Improvement of Creep Strength of 9CrODS Martensitic Steel by Controlling Excess Oxygen and Titanium Concentrations

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The effects of chemical compositions (titanium, oxygen) and consolidation temperature on high-temperature mechanical properties of 9Cr-oxide dispersion strengthened steel (9CrODS steel) were investigated. A possible high-temperature strengthening mechanism of 9CrODS steel was discussed based on the experimental results. Creep strength of 9CrODS steel at 973 K was remarkably improved when titanium concentration was 0.35 mass%. A higher amount of added titanium than 0.2 mass% was effective for providing consistently reliable manufacturing of high strength 9CrODS steel because it reduced the effect of oxygen contamination on high-temperature strength. The fraction of elongated α-ferrite grains, which had an ultra-fine oxide particle dispersion, tended to increase with increasing titanium. The elongated grains were considered to improve creep strength of 9CrODS steel. It was also found that creep strength was degraded by elevating the consolidation temperature from 1423 K to 1473 K.

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1. Introduction

9Cr-oxide dispersion strengthened martensitic steel (9CrODS steel) has been identified as an attractive candidate for fusion reactor blanket material as well as advanced fast reactor (FR) fuel cladding tubes because of its superior mechanical properties and radiation resistance. By applying 9CrODS steel to the blanket material, operation temperature of the blanket system can be elevated.1) From the viewpoint of manufacturing conditions on the mechanical properties of 9CrODS steel is an important task.

Japan Nuclear Cycle Development Institute (JNC) is engaged in developing 9CrODS steel for FR cladding tubes, and has successfully produced thin-walled tubes with this material.2,3) It was recently shown that microstructure and creep strength of 9CrODS steel is sensitive to subtle changes of oxygen and titanium concentrations.3,4) To develop a consistently reliable manufacturing procedure for high strength 9CrODS steel, it is important to clarify the effects of manufacturing conditions on the mechanical properties of 9CrODS steel. In this study, the effects of titanium concentration, excess oxygen concentration and consolidation temperature on the high-temperature strength (creep and tensile properties) of 9CrODS steel were investigated. A possible high-temperature strengthening mechanism of 9CrODS steel was discussed based on the experimental results.

2. Experimental Procedure

2.1 Manufacturing of 9CrODS steel bars

9CrODS steel rods (10 mm diameter) were produced with different concentrations of titanium and oxygen using the following procedure. The mixtures of element powder (iron (Fe), chromium (Cr), carbon (C), tungsten (W), titanium (Ti)), yttrium oxide (Y₂O₃) powder, iron-yttrium intermetallic compound (Fe₂Y) powder, and iron oxide (Fe₂O₃) powder were mechanically alloyed in an attrition-type ball mill with a rotating speed of 220 revolutions per minute (rpm) for 48 h in Ar gas atmosphere. Titanium concentration was controlled by changing the amount of titanium powder in the powder mixture. Oxygen concentration was controlled by adjusting the amount of Fe₂Y and Fe₂O₃ powders in the mixture. The Y₂O₃ powder consisted of small Y₂O₃ particles, whose diameter was approximately 20 nm.

The resulting mechanically alloyed powders (MA powders) were sealed in cans and degassed at 673 K in a vacuum of 0.1 Pa. These powders were hot-extruded and air-cooled to be consolidated into rod shape. The hot-extrusion was usually carried out at 1423 K. However, 1473 K hot-extrusion was also used to examine the effects of hot-extrusion temperature (Te) on high-temperature mechanical properties. The extruded bars were forged at 1423 K and were either normalized (N: 1323 K–1 h, air-cooling), normalized-and-tempered (NT: 1323 K–1 h, air-cooling ⇒ 1073 K–1 h, air-cooling), or else furnace-cooled (FC: 1323 K–1 h ⇒ furnace-cooling at 30 K/h). The chemical compositions of the manufactured steels were analyzed after hot-extrusion. Oxygen concentration was analyzed by an inert gas fusion method. The analyzed results are shown in Table 1, where Ex.O stands for excess oxygen, which is defined as the value subtracting oxygen concentration in Y₂O₃ powder from the total oxygen concentration in the steel.

2.2 Mechanical tests

Mechanical tests were performed after normalizing-and-tempering. Vickers hardness tests were conducted with 1 kgf loading. Uni-axial tensile and creep tests were performed with a gauge size of 6 mm diameter × 30 mm length, where stress was loaded parallel to hot-extrusion direction. Testing temperatures were set at 973 K and 1073 K for tensile test and 973 K for creep rupture test. The loaded stress in the creep test was in the range from 100 to 180 MPa.
2.3 Microstructure observation

Oxide particle observations were done using a 200 keV transmission electron microscope (TEM) for the furnace-cooled steels, while metallographic examinations were done using an optical microscope for the normalizing steels. To investigate the redistribution behavior of ferrite (α)-former elements (tungsten and chromium) during the 1423 K hot-extrusion process, EPMA (electron probe microanalyzer) mapping analysis was carried out for MA powder of ST-1 before and after quenching (WQ: 1423 K–1 h, water quenching (WQ)). Here, the annealed powder was cooled not by Ar-gas cooling but by quenching to reduce the amount of carbide precipitation.

3. Results and Discussion

3.1 Mechanical properties

3.1.1 Creep and tensile strength

Figure 1 shows 1000 hour creep rupture strength of normalized-and-tempered steels. With the 0.2 mass% titanium steels, creep strength reaches a maximum value when excess oxygen is around 0.08 mass%. High creep strength is kept, even if excess oxygen is increased to 0.17 mass%, when titanium concentration is 0.46 mass%. Therefore excess oxygen dependence of creep strength in 9CrODS steel can be weakened by increasing titanium concentration. It should be noted that a significant creep strength enhancement is achieved when titanium concentration is 0.35 mass%. This suggests that an optimum titanium concentration should exist for creep strength improvement. The ODS bars except for M-Ti(H) (0.35 mass% titanium) were hot-extruded at 1423 K; M-Ti(H) was hot-extruded at 1473 K. Elevating hot-extrusion temperature to 1473 K apparently degrades the creep strength.

Tensile test results at 973 K are shown in Fig. 2. Unlike creep strength, tensile strength is not greatly improved by increasing titanium concentration from 0.2 mass% to 0.46 mass%.

Table 1 Chemical compositions of the manufactured steel rods.

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>Chemical composition (mass%)</th>
<th>Y2O3</th>
<th>Ex.O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lo-O1</td>
<td>C 0.13, Ni 0.01, Cr 8.9, W 1.9, Ti 0.20, Y 0.27, O 0.099, N 0.014, Ar 0.005, Y2O3 0.34, Ex.O 0.026</td>
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<tr>
<td>Lo-O2</td>
<td>C 0.13, Ni 0.01, Cr 8.9, W 2.0, Ti 0.21, Y 0.28, O 0.12, N 0.012, Ar 0.006, Y2O3 0.36, Ex.O 0.044</td>
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</tr>
<tr>
<td>ST-1</td>
<td>C 0.13, Ni 0.01, Cr 8.9, W 2.0, Ti 0.21, Y 0.28, O 0.16, N 0.009, Ar 0.005, Y2O3 0.36, Ex.O 0.084</td>
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<tr>
<td>ST-2</td>
<td>C 0.14, Ni 0.04, Cr 8.8, W 2.0, Ti 0.21, Y 0.26, O 0.18, N 0.013, Ar 0.005, Y2O3 0.33, Ex.O 0.11</td>
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<td></td>
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<tr>
<td>M11</td>
<td>C 0.13, Ni 0.02, Cr 9.0, W 2.0, Ti 0.20, Y 0.29, O 0.14, N 0.013, Ar 0.003, Y2O3 0.37, Ex.O 0.06</td>
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<tr>
<td>Hi-O</td>
<td>C 0.13, Ni 0.01, Cr 8.8, W 2.0, Ti 0.21, Y 0.27, O 0.22, N 0.012, Ar 0.005, Y2O3 0.34, Ex.O 0.15</td>
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</tr>
<tr>
<td>M-Ti, M-Ti (H)</td>
<td>C 0.14, Ni —, Cr 9.0, W 2.0, Ti 0.35, Y 0.28, O 0.16, N 0.012, Ar 0.005, Y2O3 0.36, Ex.O 0.084</td>
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<tr>
<td>Hi-Ti</td>
<td>C 0.13, Ni 0.01, Cr 8.7, W 1.9, Ti 0.46, Y 0.27, O 0.24, N 0.011, Ar 0.005, Y2O3 0.34, Ex.O 0.11</td>
<td></td>
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</tr>
<tr>
<td>Hi-TiO</td>
<td>C 0.13, Ni 0.01, Cr 8.8, W 1.9, Ti 0.46, Y 0.27, O 0.24, N 0.011, Ar 0.005, Y2O3 0.34, Ex.O 0.17</td>
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</table>

Fig. 1 Effects of titanium, excess oxygen and hot-extrusion temperature (Te) on creep strength of the normalized-and-tempered steels at 973 K.

Fig. 2 Effects of titanium, excess oxygen and hot-extrusion temperature (Te) on tensile properties of the normalized-and-tempered steels at 973 K. (a) Tensile strength, (b) Uniform elongation.
0.46 mass%. Uniform elongation in 0.35 mass% titanium steel is approximately the same level as that in 0.2 mass% titanium steel when excess oxygen concentration is ~0.08 mass%. Improved tensile strength and uniform elongation are kept at high values in 0.46 mass% titanium steels even if excess oxygen is increased to 0.17 mass%, while those values in 0.2 mass% titanium steels drop as excess oxygen is increased to 0.15 mass%. A fine and dense distribution of oxide particles is an important factor for creep and tensile strength improvement, because a high number density of oxide particle blocks dislocation gliding and plastic deformation. It is supposed that the high number density distribution of oxide particles is kept in 0.46 mass% titanium steel, although excess oxygen is increased to 0.17 mass%. Further discussion will be given in section 3.2.3 from the viewpoint of nano-structures.

### 3.1.2 Vickers hardness

Figure 3 reveals an interesting correlation between creep rupture strength and the hardness of normalized-and-tempered steel. In general, creep strength is not considered to correlate with Vickers hardness. However, creep strength linearly increases with increasing hardness up to Hv385 in the 9CrODS steels. Both creep strength and Vickers hardness of the 9CrODS would be closely correlated with the number density of oxide particles. This correlation may lead to the linear relationship between Vickers hardness and creep strength. The 0.46 mass% titanium steels have higher Vickers hardness than Hv385 and deviate from the linear relationship. A different creep mechanism may work in the steels containing 0.46 mass% titanium.

### 3.2 Micro & nano structures of the manufactured 9CrODS steels

#### 3.2.1 Microstructures

Typical examples of optical microstructures of normalized steels (N) are shown in Fig. 4. A certain difference in microstructures between high creep strength steel (M-Ti, ST-1) and low creep strength steel (Hi-O) can be seen. While only equiaxed grains were observed in Hi-O (0.2 mass% titanium, 0.15 mass% excess oxygen), both equiaxed and elongated grains co-exist in ST-1 (0.2 mass% titanium, 0.08 mass% excess oxygen) and M-Ti (0.35 mass% titanium, 0.08 mass% excess oxygen).

Figure 5 shows the alloying element distributions in MA powder of ST-1 (0.2 mass% titanium, 0.08 mass% excess oxygen) obtained using EPMA. As shown in Fig. 5(a), chromium and tungsten are distributed uniformly in the powder immediately after MA. Following the heat treatment of 1423 K–1 h and WQ (Fig. 5(b)), these elements are locally segregated. Considering that chromium and tungsten are typical ferrite-former elements, the locally segregated area of chromium and tungsten must not be in the austenite (γ) phase but in ferrite (δ) phase during the 1423 K annealing. More than half of the grains seem to remain as ferrite phase in ST-1 during 1423 K annealing. More detailed discussion is described in the next section.

#### 3.2.2 A possible phase transformation process in 9CrODS steel

It was reported that severe plastic deformation in the MA process produces the MA powder matrix composed of ultra fine ferrite (α) grains. Both ferrite (α) to austenite (γ) phase transformation and grain growth proceed simultaneously in the subsequent hot-extrusion. From Figs. 4 and 5, it is considered that the hot-extrusion causes the transformation of ultra-fine α-Fe grains in ST-1 and M-Ti to a dual phase microstructure composed of austenite phase (γ) and ferrite phase (δ). If the ultra-fine α-Fe grains were completely transformed to austenite (γ) phase in the hot-extrusion process, matrix grains became totally equiaxed. Then the elongated grains are considered to be ferrite (δ) grains, which remained as ferrite-phase without transforming to austenite (γ) phase during the hot-extrusion process. This elongated ferrite phase (δ) is designated as residual-α phase in this study.

The calculated phase diagram of 9CrODS steel is shown in Fig. 6. The calculation was performed using the Thermo-calc code with TC-FE database. In general, “Fe-0.13Cr-2W-0.1Ti” steel should be completely transformed from ferrite (α) to austenite (γ) phase by heating to 1423 K as seen in Fig. 6. However, ferrite phase seemed to remain even at 1423 K in ST-1 as seen in Fig. 5. It is supposed that matrix carbon depletion by titanium carbide formation causes some of the ferrite phase to remain even at 1423 K. Titanium has a higher affinity to oxygen than to carbon. Decreasing excess oxygen enhances titanium carbide formation instead of oxide formation. This leads to solute carbon depletion in the matrix of ST-1, which contains lower excess oxygen of 0.08 mass%. On the other hand, Hi-O containing higher excess oxygen of 0.15 mass% does not have elongated residual-α grains as seen in Fig. 4. It is thought that matrix carbon depletion is small in Hi-O because Hi-O contains enough oxygen to combine with titanium. This inference is supported by previous findings that carbides containing titanium were not identified by extracted replica/EDS analysis in the higher excess oxygen-containing steel (9Cr-2W-0.2Ti-0.34Y2O3-0.14 mass% ExO, Mm13), while carbides containing titanium were identified in the lower excess oxygen-containing steel (9Cr-2W-0.2Ti-0.34Y2O3-0.06 mass% Ex-O, M11). As seen in Fig. 6, ferrite phase certainly increases at 1423 K by increasing titanium concentration to 0.46 mass%. More titanium addition causes the higher fraction of residual-
phase at 1423 K through formation of titanium carbide.

3.2.3 Nano structures

Furnace-cooling (1323 K–1 h) leads to austenite to ferrite phase transformation. To clearly observe the oxide particles, well-annealed furnace-cooled specimens were observed using TEM. Oxide particle diameters were estimated from image analysis of TEM micrographs and shown in Fig. 7. In the 0.2 mass% titanium steels, oxide particle diameter in the equiaxed grains increases with increasing excess oxygen. However, in 0.46 mass% titanium steel, the oxide particles in equiaxed grain remain fine even though excess oxygen concentration increases to 0.17 mass%. In elongated grains of both 0.2 mass% titanium steel and 0.46 mass% titanium steel, the oxide particles are much finer than in equiaxed grains. A larger oxide dispersion strengthening is expected in elon-

![Fig. 4 Optical microstructures of normalized 9CrODS steels.](image)

(a) As mechanically alloyed

![Fig. 5 EPMA mapping results of mechanically alloyed powder of ST-1 (0.2 mass% titanium-0.08 mass% excess oxygen). (a) As mechanically alloyed, (b) After quenching (1423 K–1 h, water quenching (WQ)).](image)
gated grains than in equiaxed grains. As seen in Figs. 1 and 2, creep strength and tensile strength in 0.46 mass% titanium steel are kept high even though excess oxygen concentration increases to 0.17 mass%. Higher titanium concentration is considered to be suitable for increasing the amount of elongated grains. It would concurrently make oxide particles in equiaxed grain keep fine and prevent equiaxed grain from softening even though excess oxygen increases. These would be the reason why the creep and tensile strength of 0.46 mass% steel are kept in high value even though excess oxygen increases.

A classical theory on precipitate coarsening explains that oxide particle growth is controlled by the interfacial energy between an oxide particle and matrix. If the lattice misfit between ferrite (δ) phase and oxide particles is smaller than that between austenite (γ) phase and oxide particles, the finer oxide particle precipitation in elongated grains can be interpreted by the foregoing classical theory concerning the correlation between interfacial energy and precipitate size.

3.3 A possible mechanism of creep strength improvement of 9CrODS steel

Grain boundary sliding is considered to be one of important mechanism of creep deformation of 9CrODS steel, because the microstructure of 9CrODS steel consists of fine grains. Plastic deformation inside grain near the grain boundary triple junction is thought to be necessary for grain boundary sliding. Therefore the larger oxide particle dispersion strengthening inside grain would reduce grain boundary sliding.

Initial Y₂O₃ powders and the mixed element powders dissolve in matrix during MA. In the subsequent hot-extrusion, nano-sized titanium-yttrium complex oxide particles (nano-particles) precipitate. It was reported that hot-extrusion temperature just after MA significantly influences the size and volume fraction of nano-particles. The number density of the nano-particles decreases by elevating hot-extrusion temperature from 1423 K to 1473 K in 14Cr-0.4Ti-0.25Y₂O₃ steel. The degradation of creep strength by elevating hot-extrusion temperature to 1473 K, as shown in Fig. 1, can be interpreted in terms of decreasing the number density of nano-particles.

High creep strength steels consist of hard grains (elongated grains) and soft grains (equiaxed grains). By increasing titanium concentration from 0.2 to 0.35 mass%, the fraction of elongated grains must increase as predicted from the phase diagrams in Fig. 6. It is thought that the creep strength enhancement by increasing titanium to 0.35 mass% is caused by increasing the fraction of elongated grains. When titanium concentration is increased from 0.35 to 0.46 mass%, too many elongated grains are formed. This should enhance stress concentration at the grain boundary triple junction and grain boundary sliding, which deteriorates creep strength.

Further studies to characterize microstructure of the creep ruptured specimens near grain boundary triple junction are required to confirm the above-mentioned discussion.

4. Summary

The effects of titanium concentration, excess oxygen concentration and consolidation temperature on high-temperature mechanical properties were investigated in 9CrODS martensitic steels. The obtained results can be summarized as follows.

1. The creep strength of 9CrODS steel was remarkably improved by controlling titanium concentration to 0.35 mass%.
2. The fraction of elongated grain tended to increase with increasing titanium. An appropriate fraction of elongated grain formation is considered to improve creep strength of 9CrODS steel.
3. Increasing titanium concentration from 0.2 to 0.46 mass% remarkably reduced the effect of excess oxygen on creep strength and tensile property. Increasing titanium concentration is effective to manufacture high strength 9CrODS steel.
Creep strength was found to be degraded by elevating the consolidation temperature from 1423 to 1473 K. This could be caused by decreasing number density of oxide particles.

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REFERENCES


