Microstructural Evolution of a 12Cr–2W–Cu–V–Nb Steel during Three-year Service Exposure

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Microstructural evolution of 12Cr–2W–Cu–V–Nb steel tubes (ASME SA213-T122) after one-year and three-year service exposure tests in a Japanese practical boiler has been investigated from a standpoint of the phase stability of precipitates. The test tubes consist of tempered martensite and δ-ferrite, and the main precipitates are MX-type carbonitride, M23C6 carbide and Laves phase. TEM observations on thin films show that the MX has precipitated in a plate-shaped with a coherent or semi-coherent relationship with the matrix inside grains. An estimation of the lattice misfit between MX and the matrix suggests that the coherent strain has been high enough to enhance the shear stress and then strongly interact with dislocations. Another important point is that morphology and compositions of MX have been stable under the present service conditions, thereby the creep strength as well as tensile strength has kept high after long-term service exposure.

The long-term exposure to the present service temperature has enhanced the precipitation of Fe3(W, Mo) Laves phase inside grains, resulting in a marked reduction in the dissolved W and Mo in matrix. It is found that the kinetics of W-partitioning between matrix and Laves phase can be successfully expressed by the Johnson–Mehl–Avrami type equation and applied to estimate the actual temperatures of the exposed tubes.

It is concluded that the kinetics of Laves phase precipitation and morphology of MX have mainly controlled a microstructural stability in the 12Cr–2W–Cu–V–Nb steel, and also give helpful suggestion to increase the creep resistance during the long-term service exposure.

KEY WORDS: creep; precipitation; microscopy; steel for elevated temperature service.

1. Introduction

The recent trend toward protection of global environment is accelerating the application of ultra super critical (USC) boilers, which are operated with higher heat efficiency in power generation than in conventional boilers and thus release less amount of carbon dioxide.1–2) The USC boiler requires the advanced heat resistant materials with improved creep rupture strength and corrosion resistance at the elevated temperatures, because of an increase in operating temperature and pressure of the steam. A recent majority of heat resistant steels for the USC boiler has been based on 9–12% Cr steels micro alloying Mo, W, V, and Nb so as to increase the creep strength.3–5) Among these elements, the effect of Mo and W on the creep strength has been investigated from the point of solution strengthening and precipitation hardening effect. Previous studies showed that the excess W dissolved in matrix increased the creep resistance in low Cr steels.6–7) In W-bearing 9–12% Cr steels, on the other hand, it is considered that the finer M23C6 and Laves phase precipitating along grain boundaries and martensite lath boundaries retard a recovery of martensite lath structure, resulting in an increase in creep resistance.3) V and Nb are extensively utilized to optimize the precipitation hardening effect, since finely NaCl type carbonitrides represented by VC, VN, NbC, NbN, and the mixture of them (MX type carbonitrides) are expected to precipitate inside grains with high density and then obstruct the climb of dislocations.9)

The developed 12Cr–2W–Cu–V–Nb steel (ASME SA213-T122) is characterized by its superior corrosion resistance due to high amount of Cr. In addition, the creep strength of the steel is approximately 1.3 times higher than conventional 9Cr–1Mo–V–Nb steel (ASME SA213-T91) by substituting W for a part of Mo and optimizing chemistry and microstructure.10) In order to verify a practical performance of 12Cr–2W–Cu–V–Nb steel tubes, a service exposure in a practical boiler has been conducted. The various investigations on the test tubes have shown that there are no remarkable changes in tensile properties, impact properties, and creep rupture properties after 3-year service exposure, and then it is confirmed that this steel is potentially applicable for USC boilers.10)

The main purpose of this study is to clarify the strength-
ening mechanisms of 12Cr–2W–Cu–V–Nb steels by identifying the microstructural evolution during long-term service exposure. The present article has focused on the precipitation kinetics of Laves phase, with the consequence that the microstructural evolution has been successfully quantified by time-temperature dependence of W-partitioning between Laves phase and matrix, leading to the estimation of the actual temperatures of the exposed tubes. Another focus is the strengthening mechanisms due to MX-type carbonitride, which has coherent or semi-coherent relationship with matrix. This article has also proposed a coherent strengthening model and then estimated the most effective size and morphology of MX to increase the creep strength.

2. Experimental Procedure

Chemical compositions of the test tubes are given in Table 1. The test tubes with 38.1 mm in outside diameter and 7.4 mm in thickness have been installed into superheater in a 156 MW practical boiler, in which the maximum steam pressure was 19.2 MPa, and the steam temperature was 843 K at the outlet. The fuel for this boiler was mainly blast furnace gas and the test tubes were removed after 9200 h (one-year) and 20508 h (3-year) service exposure.

The tensile specimens with 6 mm in diameter and 30 mm in gauge length were machined from the test tubes before and after 1- and 3-year exposure and the tensile tests and the creep rupture tests were carried out. The microstructures of the test tubes were examined at both light and electron optical levels. The crystal structure and compositions of the precipitates were identified by transmission electron microscope (HITACHI-U700H) operated at 100 kV with EDX (Kevex delta-s) using extracted replica samples. The orientation relationship between precipitates and matrix was characterized by transmission electron microscope (JEOL2000EX) operated at 200 kV using thin foiles. The amount of precipitates was estimated by the quantitative chemical analysis of extracted residues from the test tubes before and after exposure. In order to clarify the time-temperature-precipitation diagram, unused tubes were aged at 823, 873, and 923 K up to 10000 h. The amount of precipitates for the aged specimens was also estimated by the quantitative chemical analysis of extracted residues, and equated with the Johnson–Mehl–Avrami type equation. This equation could be used to estimate the actual temperature of the test tubes. The lattice parameter of matrix and MX was determined by X-ray diffraction analysis of polished bulk samples and extracted residues respectively.

3. Experimental Results

Figure 1 shows the tensile properties of the test tubes before and after exposure. The tensile strength and 0.2% proof stress at room temperature have been increased by a long-term service exposure. The tensile strength at 873 K, however, have been almost the same between the unused tubes and long-term exposed tubes.

Figure 2 shows creep rupture strength of the test tubes before and after exposure. It can be seen that one-year exposure little changes the creep rupture strength, though 3-year exposure significantly decreases it.

![Tensile strength](image1)

![Elongation](image2)

![Creep rupture strength](image3)

Table 1. The chemical compositions of the test tube (in mass%, bal. Fe).

| Element | C   | Cu  | Ni  | Cr  | Mo  | V   | Nb  | W   | N  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 0.10    | 0.95| 0.35| 12.40| 0.36| 0.20| 0.047| 1.89| 0.052|

Fig. 1. Tensile properties of the test tubes before and after exposure.

Fig. 2. Creep rupture strength of the test tubes before and after exposure.
year exposure leads to a slight reduction in rupture strength within the scatter data band for the unused tubes.

Optical microscope observation shows that the test tubes, that has been normalized and tempered, have consisted of tempered martensite with about 20 vol% of δ-ferrite. The long-term service exposure does not seem to affect the microstructure on the light level as shown in Fig. 3.

Figures 4 and 5 show TEM images of extracted replica from the test tubes before and after exposure. In the case of unused test tubes, M_{23}C_{6} type carbide has been extensively observed to precipitate along former austenite grain boundaries, δ-ferrite/martensite boundaries, and martensite lath boundaries. M of M_{23}C_{6} has been identified as Fe_{23−x}Cr_{60−x}Mo_{6−x}W_{10−x} (mass%) by EDX analysis. Inside grains, fine precipitate identified as MX type carbonitride has been observed with high density. After 1- and 3-year exposure, M_{23}C_{6} and MX remains without
changing its morphology, and needle-like Laves phase newly precipitates inside grains and on the martensite lath boundaries. The composition of the Laves phase has been determined as Fe_{29–Cr_{11–Mo_{20–W_{36}}} (mass%) by EDX analysis.

Figure 6 shows TEM images, diffraction pattern, and EDX spectroscopy of MX obtained from extracted replica. It is seen that the main constituent of MX is V including a small amount of Nb, and the morphology of MX is characterized by habit planes along \{001\}_{MX}. In order to clarify the crystallographic orientation relationship between precipitates and matrix, TEM observation has been carried out by using thin films of the test tubes before and after 3-year exposure. Figures 7 and 8 show bright field images and dark field images, which have been taken under an electron beam direction tilted by a few degree from \langle 001 \rangle of matrix in order to enhance the contrast due to the strain field. It is noted that the MX has homogeneously distributed inside martensite lath and \delta-ferrite and has a plate-shaped with a habit plane parallel to \langle 001 \rangle of the matrix with following crystallographic orientation relationship with matrix; \{100\}_{MX}/\{100\}_{matrix}, \langle 010\rangle_{MX}/\langle 011\rangle_{matrix}. The most significant feature on the MX is that the contrast images due to coherent strain is often observed on the bright field images under a two-beam condition, and a streak can be seen on the diffraction patterns. In addition, some dislocations have been pinned on the interface between MX and matrix. This seems to be direct evidence showing that the coherent strain

![Figure 6. TEM images of MX-type carbonitride on the extracted replica from the test tubes after 3-year exposure.](image)

![Figure 7. TEM bright field and dark field images of the test tube before exposure.](image)

![Figure 8. TEM bright and dark field images of the test tube after 3-year exposure.](image)
works on 9% Cr steels with 2% of Mo has shown that Laves phase preferentially precipitated inside grains, in which dislocations seem to act as the nucleation site. In the case of present test tubes, it is found that the Laves phase has mainly precipitated in needle-shaped with high density growing toward a specific crystallographic direction inside grains. This suggests that the actual temperature was not so high that the coarse Laves phase precipitated only along grain boundaries and martensite lath boundaries.

The actual metal temperature of the exposed tubes can be estimated by the kinetics of Laves phase precipitation as follows. EDX analysis have suggested that the Laves phase mainly consisting of Fe and W is precipitated and grown with concentration of W. Therefore, the amount of precipitated W now can correspond to the total amount of Laves phase. In order to clarify the time and temperature dependence of Laves phase precipitation, the chemical analysis of extracted residues has been carried out for the laboratory aging specimens up to 10 000 h at 873, 923, and 973 K. And W-concentration in the extracted residues has been picked up and utilized to the following simulations. The precipitation kinetics is often modeled by the Johnson–Mehl–Avrami type equation,

\[ X = 1 - \exp(-bt^n) \]  

that was modified by J. W. Cahn to explain the kinetics of pearlite precipitation.12 Where \( X \) is the fraction of transformation at time \( t \) and \( b \) is a factor including nucleation site number and/or diffusion controlling growth rate. In the present application, \( X \) in Eq. (1) applies the relative amount of precipitated W, which has been obtained from W-concentration in the extracted residues at the time \( t \) to that at the equilibrium amount of precipitated W obtained from THERMO-CALC. Figure 10(a) shows time-precipitation curves fitting the measured W-concentration in the extracted residues to Eq. (1) at 823, 873 and 923 K, where suitable \( n \) and \( b \) are given as listed in Table 2. It is found that the precipitation kinetics of W can be successfully expressed by the Johnson–Mehl–Avrami type equation and this model may be applicable for estimation of the heated temperatures. Figure 10(b) shows one of the examples for estimation of the actual metal temperature of the exposed tubes. The W-concentration in the extracted residues after 1-year and 3-year has accorded with the time-precipitation curve for 873 K, which is supposed to be the average metal temperature.

The present result shows that the precipitation of Laves phase leads to a reduction in dissolved W and Mo, and thereby the solution strengthening effect due to W and Mo might reduce after long-term service exposure. 1-year and 3-year service exposure have, however, slightly increased the tensile strength as well as yield strength at room temperatures and led to no significant changes in tensile properties at 873 K as well. It is explained that the solution strengthening effect due to W and Mo and precipitation strengthening effect due to Laves phase offsets each other, and the latter may be rather effective to increase the deformation resistance around room temperatures.

The another important precipitate to increase the deformation resistance has been MX type carbonitride finely dispersed inside martensite lath and ferrite. TEM observa-

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**Figure 9.** The amount of W, Mo, V and Nb in extracted residues in the test tubes before and after 3-year exposure.

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obstructs the mobile dislocations. The size of MX is estimated at from 5 nm to 80 nm in diameter and less than 2 nm in thickness, which have little changed during 1-year and 3-year service exposure. At the present service exposure conditions, Laves phase has also precipitated inside grains in a needle-shaped, and it seems to have some crystallographic orientation relationship with matrix.

**Figure 9** shows the amount of W, Mo, V, and Nb precipitated and dissolved into matrix, which have been determined by the chemical analysis of extracted residues from the test tubes before and after 3-year exposure. It is noted that more than 70% of W and Mo have precipitated as Laves phase, resulting in a marked reduction in dissolved W and Mo in matrix. On the other hand, the amount of precipitated V and Nb has little changed after long-term service exposure.

4. Discussion

The present works on 12Cr–2W–Cu–V–Nb steel tubes have clarified the roles of three types of precipitates; MX type carbonitride, \( \text{M}_2\text{C}_6 \) carbide, and Laves phase, on the microstructural evolution. TEM observations and quantitative analysis of extracted residues have shown that the MX phase hardening effect can be maintained to a long-term service exposure. Thereby it is considered that the MX precipitation resistance has been MX type carbonitride finely dispersed inside martensite lath and \( \delta \)-ferrite. TEM observa-

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\[ \text{Amount of W, Mo, V and Nb precipitated and dissolved (mass\%)} \]

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\[ \text{Amount of W, Mo, V and Nb precipitated and dissolved (mass\%)} \]
tion shows that the MX has precipitated in a plate-shaped
with the specific crystallographic orientation relationship;
{100}MX/{100}matrix and (110)MX||(001)matrix. In addition,
the contrast image due to coherent strain has often been ob-
served under a two-beam condition. The misfitting coheren-
cy between MX and matrix is now estimated from the dif-
fERENCE of lattice spacing among them.

Table 3 shows lattice parameter of MX and matrix determined by X-ray dif-
fraction analysis of extracted residues and chemical pol-
ished specimens respectively. From the crystallographic re-
lationship on (001)matrix and (110)matrix as shown in
Fig. 11, the lattice misfit on (001) matrix and (110)matrix is estimated to
be 1.45 and 17.2 %. These misfit parameters can predict the critical coherent size of MX, that is 20 nm in diameter and
1.2 nm in thickness of the MX platelet. As shown in Figs. 7
and 8, the size of MX has been covered from 5 to 80 nm in
diameter and less than 2 nm in thickness for both unused
and exposed test tubes. It seems that, therefore, some MX
platelets can keep coherent relationship and the others have
semi-coherent relationship with matrix during long-term
service exposure.

Following statics of dislocation–precipitate interaction, it
is possible to evaluate the most effect size of coherent parti-
cle to enhance the creep resistance. The critical stress, \( \tau_c \),
required for the dislocation to break free of the obstacle is
generally expressed by

\[
\tau_c = \frac{F_m}{Lb} \sin \frac{\theta}{2},
\]

where \( F_m \) is the maximum force that the obstacle can sus-
tain, \( L \) is inter-particle spacing, and \( b \) is Burgers vector of
the dislocation. Some advances are proposed to under-
stand the statistics of penetration of a dislocation through
an array of obstacles during creep, and the critical stress is
approximately expressed as follows;

\[
\tau_c = 0.81 \frac{Gb}{L_s}
\]

where \( G \) is shear modulus and \( L_s \) is average inter-particle
spacing. \( L_s \) is substituted by

\[
L_s = \left( \frac{2\pi}{3f} \right)^{1/2} r,
\]

when the obstacle is assumed to be sphere. Thereby, \( \tau_c \) is
substituted as follows;

\[
\tau_c = 0.81 \frac{Gb}{r} \left( \frac{3f}{2\pi} \right)^{1/2}
\]
The strengthening due to misfitting coherent precipitates occurs by the interaction between the stress fields of precipitates and dislocations. The most thoroughly modeled case is that of the edge dislocation interact with a spherical coherent precipitates of radius $r$ with a misfit parameter, $\varepsilon$, given by

$$\varepsilon = \frac{a_p - a}{a}, \hspace{1cm} \text{equation (7)}$$

where $v_p$ is Poisson’s ratio of the precipitates and $\delta$ is the difference between the lattice parameter of the precipitate; $a_p$ and matrix; $a$ and given by the following equation,

$$a_p = a \pm a_{\text{coherence}}.$$ 

In this model, the critical stress is expressed by

$$\tau_{\text{cr}} = \chi \varepsilon^{1/2} f^{1/2} \left( \frac{r}{b} \right)^{1/2}, \hspace{1cm} \text{equation (8)}$$

where $\chi$ is a constant varying between 2 and 3.

Figure 12 shows the calculated critical shear stress for spherical coherent precipitates with $\varepsilon=0.0146$ and $\varepsilon=0.172$, which correspond to the above-mentioned misfit parameter for MX. This shows that the strain field due to coherent precipitates more strongly interacts with dislocations with increasing the precipitate size. When the precipitate size exceeds $r_{\text{max}} = b/4\varepsilon$, which gives the maximum critical stress, however, the dislocation bypasses the precipitates by Orowan process resulting in the reduction in the shear stress. These considerations have suggested that the most effective size of MX to increase the shear stress is 8.5 to 15 nm in diameter and 0.7 to 1.2 nm in thickness. From the point of designing steels, controlling lattice misfit and size of MX is another important strategy to enhance the creep strength for the steels.

It is confirmed that the main constituent of M in MX is V including a small amount of Nb by EDX analysis. On the other hand, it is difficult to identify C- and N-concentration to X in MX by direct observations. From the X-ray diffraction analysis of extracted residues, the lattice parameter of the present MX has been estimated as 4.130 Å, that is closer to that VN ($a=4.14915$ Å) rather than $V_{4}C_{3}$ ($a=4.16$ Å) and NbC ($a=4.4702$ Å). In addition, the equilibrium composition of MX has been estimated as $(V_{0.79}Nb_{0.20})(N_{0.98}C_{0.011})$ in mass fraction by the calculation using THERMO-CALC. This means that VN is a dominant precipitate controlling the mechanical properties in the 12Cr–2W–Cu–V–Nb steel.

5. Conclusions
The microstructural evolution of the 12Cr–2W–Cu–V–Nb steel tubes (ASME SA213-T122) during 1- and 3-year service exposure in a practical boiler has been investigated from the standpoint of the stability and the morphology of precipitate phases. The major precipitates in the exposed tubes are MX carbonitride, Laves phase, and $M_23C_6$ carbide. One of the important points concerning the strengthening mechanisms is that the finely dispersed MX has been so stable that its size and precipitation density have little changed after long-term service exposure. In addition, the MX has precipitated in a plate-shaped keeping coherent relationship with matrix, and therefore the shear stress for creep deformation has enhanced due to its coherent strain. The statics of the interaction between dislocation and MX platelet has suggested that the most effective size of MX for an increase in the creep resistance is 8.5 to 15 nm in diameter and 0.7 to 1.2 nm in thickness. EDX and X-ray diffraction analysis has shown that the main constituent of MX is VN, which may be dominant precipitate controlling mechanical properties in 12Cr–2W–Cu–V–Nb steels.

Laves phase has precipitated during long-term service exposure and its precipitation has simultaneously led to the reduction of dissolved W and Mo in matrix. It is confirmed that precipitation strengthening effect due to Laves phase, which has precipitated inside grain and martensite lath boundaries with high density, has surpassed to solution strengthening effect due to W and Mo. As a result, there is no remarkable degradation in tensile strength and creep strength after long-term service exposure.

The microstructural evolution after long-term exposure has been quantified by time-temperature dependence of Laves phase precipitation, and its precipitation kinetics has successfully expressed by the Johnson–Mehl–Avrami type equation. The actual metal temperature of the exposed tubes has been estimated at 873 K by fitting to the time-temperature dependence of precipitation.

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