Microstructural Evolution during Creep Test in 9Cr–2W–V–Ta Steels and 9Cr–1Mo–V–Nb Steels

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(Received on January 19, 2001; accepted in final form on April 3, 2001)

In order to clarify the mechanism of remarkable creep strength of the 9Cr–2W–0.2V–Ta steels, high-Cr heat-resistant steels with Mo replaced by W and Nb by Ta for reducing induced radioactivity, the microstructural evolution during creep tests has been studied and compared with that in conventional 9Cr–1Mo–0.2V–Nb steels. Particular attention was called to quantitative analysis of solute W and Mo contents evaluated with the EDX spectra measured with the thin foil in the FE-TEM analysis.

It has been supposed that the martensitic microstructure and fine MX-type precipitates have no significant effect on the difference in creep properties between the W-containing steel and the Mo-containing steel. Moreover the creep strength of the W-containing steel can not be attributed to the larger solid solution hardening by W. Mo distribution may encourage creep strain localization in solid solution, which results in the deterioration of creep strength of Mo-containing steels. Comparing M23C6 and Laves phase, the latter is assumed to be the main governing factor.

KEY WORDS: low activation steel; ferritic steel; creep-rupture strength; toughness; tungsten; molybdenum; precipitate; Laves phase.

1. Introduction

Ferritic and martensitic steels have better void swelling resistance, lower thermal expansion coefficient, and higher thermal conductivity compared with austenitic steels as structural materials for the first wall and blanket components of a fusion reactor. Irradiation-induced embrittlement and irradiation creep/relaxation have been recognized as the most important R&D issues for these materials.

Candidate low-activation ferritic and martensitic steels have been developed based on the conventional high-Cr heat-resistant steels with Mo replaced by W and Nb by Ta in order to reduce induced radioactivity. Several of the candidate steels such as Japanese F82H and JLF-1, U.S. 9Cr–2W–V–Ta steel, and European EUROFER have similar alloy compositions. Among the candidate steels, 9Cr–2W–0.2V–0.07Ta steels, developed in the Japanese Universities fusion program and designated as JLF-1 steels, have been considered the most promising because of their good irradiation-creep resistance and low irradiation embrittlement as well as good baseline properties.

Recent work has clarified that low activation 9Cr–2W–V–Ta steels have better creep strength and toughness than conventional 9Cr–1Mo–V–Nb steels, and investigated microstructural factors governing mechanical properties of these steels. Moreover, it has been reported that W additions can improve creep strength of conventional Mo-containing heat-resistant steels (9Cr–0.5Mo–1.8W–V–Nb steels (ASTM T92, P92), 11Cr–0.4Mo–2W–V–Nb steels (ASTM T122, P122)), and therefore, fundamental studies concerning strengthening mechanism of W have been encouraged.

In this report, the role of W on the improved creep strength is discussed in a comparison of microstructural evolution during creep tests in the low-activation 9Cr–2W–0.2V–Ta steel and the conventional 9Cr–1Mo–0.2V–Nb steel.

2. Experimental Procedure

9Cr–2W–0.2V–Ta steel (Steel W3) and 9Cr–1Mo–0.2V–Nb (Steel M3) steel were melted in a vacuum-induction melting furnace. The chemical compositions are listed in Table 1. Ta and Nb concentrations are approximately the same in atomic fraction. Both steels contain 0.06 mass% N. As Ta and Nb contents balance with Nb and N contents in Steel M3 whose composition is equivalent to Mod. 9Cr–1Mo steel in atomic percentage. Nevertheless it is still in the range of chemical compositions of JLF1 steels.

Table 1. Chemical compositions of steels studied. (mass%)

| Steel   | C | Si | Cr | Mo | P | S | 0.003 | 9.01 | 2.0 | W | Ta | Nb | N   |
|---------|---|----|----|----|---|---|-------|------|-----|----|----|----|----|
| W3      | 0.10 | 0.24 | 0.50 | 0.004 | 0.003 | 9.01 | 2.0 | -   | 0.160 | - | 0.0564 |
| M3      | 0.10 | 0.24 | 0.49 | 0.004 | 0.003 | 9.13 | 2.0 | -   | 1.0 | - | 0.081 | 0.0535 |

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The TMCP process was applied for preparing sample plates. Namely, the ingots were heated to 1523 K and were hot-rolled to 20 mm-thick plates with a finish-rolling temperature of about 1323 K followed by air-cooling to room temperature. Tempering (1033 K × 1 h; air cooling) and additional heat treatment corresponding to post-weld heat treatment (PWHT; 1013 K × 8.4 h; furnace cooling) were applied to the hot-rolled plates. As described in our previous study, the TMCP steels demonstrate better mechanical properties, such as tensile strength, creep rupture strength and toughness than the normalized steels.3)

Round bar specimens for both tensile and creep rupture tests, whose gauge section was 6 mm in diameter and 30 mm in length, were taken from at the mid-thickness of the plates in the transverse direction. Tensile properties were tested at room and elevated temperature. Creep rupture tests were carried out at 873, 923 and 973 K. V-notch Charpy impact test specimens of standard size were also machined with the same manner as the tensile test specimens.

The plates were sampled before and after creep testing, and microstructures at the mid-thickness were observed by an optical microscope, a transmission electron microscope (TEM) and a scanning electron microscope (SEM). In order that the microstructural evolution at an identical creep condition for both steels could be compared, a creep interrupt test was carried out under an applied stress of 150 MPa for 5058.7 h at 872 K which corresponds to about 10 and 17% of the creep lives of Steel W3 and Steel M3, respectively.

Composition analysis of the precipitates were carried out by energy dispersive X-ray spectrocope (EDS) in FE-TEM (Hitachi HF2000, 20 kV) for both thin foil and extraction replica. Thin foil specimens for TEM observations were prepared by electropolishing in a mixture of 5% perchloric acid with 20–30 DCV at 286 K (one-step electropolishing). In addition, subsequent electropolishing is employed in a mixed solution of 135 ml of acetic acid, 7 ml of water and 25 g of chromic acid under an applied potential of 30 DCV at 290 K (two-step electropolishing). The latter procedure allows us to distinguish Laves phase and M23C6 type precipitates due to the preferential dissolution of M23C6 in electrolyte.

M23C6 is therefore observed as a white hole in the image for the two-step electropolishing whereas Laves phase is observed as a black contrast.

Specimens for optical microscopy and scanning electron microscopy were etched with picral containing 3 vol% of HCl. In SEM analysis, the specimens were taken from the gauge section apart from heavily deformed region of fractured specimens for creep rupture test of Steel W3 and were observed by backscattered electron image, in which Laves phase (Fe2W) was clearly distinguished from M23C6 due to the brighter image of Laves phase arising from the difference in mean atomic weight, which enables us to quantify the change in fraction and size distribution of Laves phase during creep.

3. Results

3.1. Mechanical Properties

The tensile strengths are shown in Fig. 1 as functions of test temperature. Steel W3 (2%W) and Steel M3 (1%Mo) has about the same level of tensile strength irrespective of test temperature. On the other hand, toughness and creep rupture strength of Steel W3 were obviously improved compared with Steel M3 as shown in Figs. 2 and 3.

As shown in Fig. 2, the prior austenite grain size is close for both steels, thus better toughness in Steel W3 can not be attributed to the finer prior austenite grain size.

In Fig. 3, the creep rupture strength is evaluated in terms of the relationship between the applied stress and Larson–
Miller parameter \((LMP = \tau(35 + \log t))\). Steel W3 alloyed with W indicates marginal effects in creep rupture properties under the high LMP conditions compared with the Mo alloyed steel (Steel M3).

It is interesting that toughness in the W-containing steel is better than that in the Mo-containing steel. However, metallurgical factors for the better toughness can not be specified with present data.

SEM observations have revealed that the brittle fracture occurs by a cleavage not by an intergranular fracture, irrespective of the steels or test temperatures. Thus, the grain size, precipitates and existence of \(\delta\)-ferrite may be considered to be the governing factors of toughness. However, no distinct differences of these metallurgical factors between the both steels were found. Namely, no \(\delta\)-ferrite is observed and the prior austenite grain size is same for both steels, as shown in Figs. 2 and 4. Also, it can not be attributed to the difference in the size of the precipitates, as shown in various TEM micrographs of the specimens before creep tests.

It is worthwhile to add a possibility of intense embrittlement during creep duration in Steel M3 compared with Steel W3, because the coarsening of M23C6 and Laves phase during creep duration is enhanced in Steel M3.

3.2. Microstructural Evolution during Creep Test

Figure 4 shows the optical micrographs of the steels with tempering and additional heat treatment corresponding to PWHT. The both steels are completely martensitic and no \(\delta\) ferrite is observed. There is little difference in prior austenite grain size, which is approximately 20 \(\mu\)m in diameter, between Steels W3 and M3 as shown in Fig. 2. The change in microstructures under the creep test including the creep interrupt test is not recognized at the scale of the optical microscope.

Figures 5 and 6 show TEM micrographs of the extraction replicas of Steels W3 and M3 before and after interrupt creep tests, respectively. The TEM micrographs clearly indicate that the size of coarse precipitates which is presumed to be existed along prior austenite grain boundaries is almost same in the both steels before creep tests, but is larger in Steel M3 after creep interrupt tests (Figs. 5(b) and 6(b)). This suggests that the growth rate of the precipitates during creep test is higher in Steel M3. This difference in the size of coarse precipitates between Steels M3 and W3 was also
verified by the TEM observation with thin foil as will be mentioned in the later part of this section. EDS analysis (Figs. 7 and 8) revealed that the coarse precipitates before creep tests in the both steels were identified as M₂₃C₆ and those after creep interrupt tests were Laves phase in addition to M₂₃C₆.

Moreover, in order to investigate the change in the amount of precipitates during creep test, the comparison between the TEM results (Figs. 5 and 6) and the amount of extracted residues (Figs. 9 and 10) was made.

As shown in Figs. 9 and 10, the contents of precipitated Fe, Cr, W and Mo, which are the constituents of M₂₃C₆ or Laves phase, increase in residues during creep tests of approximate 5 000 h at 873 K. In contrast, the contents of V, Ta and Nb, which are the constituents of MX, did not show any remarkable change. Comparing the contents Ta and Nb in extracted residues, it is assumed that volume fraction of MX is comparable in both steels. Also, it was confirmed that the size of MX was almost same in the both steels and was unchanged during creep tests with TEM observations at high magnification.

Moreover, it can be recognised from Figs. 9 and 10 that
the increment of the precipitates due to approximately 5000 h creep at 873 K in Steel W3 is larger than that in steel M3. Particularly, it should be noted that increment of W in extracted residue of Steel W3 is extremely larger than that of Mo in Steel M3. It is thus suggested that Laves phase of Steel W3 precipitates faster, or occurs at earlier stage under the creep duration than that of Steel M3. This results agrees well with the previous studies which indicate that Laves phase is a dominant one which changes in size or morphology during a creep test.

Figures 11 and 12 show TEM micrographs of Steels W3 and M3, before and after creep interrupt tests, whose specimens were prepared by the one-step electropolishing. Both steels before creep tests consist of lath martensite subgrains with high dislocation densities and precipitates mainly of MX and M23C6 type carbides. Slight decrease in the dislocation densities is observed after creep interrupt tests, but a change in size and morphology of martensite lath was not clearly observed.

In the steels before creep tests, only M23C6 is identified as relatively coarse precipitates mainly along prior austenite grain boundaries as well as along martensite lath boundaries by TEM observation. However, coarse precipitates in the specimens after creep interrupt tests include Laves phase in addition to M23C6. Figures 13 and 14 show the TEM micrographs observed with thin foil prepared by the two-step electropolishing where the trace of M23C6 can be observed as a blank. In the specimens before creep tests, there is no remarkable difference between both steels in the size and distribution of the M23C6. It is observed that M23C6 in the steels before creep tests is densely aligned along prior austenite grain boundaries but less along martensite lath boundaries. The amount of M23C6 interior of grains and lath boundaries is slightly larger in Steel M3 than in Steel W3.

In the specimens after creep interrupt tests exposed for approximately 5000 h at 873 K, it is easily found that most
precipitates sitting along prior austenite grain boundaries are remarkably coarsened during creep test, while the size of those aligned along lath boundaries are almost kept constant. Due to the two-step electropolishing technique, it could be recognized that the precipitates aligned along prior austenite boundaries are mainly Laves phase and the precipitates located at lath boundaries are M$_{23}$C$_6$.

In order to follow the evolution of Laves phase through creep duration, SEM images composed of backscattered electron were observed with the specimens of Steel W3 taken from gauge sections apart from heavily deformed regions of fractured specimens crept at 923 K, so that Laves phase composed of Fe and W is clearly distinguished from the M$_{23}$C$_6$ as previously mentioned. With these SEM micrographs, area fractions, sizes, and number densities of Laves phase were measured by an image analyzer. The size of each Laves phase particle is represented by the diameter of the circle having the same area.

**Figure 15** shows the results of the quantitative analysis. Laves phase in Steel W3 is observed in the specimens ex-

![Fig. 13. TEM micrographs of Steel W3 with thin foil prepared with two-step electropolishing. (a) before and (b) after creep interrupt tests (150 MPa for 5058.7 h at 872 K)](image)

![Fig. 14. TEM micrographs of Steel M3 with thin foil prepared with two-step electropolishing. (a) before and (b) after creep interrupt tests (150 MPa for 5058.7 h at 872 K)](image)

![Fig. 15. Quantitative analysis of evolution of Laves phase by creep duration measured with ruptured specimens of Steel W3 using SEM micrographs (images of backscattered electron). (a) fraction, (b) size and (c) number density)](image)
posed over 300 h of creep duration. As shown in Fig. 15(a), the area fraction of Laves phase in the SEM micrographs increases with the lapse of creep test time up to about 5000 h duration. Exceeding 5000 h of creep duration, the fraction of Laves phase is thought to reach plateau. On the other hand, a steep increase in the size of Laves phase was observed over 5000 h exposure of creep test at 923 K. In the specimen ruptured for about 10000 h, the mean diameter of Laves phase reached to 0.6 μm. In correspond to the significant coarsening of Laves phase for about 10000 h of creep duration, the number density of Laves phase showed gradual increase up to about 5000 h of creep duration and abrupt decrease at about 10000 h creep duration.

The above-mentioned results are probably associated mainly with M23C6 or Laves phase for which the precipitation behaviors are strongly affected by W or Mo. As governing factors of mechanical properties, especially creep properties, solid-solution hardening of W or Mo should be taken into account as well as precipitation or dispersion hardening.

In most cases, the difference between a total amount and the amount of extracted residues was used as the amount of a certain element in solution. In this study, in addition to this method, more direct method for measuring the amounts of solute W and Mo, matrix analysis by EDS, was carried out.

Figure 16 indicates W and Mo contents in the matrix measured by EDS/TEM method with the specimens before and after creep interrupt test where creep exposure was about 5000 h at 873 K. The initial solute W and Mo contents in Steels W3 and M3 were 0.3 and 0.6% in atomic percentage on the average, respectively. Both solute W and Mo contents were reduced to about a half of the initial contents by about 5000 h-creep exposure. It should be noted that the solute Mo content is largely scattered with analysing points compared with the solute W content. Especially, this scatter of contents of solute Mo was marked in the specimens before creep test where the contents of solute Mo were varied from 0.25 to 0.85 at%.

Figure 16 also shows the solute W and Mo contents obtained by two other means. One is the content estimated with the amount of extracted residues where contents of solutes are defined as the difference between the total amount and the amount of extracted residues. The other is the equilibrium values calculated utilizing THERMOCALC, a computer program for equilibrium phase-diagram calculations.9)

The estimated contents based on the amount of extracted residues indicate considerable difference compared with solute W and Mo contents measured with FE-TEM. This inconsistency is larger in the amount of solute W for Steel W3, where the contents estimated with extracted residues are higher than those measured directly with the FE-TEM method irrespective of creep conditions whether before or after creep interrupt tests. In contrast, the equilibrium values are close to solute W and Mo contents after creep interrupt tests measured with FE-TEM.

4. Discussion

As shown in Fig. 3, it is no doubt that the W-containing steel (Steel W3) has better creep rupture properties compared with the Mo-containing steel (Steel M3). This difference in creep properties can be mainly attributed to the difference in creep strength controlling mechanism between W and Mo, because the size and quantity of fine precipitates consisting of Ta or Nb are almost same in both steels and indicate no obvious change during creep tests. Indeed, another experiment10) has shown that a steel, matching Steel W3 except for the addition of Nb instead of Ta, has almost the same creep properties as those of Steel W3.

The difference of creep strength controlling mechanism between W and Mo can be hypothesized based on the difference in microstructural evolution during creep tests. Microstructural factors, assumed to influence creep properties and possibly differ in the W-containing steel and the Mo-containing steel, is exemplified as follows: martensite structures (lath size, dislocation density), precipitates (M23C6, Laves phase) and solute atoms.

As shown in Figs. 11 and 12, no remarkable difference in the martensite structure such as the lath size and dislocation density is observed between Steels W3 and M3, for both before and after creep interrupt tests. Accordingly, it is plausible to focus on the precipitation behavior of M23C6 or Laves phase composed of W or Mo, and W or Mo contents in solid solution as the governing factors for creep properties.

The TEM observations with thin foil (Figs. 11 and 12) and with extracted replicas (Figs. 5 and 6) clearly indicate that the marked increase in amount and size during creep duration can be observed only in Laves phase, not in M23C6. Furthermore, Laves phase more coarsens during creep duration in the Mo-containing steel (Steel M3) than in the W-containing steel (Steel W3). Thus, if the amount, size, morphology or distribution of precipitates are the major causes for difference in the creep strength between the W-containing steel and Mo-containing steel, Laves phase should have a major contribution. Igarashi et al. have suggested that coarsening of carbides or intermetallic compounds extends a precipitation-free zone where creep strain can be concentrated, results in the degradation of creep strength.11) This is considered to be the most agreeable
mechanism for controlling creep strength by the precipitates in the present study. However, there is a question with this hypothesis whether M$_{23}$C$_6$ or the Laves phase less densely dispersed are the major controlling factors rather than MX type precipitates such as carbo-nitrides of Nb, Ta or V.

Increase of the amount of M$_{23}$C$_6$ or Laves phase during creep tests, of course, causes decrease of the amount of W or Mo in solid solution. This is confirmed with the TEM analysis as shown in Fig. 16. The average atomic concentration of solute Mo in Steel M3 is 2–3 times higher than that of solute W in Steel W3 both for before and after creep tests. As far as the contents of solute atoms are compared using average contents, it is considered that the higher creep strength of the W-containing steel cannot be attributed to the difference of solid solution hardening between W and Mo. However, it should be noted that the scatter among each data of Mo content in solid solution is larger than that of W as shown in Fig. 16. This suggests that the nonuniform distribution of Mo atoms in solid solution may enhance localization of creep strain where solute Mo content is low, and may result in deterioration of creep strength, although this nonuniform distribution of Mo atoms has to be confirmed excluding unidentifiable ultra-fine precipitates and Mo-rich clusters by further investigations.

5. Conclusions

The role of W for improving creep strength has been studied in terms of microstructural evolution during creep tests on the low-activation 9Cr–2W–0.2V–Ta steels in contrast with conventional 9Cr–1Mo–0.2V–Nb steels. The conclusions are summarized as follows.

(1) There is no significant difference in the lath size and the dislocation density of martensite between the W-alloyed steel and the Mo alloyed steel irrespective of whether before or after creep tests. Furthermore, there is no difference in the size and amount of fine MX-type precipitates composed of Ta, Nb or V, which indicates no remarkable change in the size and amount during creep tests, for both steels.

(2) In the present study, the amount of W or Mo in solid solution is directly measured with thin foil using an FE-TEM equipped with an X-ray energy dispersive spectroscopy. The solute W or Mo contents measured with this method indicate considerable difference compared with the estimated content based on the amount of extracted residues. As far as the solute atom contents are compared based on the average contents, higher creep strength of the W-containing steel can not be attributed to the difference of solid solution hardening between W and Mo. Thus, it is concluded that the different manner of evolution of M$_{23}$C$_6$ or Laves phase between the W-alloyed steel and the Mo-alloyed steel causes different creep strength between them. Comparing M$_{23}$C$_6$ and Laves phases, the latter is assumed to be the main governing factor because the change in amount and size of the particles during creep duration is more remarkable in Laves phase than in M$_{23}$C$_6$ and coarsening of Laves phase due to creep duration is more pronounced in the Mo-alloyed steel than in the W-alloyed steel. In addition, it should be taken into consideration that the nonuniform distribution of Mo atoms in solid solution may enhance the localization of creep strain where solute Mo content is low, and may result in deterioration of creep strength.

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