High-temperature Embrittlement in Si-added Austenitic Stainless Steel

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High-temperature tensile tests, a cast-slab microstructure investigation, and an *in-situ* observation of the dissolution behavior of 17%Cr-14%Ni-4%Si-Nb steel during heat treatment were conducted. The ductility suddenly decreased at above 1 200°C. A microstructure observation near the cast-slab surface suggests that the solidification mode was a divorced eutectic ferrite-austenite; in addition, the precipitation of Fe₁₆Nb₆Si₇ (G phase) occurred inside the δ phase and at the δ/γ interface. The temperature at which solidification was completed, as calculated using DICTRA, was 1 331°C; hence, the embrittlement at about 1 200°C, observed during the high-temperature tensile tests, was different from the L-zone embrittlement caused by the residual liquid phase during solidification. The *in-situ* observations showed that liquefaction occurred from the δ phase near the δ/γ interface at above 1 180°C. The high-temperature embrittlement was attributed to compositional liquefaction, in which the G phase was precipitated inside the δ phase and at the δ/γ interface during the cooling process after solidification provided Si and Ni owing to the dissolution upon re-heating.

KEY WORDS: high-Si stainless steel; austenitic stainless steel; high-temperature embrittlement; liquefaction; eutectic melting; G phase; solidification; *in-situ* observation.

1. Introduction

Stainless steel shows excellent corrosion resistance because a passive film forms on its surface. However, the film cannot stably exist, and the corrosion rate increases in environments with high corrosion potential, for instance under a high temperature or high nitric acid concentration.¹⁾ Si was applied to stainless steel to improve the corrosion resistance under such environments,²⁾ and because high-Si stainless steel with nitric acid resistance is commercially available.³⁾

The occurrence of hot cracking in welds has been reported in high-Si stainless steel.⁴⁾ Ogawa *et al.*⁵⁾ showed that the cracking sensitivity of Si was higher in the primary γ -phase solidification compared to the primary δ -phase solidification and that Ni–Cr–Fe–Si intermetallic compounds formed between dendrites. The authors concluded that solidification cracking was caused by the melting-point reduction of the residual melt owing to the formation of Si-rich phases. They applied the primary δ -phase solidification mode to reduce the amount of γ phase and succeeded in suppressing the segregation of Si. Hot cracking during the weld solidification was prevented when the residual δ -Fe content at the weld metal was greater than 8%. Wada *et al.*⁶⁾ reported that the zero-ductility temperature was low in Si-added steel and attributed it to the partial melting of Si–Ni rich intermetallic

compounds.

Some reports have suggested that the high-temperature embrittlement of high-Si stainless steel was caused by low-melting-point intermetallic compounds, as mentioned previously; however, there have been no detailed descriptions on the identification of precipitates causing embrittlement. The residual liquid phase at the segregated part was the possible origin of high-temperature embrittlement because Si causes a large melting-point depression;⁷⁾ however, such possibility has not been investigated. Therefore, herein we present an investigation into 17%Cr-14%Ni-4%Si-Nb steel, which is an industrially used nitric-oxide-resistant high-Si stainless steel with Nb added for stabilization.

2. Experiment Procedure

2.1. Material

For the specimen, 17%Cr-14%Ni-4%Si-Nb, cast using commercial production was applied. The raw materials were melted in an electric furnace, composition adjustments were performed using argon-oxygen decarburization (AOD), the final adjustments of the composition and temperature were conducted in a ladle furnace (LF), and casting was carried out using a vertical continuous-slab casting machine. The chemical composition of the specimen is shown in **Table 1**. No internal cracking in the cast slab was found in a macroscopic structural observation of the cross-section of the slab perpendicular to the casting direction.

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2.2. Evaluation of Hot Workability

Tensile test specimens with dimensions of $\phi 10 \text{ mm} \times 120 \text{ mm}$, where the casting direction is the length direction, were cut out from the surface of the cast slab. Tests were conducted on both the as-cast and heat-treated specimens. The heat treatment was conducted at 1180°C for 60 min to simulate the slab heating prior to hot rolling. A Thermorester-W II from Fuji Electronic Industrial Co., Ltd. was used in the high-temperature tensile tests (called “thermorester tests” hereafter). As temperature profile during the tests, heating to 1200°C was applied for 60 s, then retained for 60 s, and cooled to the test temperature at a rate of 20°C/s , with a finally retaining for 60 s before starting the tensile test. For test temperatures of 1225°C and 1250°C , the specimens were heated for 60 s, retained for 60 s, and then tested. The tensile speed was 20 mm/s.

2.3. Melting Point Measurement

First, 670 g of the specimen cut out from the cast slab surface was placed into a MgO crucible with an inner diameter of 32 mm and a height of 100 mm. The melting point was determined based on the temperature increase from the release of the latent heat of the solidification during the molten steel cooling in Ar-atmosphere Tammann furnace. Heating at up to 1500°C was conducted at a rate of 20°C/min and was maintained for 30 min; melting was then confirmed, and the sample was cooled at a rate of 20°C/min .

2.4. Microstructure Observation

Specimens were cut out from the cast slab surface at the center in the width direction and then mirror-polished for optical microscopy and scanning electron microscopy (SEM) observations as well as for energy-dispersive X-ray spectroscopy (EDS). Specimens for electron backscatter diffraction (EBSD) were also polished using colloidal silica. The microstructure of each specimen was clarified for optical microscopy using oxalic acid electrolysis etching, and the amount of $\delta\text{-Fe}$ was measured using a FERITSCOPE FMP30 (Fischer Technology, Inc.).

2.5. In-situ Observation during Heat Treatment

The specimens were cut out with dimensions of $5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ to observe a position 5 mm below the surface. The surface observed was then mirror-polished. The specimens were then set in an alumina crucible with an inner diameter of 8 mm and a height of 3.5 mm. *In-situ* observations⁸⁾ were conducted using a confocal scanning laser microscope (Yonekura Manufacturing Co., Ltd.) combined with an infrared image furnace. The atmosphere in the furnace was ultra-high-purity Ar ($> 99.9999 \text{ vol\%}$). Infrared light from halogen lamps and the furnace wall was used to heat the specimen, and the temperature was controlled using a thermocouple placed under the crucible. As the temperature profile, heating was applied at a rate of 10°C/s and then maintained at between 1140°C and 1200°C for

the *in-situ* observations.

3. Results and Discussion

3.1. Evaluation of Hot Workability

Figure 1 shows the area reduction ratio used during the Thermorester tests. The as-cast specimens showed a low ductility within a low-temperature range of $900\text{--}1000^\circ\text{C}$; nevertheless, the ductility was recovered through heat treatment at 1180°C for 60 min. Figure 2 shows the microstructure of the cross-section near the fracture surface after the test. The white and gray parts indicate the γ and δ phases, respectively. During the test at 900°C , cracks formed at the δ/γ interface in the as-cast specimen. Furthermore, the amount of $\delta\text{-Fe}$ in the slab measured using a FERITSCOPE was reduced from 9 vol% to 0.9 vol% through the heat

Fig. 1. Hot ductility of high Si stainless steel.

Fig. 2. Microstructure of the cross-section near the fracture surface after the Thermorester tests. As cast specimen tested at (a) 900°C and (b) 1225°C , and heat-treated versions tested at (c) 900°C and (d) 1225°C .

Table 1. Chemical compositions of the steel used (mass%).

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Nb
0.014	4.17	0.95	0.026	0.0002	13.73	16.80	0.20	0.20	0.0088	0.413

treatment. Therefore, the improvement in ductility at 900°C by heat treatment is thought to be due to a decrease in the δ -Fe content.

The ductility of 17%Cr-14%Ni-4%Si-Nb steel suddenly decreased at above 1 200°C. In addition, an observation of the fracture surface of the 1 225°C specimens showed that cracks were formed at the δ/γ interface in the as-cast specimens and at the grain boundaries in the heat-treated specimens. It is believed that a drastic embrittlement at above 1 200°C could have occurred because the δ/γ interface and/or grain boundaries were covered by a liquid film. The melting point measured using the Tammann furnace was 1 396.4°C. When a liquid film was present owing to the liquidus temperature at 1 200°C where the ductility is restored, the coexistence of a solid–liquid phase spanned an extremely wide temperature range of approximately 200°C.

3.2. Investigation of Solidified Microstructure in Cast Slab

Figure 3 shows an equilibrium phase diagram calculated using Thermo-Calc.⁹⁾ Fe-DATA (version 6)¹⁰⁾ was used as the thermodynamic database. The 17%Cr-14%Ni-4%Si-Nb

Fig. 3. Phase diagram for 4mass%Si stainless steel computed using Thermo-Calc.

steel solidifies in ferrite-austenite (FA) mode, where the δ phase is the primary phase and the γ phase crystallizes as the second phase.¹¹⁾ Precipitation of the G phase ($M_{22}Si_7$) is expected at temperatures of below 1 160°C. The G phase is an intermetallic compound where precipitation is promoted by the addition of Si; in addition, the precipitation of the G phase consisting of Ni and Si, namely, $Ni_{16}Ti_6Si_7$, has been

Fig. 5. SEM micrograph and EDS analysis at 5 mm from slab surface. (Online version in color.)

Fig. 6. TEM image of extraction replica at low magnification.

Fig. 4. Microstructures of the cross-section at 5 mm from the cast-slab surface: (a) low and (b) high magnification.

reported in Si-added steel.¹²⁾ **Figure 4** shows the microstructures of the cross-section at 5 mm from the cast-slab surface. This is an FA-mode microstructure containing vermicular ferrite in the dendrite core, which remained after the δ/γ -phase transformation. The δ -Fe concentration measured using the FERITSCOPE was 9 vol%. Precipitates were observed on the δ -phase side of the δ/γ interface. **Figure 5** shows the results of the SEM and EDS analyses. The precipitate showed high Si and Nb amounts and was presumed to be a G phase based on the calculated phase diagram and previous studies on Si-added steel.

An extracted replica specimen obtained at 5 mm from the cast slab surface was prepared, and an investigation of the precipitates was conducted using a transmission electron microscope (TEM). The precipitates were unevenly distributed, and mostly existed in the high precipitate within

the concentration region shown in **Fig. 6**. The thickness of the high-precipitate-concentration region was 5–8 μm . The morphology and size indicated that the high-precipitate-concentration region was in a δ phase.

Figure 7 shows TEM images, electron diffraction analyses, and EDS analysis results of the high-precipitate-concentration region presumed to be inside the δ phase. Precipitates of approximately 100 nm in size were confirmed, and two types of G phase were found: $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ containing Nb and $\text{Cr}_3\text{Ni}_2\text{Si}$ containing Cr. **Figure 8** shows the TEM images and electron diffraction and EDS analysis results of the fringe of the high-precipitate-concentration region, which was most probably a δ/γ -phase interface. $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ particles were shown with a size of approximately 400 nm as well as Laves-phase Fe_2Nb and Nb(C,N), both of which are coarse and exceed 1 μm .

Fig. 7. TEM image of precipitates in δ , and its identification through EDS and electron diffraction analyses: (a) $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ and (b) $\text{Cr}_3\text{Ni}_2\text{Si}$.

Fig. 8. TEM image of precipitates at δ/γ boundary, and its identification using EDS and electron diffraction analyses: (a) $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$, (b) Fe_2Nb , and (c) Nb(C,N).

Figure 9 shows an inverse pole figure at 5 mm below the cast slab surface and $[111]$ and $[110]$ pole figures of the δ and γ phases. **Figure 10** shows inverse pole figures from the transverse direction and $[001]$ pole figures. No specific crystal orientation relations, such as a Kurdjumov–Sachs relation, were found between the δ and γ phases. The preferred growth direction of the primary crystal δ phase and the second γ phase, which were $\langle 100 \rangle_{\delta}$ and $\langle 100 \rangle_{\gamma}$, respectively, were both nearly parallel to the heat flow direction; therefore, this was a divorced eutectic where the δ and γ phases individually nucleated and grew.

3.3. Solidification Analysis

Ogawa *et al.*⁵⁾ reported that cracks during welding significantly decrease in stainless steel with 4 mass% Si if more than 8 vol% residual δ -Fe is present. In addition, 17%Cr-14%Ni-4%Si-Nb contains more than 9 vol% residual δ -Fe at 5 mm below the cast-slab surface; thus, their findings imply a low hot crack susceptibility. Indeed, no internal cracks were found in the cast slab, and the liquid phase from the solidification was not thought to remain at 1 200°C, which was the onset of embrittlement during the Thermorester tests. Therefore, a one-dimensional solidification analysis was conducted using DICTRA¹⁴⁾ to evaluate the phase formation. The cell size of the computational model was set

Fig. 9. Crystallographic orientation between primary δ and γ : (a) EBSD orientation mapping and pole figures of $[110]_{\delta}$ and $[111]_{\gamma}$.

Fig. 10. Preferred growth direction of primary δ and γ : (a) EBSD orientation mapping and (b) pole figure of $[001]_{\delta}$ and $[001]_{\gamma}$.

to one-half of the secondary arm spacing ($= 11.8 \mu\text{m}$). An analysis was carried out using the eutectic model shown in **Fig. 11** with a cooling rate of 50°C/s . The calculations were simplified by consolidating the components using Cr_{eq} and Ni_{eq} , as described by Hammar and Svensson,¹⁵⁾ and a five-component Fe-17.07%Cr-14.65%Ni-4.17%Si-0.413%Nb system was estimated.

$$\text{Cr}_{\text{eq}} = \text{Cr} + 1.37\text{Mo} + 1.5\text{Si} + 2\text{Nb} + 3\text{Ti} \dots\dots\dots (1)$$

$$\text{Ni}_{\text{eq}} = \text{Ni} + 0.31\text{Mn} + \text{Cu} + 22\text{C} + 14.2\text{N} \dots\dots\dots (2)$$

Figure 12 shows the change in the volume fraction of each phase calculated using DICTRA with Fe-DATA (version 6)¹⁰⁾ as the thermodynamic database. **Figure 13** shows the Si concentration profile at each temperature. An analysis indicates that solidification is complete at 1331°C ; the Si concentration in the liquid phase increases to 4.9 mass% at 1335°C , which occurs immediately before the completion of the solidification. The partition coefficient of Si between the δ and liquid phases, k^δ , is 0.90. This is larger than that between the γ and liquid phases, $k^\gamma (= 0.79)$. The solid solution of Si in the δ phase mitigates the micro-segregation of Si. Calculations indicate that the Si concentration at the γ -phase dendrite core at 900°C is approximately 3.6 mass%, which is almost the same as that measured using an electron probe micro analyzer (approximately 3.5 mass%). After solidification is completed, the δ phase decreases owing to the δ/γ transformation, and the partition of the alloy elements proceeds. During the δ phase, the concentration of

the ferrite former, such as Si and Cr, increases, and in austenite, the concentration of Ni, which is an austenite former, increases. A 40% residual δ -Fe was shown in the calculations, which differs significantly from that in the actual cast slab (9% at 5 mm below the surface). Furthermore, in the calculation, the Si concentration of the δ phase is approximately 4.6%, which is lower than the 5.75% measured using EDS. In the calculation, the amount of δ is larger than the actual amount, and the distribution of the alloy shows no progression, and thus it is thought that the Si concentration in the δ phase was lower than the analytical value. One possible reason for the higher amount of δ -Fe in the calculation is the one-dimensional treatment in the calculation through the δ/γ transformation of the vermicular δ phase, which has a large surface area and complex shape.

The solidification temperature range ΔT_0 when adding an alloying element with a Co concentration can be written as the follows using the liquidus slope m , solidus slope n ($= m/k$), and melting point of steel T_M :

Fig. 11. Schematic illustration of divorced eutectic solidification model.

Fig. 12. Phase fraction changes during cooling as computed using DICTRA.

Fig. 13. Si concentration distribution computed using DICTRA. Prior to solidification completion at (a) 1335°C and after solidification at (b) 1300°C to 900°C . (Online version in color.)

$$\begin{aligned}\Delta T_0 &= T_{LL} - T_{SL} = (T_M + mC_0) - (T_M + nC_0) \\ &= C_0(m - n) = mC_0(1 - 1/k) = mC_0((k-1)/k) \dots (3)\end{aligned}$$

Kagawa *et al.*⁷⁾ reported that the liquidus slope of Si during primary δ phase solidification was -14.39 ; thus, ΔT_0 is 6.7°C when 0.9 is used as k^δ . By contrast, when a primary γ phase solidification is assumed, $\Delta T_0 = -18.9^\circ\text{C}$ with $m = -17.1$ ⁷⁾ and $k^\gamma = 0.79$. Although this value is larger than that of the δ -phase solidification, the increase in ΔT_0 with Si is limited, and the liquid phase is not expected to remain at $1\,200^\circ\text{C}$.

3.4. In-situ Observation of Change in Microstructure

The 17%Cr-14%Ni-4%Si-Nb steel showed high-temperature embrittlement owing to liquefaction during heat treatment. Therefore, an *in-situ* observation of the changes in the microstructure and dissolution behavior was carried out using a confocal scanning laser microscope.⁸⁾

Figure 14 shows the change in microstructure when the temperature was retained at between $1\,140$ and $1\,200^\circ\text{C}$. Upon heating toward retention at $1\,200^\circ\text{C}$, a liquid phase instantaneously formed from the δ/γ interface at near $1\,190^\circ\text{C}$, and melting immediately appeared after reaching $1\,200^\circ\text{C}$. The melt was thought to originate from the precipitates at the δ/γ interface or the molten δ phase. Such liquefaction at the δ/γ interface was confirmed after heating to above $1\,180^\circ\text{C}$, and was not found when the heating temperature was $1\,160^\circ\text{C}$ or less. Instead, dissolution of the δ phase and precipitation at the δ/γ interface, which was estimated to be a G phase, was observed upon heating to $1\,160^\circ\text{C}$ or less.

A phenomenon similar to liquation cracking occurring in the weld of Ni-based alloys¹⁶⁾ could be the mechanism for

the melt formation at the interface. NbC precipitation at the interface was considered the origin of liquation cracking in the Alloy 718. Heating at a relatively high rate forced a precipitate phase that should completely dissolve to remain in a non-equilibrium state. This precipitate phase became the source of the solute during the solidification of the solution, and liquation cracking occurred through eutectic melting at a temperature much lower than the melting point of the precipitate phase.

Intermetallic compounds such as $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ and $\text{Cr}_3\text{Ni}_2\text{Si}$ were present in the δ phase and at the δ/γ interface in 17%Cr-14%Ni-4%Si-Nb steel. These intermetallic compounds provided Si, Ni, or Nb for compositional liquefaction. Therefore, equilibrium calculations of three phases, namely, liquid, BCC (δ), and G phases, were conducted using Fe-DATA (version 6)¹⁰⁾ as the thermodynamic database. **Figure 15** shows a phase diagram in which the horizontal axis indicates the Si concentration. The eutectic zone between the δ and G phases starts at a Si concentration of 8.15 mass% and a temperature of $1\,332^\circ\text{C}$, and the solidus temperature rapidly decreases at Si concentration > 11 mass%. The Si concentration must locally attain 13.5 mass% for eutectic melting to occur at $1\,180^\circ\text{C}$, which is the temperature at which a melt formation was confirmed during the *in-situ* observations.

Next, the possibility of a solid solution with the G phase liquefaction of the δ phase with a locally high Si concentration was investigated. **Figure 16** shows a phase diagram considering the liquid and δ phases. The two-point average of the Cr and Ni concentrations found in the δ phase in SEM-EDS (Cr = 22.46% , Ni = 8.17% , and Si = 5.79%) was used. The Si content in the δ phase must exceed 9.05 mass% to achieve liquefaction at $1\,180^\circ\text{C}$. This value is lower than both the Si concentration for the eutectic melting discussed

Fig. 14. *In-situ* observation of microstructure changes during elevated temperature holding at $1\,140^\circ\text{C}$ to $1\,200^\circ\text{C}$.

Fig. 15. Phase diagram for Fe-16.8Cr-13.73Ni-0.413Nb computed using Thermo-Calc. (Online version in color.)

Fig. 16. Liquidus and solidus for Fe-22.46Cr-8.17Ni-0.413Nb computed using Thermo-Calc.

previously and the Si concentration in the G phase; thus, this scenario can cause sufficient liquefaction. Ni and Nb in the G phase also lower the solidus curve of the δ phase. The local concentration of these solute elements in the G phase contribute to a liquefaction of the δ phase.

4. Conclusions

The high-temperature embrittlement mechanism of 17%Cr-14%Ni-4%Si-Nb steel was investigated and the following results were obtained:

(1) A microstructural observation of the cast slab showed that 17%Cr-14%Ni-4%Si-Nb solidified in FA mode, and a secondary γ phase formed as a divorced eutectic. The $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ phase precipitated at the δ/γ interface and $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ and $\text{Cr}_3\text{Ni}_2\text{Si}$ precipitated in the δ phase. These were thought to precipitate after solidification.

(2) The heating of 17%Cr-14%Ni-4%Si-Nb steel at above 1200°C resulted in significant embrittlement. According to the solidification analysis, the liquid phase disappeared at 1331°C; thus, the embrittlement at 1200°C could not be I-zone embrittlement of which the residual liquid phase during solidification played a role.

(3) Embrittlement of 17%Cr-14%Ni-4%Si-Nb steel during heating was presumed to originate from local compositional liquefaction in the δ phase, which was caused by Si and Nb supplied by the solid solution. The G phase, such as $\text{Fe}_{16}\text{Nb}_6\text{Si}_7$ and $\text{Cr}_3\text{Ni}_2\text{Si}$, precipitated at the δ/γ interface and in the δ phase during cooling, and released these elements through dissolution during heating. The heating temperature must be controlled at below 1160°C to prevent embrittlement at above 1200°C.

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