Microstructural Evolution and the Effect on Mechanical Properties of S30432 Heat-resistant Steel during Aging at 650°C

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In this paper, the mechanical properties and microstructural evolution of S30432 heat-resistant steel during aging at 650°C were investigated, and the effect of microstructural evolution on the yield strength, tensile strength, hardness and impact toughness was discussed. The results show that, the change of strength and hardness can be divided into three stages. In the first stage (before 500 h), the precipitation of fine \(\varepsilon\)-Cu plays a main role in the significant increase of the strength and hardness. In the second stage (500–5 000 h), the coarsening of \(\varepsilon\)-Cu is the key factor to decrease the strength and hardness. After 5 000 h of aging, there is no obvious change in the strength and hardness. Similarly, the change of impact toughness during aging of S30432 steel at 650°C can also be divided into three stages. The sharp decrease of impact toughness in the first stage results from the precipitation of \(M_{23}C_6\) and \(\varepsilon\)-Cu particles. At stage II, the impact toughness keeps on declining as a result of gradual coarsening of \(M_{23}C_6\), \(\varepsilon\)-Cu and \(Nb(C, N)\). Finally, \(M_{23}C_6\), \(\varepsilon\)-Cu and \(Nb(C, N)\) are relatively stable, so that the impact toughness tends to be stable gradually.

KEY WORDS: heat-resistant steel; aging; microstructural evolution; mechanical properties; \(\varepsilon\)-Cu particles.

1. Introduction

In recent years, the development of ultra super critical (USC) plants is accelerated by the demands of environment protection and energy saving, and USC plants with steam temperature and pressure conditions in excess of 593°C and 24.1 MPa respectively were constructed. In Japan, the ultimate steam conditions are targeted at 650°C and 34.3 MPa. To achieve the goal, it is important to develop new materials with excellent high temperature strength, superior resistance to oxidation and corrosion at high temperature. Besides, it is essential that the properties of used materials should not be deteriorated at elevated temperature, and their cost must be low enough to meet the requirement of plants.

Many new heat-resistant steels with good comprehensive properties have been developed. S30432 (0.1C–18Cr–9Ni–3Cu–0.4Nb–0.08N) is a promising austenitic heat-resistant steel, which is suitable to be used in USC boilers operating at pressure in excess of 30 MPa and temperature higher than 630°C. It has more than 30% higher creep rupture strength at 600–700°C compared with TP347H. This excellent strength is based on the finely precipitated particles such as Cu-rich phase, \(M_{23}C_6\), NbCrN and Nb(C, N). The resistance to oxidation and corrosion of S30432 at high temperature is superior to TP321H. S30432 still exhibits a good performance in spite of more than ten years when used for superheater and reheater tubes in Japanese USC plants.

It is well known that the mechanical properties of heat-resistant steels tend to degrade owing to microstructural evolution after long-term service at high temperature. However, it is not clear that how the microstructural evolution affects the mechanical properties of S30432 heat-resistant steel during aging. In this paper, the mechanical properties and microstructural evolution of S30432 steel during aging at 650°C were investigated, and the effect of microstructural evolution on the yield strength, tensile strength, hardness and impact toughness was discussed.

2. Materials and Experimental Methods

S30432 heat-resistant steel tubes were produced by Baoshan Iron and Steel Co., Ltd. The chemical composition is given in Table 1. The heat treatment included the so-

<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Al</th>
<th>B</th>
<th>P</th>
<th>V</th>
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</tr>
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<tr>
<td>0.084</td>
<td>18.28</td>
<td>8.81</td>
<td>2.94</td>
<td>0.60</td>
<td>0.84</td>
<td>0.28</td>
<td>0.096</td>
<td>0.010</td>
<td>0.004</td>
<td>0.013</td>
<td>0.010</td>
<td>0.005</td>
</tr>
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Table 1. Chemical composition of S30432 steel (mass%).
olution heat treatment at 1,150°C and water-cooling. The specimens were aged for 50, 100, 300, 500, 1,000, 3,000, 5,000, 8,000 and 10,000 h at 650°C, respectively. Both the as-supplied and as-aged specimens were used to carry out the tensile test, Charpy impact test and hardness measurement. In order to investigate the effect of microstructural evolution on the mechanical properties, the microstructure of as-supplied and as-aged specimens was examined by means of Nikon EPIPHOT 300 optical microscope (OM), JSM-5510 scanning electron microscope (SEM) and JEM-200CX transmission electron microscope (TEM).

3. Results

3.1. Mechanical Properties of S30432 Heat-resistant Steel Aged at 650°C

The mechanical properties of S30432 steel aged at 650°C are shown in Fig. 1. The change of strength and hardness with the aging time is similar, and can be divided into three stages. In the first stage (before 500 h), the yield strength, tensile strength and hardness gradually increase and reach the maximum at 500 h. In the second stage (from 500 to 5,000 h), they decline slowly. In the third stage (after aging for 5,000 h), there is no obvious change in the strength and hardness. The impact toughness can also be divided into three stages. It decreases quickly before 500 h. Then it keeps on decreasing but the velocity diminishes from 500 to 5,000 h. Finally, it tends to be stable after aging for 5,000 h.

3.2. Microstructure of As-supplied S30432 Heat-resistant Steel

The microstructure of as-supplied S30432 steel is typical austenite, and some twins can be observed (Figs. 2(a), (b)). A lot of fine particles are dispersed inside the grains and they are not uniform in size, approximately 20–100 nm in diameter, as shown in Fig. 2(c). Electron diffraction patterns indicate that the fine particles belong to only Nb(C, N). There are also a small amount of undissolved Nb(C, N) bigger than 300 nm inside the grains and at the grain boundaries (Fig. 2(d)). No Cu-rich phase, M₂₃C₆ or NbCrN is found in the as-supplied S30432 steel.

3.3. Microstructure of S30432 Heat-resistant Steel Aged at 650°C

Compared with the as-supplied microstructure, the S30432 steel aged at 650°C is still typical austenite and the grain size doesn’t change significantly (Fig. 3). SEM observation shows that many particles precipitate once aging and they tend to coarsen with the increase of aging time. After 50 h of aging, most of them precipitate along the grain boundaries (Fig. 3(a)). There are more and more particles at the grain boundaries after 100 h of aging. With the increase of aging time, the particles also precipitate inside the grains obviously. After aging for 500 h, there are a large amount of precipitations along the grain boundaries and inside the
grains (Fig. 3(b)). With further aging, the particles both at the grain boundaries and inside the grains coarsen continuously. In the specimen aged for 5 000 h, the coarsening of the precipitations at the grain boundaries and inside the grains is serious, and a large amount of large spherical particles are observed along the grain boundaries in the form of chain, as shown in Fig. 3(c). The particles coarsen slightly with further aging.

The newly formed precipitations in S30432 steel during aging are primarily $\varepsilon$-Cu and $M_23C_6$ identified by electron diffraction patterns. Figure 4 shows TEM micrographs of $\varepsilon$-Cu particles, indicating that fine and spherical $\varepsilon$-Cu are dispersed in the matrix. The average radius of $\varepsilon$-Cu particles is only 5 nm after aging for 500 h (Fig. 4(a)). With the increase of aging time, $\varepsilon$-Cu particles grow up gradually. When the aging time reaches 5 000 h, the average radius of $\varepsilon$-Cu particles is about 13 nm (Fig. 4(c)). In the following aging process, $\varepsilon$-Cu particles still tend to grow up, but the coarsening velocity diminishes greatly. The average radius of $\varepsilon$-Cu particles is only 15 nm even after aging for 10 000 h (Fig. 4(d)).

In addition to $\varepsilon$-Cu, $M_{23}C_6$ particles are also found to precipitate in the as-aged samples. Considering that $\varepsilon$-Cu and Nb(C, N) are too fine to be observed by SEM, most of the precipitations observed in Fig. 3 belong to $M_{23}C_6$. SEM observation shows that $M_{23}C_6$ particles precipitate firstly along the grain boundaries and then inside the grains. When the aging time prolongs from 500 to 5 000 h, $M_{23}C_6$ particles coarsen quickly. Further aging only leads to a slight increase in the size of $M_{23}C_6$. The change of $M_{23}C_6$ particles during aging can be further proved by TEM, as shown in Fig. 5. There is no $M_{23}C_6$ in as-supplied S30432 steel, see Fig. 5(a). However, aging at 650°C results in the precipitation of $M_{23}C_6$. Most of $M_{23}C_6$ particles are distributed at the grain boundaries in the specimen aged for 100 h, see Fig. 5(b). With the increase of aging time, the coarsening of $M_{23}C_6$ is easier than $\varepsilon$-Cu. Compared with 100 h, the size of $M_{23}C_6$ is much larger after aging for 5 000 h (Fig. 5(c)).

Nb(C, N) particles are observed in the as-supplied microstructure (Fig. 2(c)), and they are not uniform in size.

4. Discussion

Aging of S30432 steel at 650°C results in the precipitation of $\varepsilon$-Cu and $M_{23}C_6$, and $\varepsilon$-Cu, $M_{23}C_6$ and Nb(C, N) tend to coarsen during aging. The change in mechanical properties is related to the microstructural evolution of S30432 during aging.
4.1. Effect of Microstructural Evolution on Strength and Hardness

Yield strength, tensile strength and hardness of S30432 steel increase gradually in the first stage of aging. There is no change in Nb(C, N) particles at stage I, while the pronounced microstructural evolution of S30432 is the precipitation and coarsening of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) carbides. Hence, the hardening behavior at stage I results from the precipitation strengthening of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\).

According to the interaction between dislocations and particles, the precipitation strengthening can be divided into cutting mechanism and Orowan bypass mechanism. When the particles are small enough to be sheared by the dislocations, the cutting mechanism is dominant. Once the size of particles exceeds a critical value, Orowan bypass mechanism dominates. Considering that the average radius of \(\epsilon\)-Cu in the specimen aged for 500 h is 5 nm, \(\epsilon\)-Cu can probably be sheared by the dislocations. Thus the precipitation hardening by elastically strained \(\epsilon\)-Cu particles helps to increase the strength and hardness in the early stage of aging. However, the average radius of M\(_{23}\)C\(_6\) in the specimen aged for 500 h is 50 nm, which is relatively big and should be non-shearable, the dislocations tend to bypass M\(_{23}\)C\(_6\) particles by Orowan process. In order to compare the contribution of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) to the hardening at stage I, the interaction between dislocations and particles was calculated. For simplification, the pinning force \(\Delta\tau\) by \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) can be estimated by Eq. (1) \(^{12}\) when supposing that the particles are non-shearable.

\[
\Delta\tau = \frac{\alpha G b}{\lambda} \quad \text{(1)}
\]

Where \(\alpha\) is a constant and can be roughly estimated to be about 0.8, \(G\) is the shear modulus of matrix (about 51.5 GPa at 650°C), \(b\) is the Burgers vector of dislocation (about 0.25 nm) and \(\lambda\) is the mean free path among dispersed particles. \(\lambda\) can be given by Eq. (2) as a function of the volume fraction \(f\) and average radius of dispersed particles \(r\): \(^{13}\)

\[
\lambda = 2r(1 - f^{1/3}) f^{1/3} \quad \text{(2)}
\]

From Eqs. (1) and (2),

\[
\Delta\tau = 5.15 \frac{f^{1/3}}{1 - f^{1/3}} \frac{1}{r} \quad \text{(3)}
\]

Therefore, the pinning force \(\Delta\tau\) will be stronger if there are more particles with small size. After 500 h of aging at 650°C, the average radius of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) in S30432 steel is separately 5 nm and 50 nm. Thermo-Calc software can be used to calculate the volume fraction of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) in S30432 steel under equilibrium state at 650°C, \(f_{\epsilon-Cu} = 0.019046, f_{M_{23}C_6} = 0.00163.\) Obviously, the volume fraction of \(\epsilon\)-Cu is much higher than M\(_{23}\)C\(_6\) and the size of \(\epsilon\)-Cu is much smaller than M\(_{23}\)C\(_6\) so the pinning force caused by \(\epsilon\)-Cu will be much stronger than M\(_{23}\)C\(_6\). The pinning force of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) was calculated using Eq. (3), showing that the contribution of \(\epsilon\)-Cu to the strength of S30432 steel after aging for 500 h is 27 times as strong as that of M\(_{23}\)C\(_6\). This indicates that although the precipitation of \(\epsilon\)-Cu and M\(_{23}\)C\(_6\) plays a role in the increase of the strength and hardness in the first stage, the precipitation strengthening of fine \(\epsilon\)-Cu is the main factor.

In the second stage, the coarsening of \(\epsilon\)-Cu, M\(_{23}\)C\(_6\) and Nb(C, N) leads to the increase of the mean free path \(\lambda\) and thus the decrease of the pinning force \(\Delta\tau\). Therefore, the strength and hardness of S30432 steel decrease in the second stage during aging.

During overaging the volume fraction of precipitations \(f\) is assumed to be constant, \(^{14}\) thus

\[
\frac{df}{dt} = \frac{1}{5.15} \frac{1}{1 - f^{1/3}} \frac{1}{r} \quad \text{(4)}
\]

Equation (4) implies that the pinning force decreases more quickly for the precipitations with smaller size, faster coarsening velocity and higher volume fraction, and the effect of particle size on \(df/dt\) is more than the coarsening velocity and volume fraction.

In order to understand the effect of \(\epsilon\)-Cu, M\(_{23}\)C\(_6\) and Nb(C, N) on the strength in the second stage, the changes of particle size and pinning force of \(\epsilon\)-Cu, M\(_{23}\)C\(_6\) and Nb(C, N) with aging time are given in Fig. 7. It can be seen that the coarsening of \(\epsilon\)-Cu, M\(_{23}\)C\(_6\) and Nb(C, N) results in the decrease of pinning force at stage II. Especially the pinning force of \(\epsilon\)-Cu decreases more quickly. In Eq. (4), \(f^{1/3}/(1 - f^{1/3})\) of \(\epsilon\)-Cu, Nb(C, N) and M\(_{23}\)C\(_6\) is 0.36, 0.26, 0.13, respectively. Compared with M\(_{23}\)C\(_6\), the coarsening velocity of \(\epsilon\)-Cu is much lower, but the radius of \(\epsilon\)-Cu is much smaller and \(f^{1/3}/(1 - f^{1/3})\) is bigger, so the pinning force owing to the coarsening of \(\epsilon\)-Cu is reduced much more than M\(_{23}\)C\(_6\). Besides, the decrease of pinning force due to the coarsening of Nb(C, N) particles is not as significant as \(\epsilon\)-Cu because the radius of \(\epsilon\)-Cu particles is smaller than Nb(C, N). In conclusion, the coarsening of \(\epsilon\)-Cu is the key factor to decrease the strength and hardness at stage II since the radius of \(\epsilon\)-Cu is the smallest and the value of \(f^{1/3}/(1 - f^{1/3})\) is the biggest, although the coarsening velocity of \(\epsilon\)-Cu during aging is low.

In the third stage, the coarsening velocity of \(\epsilon\)-Cu, M\(_{23}\)C\(_6\) and Nb(C, N) is so slow that there is no obvious change in

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the strength and hardness.

4.2. Effect of Microstructural Evolution on Impact Toughness

Impact toughness is strongly dependent on microstructural variables such as the size, volume fraction and distribution of the precipitations (especially at the grain boundaries). The impact toughness of S30432 steel decreases during aging at 650°C, which can be directly attributed to the precipitation and coarsening of particles.

Generally speaking, the increase in strength during aging is accompanied by the decrease in impact toughness, because the extent to which the stress concentration ahead of the notch relaxed by plastic deformation decreases when the yield stress increases. It can be seen from Fig. 1 that the impact toughness of S30432 steel decreases in the first stage, whereas the strength increases during aging at 650°C. The above-mentioned experimental results show that in the first stage of aging, more and more \( \varepsilon \)-Cu and \( M_23C_6 \) precipitate with the prolonging of aging time. The increase of hardness and strength owing to the precipitation of \( \varepsilon \)-Cu and \( M_23C_6 \) makes the specimen more brittle, and correspondingly the impact energy decreases since less plastic work can be done before the strain in the plastic zone is sufficient to fracture the test specimen. Impact toughness decreases with the increase of precipitation volume fraction. In the first stage of aging the impact toughness of S30432 decreases accompanied by the precipitation of more and more \( \varepsilon \)-Cu and \( M_23C_6 \). Therefore, the sharp decrease of impact toughness in the first stage results from the precipitation of \( \varepsilon \)-Cu and \( M_23C_6 \). Especially the precipitation of \( M_23C_6 \) at the grain boundaries is very harmful to the impact toughness during aging due to the reduction in the cohesive strength of grain boundaries.

In the second stage, the obvious microstructural change is the coarsening of \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N). Regardless of the particles at the grain boundaries or inside the grains, the toughness will decrease when they coarsen. Hence, the impact toughness keeps on declining as a result of gradual coarsening of \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N) in the second stage. Especially, the size of \( M_23C_6 \) particles is larger and the coarsening is easier in contrast to \( \varepsilon \)-Cu and Nb(C, N), thus the decrease of impact toughness is mainly attributed to \( M_23C_6 \) since the matrix is easier to be divided by larger particles. However on the whole, the volume fraction of \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N) hardly changes, and the strength and hardness decline slowly at stage II. Besides, the spheroidization of \( M_23C_6 \) may weaken the decrease of impact toughness. Therefore, the declining velocity of the impact toughness diminishes in the second stage although it keeps on decreasing.

In the third stage, there is a slight coarsening of \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N) and they are relatively stable, so that the impact toughness tends to be stable gradually.

5. Conclusions

(1) The microstructure of the as-supplied and as-aged S30432 steel is austenite. In the as-supplied S30432 steel, the main precipitation consists of only Nb(C, N). Aging results in the precipitation of \( \varepsilon \)-Cu and \( M_23C_6 \). With the increase of aging time \( \varepsilon \)-Cu particles grow up gradually, but the growth velocity of \( \varepsilon \)-Cu particles diminishes greatly and they are still very fine in the long-term aging range. Fine Nb(C, N) tends to grow very slowly and become relatively uniform in the size during aging. The size of \( M_23C_6 \) is larger and the coarsening is easier than \( \varepsilon \)-Cu and Nb(C, N).

(2) The change of strength and hardness during aging of S30432 steel at 650°C can be divided into three stages. At stage I (before 500 h), the precipitation of \( \varepsilon \)-Cu and \( M_23C_6 \) plays a role in the increase of the strength and hardness, but the precipitation of fine \( \varepsilon \)-Cu is the main factor. At stage II (500–5 000 h), the coarsening of \( \varepsilon \)-Cu, \( M_23C_6 \) and Nb(C, N) result in the decrease of strength and hardness, but the coarsening of \( \varepsilon \)-Cu is the key factor. At stage III (after 5 000 h), the coarsening velocity of \( \varepsilon \)-Cu, \( M_23C_6 \) and Nb(C, N) is so slow that there is no obvious change in the strength and hardness.

(3) The change of impact toughness during aging of S30432 steel at 650°C can also be divided into three stages. The sharp decrease of impact toughness in the first stage results from the precipitation of \( M_23C_6 \) and \( \varepsilon \)-Cu particles. At stage II, the impact toughness keeps on declining as a result of gradual coarsening of \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N). Finally, \( M_23C_6 \), \( \varepsilon \)-Cu and Nb(C, N) are relatively stable, so that the impact toughness tends to be stable gradually.

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