in the pre-aging condition A applying that value of \( \omega \) as 1.5. From that value of \( \tau_0 \), the initial size of \( r_{om} \) is calculated as 4.8 um applying the values of \( D_0 \) and \( \omega \) to Eq. (11).
In case of the pre-aging condition A in 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel, the initial fraction of sigma phase of $V(0)/V_0$ and size $r_{0m}$ were 0.22 and 4.8 $\mu$m, respectively. Therefore, the density of sigma phase of $N_{pin}$ is $4.8 \times 10^{14}$ $m^{-3}$ referring Eq. (9). The density of $4.8 \times 10^{14}$ $m^{-3}$ corresponds to the grain size of $R_G$ of 19 $\mu$m referring Eqs. (10) and (12). Significant deviations for that value of $R_G$ are not observed comparing with the actual microstructure, therefore that evaluation regarding the size of initial is considered to be valid. Next, in the case of the pre-aging condition B in 25%Cr-7%Ni-3%Mo-2%W-0.3%N steel, the initial fraction of sigma phase of $V(0)/V_0$ and size $r_{0m}$ were 0.42 and 5.0 $\mu$m, respectively in the same way to the pre-aging condition A. Consequently, the density of sigma phase of $N_{pin}$ corresponds to $8.3 \times 10^{14}$ $m^{-3}$ referring Eq. (9). That value of the density obtained corresponds to the grain size of $R_G$ of 16 $\mu$m referring Eqs. (10) and (12). That value also has not so large deviation from the actual microstructure, therefore that evaluation regarding the size of initial is considered to be valid.

In conclusion, applying the value of $r_{0m}$ obtained with the sigma phase fraction of $V(0)/V_0$, $N_{pin}$ was calculated as shown in the above, and the value of $\omega$ from thermodynamic data, the dominant value of $\tau_0$ to determine the critical condition of the sigma phase dissolution can be assumed without the experiment of solution treatment test.

### 4.3. Applicability of Critical Condition of Sigma Phase Dissolution

The applicability of critical condition of the sigma phase dissolution for the steels consisting of other chemical compositions was considered. When the initial fraction of sigma phase $V(0)/V_0$ is known, the values of $r_{0m}$ is calculated using Eq. (11) on the basis of the above manner, and then the value of $\tau_0$ is calculated. The results in the 25%Cr-6%Ni-3%Mo-2%W-0.3%N and 25%Cr-7%Ni-4%Mo-0.3%N steels are shown in Table 2. The parameters necessary such as $V(0)/V_0$ and $\omega$ in those steels have been obtained in the previous work and in Fig. 10, respectively. The results of critical condition using those values of $\tau_0$ were shown as a solid line in Figs. 11 and 12, respectively with the experimental data. The results of critical condition calculated was

<table>
<thead>
<tr>
<th>Steel</th>
<th>$T_{eq}$ (K)</th>
<th>$\varphi$ (J/mol)</th>
<th>$V(0)/V_0$</th>
<th>$R_G$ ($\mu$m)</th>
<th>$r_{0m}$ ($\mu$m)</th>
<th>$\omega$</th>
<th>$\tau_0$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25Cr-7Ni-3Mo-2W-0.3N</td>
<td>1339</td>
<td>200</td>
<td>0.22</td>
<td>19</td>
<td>4.8</td>
<td>1.50</td>
<td>3.24E-08</td>
</tr>
<tr>
<td>25Cr-6Ni-3Mo-2W-0.3N</td>
<td>1320</td>
<td>200</td>
<td>0.17</td>
<td>17</td>
<td>4.5</td>
<td>1.30</td>
<td>3.22E-08</td>
</tr>
<tr>
<td>25Cr-7Ni-4Mo-0.3N</td>
<td>1314</td>
<td>250</td>
<td>0.21</td>
<td>10</td>
<td>3.8</td>
<td>0.83</td>
<td>3.57E-08</td>
</tr>
</tbody>
</table>
agreed the experimental ones, because the value of $R_2$ was determined as fitting parameters to calculate $N_{\text{pin}}$. When the density of sigma phase of $N_{\text{pin}}$ is determined, the critical condition of the sigma phase dissolution can be predicted using the model proposed without the experiment of solution treatment test.

5. Conclusion

The condition to dissolve the sigma phase into matrix in duplex stainless steels by solution treatment was investigated, and the following findings were obtained.

(1) The critical condition of the complete dissolution of sigma phase by solution treatment was influenced by the initial microstructure before solution treatment. The solution treatment at the higher temperature and for the longer heating time was necessary for the complete dissolution of the retained sigma phase in the initial microstructure consisting of two phases of austenite and sigma without ferrite compared to that in the initial microstructure consisting of three phases of ferrite, austenite and sigma.

(2) The critical condition necessary for the complete dissolution of the sigma phase by the experimental results was described as a linear function of the inverse of solution temperature and the logarithm of holding time. That function was $1/T = 2.303R/Q[\log(t) + \log(1/t_0)]$ and that was determined uniquely with the diffusion coefficient of Cr atom in the dominant phase and the constant $t_0$ consisting of the initial size of the sigma phase.

(3) The effect of the chemical composition of steel on the critical condition necessary for the complete dissolution of the sigma phase was suggested to be reflected in the value of constant $t_0$ in the function proposed.

REFERENCES