Dependence of Elevated Temperature Intergranular Cracking on Grain Size and Bulk Sulfur Content in TP347H Austenitic Stainless Steels

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(Received on January 4, 2016; accepted on February 5, 2016)

Regardless of the bulk sulfur content, heat–resistant TP347H austenitic stainless steels of the smaller grain size show a ductile fracture after rupture test, while the steels of the larger grain size show a typical intergranular cracking. The intergranular cracking is mainly due to the sulfur segregated at grain boundaries, and it is not inhibited even by the extremely low bulk sulfur content of 7 ppm. In steels showing the intergranular cracking, the time to failure is rather longer in the steel of the higher bulk sulfur content. This is due to MnS precipitates incoherently formed within the matrix, the interface of which acts as a strong sink of free sulfur segregating to grain boundaries. The fracture mode and the time to failure are determined by the combination of bulk sulfur content and grain size influencing the creep resistance and the equilibrium grain boundary segregation concentration of sulfur.

KEY WORDS: heat-resistant austenitic stainless steel; intergranular cracking; grain size; sulfur segregation; MnS precipitation reaction.

1. Introduction

Elevated temperature intergranular cracking in heat-resistant alloys has been generally explained in the light of the formation and coalescence of voids in the soft denuded zone which is caused by grain boundary precipitates.1,2) However, the mechanism for the formation of closed voids at grain boundaries normal to the tensile stress and their development to the intergranular cracking are not still clear. It has been proposed that the intergranular cracking in metals is their intrinsic property occurring at elevated temperatures3) due to the intergranular fracture strength lower than the yield strength (exactly speaking, the flow stress), and the segregation of impurities (P and S) to the grain boundaries accelerates the intergranular cracking by lowering the grain boundary cohesion strength.3–10) The bulk content of impurities (especially, sulfur) has been, therefore, reduced to below 10 ppm to minimize the possibility for the intergranular cracking.

On the other hand, one of the reasons for the poor hot ductility observed in low alloy steels during continuous casting is the austenite grain boundary segregation of sulfur which decreases the grain boundary cohesion strength.11,12) Under such a situation in which the grain boundaries are embrittled by the segregated sulfur, the formation of region of the heat-affected zone. Compared to the expected creep life of 10 years, the service exposure time for the premature cracking was about 1 year.

Fig. 1 shows such a typical premature cracking in the heat-resistant TP347H austenitic stainless steel tube which occurs within the coarse-grained

Fig. 1. Premature intergranular cracking which occurred in a final reheater tube of a fossil power plant of Korea which is made of the heat–resistant TP347H austenitic stainless steels: (a) macrostructure and (b) microstructure.
 Nb(C,N) particles, which strengthens the matrix, accelerates the hot ductility loss.\textsuperscript{13} The hot ductility is recovered due to not only the matrix softening arising from the coarsening of the Nb(C,N) precipitates but also the decrease in segregation concentration of sulfur at the grain boundaries which is accompanied by the MnS precipitation. Because the interface between the MnS precipitates and the neighboring matrix acts as a strong sink of the free sulfur segregating towards the grain boundaries,\textsuperscript{14} the formation of a highly dense MnS precipitates within the matrix increases the recovery rate of the hot ductility.\textsuperscript{12}

It is the purpose of this research to clarify effects of grain size and bulk sulfur content on elevated temperature intergranular cracking occurring in TP347H austenitic stainless steels.

2. Experimental Procedures

Two kinds of TP347H austenitic stainless steels, the compositions of which are different mainly in the bulk sulfur content, were prepared using a vacuum induction melting. Chemical compositions of the steels are shown in Table 1. The ingots were homogenized at 1 150°C for 2 h, hot rolled to 15 mm thick plates, and subsequently cold-rolled to 12 mm after pickling. For stress rupture test, cylindrical specimens with a dimension of 15 mm gauge length and 6 mm gauge diameter were machined from the cold-rolled plates in the rolling direction. These specimens were induction-heated to 1 300°C at a heating rate of 10°C/s under an argon atmosphere and rapidly cooled to room temperature after holding at the temperature for some times. Specimens of 50 and 250 μm grain sizes were obtained from the heat treatment held at 1 300°C for 5 s and 3.3 h, respectively. The rupture test was performed using conventional creep testers. In order to accelerate the rupture test, the test temperature was fixed at 750°C much higher than the service temperature, about 600°C, of fossil power plants, and the stress range of 80 to 150 MPa was chosen. The rupture test specimens to which a K-type thermocouple was attached were heated to the test temperature at a heating rate of 1 200°C/h. The test was carried out without soaking at the temperature. Reduction in area after rupture test was measured using conventional methods. The fracture surface of ruptured specimens was investigated using a scanning electron microscope (SEM, JEOL JSM-6610). Analyses of carbides and MnS precipitates were carried out in a Cs-corrected 200 kV field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F). Segregation behaviors of impurities were investigated using an ion-sputtering method\textsuperscript{15} in an Auger electron spectroscope (Perkin Elmer 700).

3. Results and Discussion

Figure 2 shows changes in time to failure of the ruptured HS steel specimens, reduction in area and representative fracture mode with grain size. As shown in Fig. 2(a), the time to failure increases with decreasing applied stress. As shown in Figs. 2(a) and 2(b), although the composition is same, the time to failure is longer in the larger grain size, but the reduction in area is much lower in the larger grain size. As shown in Figs. 2(c) and 2(d), the fracture mode of the smaller grain size is ductile, regardless of the time to

| Heats | C    | Mn   | S    | Cr   | Ni   | Nb   | P    | Si    | Fe    |
|-------|------|------|------|------|------|------|------|-------|-------|
| LS    | 0.071| 1.46 | 0.0007| 18.14| 10.03| 0.49 | 0.025| 0.656 | Balance|
| HS    | 0.071| 1.51 | 0.0093| 18.12| 10.05| 0.48 | 0.030| 0.609 | Balance|

Fig. 2. Changes in time to failure, reduction in area and representative fracture mode with grain size in ruptured HS specimens: (a) time to failure, (b) reduction in area, (c) ductile fracture in the grain size of 50 μm, and (d) intergranular fracture in the grain size of 250 μm.
failure, while that of the larger grain size is intergranular.

As shown in Fig. 3, the more severe plastic deformation during the rupture test has occurred in the HS specimen of the smaller grain size than that of the larger grain size. The ion-sputtering result obtained from the intergranular fracture surface of the HS specimen exposed after rupture test is shown in Fig. 4. A strong sulfur peak is observed from the intergranular fracture surface. The oxygen peak is from the surface oxide, and the carbon peak is due to the surface adsorption of oxygen from the atmosphere. The ion-sputtering result supports that the elevated temperature intergranular cracking of the HS specimens is mainly due to the sulfur segregated at the austenite grain boundaries.16–19)

Figure 5 shows changes in time to failure and fracture mode with grain size and bulk sulfur content. As shown in Fig. 5(a), the time to failure of the smaller LS and HS specimens is similar, irrespective of the bulk sulfur content and the applied stress. The fracture mode in both cases is ductile, as shown in Fig. 5(c). At the larger grain size of 250 μm, the time to failure is, as shown in Fig. 5(b), shorter in
the LS steel than the HS steel, while the fracture mode is, as shown in Fig. 5(d), typically intergranular, irrespective of the bulk sulfur content.

After holding at 1300°C for 5 sec and rapid cooling to room temperature, MnS precipitates are little observed in the specimens and only NbC carbides are observed, as shown in Fig. 6. After rupture test at 750°C under 80 MPa, the MnS and NbC precipitates formed within the HS and LS steels are shown in Figs. 7 and 8, respectively. The oversaturated sulfur is consumed to form the equilibrium phase MnS precipitate. The round-shaped MnS precipitates are denser in the HS steel of the higher sulfur content. As reported in a research,20) the MnS precipitate and the NbC carbide are formed as a complex precipitate.

3.1. Time to Failure and Fracture Mode Which are Determined by the Competition between Creep Rate and Grain Boundary Embrittlement Rate during Rupture Test

Changes in fracture mode and time to failure with grain

![Fig. 6. Microstructure (a) and energy-dispersive spectroscopy (EDS) analyses (b) of the HS steel rapidly cooled after holding at 1300°C for 5 sec.](image)

![Fig. 7. HAADF-STEM image (a) and EDS analyses (b) of the HS specimen ruptured under 80 MPa.](image)

![Fig. 8. HAADF-STEM image (a) and EDS analyses (b) of the LS specimen ruptured under 80 MPa.](image)
size, which are shown in Figs. 2 and 5, need to be understood. If the grain boundary embrittlement by impurities is excluded, the time to failure is absolutely longer in a coarse-grained material due to the higher creep resistance. The creep resistance is a material’s ability to resist any kind of distortion, while an extended period of time is given to the material under a load. Therefore, the creep behavior is one of the factors that limit the maximum application temperature of the material. As shown in Fig. 1, the premature intergranular cracking in heat resistant steels occurs however at the heat-affected zone of the larger grain size without any exception. The fine-grained heat resistant steels have therefore been preferred. During the creep rupture test, the increase of plastic strain within the gauge length part of the specimens increases the true stress, because the load is fixed but the cross-sectional area decreases with increasing time. Meanwhile, the equilibrium segregation concentration of impurities decreases abruptly with decreasing grain size.\(^{21}\)

During creep rupture test, the creep resistance is lower in the smaller grains, and the grain boundary embrittlement rate is lower in the smaller grains. Such a situation is favorable for ductile fracture during rupture test, as shown in Figs. 2(c) and 5(c). The intergranular fracture in the larger grain size is mainly due to the higher creep resistance and the higher grain boundary segregation concentration of sulfur of Fig. 4. However, whether the fracture mode is ductile or intergranular, the time to failure in the present study is mainly determined by the competition between the creep resistance and the grain boundary embrittlement rate.

Generally, residual stress after welding is mainly confined around the welding part. Within the boiler of fossil power plants, the temperature difference between locations causes a thermal tensile stress in tubes. During creep rupture test, thinning in the gauge section by the creep increases the stress in the gauge section due to the fixed dead load. However, the plastic deformation within the tube during the service exposure releases largely the tensile stress which arises from the residual and thermal stresses. Considering the same location of a tube within the boiler, the total tensile stress at a time \(t\) is therefore higher in the tube of the larger grain size due to the higher creep resistance. This accelerates the grain boundary segregation kinetics of impurities, causing the premature intergranular cracking. Therefore, the best way to inhibit the premature intergranular fracture is to decrease the grain size as far as possible. This is the reason why the premature intergranular cracking occurs always within the coarse-grained region of the heat-affected region and also the intergranular cracking is observed generally under a condition of low temperature and low stress range. Based on the current concept, a harder steel of the larger grain size is paradoxically the worst case against the premature intergranular cracking, probably due to the higher creep resistance and the higher thermal stress which accelerates the grain boundary segregation of sulfur. Such an explanation has been well detailed in the previous research.\(^{22}\)

With little consideration of the fracture mode, the judgment of the better creep-resistant material has usually been based on the time to failure which is simply determined from the conventional creep rupture test. Based on such a simple judgment, the steels of the larger grain size in Figs. 2 and 5, which show the intergranular fracture mode, should be chosen as the better creep-resistant materials due to the longer time to failure. Because the premature cracking occurs always within the coarse-grained region of the heat-affected zone, such a simple determination of the better creep-resistant material is very risky from the viewpoint of the premature intergranular cracking.

### 3.2. Role of Incoherent MnS Interface on Grain Boundary Segregation of Sulfur

Due to the detrimental effect of sulfur on the grain boundary cohesion strength, the bulk sulfur content has been decreased to an extremely low level below 10 ppm. As shown in Fig. 5(b), the rupture life in the larger grain size showing intergranular cracking was, however, rather shorter in the LS steel than the HS steel. Such a phenomenon can be understood on the basis of the previous research,\(^{12,14}\) which report the role of MnS precipitates acting as a strong sink of free sulfur segregating to the interfaces.

If a precipitation reaction related to the segregating species occurs in the matrix, the precipitation reaction causes the anomalous segregation kinetics of the species.\(^{14,23–30}\)

Schematic diagrams for explaining the difference in segregation concentration of sulfur in the LS and HS steels are shown in Fig. 9. These are based on Fe–Ni–(Mn,Ti) steels\(^{23,24}\) age-hardened by the coherent \(\theta\)-MnNi or \(\eta\)-NiTi precipitates and Fe-3%Si steels\(^{40}\) showing the MnS precipitation reaction. In order to simplify the explanation, it is assumed that the bulk sulfur content of the LS steel corresponds to the solubility of sulfur at the rupture test temperature \(T_o\). Concentrations \(C_{S}(t)\) and \(C_{ES}\) are the grain boundary segregation concentration of sulfur at a time \(t\) and the equilibrium grain boundary segregation concentration of sulfur in the LS steel, respectively. \(C_{FS}\) of Fig. 9 is the grain boundary segregation concentration of sulfur which corresponds to the intergranular cracking under the same applied stress. As a result, \(C_{FS}\), which causes the intergranular cracking, is same in both steels.

The grain boundary segregation concentration of sulfur in the LS steel increases gradually with increasing time and is saturated at \(C_{ES}\), as shown in Fig. 9(a). During the active MnS precipitation in the HS steel of the oversaturated sulfur, if the interface is coherent, some sulfur moves toward the precipitate for its growth. The other dissolved sulfur segregates actively to the grain boundaries, resulting in the segregation profile\(^{23,24}\) of Fig. 9(b).

![Schematic diagrams for explaining the difference in segregation concentration of sulfur in the LS and HS steels of the large grain size during rupture time and the resulting time to failure.](image-url)
(2) The elevated temperature intergranular cracking is mainly due to the sulfur segregation to grain boundaries.
(3) The time to failure is on the whole shorter in the steel of the smaller grain size in the present experimental condition. However, it is generally determined by the competition between the creep resistance and the grain boundary embrittlement rate.
(4) The fracture mode and the time to failure are determined by the combination of the bulk sulfur content and the grain size influencing the creep resistance and the equilibrium segregation concentration even at the same bulk sulfur content.
(5) The time to failure in the intergranular cracking is rather longer in the steel of the higher bulk sulfur content. This is attributed to the active incoherent MnS precipitation reaction within the matrix, the interface of which acts as a strong sink of the free sulfur segregating to the grain boundaries.

Acknowledgment
The authors are grateful to Mrs. J. H. Yoon in KIST for the AES analyses.

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