Dependence of Solvus Temperature of the Laves Phase on (Mo+W+Re) Contents in High Cr Ferritic Steels

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The solvus temperatures of the Laves phase were investigated in heat resistant 10Cr ferritic steels containing 2.3–4.7 mass% (Mo+W) and 0–1.7 mass% Re. The measured solvus data was approximately represented as a solvus curve in the pseudo-binary system of Fe–W (− Mo). The solvus temperatures increased with increasing content of Mo+W in the steels, for example, 1 020 K for 2.3 mass% (Mo+W) steel, 1 130 K for 3.7 mass% (Mo+W) and 1 145 K for 4.7 mass% (Mo+W) steel. It was suggested from the measured solvus curve that the Laves phase precipitated at 923 K granularly in a 2 mass% W steel, but finely in a 4.5 mass% W steel. On the other hand, the solvus temperature did not change with the Re addition up to 1.7 mass%.

KEY WORDS: ferritic steel; heat resistant; Laves phase; fine Laves; solvus temperature; W containing steel; Re containing steel.

1. Introduction

It is well known that interstitial elements, C and N, give a significant influence on the strength of steels. Besides these elements, Fujita et al. have reported that a nonmetallic element, B, improves considerably a long-term creep strength of heat resistant ferritic steels.1) This is because the presence of B in the steel could stabilize M 23C6 carbide to form M23(C, B)6, resulting in the lowering of its coalescence rate.2,3) However, the B addition increases remarkably even a short-term creep strength of the steels, which can not be explained by the stabilization of M 23C6 carbide alone. Azuma et al. have reported that the B addition changes spatial distribution of the MX carbonitrides in the steel.4)

In the high Cr ferritic steels containing Mo and W in a relatively high compositional level, it is known that a (Fe, Cr)2(W,Mo) type Laves phase precipitates in the steels5) together with M23C6 carbide and the MX carbonitride. Recently, we have observed the fine coherent precipitation of the Laves phase inside the martensite in an as-tempered state of the steels containing W more than 3.5%.6) On the other hand, it has been shown that a refractory element, Re, is effective in improving the creep strength of the steels,7) and the Re containing steel has been developed.8,9)

It has been found in late years that for high Cr heat resistant ferritic steels the long-term creep strength at 923 K (650°C) becomes weaker, as compared to the value extrapolated from the short-term creep tests.10) This phenomenon is considered to relate the behaviour of microstructure change of the martensite, the Laves phase, etc. during the creep test. Therefore, it is important to evaluate quantitatively such a microstructure change including the precipitation behaviour of the Laves phase in order to design advanced ferritic steels sustaining the high creep strength even after long duration. Generally, the precipitation behaviour of a phase is understood in terms of TTP (Time-temperature-precipitation) diagram which is determined on the basis of the solvus temperature of the phase. The purpose of this study is to determine the solvus temperature of the Laves phase in high Cr ferritic steels containing Mo, W and Re, all of which are the Laves phase-forming elements in the steels.

2. Experimental Procedure

2.1. Experimental Steels

Ten ferritic steels used in this study were 0.1C–10Cr–3Co based systems containing (1.9–4.6) mass% W and (0–1.7) mass% Re. Their chemical compositions are listed in Table 1. Hereafter, the composition is expressed in mass% unless otherwise noticed. Each steel was named by reflecting the compositions of W and Re, e.g., 1.9W0.6Re steel contains 1.9% W and 0.6% Re. The Md parameter is an average d-orbital energy level to be used for predicting the phase stability of the steel. The Md values are also given in the table. No δ ferrite was formed in any experi-
mental steels, because their \( \bar{M}d \) values were controlled to be less than a critical value, 0.86, for the \( \delta \) ferrite formation in the steel containing 3\% Co. 6)

The 50 kg ingot of each steel listed in Table 1 was made using a vacuum induction furnace and the ingot was forged into a plate of 35 mm in thickness. The plate was heat-treated at 1 373 K for 18 ks and at 993 K for 72 ks so as to control the grains in proper sizes. In this case, the grain size number was about 2–3. For normalized heat treatment, it was austenitized at 1 343 K for 18 ks followed by tempering at 843 K for 72 ks in the first step and at 953 K for 72 ks in the second step.

A series of experiments was carried out with the specimen cut from the grip part of the specimen creep-ruptured at 923 K (650°C). The creep rupture life was 17.658 Ms (4 905 h) for 1.9 W steel, 13.543 Ms (3 762 h) for 3.6 W steel, and 12.226 Ms (3 396 h) for 4.6 W steel. For the grip part, the rupture life corresponds to the aging time without applied any loads at 923 K (650°C). The precipitates such as the Laves phase in the steels are considered to be nearly equilibrium state because of such a long aging time.

### 2.2. DTA Measurement

Differential thermal analysis (DTA) was carried out to measure the solvus temperature of the Laves phase. The DTA was performed during heating of the grip part specimen, because the superheating seldom occurred in solid-state reaction, and hence the solvus temperature could be measured accurately. A column sample with about 3 mm in diameter, about 4 mm in length, and about 2 \( \times 10^{-4} \) kg in weight was cut from the grip part. Pure Pt specimen of about 2 \( \times 10^{-4} \) kg was used as a standard sample, and DTA experiment was carried out in a high purity Ar gas atmosphere at a constant heating rate of 8.3 \( \times 10^{-2} \) K/s (5 K/min).

### 2.3. TEM Observation and EDX Analysis

A sample cut from the grip part was heated up at a rate of 8.3 \( \times 10^{-2} \) K/s (5 K/min) in vacuum using a radiation furnace and kept at various temperatures, \( T \), for 5.4 ks, followed by quenching into water. The heating temperatures, \( T \), vary according to the content of the refractory elements in the steel, but each temperature range, in which the solvus temperature of the Laves phase was included, was about 150 K. The thermal history is shown in Fig. 1. Extraction replica was prepared from the quenched specimen and TEM observation was performed at 200 kV. Also, the precipitates extracted were analyzed using an EDX analyzer attached to the TEM instrument.

### 2.4. X-ray Diffraction

By means of the SPEED method 11) using a 10\% hydrochloric acid–methanol solution, extracted residues were taken from the samples quenched from various temperatures as mentioned above. X-ray diffraction experiment was carried out with the residues by using a conventional \( \theta - 2\theta \) method.

### 3. Experimental Results

#### 3.1. DTA Measurement

Typical DTA curves obtained during heating of the 1.9W and 3.6W steels were shown in Figs. 2(a) and 2(b), respectively. Two endothermic peaks were observed in the vicinity of 1 040 and 1 110 K. The peak at 1 040 K, which is of a typical \( \lambda \) type in shape, is attributable to the magnetic transformation (A2), whereas the peak at 1 110 K is probably interpreted as due to the A3 transformation, because an endothermic peak also appear in DTA curve by the A3 transformation of pure iron. A DTA endothermic peak due to the dissolution of the Laves phase was not observed in any experimental steels. This is probably because the peak is very small or the peak temperature overlaps the onset temperature of either A2 or A3 transformation. Thus DTA was not suitable for measuring the solvus temperature of the Laves phase in the present experimental steels.

#### 3.2. TEM Observation and EDX Analysis

As shown in Fig. 3, the microstructures were observed by TEM for the 4.6W steel before the heating treatment, (a), and quenched from the temperature of (b) 1 073, (c) 1 123 and (d) 1 163 K. The microstructure before the heating treatment consisted mainly of \( \text{M}_{23}\text{C}_{6} \) carbide, the fine Laves phase and the granular Laves phase 12) (Fig. 3(a)). As shown in Figs. 3(b) and 3(c), the morphology of the granular Laves phase changed into the particle with smooth surface by the heating treatment (see Fig. 1). Also, the size of the granular Laves phase decreased with increasing the heating temperature (Figs. 3(b) and 3(c)), because the vol-

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**Table 1.** Chemical compositions of experimental steels used in this study, mass%.

<table>
<thead>
<tr>
<th>Steel Name</th>
<th>C</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>W</th>
<th>Co</th>
<th>B</th>
<th>Re</th>
<th>N</th>
<th>Fe</th>
<th>( \bar{M}d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9W</td>
<td>0.12</td>
<td>---</td>
<td>10.1</td>
<td>0.4</td>
<td>0.2</td>
<td>0.08</td>
<td>1.9</td>
<td>3.0</td>
<td>0.006</td>
<td>---</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.852</td>
</tr>
<tr>
<td>3.6W</td>
<td>0.09</td>
<td>0.21</td>
<td>10.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.06</td>
<td>3.6</td>
<td>3.0</td>
<td>0.011</td>
<td>---</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.856</td>
</tr>
<tr>
<td>4.6W</td>
<td>0.11</td>
<td>0.20</td>
<td>10.0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.08</td>
<td>4.6</td>
<td>3.0</td>
<td>0.011</td>
<td>---</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.859</td>
</tr>
<tr>
<td>1.9W0.3Re</td>
<td>0.12</td>
<td>---</td>
<td>11.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.08</td>
<td>1.9</td>
<td>3.0</td>
<td>0.009</td>
<td>0.3</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.855</td>
</tr>
<tr>
<td>1.9W0.9Re</td>
<td>0.12</td>
<td>0.02</td>
<td>10.0</td>
<td>0.4</td>
<td>0.2</td>
<td>0.08</td>
<td>1.9</td>
<td>3.0</td>
<td>0.009</td>
<td>0.9</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.853</td>
</tr>
<tr>
<td>1.9W1.7Re</td>
<td>0.11</td>
<td>---</td>
<td>11.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.08</td>
<td>1.9</td>
<td>3.0</td>
<td>0.006</td>
<td>1.7</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.856</td>
</tr>
<tr>
<td>3W</td>
<td>0.11</td>
<td>0.21</td>
<td>10.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.08</td>
<td>3.0</td>
<td>3.1</td>
<td>0.010</td>
<td>---</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.854</td>
</tr>
<tr>
<td>3W1Re</td>
<td>0.10</td>
<td>0.25</td>
<td>10.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.06</td>
<td>3.0</td>
<td>3.0</td>
<td>0.010</td>
<td>1.0</td>
<td>0.02</td>
<td>Bal.</td>
<td>0.855</td>
</tr>
<tr>
<td>4W</td>
<td>0.09</td>
<td>0.20</td>
<td>10.1</td>
<td>---</td>
<td>0.2</td>
<td>0.06</td>
<td>4.0</td>
<td>3.0</td>
<td>0.007</td>
<td>---</td>
<td>0.03</td>
<td>Bal.</td>
<td>0.855</td>
</tr>
<tr>
<td>4W0.2Re</td>
<td>0.09</td>
<td>0.21</td>
<td>10.2</td>
<td>---</td>
<td>0.2</td>
<td>0.06</td>
<td>4.0</td>
<td>3.0</td>
<td>0.007</td>
<td>0.2</td>
<td>0.03</td>
<td>Bal.</td>
<td>0.855</td>
</tr>
</tbody>
</table>
Laves phase, because $M_{23}C_6$ carbide coexists with the Laves phase even at the heating temperatures.

EDX spectra corresponding to the precipitates of Fig. 3 are shown in Fig. 4. For example, the spectrum shown in Fig. 4(a) was taken from the precipitate arrowed in Figs. 3(b) and 3(c). Here, the Cu spectrum observed in Fig. 4 was attributable to the Cu mesh used for supporting the extraction replica. The results of semi-quantitative analysis excluding Cu are also shown in Fig. 4. From the result, the composition was estimated to be about $(\text{Fe,Cr})_2(W,\text{Mo})$, which was very similar to the composition of the Laves phase. Here, Mo spectrum was not obvious in Fig. 4 due to very small quantity of Mo in the experimental steels.

On the other hand, the precipitates observed in Fig. 3(d) were much larger and thinner than those observed in Figs. 3(b) and 3(c). The EDX spectrum obtained from a precipitate marked by an arrow in Fig. 3(d) is shown in Fig. 4(b). In the spectrum, the W peak was higher than the Fe peak, indicating that this is not the Laves phase shown in Fig. 4(a). This large precipitate is the Fe$_3$W$_3$C type M$_6$C carbide judging from the fact that the composition of the metal elements estimated from the spectrum shown in Fig. 4(b) was about $(\text{Fe,Cr})W$. This result was confirmed further by the X-ray diffraction experiment as explained later (Fig. 6(a)). Therefore, the solvus temperature of the Laves phase in the 4.6W steel was above 1163 K. In a similar way, the solvus temperatures of the other experimental steels were determined experimentally.
3.3. X-ray Diffraction

X-ray diffraction experiment was performed with the extracted residues prepared from the specimens quenched from the temperatures above and below the solvus temperature of the Laves phase. The results obtained from the 1.9W steel and the 4.6W steel are shown in Figs. 5 and 6, respectively. In the both figures, (a) and (b) correspond to the diffraction pattern of the specimen quenched from the temperature above and below the solvus temperature, respectively. In Fig. 5(a), there are diffraction peaks from the M23C6 carbide but no peaks from the Laves phase. In the case of 4.6W steel, the Laves phase, M23C6 and NbC are observed in Fig. 6(b), whereas M23C6, M6C and NbC carbides are observed in Fig. 6(a).

3.4. Solvus Temperature of the Laves Phase

The X-ray diffraction experiments as well as the TEM/EDX observations show that the Laves phase existed in the 4.6 W steel when quenched from 1 123 K, but did not exist when quenched from 1 163 K. This result clearly indicated that the solvus temperature of the Laves phase lay between 1 123 and 1 163 K in the 4.6 W steel. In the same way, the solvus temperature lay between 1 033 K and 1 003 K in the 1.9 W steel, and between 1 113 K and 1 143 K in the 3.6 W steel. The solvus temperatures are plotted against the Mo+W contents in the steel as shown in Fig. 7.

**Fig. 5.** X-ray diffraction patterns obtained from the extracted residue taken from the 1.9W steel aged at 923 K for 17.658 Ms, followed by heating up to the temperature of (a) 1 033 K and (b) 1 003 K.

**Fig. 6.** X-ray diffraction patterns obtained from the extracted residue taken from the 4.6W steel aged at 923 K for 12.226 Ms, followed by heating up to the temperature of (a) 1 163 K and (b) 1 123 K.

**Fig. 7.** Relationship between the solvus temperature of the Laves phase and Mo+W content in high Cr ferritic steels.
tently to these calculated values on lower Mo+W content.

In a similar way, the solvus temperature of the Laves phase was estimated for the Re containing steels. The results are listed in Table 2 together with those from the Re-free steels. The solvus temperatures are plotted against Mo/W/Re content in high Cr ferritic steels.

<table>
<thead>
<tr>
<th>Steel Name</th>
<th>Laves phase prone</th>
<th>Laves phase free</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9W</td>
<td>1000K</td>
<td>1023K</td>
</tr>
<tr>
<td>3.6W</td>
<td>1113K</td>
<td>1143K</td>
</tr>
<tr>
<td>4.6W</td>
<td>1123K</td>
<td>1163K</td>
</tr>
<tr>
<td>1.9W0.3Re</td>
<td>950K</td>
<td>1000K</td>
</tr>
<tr>
<td>1.9W0.9Re</td>
<td>950K</td>
<td>1000K</td>
</tr>
<tr>
<td>1.9W1.7Re</td>
<td>950K</td>
<td>1000K</td>
</tr>
<tr>
<td>3W</td>
<td>1100K</td>
<td>1150K</td>
</tr>
<tr>
<td>3W1Re</td>
<td>1100K</td>
<td>1200K</td>
</tr>
<tr>
<td>4W</td>
<td>1150K</td>
<td>1200K</td>
</tr>
<tr>
<td>4W0.2Re</td>
<td>1140K</td>
<td>1150K</td>
</tr>
</tbody>
</table>

In contrast to the case shown in Fig. 7, no correlation was found between the solvus temperature and the total amount of the refractory elements. Then, by choosing the Re content as another horizontal axis, the solvus temperature surface was made as in Fig. 9. This is a three-dimensional presentation constructed on the basis of the data listed in Table 2. Each steel number was located in its compositional position on the isothermal plane at 923 K (650°C) in the figure. In addition, the upper-limit temperature for the precipitation of the fine coherent Laves phase was drawn using a shadowed surface, which was deduced from the calculations following the system free energy concept. As is evident from Fig. 9, the solvus temperature of the Laves phase scarcely changes with Re content up to 1.7 mass% Re. Furthermore, several broken lines are drawn in the basal plane in Fig. 9, which represent iso-content lines with respect to the total amount of Mo+W+Re. This indicates that the soluble amount of the total refractory elements in the steel increases with increasing Re content in it. In other words, the increase of the total amount of the refractory elements in the solid solution of the steel is caused by the increase of Re content in the matrix.

4. Discussion

Recently, in order to increase high temperature strength, refractory elements such as Mo and W have been added into high Cr ferritic steels, resulting in the formation of the intermetallic compounds such as the Laves phase in them. It has been recognized that the intermetallic compounds precipitate granularly on the martensite-lath, -block and -packet boundaries of the steels. But the fine coherent Laves phase also precipitated in the martensite lath. This can be explained from the present results as follows. For example, recent heat resistant high Cr ferritic steels contain refractory metals of about 1.5 mass% in terms of the Mo equivalent. This quantity is equivalent approximately to 0.8–1.0 mol%. In this composition range, the creep temperature, 923 K (650°C), is close to the solvus temperature of the Laves phase, as is seen in Fig. 7. In such a case, large precipitates tend to form as is understood by the general nucleation theory. In commercially available steels, P92 and P122, the content of Mo equivalent is about 1.5 mass%, so that their solvus temperature is about 1 000 K. Therefore, when these steels are held at 923 K (650°C), the large Laves phase will precipitate incoherently in the matrix martensite phase. In fact, this is consistent with the result reported previously in these steels.

Figure 10 shows a TEM microstructure taken from an extracted replica of the 1.9W steel aged at 923 K (650°C) for 36 ks after austenitizing at 1 323 K, followed by quenching into water and then holding in liquid nitrogen for subzero treatment. In the figure, fine precipitates were identified as M23C6 carbide and large lump-shaped precipitates as the Laves phase. This morphology of the Laves phase was understood well with the knowledge of the solvus temperature shown in Fig. 7 and our previous study. Thus it is supposed that such a large Laves phase never strengthen high Cr ferritic steels. On the other hand, when the steel contains 1.4 mol% (4.6 mass%) W, fine precipitates of the Laves phase were distributed uniformly and coherently in the martensite lath, which works to strengthen the steel.

As shown in Fig. 9, Re scarcely changed the solvus temperature of the Laves phase with alloying in high Cr ferritic steels, indicating that the soluble amount of the total refractory elements in the steel increases with increasing Re content in it. This is consistent with the previous result obtained from ICP emission spectrochemical analysis that the
increase of the total amount of the refractory elements is caused by the increase of the dissolved Re in the matrix of high Cr ferritic steels. From these results, it can be said that Re is a unique element as contrasted with Mo and W. For example, the Re addition suppresses to decrease a long-term creep strength at 923 K. This is probably due to the fact that the total amount of the soluble refractory elements in the matrix increases with Re content in high Cr ferritic steels. This increase may cause not only the solid solution strengthening but also the stabilization of the intermetallics in them.

As to a long-term creep property of the high Cr ferritic steel, it is most important to stabilize the microstructure in the steel. The future work is needed to examine the coalescence kinetics of the precipitates following the quasi-binary phase diagram shown in Fig. 9.

5. Summary

The changes in the solvus temperature of the Laves phase with alloying elements, Mo, W and Re were investigated experimentally in high Cr ferritic steels. The obtained results are summarized as follows.

1. The solvus temperature of the Laves phase increased with increasing Mo+W content in the steels.
2. The solvus temperature did not change with the Re content up to 1.7 mass%.
3. Incoherent large Laves phase was suggested to be formed in both P92 and P122 when they were tempered at 923 K, because this temperature is very close to the solvus temperature (about 1000 K).

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Fig. 10. TEM microstructure of extraction replica taken from the 1.9W steel aged at 923 K for 360 ks after quenching from 1323 K into water followed by sub-zero treatment in liquid nitrogen.