Identification of Precipitate Phases in an 11\%Cr Ferritic/martensitic Steel after Short-term Creep

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To further increase steam temperature in ultra-supercritical power plants, 9–12\%Cr ferritic/martensitic (FM) steels with target operating temperatures up to 650\°C and higher are being developed. An 11\% Cr F/M steel was prepared by reference to the nominal chemical composition of SAVE12 steel with an expected maximum use temperature of 650\°C. Precipitate phases in the 11\%Cr FM steel after a short-term creep at 600\°C/180 MPa for 1 100 h were investigated by transmission electron microscopy with energy dispersive X-ray spectrometers. Precipitate phases in the crept steel were identified to be Fe-W-Cr-rich M\textsubscript{6}C carbide, Cr-rich M\textsubscript{23}C\textsubscript{6} and M\textsubscript{2}X carbides, Fe-rich Laves phase, Nb-Ta-rich/Ta-Nb-rich/V-rich MX phases, as well as Fe-Cr-rich sigma phase. The identified M\textsubscript{6}C carbides with a f.c.c. crystal structure have a metallic element composition of about 41Fe, 31W, 20Cr, and 4Ta (in at.\%) and an irregular block-like morphology with sizes ranging from 70 to 310 nm in diameter. The M\textsubscript{6}C and Cr-rich M\textsubscript{23}C\textsubscript{6} carbides, as well as Fe-W-rich Laves phases are considered to be formed during the creep. The present investigation reveals that the M\textsubscript{6}C carbide is a dominant phase in the steel after the creep. The formation of the M\textsubscript{6}C carbide in the crept steel is also discussed.

KEY WORDS: precipitate phases; M\textsubscript{6}C carbide; high-Cr ferritic/martensitic steel; high temperature short-term creep; transmission electron microscopy.

1. Introduction

9\% Cr ferritic/martensitic (FM) steels have been used in ultra-supercritical (USC) power plants with maximum operating steam temperatures of about 600\°C to 610\°C.\textsuperscript{1,11} The operating temperature of 9\% Cr FM steel is limited by rapid decreases in mechanical properties as well as oxidation and corrosion resistance during long-term creep when the temperature is higher than 600\°C. Higher steam parameters lead to higher thermal efficiency and hence lower coal consumption and air pollution. Therefore, studies on elevating the operating temperature of 9–12\%Cr FM steels up to 650\°C and higher are required for USC power plants.\textsuperscript{2,3} An 11\%Cr FM steel SAVE12 with a 105 h creep rupture strength of 600\°C and a higher desired operating temperature of 650\°C has been experimentally developed in Japan.\textsuperscript{4–6}

Since 1960’s, the precipitation behavior in steel has been of continuing concern.\textsuperscript{7} 9–12\%Cr FM steels are generally subjected to a final heat treatment process by normalizing at 1 050\°C to 1 100\°C and tempering at 650\°C to 780\°C.\textsuperscript{8} After the heat treatment process, the microstructure of 9–12\%Cr FM steels reveals tempered martensite constituted by fine ferrite subgrains with a high density of dislocations, and different kinds of precipitates. Some precipitates, like M\textsubscript{23}C\textsubscript{6} and MX precipitates,\textsuperscript{8} as well as M\textsubscript{2}X precipitates in some cases\textsuperscript{10,11} (where M denotes the metallic atoms, C is the carbon atoms, and X denotes the carbon and nitrogen atoms), in 9–12\%Cr FM steels restrain the dislocation motion and thus improve the mechanical properties of the steels owing to a precipitation strengthening effect.\textsuperscript{1,12} Contrarily, the precipitation of some precipitates with poor stability during the creep of high Cr martensitic steels, such as Z-phase, M\textsubscript{2}X carbonitrides and Laves phase, results in a degradation in long-term creep strength\textsuperscript{13} and consumption of the existing fine M\textsubscript{2}X and MX precipitates.\textsuperscript{14–19} These indicate that the types, size distribution and thermal stabilization of precipitate phases may strongly affect the creep resistance of creep-resistant steels. Therefore, it is necessary to study the precipitate phases in 9–12\%Cr FM steels in order to understand the influence of precipitates on creep rupture strength of the steels.

It is worth noting that the microstructural evolution of SAVE12 steel during creep has been rarely reported previously. In this work, we have made the qualitative analysis of precipitate phases in an 11\% Cr FM steel similar with SAVE12 after a short-term creep. This work aims at acquiring the basic data of microstructural stability of 9–12\%Cr FM steels during long-term service under high-temperature environment and providing important reference to evaluate the service ability of 9–12\%Cr FM steels under high temperature long-term creep condition. The purpose of this paper is to report the identified precipitate phases in the 11\%Cr FM steel after a short-term creep at 600\°C at
180 MPa for 1 100 h, including one kind of Fe-W-Cr-rich M₆X carbide phase, which appears to have not been identified in high Cr FM steels with a short-term creep condition.

2. Experimental Procedures

The initial material used in this investigation was an 11%Cr FM steel prepared by reference to the nominal chemical composition of SAVE12 steel. Table 1 lists the chemical composition of the experimental steel along with SAVE12. A 100 kg ingot of the steel was prepared via vacuum induction melting method. The ingot was subjected to a 3-hour-homogenization at 1 180°C. The homogenization-treated ingot was then hot-rolled at 940°C to 1 050°C to a plate with 30 mm thick. The plate was normalized at 1 050°C for 0.5 h followed by air cooling, and subsequently tempered at 780°C for 1.5 h followed by air cooling. Creep test was conducted for 1 100 h at 600°C under an applied stress of 180 MPa (without break). Metallographic samples were cut from the normalized-and-tempered steel plate and the crept specimen by spark erosion. The samples were chemically etched in a solution of 5 ml hydrochloric acid plus 1 g picric acid in 100 ml ethyl alcohol. Extraction carbon replicas were made by standard method. Thin foil samples were twin-jet electropolished at 50–60 V in a 5% perchloric acid plus 95% ethyl alcohol solution cooled to temperatures ranging from −20°C to −30°C. The etched metallographic samples were observed in optical microscope (OM). The replicas and thin foils were examined in JEM-2100 transmission electron microscopy (TEM) and in Talos F200X TEM equipped with energy dispersive X-ray (EDX) spectrometers operating at 200 kV. Precipitate phases were identified via a combination of selected area electron diffraction (SAED), EDX analysis and the Powder Diffraction File database of the Joint Committee on Powder Diffraction Standards (JCPDS). The size of precipitate particles was measured from TEM micrographs.

3. Results and Discussion

The optical microstructure of the 11%Cr FM steel with the normalized and tempered condition is shown in Figs. 1(a), 1(b), revealing tempered martensite laths, δ-ferrite grains with a bamboo-like shape, and precipitates. Figures 1(c), 1(d) show the optical micrographs of the 11%Cr FM steel after the creep test. In the steel after the creep test, δ-ferrite grains were found to be significantly decreased in their amount and size compared with those in the normalized-and-tempered steel. By analyzing thirteen micrographs randomly taken from the metallographic sample with the aid of the Image Tool, the amount (area fraction) of δ-ferrite in the 11%Cr FM steel before and after the creep test was determined to be about 6.1% and 1.5%, respectively. This indicates that δ-ferrite in the 11%Cr FM steel was incompletely dissolved after the present creep exposure.

Table 1. Chemical composition of 11% Cr FM steel along with SAVE12 steel (in wt.%).

| Steels    | C   | Si   | Mn   | Cr   | W    | Co   | V    | Nb   | Ta   | Nd  | B   | N    |
|-----------|-----|------|------|------|------|------|------|------|------|-----|-----|------|
| 11%Cr FM Steel | 0.10 | 0.24 | 0.24 | 11.2 | 3.16 | 2.94 | 0.22 | 0.068 | 0.07 | 0.03 | 0.006 | 0.032 |
| SAVE12    | 0.10 | 0.30 | 0.20 | 11.0 | 3.0  | 3.0  | 0.20 | 0.07  | 0.07 | 0.04 | –    | 0.04 |

Fig. 1. The optical micrographs of 11% Cr FM steel with different condition. (a,b) the normalized and tempered condition, showing many large-sized δ-ferrite grains. (c,d) after a short-term creep at 600°C/180 MPa for 1 100 h, showing a few relatively small-sized δ-ferrite grains.
Figures 2(a), 2(b) show the typical TEM micrographs of carbon replicas prepared from the 11%Cr FM steel before and after the creep, respectively. After the creep test, there was a significant increase in the amount of precipitates of the steel, meanwhile a great quantity of massive precipitates was observed in the crept steel. The number density/area fraction of precipitate particles was estimated to be about $8.84 \times 10^{12} \text{m}^{-2}/4.03\%$ for the tempered steel and $1.02 \times 10^{13} \text{m}^{-2}/12.15\%$ for the crept steel, respectively. Further, the average size of precipitate particles was estimated to be about 70 nm for the tempered steel and 110 nm for the crept steel.

3.1. Fe-W-Cr-rich M$_6$C Phase and Cr-rich M$_2$3C$_6$ Phase

Figure 3(a) is a TEM micrograph taken from carbon replica prepared from the 11%Cr FM steel after the creep, showing a large arrow-marked precipitate P1 with an irregularly block-like shape. EDX analysis revealed that metallic element composition in precipitate P1 was about 46Fe, 29W, 21Cr, and 2Co (in at.%). By analyzing the SAED pattern in Fig. 3(b) taken from precipitate P1, it was found that this pattern matched well with the electron diffraction pattern from Fe$_3$W$_3$C (JCPDS 41-1351, face-centered cubic (f.c.c.) crystal structure with a lattice parameter $a=1.11094$ nm) in the zone axis of [123]. Precipitate P1 can be identified as a Fe-W-Cr-rich M$_6$C carbide with a f.c.c. crystal structure. We noticed that this pattern also matched with the electron diffraction pattern from Cr$_{23}$C$_6$ (JCPDS 35-0783, f.c.c. crystal structure with a lattice parameter $a=1.06599$ nm) in the zone axis of [011]. Since Fe$_3$W$_3$C and Cr$_{23}$C$_6$ phases have the same f.c.c. crystal structure and similar lattice parameters, it seems to be difficult for distinguishing Fe$_3$W$_3$C and Cr$_{23}$C$_6$ phases according the SAED pattern in Fig. 3(b). However, the metallic element composition of precipitate P1 is completely different from that of Cr-rich M$_2$3C$_6$ carbide observed in high Cr FM steels. In fact, we also detected many Cr-rich M$_2$3C$_6$ carbides on the replica taken from the same crept steel sample. Figure 4(a) shows a TEM micrograph taken from carbon replica prepared from the 11%Cr FM steel after the creep, showing an arrow-marked precipitate P2 having a metallic element composition of 57Cr, 27Fe, 14W, and 1V (in at.%). From SAED pattern in Fig. 4(b), precipitate P2 was identified to be a Cr-rich M$_2$3C$_6$ carbide with a f.c.c. crystal structure.

In the present TEM examination, the average metallic element composition of Cr-rich M$_2$3C$_6$ carbides observed in the 11%Cr FM steel after the creep was determined to be about 61Cr, 27Fe and 8W (in at.%). Before the creep test, the metallic element composition of Cr-rich M$_2$3C$_6$ carbides in the present steel is about 58Cr, 26Fe, 10W, 3Ta, and 2Co (in at.%), which is similar with that in the crept steel. This result is consistent with the results from other studies on M$_2$3C$_6$ phase in high-Cr FM steels. In addition, the metallic element composition of precipitate P1 appears to be similar with the composition of Laves intermetallic compound Fe$_2$W ((Fe,Cr)$_2$W). However, the diffraction pattern in Fig. 3(b) does not match with patterns from Fe$_2$W (JCPDS 65-3570, 03-0920) Laves phase in any zone axis. Therefore, precipitate P1 does not belong to Cr-rich M$_2$3C$_6$ carbide or Laves phase, but it was identified as a Fe-W-Cr-rich M$_6$C carbide with a f.c.c. crystal structure.

In all of the precipitates analyzed from the 11%Cr FM steel with creep condition, there were 65 precipitates having similar metallic element compositions with precipitate P1. These precipitates are believed to belong to the Fe-W-Cr rich M$_6$C carbide like precipitate P1. The metallic element composition of the 65 M$_6$C carbides was averaged to be about 41Fe, 31W, 20Cr, and 4Ta (in at.%). Figure 5 shows some of the detected M$_6$C carbides with various morpholo-
gies. In the present study, the observed Fe-W-Cr-rich M_{6}C carbides have an irregular block-like morphology and sizes ranging from 70 to 310 nm in diameter.

M_{6}X phase has been reported to exist in 10%Cr martensitic steel with 2% W during initial stage of tempering at 770°C,\(^{23}\) in 9%Cr martensitic steel with 4% W after tempering at 800°C,\(^{24}\) and in 4% Cr M50 steel with the annealed condition.\(^{25}\) In our previous work, the Fe-W-Cr rich M_{6}C carbide phase has not been detected in the 11%Cr steel with the normalized and tempered condition. M_{6}X phase has also been reported to form in a 12%Cr martensitic steel after long-term creep exposures at 475°C/550°C for 39 287 h/24 024 h,\(^{16}\) and in a 9%Cr martensitic steel\(^{27}\) and 17–18%Cr AISI 316LN steels\(^{26}\) after long-term creep exposures at 650°C for times up to about 10 000 h. However, M_{6}C carbide phase seems not have been reported previously in high-Cr FM steels after a short-term creep exposure. The present result indicated that a large amount of M_{6}C carbides formed in the 11%Cr FM steel after a short-term creep at 600°C for 1 100 h.

The presence of the Fe-Cr-W-rich M_{6}C carbide phase in the present steel after the creep test may be related to δ-ferrite in the steel. Because Cr and W are ferrite forming elements, the concentration of solutes Cr and W in δ-ferrite matrix should be higher than that in martensite matrix of the steel after the normalization. We found that no precipitate was formed in δ-ferrite of the present steel before the creep test, and the average content of Cr and W in δ-ferrite grains was about 12 and 6 in weight pct, respectively. Meanwhile, the average content of Cr and W in the martensite matrix of the present steel with the normalized and tempered condition was about 10.5 and 3.7 in weight pct, respectively. Because the observed M_{6}C carbides in the steel are Fe, Cr and W-rich phase, the driving force for precipitation of the Fe-Cr-W-rich M_{6}C carbide phase might be large in δ-ferrite regions having a relatively high content of of W and Cr solute atoms. Therefore, it can be expected that δ-ferrite matrix therefore is comparatively appropriate for the formation of Fe-Cr-W-rich M_{6}C carbides, and the M_{6}C carbides was first formed within δ-ferrite grains during the short-term creep exposure. The formation mechanism of M_{6}C carbide phase in the present 11%Cr FM steel during the short-term creep exposure needs to be further investigated in our next work.

### 3.2. Cr-rich M_{7}C_{3} Phase

Figure 6(a) is the TEM micrograph of carbon replica prepared from the 11%Cr FM steel after the creep, showing a precipitate P3. The metallic element composition of precipitate P3 was determined to be about 59Cr, 26Fe, 10W, and 3Ta (in at.%). Figure 6(b) is the SAED pattern taken from precipitate P3. We noticed that the composition of precipitate P3 is similar with that of precipitate P2, which has been determined to be a Cr-rich M_{23}C_{6} carbide. However, the SAED pattern in Fig. 6(b) is not consistent with the electron diffraction patterns from the Cr_{23}C_{6} (JCPDS 35-0783) in any zone axis. Instead, this pattern matched well with the electron diffraction pattern from Cr_{3}C_{6} (JCPDS 11-0550, hexagonal crystal structure with lattice parameters a/c =1.398/0.4523 nm) in the zone axis of [012]. Therefore, precipitate P3 was identified as hexagonal Cr-rich M_{3}C_{6} phase. Furtado et al.\(^{27}\) also detected M_{3}C_{6} phase in a 9%Cr steel after creep tests at 566°C for 5 127 h and 7 308 h. The Cr-rich M_{3}C_{6} phase has not been detected so far in the 11%Cr steel with the normalized and tempered condition. Whether or not the M_{3}C_{6} phase was formed during the creep test requires further confirmation.

### 3.3. Fe-rich Laves Phase

Laves phase has been reported to form in 9–12%Cr martensitic steels during high-temperature creep tests.\(^{28–31}\) Laves phase was also detected in the 11%Cr steel after the creep. Figure 7(a) is the TEM micrograph of carbon replica prepared from the creep 11%Cr FM steel, showing an irregularly block-like precipitate P4 with a metallic element composition of about 40Fe, 35W, 17Cr, 6Ta, and 2Co (in at.%). SAED pattern in Fig. 7(b) was taken from precipitate P4. This pattern matched with the electron diffraction pat-
tern from Fe,W (JCPDS 65-3570, hexagonal crystal structure with lattice parameters a/c = 0.4737/0.7719 nm) Laves phase in the zone axis of [223]. Precipitate P4 was identified to be a hexagonal Fe-W-rich Laves phase. The metallic element composition of the observed Laves phase particles in the crept steel was averaged to be about 40Fe, 32W, 18Cr, 6Ta, and 2Co (in at.%). The observed Laves phase particles have an irregular block-like morphology and sizes ranging from about 30 to 200 nm in diameter. Since the Laves phase has not been detected in the 11%Cr steel with the normalized and tempered condition, it can be considered to form during the creep of the 11%Cr FM steel.

3.4. Nb-Ta-rich and Ta-Nb-rich MX Phases

Figure 8(a) shows the TEM micrograph of carbon replica from the 11%Cr steel after the creep, revealing an arrow-marked spherical precipitate P5 with a metallic element composition of about 39Nb, 24Ta, 14V, 10Cr, 6Fe, 5W, and 1Co (in at.%). The SAED pattern recorded from precipitate P5, as shown in Fig. 8(b), matched with the electron diffraction pattern from NbC, (JCPDS 38-1364, f.c.c. crystal structure with a lattice parameter a = 0.4469 nm) in the zone axis of [001]. Thus, precipitate P5 was determined to be a Nb-rich MC carbide with a f.c.c. lattice. Except for the Nb-rich MC carbide, spherical Ta-rich MC carbide, and irregularly block-like V-rich MC carbide was also observed on carbon replicas prepared from the 11%Cr FM steel after the creep. These MX phases have also been identified in the 11%Cr steel with the normalized and tempered condition.\(^{32,33}\) Among all 39 MX precipitates detected in the crept steel, 21, 16 and 2 of them were rich in Nb, Ta, and V, respectively. The average metallic element composition of Nb-rich and Ta-rich MC carbides was determined to be 55Nb, 25Ta, 7V, 5Cr, 5W, 3Fe, and 48Ta, 24Nb, 10Fe, 8Cr, 4W, 4V, 3Co (in at.%), respectively. The metallic element composition of V-rich MC carbides was about 35V, 25Ta, 21Cr, 12Nb, 5Fe, and 2Co (in at.%).

From the TEM images taken from the 11%Cr FM steel after the creep, the size range and average size of MX precipitates were measured to be about 10–50 nm and 20 nm in diameter, respectively. Rod-like and fine-block-like MX phases were also occasionally observed, while most of MX phases have a spherical shape. The size statistics of MX precipitates in the steel before the creep test were also studied. The result shows that most of MX precipitates in the tempered steel have sizes ranging from 20 to 70 nm in diameter, and the average size of these precipitates is about 50 nm in diameter. It is obvious that the size of MX phases decreased after the creep test. This result indicates that part of pre-existing MX precipitates was dissolved during the creep test. In addition, there was no obvious change in the chemical composition of MX phase the 11%Cr FM steel after the present creep test.

3.5. Fe-Cr-rich Sigma Phase

Sigma phase was observed in the 11%Cr FM steel after the creep. Figure 9(a) is the TEM micrograph of carbon replicas from the 11%Cr FM steel after the creep test, showing an arrow-marked precipitate P6 with an irregularly block-like shape. The chemical composition of precipitate P6 was determined to be about 41Fe, 40Cr, 10W, 5Ta, and 2Co (in at.%). The SAED pattern of precipitate P6, as shown in Fig. 9(b), was found to match with the diffraction pattern from both \(\sigma\)-FeCr (JCPDS 05-0708, simple tetragonal crystal structure with the lattice parameters \(a/c = 0.8799/0.4544\) nm) and \(\sigma\)-FeCrMo, (JCPDS 09-0650, simple tetragonal crystal structure with lattice parameters \(a/c = 0.9170/0.4741\) nm) in the zone axis of [110]. Sigma phases, \(\sigma\)-FeCr and \(\sigma\)-FeCrW with a composition of about 49Fe, 48Cr, 2Co and 40-62Cr, 23-35Fe, 5-15W, 3-15Ta, 1-4Co respectively, have been identified in the 11%Cr FM steel with the normalized and tempered condition.\(^{30}\) Considering the composition of precipitate P6, it is likely to be the \(\sigma\)-FeCr (JCPDS 05-0708) phase containing W and Ta. In the present TEM examination, some precipitates with a composition of about 50-60Cr, 20-35Fe, 5-15W, and 2-10Ta (in at.%) were also detected on carbon replicas prepared from the 11%Cr FM steel after the creep. These precipitates are likely to be a \(\sigma\)-FeCrW phase containing Ta.

Regarding the amount of precipitate phases identified in the 11%Cr FM steel after the creep, the quantitative analysis of these phases is difficult only by the present TEM examination. However, according to the examination it seems that the amount of the Fe-W-Cr-rich M$_2$C carbide phase was the largest compared to other kinds of precipitate phases, whilst the amount of the \(\sigma\)-FeCr/\(\sigma\)-FeCrW phases was the smallest among the precipitates on the present replica samples of the
11%Cr FM steel after the creep. In fact, we have randomly analyzed 184 precipitate particles of the creep 11%Cr FM steel, revealing that 65 particles were the Fe-W-Cr-rich M6C carbide, but only 11 particles belong to the sigma phases. Thus, according to the present TEM work the Fe-W-Cr-rich M6C carbide is considered to be one of the dominant phases in the 11%Cr FM steel after the present short-term creep. The amount of the identified precipitate phases and the precipitation sites of these phases in the crept steel should be further studied by a combination of the use of thin foil specimens in our next experimental work.

Igarashi and Sawaragi\(^4\) reported that the precipitate phases detected in the SAVE12 steel were M23C6, M2C3 and MX phases for the tempered steel samples, and Fe-W\(_6\) type \(\mu\) phase, \(\chi\) phase, M23C6 and M2C3 phases for steel samples aged for 10 000 h at 650°C and 700°C. The precipitates of the present steel with the normalized and tempered condition were identified to be B22C6\(_b\), MX, M2C3, M2C5, M6C and sigma phases.\(^{33-36}\) In the present investigation, M6C, M2C3, M23C6 and Nb-\(\gamma\)/V-\(\gamma\)-rich MC carbides, Laves phase and sigma phases were observed in the present steel after the short-term creep. In the present steel with the creep condition, \(\mu\) phase and \(\chi\) phase have not been detected so far. There are some differences between the precipitate phases we identified in our experimental steel and the ones they determined in the SAVE12 steel. These differences may be resulted from the differences in steel composition, steel preparation process including heat treatment and hot-working, experimental methods and temperatures.

As mentioned above, \(\delta\)-ferrite in the present steel was incompletely dissolved after the present creep exposure. This may be explained as follows. As ferrite formers, W and Cr atoms are enriched in the ferritic regions. The content of W and Cr atoms in \(\delta\)-ferrite grains was higher than that in martensite matrix, as measured in this work. \(\delta\)-ferrite matrix therefore is comparatively appropriate for the formation of Fe-W-Cr-rich M6C carbides and sigma phases \(\sigma\)-FeCr and \(\sigma\)-FeCrW. The formation of a large amount of the M6X precipitates in addition to the sigma phases would consume solute W and Cr atoms in \(\delta\)-ferrite matrix, resulting in a decrease in the stability of \(\delta\)-ferrite and finally leading to a reverse-transformation of \(\delta\)-ferrite back to austenite. This is a possible explanation for the dissolving of \(\delta\)-ferrite in the present steel during the creep exposure.

The precipitation of M6X phase is generally considered to be deleterious to heat-resistant steels during creep. The dimensional stability of M6X particles is generally bad,\(^{13}\) and coarse M6X particles can accelerate the forming of creep cavities.\(^{20}\) On the other hand, since tungsten plays a vital role in the solid-solution strengthening mechanism of 9–12% Cr FM heat resistant steels, the precipitation of a large amount of W-rich M6X phase can consume solute W atoms in matrix, leading to a weakening in solid-solution strengthening effect and a deterioration in the creep resistance of steel.\(^{37,38}\) Because the Fe-W-Cr-rich M6C carbides observed in the creep 11%Cr FM steel have a relatively large size and higher tungsten content, the formation of a large amount of M6C carbides is not expected to play a favorable role in the 11%Cr FM steel during a long-term creep.

The present investigation confirms the existence of M6C carbide phase in the 11%Cr FM steel after the short-term creep. More importantly, during the creep exposure \(\delta\)-ferrite contained in the steel seems to accelerate the formation of M6C carbide phase due to its dissolution accompanied by an increase in W solutes in the matrix. The formation of M6X phase is considered to have a negative effect on the long-term creep resistance of the steel. Therefore, a careful control of \(\delta\)-ferrite formation through alloy design and appropriate steel processing is practically necessary to avoid a premature formation of M6X phase in high-Cr FM steels so as to prevent its detrimental effects on long-term creep properties of the steels.

4. Conclusions

Eight types of precipitate phases have been identified in the 11%Cr FM steel after the short-term creep. They are Fe-W-Cr-rich M6C carbide with a f.c.c. crystal structure and a metallic element composition of about 41Fe, 31W, 20Cr, and 4Ta (in at.%); Cr-rich M2C3 carbide with a hexagonal crystal structure; Fe-W-rich Laves phase with a hexagonal crystal structure; Cr-rich M23C6, Nb-rich MC, Ta-rich MC, and V-rich MC carbides with a f.c.c. crystal structure; Sigma phases, \(\sigma\)-FeCr and \(\sigma\)-FeCrW, with a simple tetragonal crystal structure. The Fe-W-Cr-rich M6C and Cr-rich M2C3 carbides along with Fe-W-rich Laves phase are considered to be formed during the short-term creep. The present TEM examination reveals that the amount of Fe-W-Cr-rich M6C carbide is larger than that of other precipitate phases, and the Fe-W-Cr-rich M6C carbide is a dominant phase in the crept steel. The formation of the Fe-Cr-W-rich M6C carbide in the present steel during the short-term creep may be related to \(\delta\)-ferrite. The presence of \(\delta\)-ferrite in high-Cr FM steels probably leads to a premature formation of Fe-Cr-W-rich M6C carbides, and hence a careful control of \(\delta\)-ferrite formation is needed in high-Cr FM steels to prevent the detrimental effects of M6X phase on long-term creep properties of the steels.

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