Effect of Ti and W on the Mechanical Properties and Microstructure of 12% Cr Base Mechanical-alloyed Nano-sized ODS Ferritic Alloys

Ick-Soo KIM, Byung-Young CHOI, Chang-Yong KANG, Takanari OKUDA, Phil J. MAZIASZ and Kazuya MIYAHARA

School of Advanced Materials and the Research Center of Industrial Tech., Engineering Research Institute, Chonbuk National University, Chonju, 561-756 Korea. 1) Dept. of Mater. Sci. and Eng., Pukyung National University, Pusan, 608-031 Korea. 2) Materials Research Inst., Kobe Steel Ltd., Kobe 651-2271 Japan. 3) Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA. 4) Dept. of Molecular Design and Eng., Nagoya University, Nagoya 464-8603 Japan.

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In recent years, research and development of high-temperature structural materials for ultra-super critical pressure plant with increased energy efficiency have actively been in progress so as to solve global environmental pollution and resource exhaustion issues. Oxide-dispersed-strengthened (ODS) ferritic alloys produced by mechanical alloying (MA) have been developed as alternative materials with very high-temperature strength at the ultra-super critical pressure.

In this study, Fe–12%Cr ODS based alloys containing Ti and W have been made and the effects of Ti and W on the high-temperature strength of the alloys were investigated. The results show that high-temperature tensile strength and creep rupture strength of the 12YWT steel containing 0.4 % Ti and 3 % W were the highest. This is mainly due to the formation of fine complex oxides of Ti–Y–O by the addition of Ti and their homogeneous distribution. It is also suggested that solid solution hardening by W occurs as a result of uniform distribution of W in solution.

KEY WORDS: ferritic alloy; mechanical alloying; oxide dispersion strengthening (ODS); yttria; titania; microstructure; high-temperature strength; atom probe; mechanical properties; creep; nano-sized oxides.

1. Introduction

It has been reported by a number of researchers1–9) that MA ODS alloys possess excellent creep strength at high temperatures and high resistance to swelling in radioactive radiation. Oxide dispersion strengthened (ODS) ferritic alloys produced by mechanical alloying (MA) have been found to be effective for increasing high-temperature strength. They are strengthened by dispersion hardening of oxide particles and by solid solution hardening. Though, precipitation hardening is similar to particle dispersion hardening, the hardening effect of the precipitates decreases because of thermal instability such as: re-solution, coarsening, etc, which occur during long term exposure at high temperatures. Comparatively, oxides in Fe-base alloy does not change in size or state of dispersion even after long term exposure at high temperatures, and also possible for it to maintain an excellent high-temperature strength near to the melting point.

In previous researches10–11) the authors have investigated the effects of types and sizes of oxides, thermomechanical treatments, and matrix structure on the mechanical properties of Fe–17%Cr ferritic alloy. Among the oxides, Y2O3 particles were found to be the finest in size and uniform in dispersion. In the long course of our studies, the strength of ODS steels was found to be changed significantly by different thermomechanical treatments.

The present research emphasizes the oxides dispersion behavior, the matrix structure stability, and the effect of single and complex oxides on the high temperature strength of Fe–12%Cr ODS alloys. The effects of W and Ti on the Orowan stress in the materials is also investigated.

2. Experimental Procedures

Three ODS alloys (12Y1, 12YW, 12YWT) have been used in this study. Table 1 shows the alloys compositions. Hereafter, mass% is used in this study. The 12YW alloy is a version of modified 12Y1 alloy having a basic composition with 3% W. The 12YWT alloy is another version of modified 12Y1 alloy with 3% W and complex oxides of Y and Ti which have been developed recently12–14) and was provided by Kobe Steel Ltd. in Japan. Y2O3 serves as an accelerator, and the content of Y2O3 was limited to about 0.25% (powder diameter: about 20 nm) in order to improve recrystallization behavior.13) The manufacturing process of these alloys is shown in Figure 1. Raw materials used were electrolytic iron and pure metal powder (average size 70 μm).
The ball mill charge consisted of about 98.1 N of powder and 1.470 N of hard steel ball. The mechanical alloying was carried out for up to 48 h in argon gas atmosphere at a speed of 250 rpm. The tank temperature was controlled as 353 to 373 K. The mechanically alloyed powders were degassed at 673 K in a vacuum for 2 h, and consolidated from f67 to f30 (extrusion ratio 5) in diameter by hot-extrusion at 1423 K, followed by hot rolling at 1123 K to plates with thickness of 7.0 mm. The plates were annealed for 1 h at 1323 K in vacuum. The 12Y1 plates were sliced to thinner plates with thickness of 4.0 mm and cold rolled to sheets with thickness of 2.7 mm. The 12YW alloys were warm rolled at 873 K and the 12YWT alloys were annealed at 1323 K for 1 h in vacuum.

Microstructural changes and recrystallization behavior of the specimens were observed by optical microscopy and TEM (H-800). After the final heat treatment, the materials were machined to flat creep and tensile specimens with a gauge partition of 2.0 mm width, 2.0 mm thickness and 10.0 mm length. Tensile tests were performed at a strain rate of 8.3×10^-3/s at temperature range of 298 to 1173 K. High-temperature long time creep tests were carried out with an Instron-machine type tester at 973 K. Characteristic of super fine cluster were investigated by means of 3D-Atom Probe imaging.15)

3. Experimental Results and Discussion

3.1. Oxide Dispersion and Strength Characteristics
ODS alloys have characteristics of not only solid solution and precipitation hardening but also high strength as a result of interruption caused by dislocation movement of the dispersed oxide particles.16) One of the important parameters of oxide dispersion strengthening is the inter particle spacing. If the amount of dispersed particles is the same, strengthening effect increases as the distance between particles decreases. Figure 2 shows TEM photographs of dispersed particles distribution in the 12Y1, 12YW and 12YWT alloys. Oxide particles of the 12Y1 and 12YW were formed as large particles with diameters of 10–30 nm, and a particles distribution with about 10^20–10^21 m^-3. While the size of oxide particles in the 12YWT remained constant as 1–10 nm in diameter. The cluster density of the 12YWT alloy was assumed to be 1–2×10^23 m^-3, and this assumption is based on the result of calculating white and black dots by strain-contrast at weak-beam dark image. The particles in the 12Y1 and 12YW alloys were larger than those of the 12YWT and their particles density were relatively lower. The dislocation density of the 12YWT showed the highest of 10^16 m^-3 while the 12Y1 showed 10^15 m^-3.

Figure 3 is the tensile-testing result starting at room temperature to 973 K. The highest 0.2% proof stress and ultimate tensile strength were obtained in the 12YWT alloy. The reason for this highest value can be attributed to the fine dispersion achieved by the addition of W and Ti. Generally, it is well known that the strength of ODS alloys increases because of obstacle of dislocation migration by Orowan model,17) cross slip model,18) particle shear model19) and dislocation climb model,20) etc. The highest tensile strength in the 12YWT alloy can be explained by very small interparticle spacings of oxides and by dislocation migration interrupted by Orowan model.

Figure 4 shows the relationship between steady state creep strain rate and stress at 973 K. The creep strain rate of the 12YWT (10^-12/s^-1) is lower than those of the 12Y1 and 12YW in the condition of applied stress of 250 MPa. The threshold stress of the 12YWT is the highest at a range of

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### Table 1. Chemical compositions of the materials used (mass%).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>O</th>
<th>Si</th>
<th>N</th>
<th>Ti</th>
<th>W</th>
<th>Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Y1</td>
<td>Bal</td>
<td>12.35</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Y2O3(0.248)</td>
</tr>
<tr>
<td>12YW</td>
<td>Bal</td>
<td>12.30</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>Y2O3(0.248)</td>
</tr>
<tr>
<td>12YWT</td>
<td>Bal</td>
<td>12.29</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>&lt;0.01</td>
<td>0.39</td>
<td>-</td>
<td>3</td>
<td>Y2O3(0.248)</td>
</tr>
</tbody>
</table>

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Fig. 1. Manufacturing process of the 12Cr ODS–MA ferritic alloys.
184–281 MPa. Here, threshold stress was calculated using the following equation where \( \lambda \) is the average distance between face to face particles on the slip plane, and is given as a function of the average particle radius \( r_s \) and the average distance \( l_s \) between center to center of the particles cut by the slip plane,

\[
\lambda = 1.25l_s - 2r_s \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

\[
l_s = \left( \frac{2 \pi r^3}{3 f r} \right)^{1/2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

\[
r_s = \left( \frac{\pi}{4} \right) \cdot \left( \frac{r^2}{r} \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]

where \( f \) is the volume fraction of the dispersed particles.
0.39,16) and $r$ is the average particle radius considering the size distribution of the assumed particles. Figure 5 shows particle size distribution in three kinds of specimens, which can be considered homogeneous dispersion. The calculated parameters are shown in Table 2. Even if several methods for calculating Orowan stress ($\sigma$) have been reported, the Orowan stress ($\sigma$) shown in the present work can be evaluated by the following equation based on the Scattergood and Bacon’s equation,16,22) which takes into account the interaction between the branches of the bowed out dislocation around a particle.

$$\sigma = \frac{G}{2(1-\nu)\pi} \left[ \ln\left( \frac{D}{r_0} \right) + B \right]$$ ..............(4)

where $G$ is the shear modulus (50 600 MPa),16) $\nu$ is the Poisson’s ratio (0.334),16) $M$ is the Taylor factor (3.0),23) $b$ is the magnitude of Burgers vector (2.48 $\times 10^{-10}$,16) and $r_0$ is the inner cut-off radius of dislocation core which is usually taken as $b–3b$.

In the above equation, the values of $A$ and $B$ are as follows.

In case of screw dislocation: $A=(1+\nu\sin^2\phi)\cdot \cos\phi/(1-\nu), B=0.6$

In case of edge dislocation: $A=(1-\nu\sin^2\phi)/(1-\nu), \cos\phi, B=0.7$

Also $\phi$ in this equation is the critical angle at which the dislocation detaches from particles, $\phi=46$ degrees in case of screw dislocation and $\phi=19$ degrees in case of edge dislocation.16) $D$ is the harmonic mean of $l, rs,$ and to be calculated from $D=2ab/(a+b)$ equation. Orowan stresses calculated from these equations were in good agreement with the measured values at various creep strain rate as shown in Figure 6. Larson–Miller-Plot (LMP) comparing the creep rupture strength of the 12YWT with those of similar alloys (The arrows indicate that creep tests are still running).

![Fig. 6. Larson–Miller-Plot (LMP) comparing the creep rupture strength of the 12YWT with those of similar alloys. (The arrows indicate that creep tests are still running.)](image)

![Fig. 7. Distributions of Ti, O, Y and W determined by three-dimensional atom probe analysis of the 12YWT alloy.](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>$l \times 10^{-9}$</th>
<th>$r \times 10^{-9}$</th>
<th>$B \times 10^{-9}$</th>
<th>$D \times 10^{-9}$</th>
<th>Void-hardening stress (MPa)</th>
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</thead>
<tbody>
<tr>
<td>12Y1</td>
<td>15</td>
<td>22.5</td>
<td>338</td>
<td>34.8</td>
<td>11.8</td>
</tr>
<tr>
<td>12YW</td>
<td>13</td>
<td>16.9</td>
<td>220</td>
<td>30.1</td>
<td>10.2</td>
</tr>
<tr>
<td>12YWT</td>
<td>2.27</td>
<td>0.77</td>
<td>215</td>
<td>6.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 2. Dispersion parameters and void-hardening stress evaluated from transmission electron micrographs.

This result also shows the same
tendency in comparison with the results of tensile testing, and the creep rupture strength of the 12YWT is higher than that of MA–ODS ferritic alloy. These cause a concern to form complex oxides of Y–Ti–O by added Ti, the finest of oxide particles (average in radius: about 5–10 nm).

Figure 7 shows the characteristics of nano-sized ultra fine cluster of the 12YWT by Atom–Probe analysis. It can be considered that the complex oxides of Y–Ti–O were formed because of a good agreement of Y, Ti and O distribution. This result is explained in detail. Also solid solution can be recognized from homogeneous distribution of W in the specimen, suggesting solid solution strength effect by added W.

3.2. Microstructure of Matrix and Recrystallization Behavior

Figure 8 shows the TEM photographs of the specimens air cooled after annealing at 1323 K for 1 h. Figure 9 shows TEM photographs of the same specimens re-annealed at 1523 K for 10 h and showing the observation of recrystallization behavior. The results showed that matrix microstructures of the 12Y1 and 12YW specimens were recrystallized, followed by grain growth, up to the average size of about 10–20 μm. However, the microstructures of the 12YWT specimens were recrystallized partially and retarded in grain growth. This can also be observed in the optical micrographs of Figs. 10–12. From the rolling condition specimen, specimens aged at 1523 K for 1 h, 3 h, and 10 h, 12Y1 and 12YW proceeded in recrystallization as time went on. But there was almost no grain growth in 12YWT. The cause for such behavior can be explained in terms of the interference of the complex oxides of the fine Y–Ti–O migrating of grain boundaries. Okuda and co-workers reported that grain growth was dependent on Y2O3 content and excessive oxygen content. Y2O3 content for cold rolling and subsequent recrystallization is limited to 0.25 wt% in ODS ferritic alloys. If Y2O3 content is within this range, long life fuel cladding is possible by cold rolling process. Also Miodowni and his co-workers reported that recrystallization should rarely occur as oxide particle size was reduced and the density of particles was increased. Given the above reasons, grain growth of the 12YWT is affected by added Ti. From these results, the effect of Ti addition is considered to be none other than it promotes the for-
4. Conclusions
Effects of oxide distribution behavior, microstructure stability of matrix and added elements on the strength characteristics of ODS ferritic alloys were investigated for the 12YWT and two other different specimens.

The results obtained from this experiment are as follows:
(1) Oxide particles of the 12YWT are the finest and distributed homogeneously.
(2) The 12YWT has the highest high-temperature ten-
sile strength and creep rupture strength. These results were explained by the formation of fine complex oxides of Ti–Y–O by added Ti. Also, W atoms show homogeneous distribution in the matrix, suggesting solid solution strengthening effect.

(3) The fine complex oxides of Ti–Y–O interfered with grain growth of matrix and increased thermal stability of matrix during high-temperature exposure.

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REFERENCES