Temper Embrittlement of Type 13Cr-4Ni Cast Steel

By Yoshitaka IWABUCHI**

Synopsis

The mechanism of toughness degradation by temper embrittlement is studied in 13Cr-4Ni martensitic stainless cast steel. The variation of toughness, brittle fracture mode and fraction of retained austenite are examined as a function of tempering temperature and the subsequent isothermal treatment in the range 550~450°C. Temper embrittlement is referred to as increases in FA TT and fraction of intergranular fracture after tempering at lower temperatures and subsequent isothermal treatment at higher temperatures. The embrittlement is found to be related to the intergranular fracture and precipitation of carbide along prior austenite grain boundary. The precipitation of intergranular carbides is resulted from the decrease of carbon solubility in the reverted austenite during tempering. Susceptibility to temper embrittlement in this steel is suppressed as tempering temperatures are raised.

Key words: martensitic stainless steel; castings; temper embrittlement; carbide precipitation; intergranular fracture; fracture appearance transition temperature.

I. Introduction

Soft martensitic stainless 13Cr-4Ni cast steels are widely used for hydraulic turbine runner castings, since they possess excellent resistance to cavitation erosion and high toughness.1-4 Proper choice of the chemical composition and heat treatment can produce a good combination of strength and toughness. However the impact notch toughness has been found to deteriorate in the steels slowly cooled from tempering temperatures.5-7 Such toughness deterioration known as temper embrittlement imposes many practical problems. Recent demands for higher strength materials make difficult the optimum selection of tempering condition to guarantee high toughness.

The present study was intended to clarify the condition and mechanism of temper embrittlement of 13Cr-4Ni cast steels in the tempering and the subsequent isothermal treatments.

II. Experimental Procedure

The experimental material used in this study was type ASTM A296 CA-6NM-13Cr-4Ni martensitic cast steel with the composition shown in Table 1. The steel was melted in a basic electric furnace and cast in a cold-setting sand mold of 80×260×160 mm³, followed by the heat treatments shown in Fig. 1. After annealing at 1 050°C for 10 h, the material was austenitized at 950°C for 10 h followed by air cooling and then tempered for 10 h at a temperature range from 580 to 630°C followed by furnace cooling to 550, 500 or 450°C for 25~100 h to induce temper embrittlement. Charpy V impact specimens were machined parallel to the top–bottom direction of the material which had already been subjected to the embrittling heat treatment, and the impact testing was carried out at a temperature between −100 and 100°C. Transformation behavior of 13Cr-4Ni cast steels has been reported5,6,7 and the reversion of austenite occurred during tempering above 550°C.

Thin foils and carbon extraction replicas taken from the impact tested specimens were examined with transmission electron microscopy (TEM), and partitions of elements in ferrite and austenite phases were determined by an energy dispersive X-ray analyser (EDX). The fracture surfaces of Charpy specimens were examined with scanning electron microscopy (SEM). The embrittled specimens were fractured at a pressure as low as 10⁻¹⁰ torr in the vacuum chamber of an Auger electron spectrometer. Auger electron spectroscopy was made on the freshly exposed surface of prior austenite grain boundary: acceleration voltage 5 kV, beam diameter 20 µm, beam current 1 µA, time constant 0.1 s, sweep rate 6 eV/s. Amounts of retained austenite of the embrittled specimens were measured by X-ray diffraction method.

III. Experimental Results

Figure 2 shows the Charpy impact transition curves of embrittled specimens together with the 50 % shear fracture appearance transition temperature (FATT).

Table 1. Chemical composition of a cast steel used for this study. (wt%)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.44</td>
<td>0.64</td>
<td>0.028</td>
<td>0.028</td>
<td>3.70</td>
<td>11.67</td>
<td>0.10</td>
<td>0.26</td>
</tr>
</tbody>
</table>

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Figure 3 shows variations of FATT and $\Delta$FATT as a function of embrittling time for various tempering and embrittling temperatures. The values $\Delta$FATT represent as the shift of FATTs for the embrittled specimens from those quenched after tempering at 580, 600 and 630°C. It is clear that both FATT and $\Delta$FATT rise with increasing embrittling time and also with lowering of prior tempering temperature; the raising rate of FATT and $\Delta$FATT is higher with the embrittling temperature. The values of FATT and $\Delta$FATT also become high with the drop of tempering temperature. As the hydraulic turbine runners are operated above 0°C, the upper shelf energy of materials used for these parts should be lower than -30°C. Fig. 4 illustrates the diagram of embrittling time-embrittling temperature-FATT of -30°C on the basis of Fig. 3. For evaluation of the requirement in terms of FATT of -30°C, this steel embrittles most severely when tempered at 580°C and then iso-
T°C x 10h → 550°C x 25h → F.C.

580°C 600°C 630°C

Tempering temperature (T)

Fig. 5. Scanning electron micrographs of brittle fracture surfaces of Charpy impact specimens tested at a temperature corresponding to FATT.

thermally held at 550 or 500°C. Figure 5 is the scanning electron fractographs of brittle fracture appearance of Charpy impact specimens tested at a temperature corresponding to FATT. Each specimen shows a mixture of cleavage and intergranular fracture; lower tempering temperature leads higher fractions of intergranular mode. Figure 6 shows the relation between FATT and the fraction of intergranular fracture measured with SEM in the middle region of the fracture surface; FATT is directly correlated to the fraction of intergranular fracture. The fraction of intergranular fracture increases with lowering of tempering temperature and rising of embrittling temperature.

Auger electron spectroscopy (AES) detects an enrichment of phosphorous on intergranular fracture surfaces. In Fig. 7, each peak height of P(120 eV) is converted into the height (RPH) relative to the Fe peak height (703 eV). These RPHs plotted in Fig. 7 are the average values of three individual RPH measured at different intergranular fracture surfaces of the samples. The fraction of intergranular fracture of the analysed samples ranges between 25 and 70 %, while the values of RPH remain constant for a variety of tempering temperature and embrittling temperature. From this result, it is suggested that the variation of FATT and intergranular fracture with embrittling treatment is not related only to the segregation of phosphorous on prior austenite grain boundary.

IV. Discussions

In previous works, the author has suggested that the temper embrittlement in 13Cr-4Ni cast steels is related to carbides precipitated at prior austenite grain boundary. This type of carbide precipitates is observed by immersing the as-polished specimen in a dilute nitric acid aq. solution. Figure 8 gives the corrosion loss after immersion in a boiled 4.4 % HNO₃ aq. solution for 24 h for the specimens described in Fig. 3 coupled with the specimens embrittled for 200 h. The optical micrographs of the specimens after these tests are attached to in Fig. 8; the temper
embrittlement is associated with the groove along austenite grain boundary and the magnitude of corrosion loss becomes large with increasing temperature and time of embrittlement. Also the corrosion loss gets higher with lowering of tempering temperature. The variations of FATT and 4FATT with embrittling treatment are similar to those of the corrosion loss.

Figure 9 shows the transmission electron micrographs of carbon replicas extracted from specimens embrittled at 550°C for 25 h or 100 h after tempering at 580, 600 and 630°C.

Fig. 8. Variation of corrosion loss with embrittling treatments for specimens after tempering at 580, 600 and 630°C.

Fig. 9. Transmission electron micrographs of carbon replicas extracted from specimens embrittled at 550°C for 25 h or 100 h after tempering at 580, 600 and 630°C.
is induced as the result of carbide precipitation, the precipitates are presumably chromium carbides from Figs. 8 and 9. Morphology and number of carbides vary during cooling after tempering, although the structure of tempered carbides depends on both time and temperature for the as-quenched materials tempered at temperatures of partial reversion of austenite. Elevation of tempering temperature for as-quenched materials produces a maximum amount of carbides, then the carbides decompose as well as the occurrence of reverted austenite and finally dissolves in austenite. The temperature and time of tempering also affect the stability of reverted austenite which appears along prior austenite grain and martensite lath boundaries, and consequently determine the amount of retained austenite.

Figure 10 shows the transmission electron micrographs of the specimens tempered at temperatures of 580, 600 and 630°C and embrittled at 550°C for 25 h, accompanied by the variation of retained austenite in differently embrittled specimens. Amount of retained austenite is influenced by tempering and embrittling conditions; the maximum value is obtained for the specimen tempered at 600°C and followed by embrittling of 550°C×100 h, and the minimum for the specimen tempered at 630°C and followed by embrittling of 450°C×24 h. The fraction of retained austenite increases as the embrittling temperature and time are higher. The retained austenite film is observed at inter-lath boundary. The variation of the amount of retained austenite with embrittling treatments is presumably due to the difference in stability among reverted austenite phases. It is suggested that stable austenite transforms to fresh martensite during cooling. Figure 11 summarizes the results of EDX analyses of ferrite and austenite phases in embrittled specimens by using thin films prepared from the specimens tempered at 580 and 630°C followed by embrittling treatment of 550°C×25 h. The nickel content is higher in austenite than in ferrite that contains somewhat a lower nickel content than the initial concentration, although there is little difference in the chromium concentration between two phases. It is presumed that the nickel enrichment in austenite is a result of the difference in solubility of nickel between ferrite and austenite.

The influence of alloying element on carbide precipitation can be discussed on the basis of Figs. 9 to 11. Carbon solubility, \( C_a \), in austenite is expressed

\[
\log C_a = \frac{-\Delta H}{2.3RT} + B \tag{1}
\]

where, \( \Delta H \): the free energy of heat

\( B \): the enthalpy term.

This equation suggests the decrease in carbon solu-
bility with drop of temperature. Nishino and Kagawa used Ni–Cr steels to estimate the carbon solubility in austenite phase and indicated that the enthalpy term varies with the chromium and nickel contents as

$$\log G_m = \frac{-\Delta H}{2.3RT} + A(Cr+Ni) \quad \ldots \ldots (2)$$

where, $A$: a constant.

Figure 12 schematically represents the change of carbon solubility in austenite during cooling from tempering temperatures of 630, 600 and 580°C to an embrittling temperature of 550°C. As the tempering temperatures are elevated, the amount of reverted austenite is also increased, coupled with the increase of nickel concentration which leads the dilution of carbon concentration in the reverted austenite, and consequently results in the reduction of carbon content rejected from the austenite. Therefore carbide precipitation during cooling is suppressed. Outflow of the dissolved carbon from reverted austenite and accompanied carbide precipitation during cooling are schematically shown in Fig. 13. Since the content of carbon rejected from reverted austenite is decreased because of increasing amounts of austenite and nickel when the tempering temperature is elevated, the nose of carbide precipitation is presumed to be shifted to the right side in the embrittling time–embrittling temperature–carbide precipitation diagram. The degree of temper embrittlement becomes more pronounced, since grain boundaries between reverted austenite and prior austenite are sufficiently covered with carbides when the steels are tempered at low temperature and subsequently held at high temperature.

V. Conclusions

The experimental results obtained in this work lead to the following conclusion on temper embrittlement in 13Cr–4Ni cast steel during tempering.

1. Impact properties of 13Cr–4Ni cast steels degrade by isothermal treatment in the range between 450 and 550°C during cooling from tempering temperatures.

2. Embrittlement in prior austenite grain boundary is affected by both temperatures of temper-
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(3) The temper embrittlement is presumed to be associated with carbide precipitation on the grain boundaries between prior austenite and reverted austenite during tempering.

(4) Susceptibility to temper embrittlement in 13Cr–4Ni cast steels is suppressed by reducing carbon concentration in reverted austenite when the temperature is higher.

Acknowledgements

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Fig. 12. Schematic diagram showing carbon rejection from reverted austenite for 13Cr–4Ni cast steel.

Fig. 13. Schematic representation of temper embrittlement as a result of carbide precipitation along grain boundary between reverted austenite and prior austenite.