Effect of long term aging on Microstructure and precipitates of valve bolts in power plant

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Abstract. 10Cr11Co3W3NiMoVNbNB is used as the materials of Intermediate Pressure Control Valve, High Pressure Control Valve, and Main Stop Valve in some thermal power plant. After 45,000 hours of operation, the mechanical properties of this those materials has have been decreased greatly. By means of scanning electron microscopy, transmission electron microscopy and thermodynamic software simulation analysis, the conclusions can be drawn: under this operation environment, the coarsening of martensite lath and the dissolution-reprecipitation of second phases such as M23C6 carbides and MX phases are the main reasons which result in the decrease both in the room mechanical properties and high temperature mechanical properties of materials.

Keywords: Co3W3; valve bolts; mechanical properties; M23C6; MX phases.

1. Introduction
10Cr11Co3W3NiMoVNbNB steel, a kind of the martensitic steels, are favored for high temperature applications, such as boiler and thermal turbine components in power plants, due to their stable structure and excellent oxidation-resistant and corrosion resistance properties [1-5]. It is widely used for blades, valve bolts in some manufacturing companies [6-10]. However, after long-term service at such a high temperatures, the evolution of microstructure and the precipitation and growth of carbides will seriously affect the mechanical properties of materials, which will lead to the failure of parts. Therefore, many scholars and researchers devote to improve the stability of precipitates and prevent the evolution of microstructure of martensitic heat-resistant steel.

It is generally considered that M23C6 carbides and MX particles are the most common precipitates in many kinds of precipitates of 9-12%Cr martensitic heat-resistant steel. Among M23C6 carbides mainly precipitate along the prior austenite grain boundary and large angle grain boundary, such as martensitic plate strip and lath boundary. The precipitation of M23C6 carbides at grain boundary is the obstacle of microstructure evolution, which has great influence on grain boundary strengthening. Significantly, during the long term creep process, the coarsening of M23C6 is tended to happened due to the fact that...
Fe and Cr atoms in solid solution are the main components of M$_{23}$C$_6$ carbides [11]. Therefore, preventing the coarsening of M$_{23}$C$_6$ carbides is the key to improving the creep strength. As described in previous papers, Abe [12] noted that the coarsening of M$_{23}$C$_6$ carbides containing tungsten is slow and its creep life is more likely to prolong because of the low diffusion coefficient of tungsten. Another family of precipitated phases of crucial importance for mechanical performance is that of MX phases. Liu [13] has pointed out that MX particles are not easy to grow during long-term creep at high temperature due to the small solid solution rate of Nb and V which are main components in MX particles in ferrite matrix. Many studies [14-15] have reported that they have a B1 (NaCl) crystal structure and were classified according to their morphology and chemical composition in the following way:

- Type I precipitates are cuboids or spheroid-like and Nb-rich.
- Type II precipitates are plate or rod shaped and V-rich.
- Type III precipitates are the so-called “wings”, in which V-rich rods, ellipsoids or plates grow after nucleating on the sides of a Nb-rich spherical core.

Unfortunately, the effect of precipitates on bolt performance during long-term service in the actual power plant has not been sufficiently investigated by statistically methods. In this paper, the valve bolts which are located in the different positions were investigated and an explanation for the degraded toughness under 36,000 service hours was proposed.

2. Experimental details

The following test steels were collected from Intermediate Pressure Control Valve, High Pressure Control Valve and Main Stop Valve (hereinafter referred to as IP.CV, HP.CV, MSV respectively) of a 600℃ thermal steam turbine unit in a power plant which have ran over 36,000hours. The contrast sample is completely heat-treated bar without service. Chemical composition of these steels are listed in Table 1.

![Table 1. Chemical composition of 10Cr11Co3W3NiMoVNbNB steels (wt %)](image)

These steels were sampled for mechanical properties testing with the size of 50×100×100mm V-notch Sharpy impact sample and in diameter of 10 mm tensile sample (including room temperature and high temperature) and 6.4mm short time rupture sample relatively. The Impact sample residue for optical microscopy (OM, Leica DM6M) and scanning electron microscopy (SEM Hitachi S4300) were polished and etched by FeCl$_3$;HCl;H$_2$O=5g;50ml;100ml solution. More detailed microstructure observation was carried out on transmission electron microscopy (TEM, Hitachi H800). Thin films for TEM specimens were prepared using mechanical milling and conventional dual-jet electropolishing in the solution of HClO$_4$+CH$_3$CH$_2$OH at a temperature of -25℃, then further thinned by ion beam milling.

Thermodynamic calculations on equilibrium phase relationships and the numbers of the carbides were carried out under the CALPHAD (CALculation of Phase Diagrams) approximation with the software Thermocalc, for the composition of the original sample and MSV reported in the above quoted literature.
3. Results and discussion

3.1. Mechanical properties

Mechanical properties of 10Cr11Co3W3NiMoVNbNB steels at room temperature are given in Table 2. As obtained from mechanical properties testing result, Brinell hardness of all the valve bolts were tested about 250 HBW, which is obviously lower than original sample’s counterpart (293HB). The tensile strength also decreased to 838, 864 and 831MPa, respectively, whereas original sample’s compartment is 955MPa, which means the tensile properties decreased by approximately 13% at the room temperature. However, it can be seen from the Table 2 that the impact toughness after service is similar to that without service, and there is no obvious decrease.

The high temperature tensile properties test was carried out at 600°C for three valve bolts sample and original sample, as shown in Table 3. Compared with original sample, all the serviced sample are decreased in different degree, where MSV is the one with the most decrease in tensile properties of all valve bolts, dropping to 352MPa. Rm of IP.CV and HP.CV also decreased to 381 and 406, respectively.

| Type         | Rp0.02 | Rm  | A   | Z   | KV2 | HB     |
|--------------|--------|-----|-----|-----|-----|--------|
| Original Sample | 378 | 476 | 21  | 73  |      |        |
| IP.CV        | 299 | 381 | 24  | 81  |      |        |
| HP.CV        | 303 | 406 | 32  | 84  |      |        |
| MSV          | 238 | 352 | 31  | 89  |      |        |

3.2. Short-term creep rupture property

Short-term creep rupture property testing was carried out on original sample and three serviced sample at 600°C, and testing stress was 245MPa, according to the enterprise material standard. The results are shown in Table 4. Testing data suggest that normal material, that is to say original sample’s short-term creep rupture life is more than 100-hour. However, after 36,000 hours operation, short-term creep rupture property of all valve blots decreased drastically. Among them, MSV broke after only 0.3 hours under this test parameter, which was far below the 100-hour standard set by the enterprise.
Table 4  Short-term creep rupture property of 10Cr11Co3W3NiMoVNbNB steels at 600℃

| Type      | Temperature  | Stress | Time |
|-----------|--------------|--------|------|
| Original sample | 600          | 245    | 101  |
| IP.CV     | 600          | 245    | 11.3 |
| HP.CV     | 600          | 245    | 18.8 |
| MSV       | 600          | 245    | 0.3  |

Fig 1  Mechanical properties and short-term creep rupture property of 10Cr11Co3W3NiMoVNbNB.

3.3. Organizational changes after service
In order to facilitate the observation of the changes in the metallographic structure of the material after long-term service, the metallographic structure inspection and SEM scanning observation were carried out on the original sample and the three serviced valve bolts. The test results are shown in Fig 2 below. It is worth to notice that the metallographic microstructure of this material is typical tempered lath martensite. However, after a long service of the three valve bolts, it can be seen that the metallographic structure has changed significantly, the number of dispersion precipitates in the grain increased significantly, coincidently with the number of precipitates in the grain boundary also increased. Meanwhile, dispersed carbides began to grow along grain boundaries, and their sizes are obviously larger, especially for MSV. Compared with original sample, the morphology of matrix structure also changed obviously for three valve bolts.
Fig 2 Microstructure of three valve bolts and original sample
TEM scanning was carried out for the original sample and MSV to further analyze the changes of the microstructure of valve bolts after service, as shown in Fig 3. The TEM observation indicated that typical morphology of lath martensite appeared in original sample, with a little precipitate, along the grain boundaries. Whereas for MSV, the morphology of lath martensite had changed significantly: Lath martensite began to disappear, and some Y-junctions appeared, which is consistent with the results observed by F. Abe [16] in 9Cr-W steel. The movement of Y-junction has been discussed first by Dunn and Daniels [17] for the subgrain growth of polygonized silicon iron crystals and later by Gilman [18] for bent zinc monocrystals. It should be taken into account that there are a lot of precipitates formed at the Y-junction and the boundary of the lath martensite, which is slightly different from the experimental results of F. Abe. What’s more, the size of the precipitates is obviously larger than that of original sample’s counterpart, indicating that the precipitates continue to precipitate, dissolve and re-precipitate in the repeated movement of the lath martensite matrix boundary, which results in the continuous increase of its size, as shown in Fig 3(b).

![Fig 3 TEM of Martensite matrix in MSV and original sample](image)

3.4. Type and size of precipitate
Since MSV is the most mechanical property degradation of all valve bolts, and the microstructure had also changed, the main purpose of the further study on the precipitates of MSV is to compare with the original sample. Equilibrium compositions calculated by means of Thermocalc are also included.

Under TEM scanning electron microscope, we can clearly see the difference of morphology between MSV and the original sample after long-term service at 600℃. Meanwhile, M23C6 carbides, MX (V-rich and Nb-rich) and Laves phases were also found under electron microscope, and their morphology pictures are shown in Fig. 3. The results indicate that M23C6 carbides has found in the middle of the photo, whose morphology is shown in Fig 4(a). It is a black ellipse under the electron microscope, with a particle size of about 150nm, which is significantly larger than the size of the residual carbides in the normal Co3W3 material, and is distributed in the lath martensite grain boundaries and grains. At the same time, the MX phase was also observed, which is gray-black elliptical, with a particle size between 220nm-250nm, slightly larger than M23C6. In generally, MX phases has two types, namely V-rich phases and Nb-rich phases[19]. Fig 4(b) shows the morphology of Nb-rich MX phases in MSV, which has the same characteristics as the Type I precipitates mentioned above. After serving at 600℃, Laves phases were detected in the matrix, as shown in Fig 4(c). It can be seen from the figure that Laves phases were formed along the martensite grain boundary, adjacent to the M23C6 precipitate, with a size between 100 and 200 nm.
Through Thermocalc simulation calculation, the changes in the amount of M23C6 precipitates in MSV after service and the original sample can be intuitively seen, as shown in Fig 5. The results show that between 500°C and 800°C, as the temperature increased, the amount of M23C6 precipitates did not change significantly, which means that the phase equilibrium was reached in this temperature range. At a service temperature of 600°C, the molar fraction of the phase content of M23C6 is 0.029, which is higher than the phase content of M23C6 in original sample (0.026), indicating that after long-term service at this temperature, the M23C6 in the matrix was continuously dissolved-re Precipitate, gathered and grew up. Fig 7 shows the chemical composition changes of M23C6 in MSV and the original sample. As can be seen in the figure, after 36,000 hours of service at 600°C, the mole percentage of Cr in M23C6 increased from 0.632 to 0.643, with Fe and C elements also increased.

Kinetically, in the second phase, precipitates in the steel coarsen. This phase is characterised mainly by the increasing size of the precipitated phase. In the previous stage, precipitation phase reaches equilibrium, i.e. no further increase in the volume fraction of precipitates. In the second stage, although not increasing the volume fraction of precipitates, the precipitates can increase in size, to follow the law of Ostwald ripening. Large precipitates consume small size precipitates while increasing in size. This process is mainly controlled by diffusion of solute atoms to and from precipitates. The small size precipitates have continuous dissolution. Atoms through diffusion reach to the surface of the large size precipitates.

Grain boundary M23C6 precipitates are significantly larger than the size of precipitates in the grain. As there is no increase in the number of precipitates, precipitation hardening effect has been exhausted. Because precipitates coarsen, precipitation strengthening effect will be weakened. Therefore, with further extension of ageing time, the strength of steel shows a declining trend, as shown in Table 2 and 3.
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4. Conclusion
The microstructure observation and analysis of the three valve bolts whose mechanical property all decreased revealed that after 36,000 hours of service at 600°C, the tempered martensite of valve bolts basically recovered. Specifically, the continuous movement of the lath martensite during the coarsening process makes the boundary converge to form a Y-junction. At the same time, precipitation-strengthened alloying elements Cr, V, Nb, etc. in the solid solution are precipitated, and under the mechanism of dislocation movement, V-rich, Nb-rich MX phases are formed. Moreover, The M$_2$C$_6$ precipitate continuously dissolves and re-precipitates during the recovery process of the matrix, aggregates and grows, resulting in a significant decrease in the hardness of the material. In the study, it is observed that a small amount of Laves phase was formed along the grain boundary. In summary, the fundamental
reasons leading to the decrease in the mechanical properties of valve bolts are: 1. The lath boundaries in the matrix are coarsened, that is to say the phenomenon of matrix recovery occurs; 2. The precipitation-strengthened alloy elements in the martensite precipitate to form MX phase and M₂₃C₆ precipitation Phase, and a small amount of Laves phase.

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