

Mechanical Properties and Microstructures of Low-C Austenitic Heat Resistant Steel S34752 After Aging Heat Treatment

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Abstract

In petroleum refinery plants, materials with both high sensitization resistance and high creep strength are required for high temperature operation units such as a delayed coker. UNS No. S34752 (low C 18Cr-11Ni-3Cu-Mo-Nb-B-N) has been developed to meet this requirement. This study reports on the mechanical properties and microstructures of several aged specimens. It revealed that there were only a few coarse precipitates that assumed the sigma phase even after aging at 700°C for 30 000 h. This indicates that S34752 has superior phase stability. The developed steel increased its Vickers hardness by aging heat treatments, which may be due to the Cu-rich phase precipitation. S34752 demonstrated excellent creep rupture strength even in the long-term tests of approximately 70 000 h, which is attributed to these precipitates.

1. Introduction

In oil refinery plants, polythionic acid stress corrosion cracking (PTA-SCC) has become a serious problem. Materials with high sensitization resistance are required for this application. TP347H and TP321H, which are stabilized heat treated materials to precipitate fine NbC and TiC within the grains, have been used so far. In that case, post-weld heat treatment is required.¹⁻⁶⁾ TP347H and TP321H without post-weld heat treatment are very sensitive to PTA-SCC. This is because $M_{23}C_6$ carbides with Cr as the main component precipitate along the grain boundaries of the heat-affected zone where the grains are coarsened during the welding process. Consequently, Cr-depleted regions are created. In contrast, 347AP (18Cr-11Ni-Nb-N, ASME Code Case 2196-4) does not require post-weld heat treatment and has excellent sensitization resistance. This high sensitization resistance is derived from the low C content.^{7,8)} Furthermore, 347AP exhibits a higher maximum allowable stress than the conventional low-C austenitic steel TP304L (ASME, SA-213).

However, in high-temperature applications such as heavy oil thermal cracking equipment, superior creep strength is demanded in addition to sensitization resistance. To meet this demand, a low C 18Cr-11Ni-3Cu-Mo-Nb-B-N steel (UNS No. S34752) was developed.⁹⁾ The creep strength of S34752 is significantly higher than that of 347AP and TP347H. Previous studies have suggested that this high creep strength is derived from precipitation strengthening of the Cu phase and the Z phase (NbCrN). However, the detailed precipitation behavior of these phases at high temperatures has yet to be clarified. This report focuses on the precipitation behavior of the phases during the aging heat treatment of S34752 and the associated changes in the mechanical properties of S34752.

2. Body

2.1 Test steels and manufacturing method

Table 1 shows the chemical composition of the test steel S34752. Cylindrical billets produced by vacuum induction melting

Table 1 Chemical composition of tested steel

	C	Si	Mn	Ni	Cr	Cu	Nb	Mo	N	B	Fe
S34752	0.005–0.020	≤0.60	≤2.00	10.0–13.0	17.0–19.0	2.50–3.50	0.20–0.50	0.20–1.20	0.06–0.12	0.001–0.005	Bal.

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and hot forging were used as the test samples. Each billet was hot-extruded into a tube with an outer diameter of 73 mm and a wall thickness of 9.5 mm and solution heat treated.

Specimens were cut from the obtained steel tubes and aging heat treated at 550 to 750°C for 300 to 30000 h. The aged specimens were subjected to optical microscopy, extraction residue analysis, a Vickers hardness test, and Charpy impact test. The extraction residue analysis used a 10% AA-based electrolyte (10 vol% acetylacetone+1 mass% tetramethylammonium chloride+methanol solution). The Vickers hardness test was conducted with a load of 10 kg. The Charpy impact test was conducted on half-size V-notched specimens at 0°C. Furthermore, solution heat treated specimens were creep tested and creep rupture tested at 600 to 750°C. The microstructural observation of creep ruptured specimens used an optical microscope and a transmission electron microscope (TEM). Electrolytically polished thin film specimens were used for TEM observation.

2.2 Results and discussion

Figure 1 shows an optical micrograph of a specimen aged at 700°C for 30000 h. Even after long-term heat treatment, there are only a few coarse precipitates that appear to be the σ phase (FeCr).

To predict precipitates other than the σ phase, thermodynamic equilibrium phase calculations were performed using Thermo-Calc[®]. **Figure 2** shows the calculation results. The version of Thermo-Calc[®] used in the calculations was 2022a, the database was TCFE10, and the chemical composition was that of the test steel. For simplicity, the σ phase is not shown in Fig. 2. In the test steel, the Z phase, Cr₂N, M₂₃C₆, Cu phase, and Cr₂B are expected to precipitate. Since the Z phase precipitates even at high temperatures of 900°C or more, it is considered to contribute to the pinning effect and suppress grain growth during solution heat treatment. It has been reported that almost no Cr₂N is observed in S34752, which is free from impurities.¹⁰⁾ So, it is unlikely that Cr₂N precipitates in this test steel. Since the amount of M₂₃C₆ precipitated is very small, the effect of M₂₃C₆ on the mechanical properties of the material is also considered to be small.

In the following, the data obtained from the aged specimens is organized using the time-temperature parameter P . The time-temperature parameter P is expressed by the following equation using the Orr-Sherby-Dorn equation:

$$P = \log t - \frac{Q}{RT} \cdot \log e \quad (1)$$

where t is time (h), Q is activation energy (kJ/mol), R is gas constant, and T is temperature (K). In this report, the activation energy Q was set to 264 kJ/mol, which is the activation energy for Cr diffusion in γ -Fe.¹¹⁾

The precipitation amount of Cr and Nb determined by the extraction residue analysis was organized by the precipitation ratio X . The precipitation ratio X is the aging heat treatment-induced precipitation amount divided by the Thermo-Calc[®] calculated equilibrium precipitation amount and is expressed by:

$$X = \frac{M - M_0}{M_c - M_0} \quad (2)$$

where M is the precipitation amount in the aged specimen, M_0 is the precipitation amount in the solution heat treated specimen, and M_c is the equilibrium precipitation amount calculated by Thermo-Calc[®]. The values obtained by the extraction residue analysis were used for M and M_0 . In addition, M_c was defined only as the precipitation amount of the Z phase and M₂₃C₆.

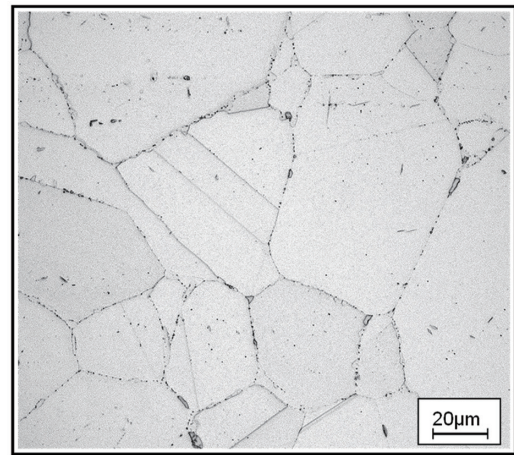


Fig. 1 Microstructure of tested steel aged at 700°C for 30000 h

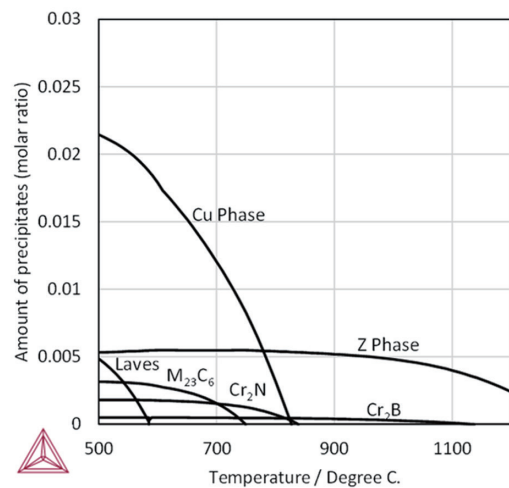


Fig. 2 Equilibrium amount of precipitates calculated by Thermo-Calc[®]

Figure 3 shows the precipitation ratio X of Cr and Nb organized by the time-temperature parameter P . In the figure, as the parameter P increases, the temperature and time increase. Nb is one of the constituent elements of the Z phase and not much of it is contained in M₂₃C₆. The precipitation amount of Nb begins to increase when the parameter P exceeds -13.0 and remains approximately constant when the parameter P is above -11.0 . When the parameter P is -11.0 , the residue amount of Nb is 0.28 mass% and practically equal to the total Nb content of 0.30 mass% in the test steel. This suggests that when the parameter P is -11.0 or higher, the amount of solute Nb is small, and the precipitation amount of the Z phase is saturated. On the other hand, Cr is a constituent element of both the Z phase and M₂₃C₆. Therefore, the precipitation of Cr is considered to be derived from the Z phase and M₂₃C₆. Compared to Nb, Cr increases slowly and monotonically. This is thought to be due to the phase transition from the MX phase to the Z phase during aging heat treatment.^{12,13)} Yoshizawa et al. stated that Cr and Fe begin to concentrate as M₂N₂ in MX during aging, change continuously to M₂N_(2-a), then to the ordered lattice tetragonal M₂N, and finally to the disordered lattice tetragonal M₂N that is the Z phase.¹³⁾ When the present specimens are held at the same temperature, for exam-

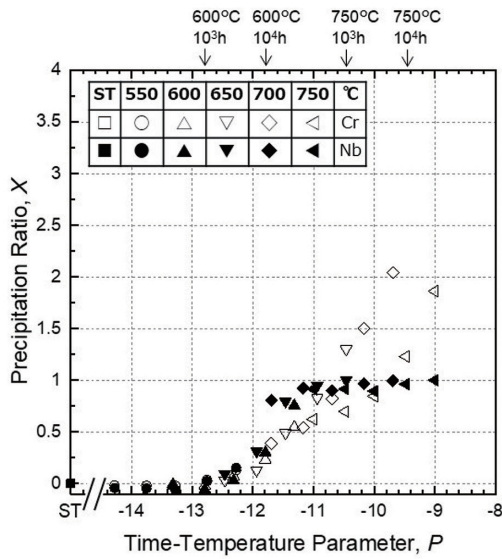


Fig. 3 Relationship between time-temperature parameter and precipitation ratio of Cr and Nb

ple, it is considered that MX with a high Nb concentration precipitates first. Cr is gradually enriched in the precipitate, and finally, MX transitions to a stable Z phase. When the parameter P exceeds -10.5 at temperatures above 650°C , the Cr precipitation ratio increases significantly. This may be ascribed to the precipitation of the σ phase observed with an optical microscope.

Figure 4 shows the Vickers hardness organized by the time-temperature parameter P . The Vickers hardness shows a larger variation than the precipitation ratio X . This is because the Vickers hardness is affected by both the precipitation amount and distribution. As shown in Fig. 4, even if the parameter P is -13.0 or less, the aged specimens are harder than the solution heat treated (ST) specimens. Since neither $M_{23}C_6$ nor the Z phase precipitates when the parameter P is -13.0 or less, it is considered that the test steel was hardened by the precipitation of the Cu phase that cannot be extracted with the 10% AA electrolyte solution. When the precipitation amount of the Z phase is saturated at the parameter P of -11.0 or higher, the test steel softens. This result suggests the softening of the material by the Ostwald growth of the precipitates.

Figure 5 shows the Charpy impact values organized by the parameter P . When the parameter P is -13.0 or less, the Charpy impact value of the aged specimens is equivalent to that of the ST specimens. This suggests that the effect of the Cu phase precipitation on the Charpy impact value is small. As the time-temperature parameter P increases from -13.0 to -11.0 , the Charpy impact value gradually decreases. This is presumed to be attributable to the precipitation of the Z phase and $M_{23}C_6$. As the parameter P exceeds -11.0 , where the precipitation amount of the Z phase is saturated, the Charpy impact value continues to decrease. The aging heat treatment for 30000 h at any temperature markedly decreases the Charpy impact value. The existing austenitic heat-resistant steel HR3C is reported to decrease in toughness when aging heat treated at 700°C for a long time. The causes of this embrittlement are reported to be the grain boundary segregation of S and the precipitation of $M_{23}C_6$.¹⁴⁾ The decrease in the toughness of the test steel after aging heat treatment may also be ascribed to the segregation of S and the grain boundary precipitation of the σ phase, Z phase, or $M_{23}C_6$.

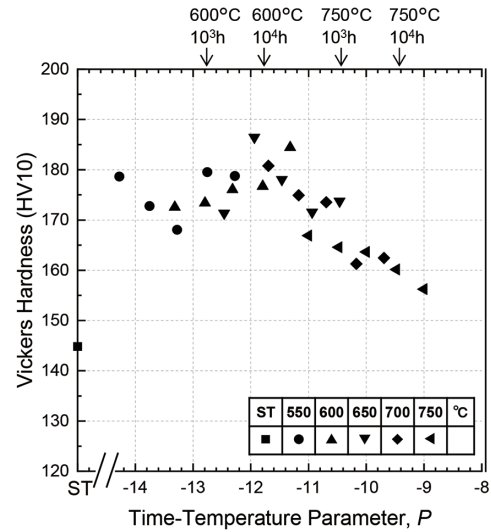


Fig. 4 Relationship between time-temperature parameter and Vickers hardness

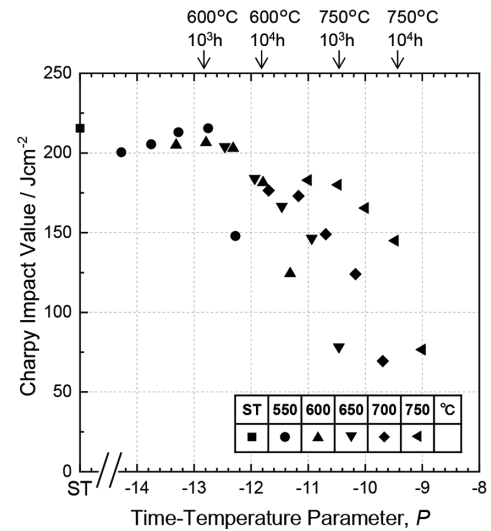


Fig. 5 Relationship between time-temperature parameter and Charpy impact value

However, when aging heat treated at 700°C for 30000 h, the test steel still exhibited an excellent Charpy impact value of 69.4 J/cm^2 , which is sufficiently high compared to that of HR3C. At 750°C , the Charpy impact value decreases more slowly than at other temperatures. This suggests that the nose temperature for the σ phase precipitation is lower than 750°C .

Figure 6(a) shows the stress-time to rupture curves of the test steel. Even in the range of over 70000 h, the test steel shows no significant decrease in strength and exhibits excellent creep strength. This high creep strength may be ascribed to the contribution of precipitates such as the Cu phase, Z phase, and $M_{23}C_6$. Figure 6(b) shows the creep strength normalized by Young's modulus with respect to the time-temperature parameter P . The test steel exhibits excellent creep strength even when the parameter P is -11.0 or more, which is the region where the σ phase precipitation and the Ostwald growth occur. When the normalized stress exceeds 0.7, the

creep strength increases as the temperature decreases. This normalized stress corresponds to 50 to 65% of the 0.2% proof stress at each test temperature, so below this value, plastic deformation is unlikely to occur. Therefore, the temperature dependence is considered to be small when the normalized stress is 0.7 or less. The time-temperature parameter P can be used to estimate the stress exponent n . The

stress exponent n is defined as follows:

$$P = -n \log \sigma_n + C \quad (3)$$

where σ_n is the normalized creep strength, and C is the material constant. The stress exponent n obtained by the regression analysis of the experimental data with a normalized creep strength of 0.7 or less was 3.6. This value falls within the range of 3.0 or higher, indicating dislocation creep.

Microstructural observation was performed on the creep rupture specimen shown in red in Fig. 6(b). This specimen ruptured after 29380.6 h at 750°C under a stress of 50 MPa. Figure 7 is an optical micrograph of the gauge portion of the fractured specimen. Cracks, which are presumed to be caused by creep deformation, can be seen at the grain boundaries nearly perpendicular to the tensile direction.

A bright field image of the gauge portion of the same creep rupture specimen is shown in Fig. 8. As shown in Fig. 8(a), the dislocations are accumulated along the grain boundaries. Since the strain is concentrated at the grain boundaries due to deformation, cracks are presumed to eventually form along the grain boundaries, as shown in Fig. 7. Figure 8(b) shows a bright field image of inside the grain. There are two types of precipitates: one is a fine precipitate marked by a yellow arrow, and the other is a spherical precipitate marked by a red arrow. Since both precipitates are associated with dislocations, it is suggested that both precipitates contribute to the creep strengthening of the test steel. Figure 8(c) shows an electron diffraction pattern of the fine precipitates. This electron diffraction pattern matches

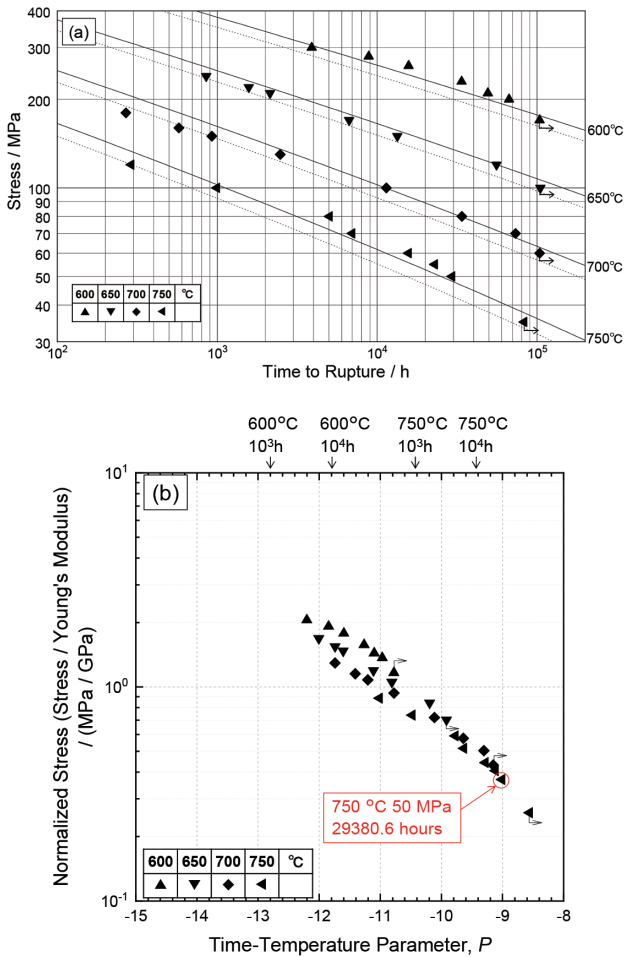


Fig. 6 (a) stress-time to rupture curves (b) effect of time-temperature parameter on creep strength

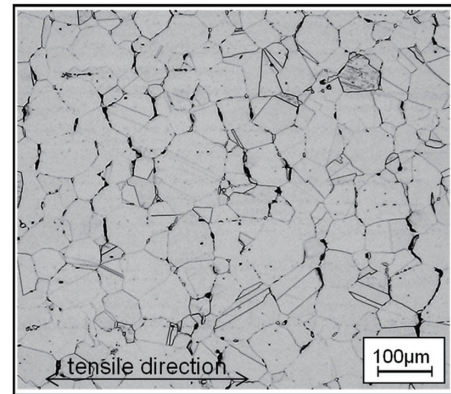


Fig. 7 Microstructure of gauge portion of tested steel ruptured at 750°C after 29380.6 h

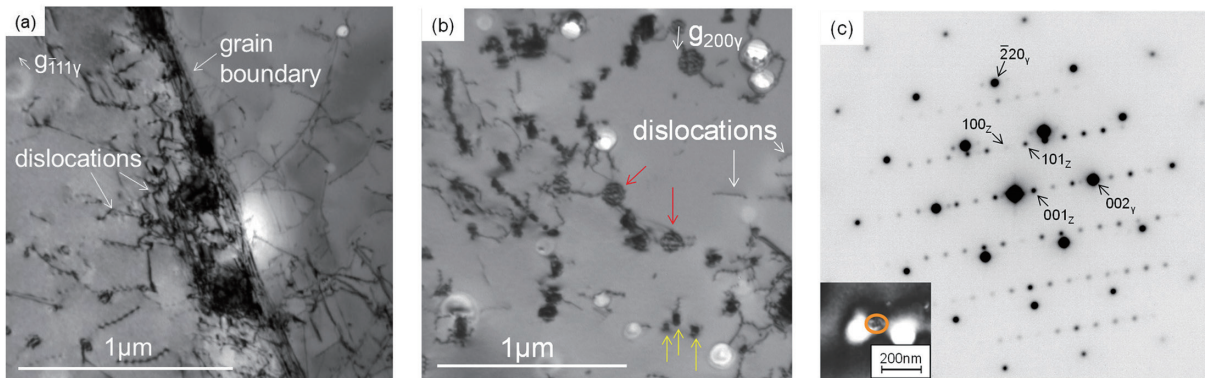


Fig. 8 (a) bright field image around grain boundary of ruptured steel (b) bright field image of inside grain of ruptured steel (c) selected area diffraction pattern of fine precipitate marked in yellow

the electron diffraction patterns of the Z phase incident from $[010]_Z$ and the austenite phase incident from $[110]_Z$. From Fig. 8(c), it can be said that there are orientation relationships of $[010]_Z//[110]_Z$ and $[001]_Z//[001]_Z$. This result matches that of a previous study.¹⁵⁾ Figure 9 shows a transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) map of the creep ruptured specimen. The distribution of Nb is shown in pink, and the distribution of Cu is shown in blue. The fine precipitates contain Nb. From the EDS mapping and the electron diffraction pattern in Fig. 8(c), the fine precipitates are identified as the Z phase. MX was not detected in the creep ruptured specimen. Since the spherical precipitates contain a large amount of Cu, they are considered to be the Cu phase. Since their size and shape are similar to those of the Cu phase, the white holes in the microstructure are thought to be traces of the Cu phase detached during electrolytic polishing. Since the TEM observation did not detect $M_{23}C_6$, the precipitation amount of $M_{23}C_6$ is suggested to be smaller than that of the Cu and Z phases.

3. Conclusions

We investigated the effects of aging heat treatment on the mechanical properties and microstructure of the UNS No. S34752 steel (low C 18Cr-11Ni-3Cu-Mo-Nb-B-N). The results obtained are summarized below.

- (1) In the S34752 steel, the precipitation amount of the σ phase is small even after aging heat treatment at 700°C for 30 000 h.
- (2) The Cu phase precipitates when the time-temperature parameter P is -14.0 or less. When the time-temperature parameter ranges from -13.0 to -11.0 , the Z phase and a small amount of $M_{23}C_6$ precipitate. The Vickers hardness increases with the precipitation amount, but after long-term aging heat treatment, it decreases due to the Ostwald growth. The S34752 steel shows an excellent Charpy impact value even after long-term aging heat treatment, which causes the precipitation of the Z phase, σ phase, $M_{23}C_6$, and the Ostwald growth.
- (3) The S34752 steel exhibits excellent creep strength even under prolonged exposure to high temperatures. This remarkable strength is attributed to the precipitation of the Cu phase and Z phase.

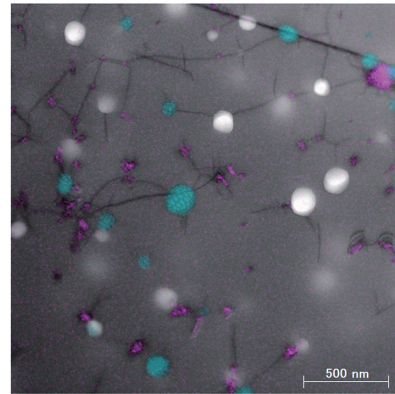
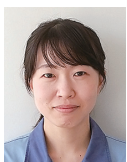


Fig. 9 TEM-EDS mapping on bright field image (pink indicates Nb, blue indicates Cu)

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