Effect of Aging on the Tensile Properties of High-Purity Fe–50Cr Alloys

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The effects of strain rate and aging on the tensile properties of high-purity Fe–50 mass%Cr and 166 mass ppm carbon-doped Fe–50 mass%Cr alloys were investigated by tensile tests and microstructural observations. The serration occurring by dynamic strain aging on the stress-strain curve disappears at the strain rate below $4.2 \times 10^{-3} \text{ s}^{-1}$ and above $1.7 \times 10^{-2} \text{ s}^{-1}$ at 773 K in a high-purity Fe–50 mass%Cr alloy with the grain size of 29 µm. The deformation twinning in a high-purity Fe–50 mass%Cr alloy with the grain size of 108 µm at 773 K occurs at the same stress of 480 MPa, independent of strain rate. The pre-strained specimen of high-purity Fe–50 mass%Cr alloy shows static strain aging after aging at 573 K. The aging treatment at 773 K causes the precipitation of carbides and thereby the formation of deformation twins in tensile tests. In a carbon-doped high-purity Fe–50 mass%Cr alloy, the heat treatment for precipitating carbides on grain-boundaries restrains the formation of deformation twins at 773 K.

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Keywords: aging, Fe–50Cr alloy, high-purity alloy, tensile property, carbide

1. Introduction

In Fe–Cr alloys, an increase in chromium content improves corrosion resistance and strength at elevated temperatures, while the ductility of conventional-purity Fe–Cr alloys decreases with increasing chromium content. Recently many kinds of properties of high-purity Fe–50 mass%Cr alloys have been reported, since Abiko and co-workers developed ductile Fe–50 mass%Cr alloys by purification.1 We reported that high-purity Fe–50 mass%Cr alloys show specific deformation properties: deformation twinning occurs continuously at 773 K up to 10% strain during the plastic deformation in tensile tests.2 Furthermore we reported that, by decreasing grain size, the deformation mode at 773 K is changed from the continual formation of deformation twins to Portevin-Le Chatelier (P-L) mechanism by dislocation slip.3 P-L mechanism is caused by the interaction between mobile dislocations and interstitial atoms, and thereby serration is observed in the stress-strain curve, which is called dynamic strain aging.4 Yoshinaga and Morozumi reported that the friction stress of mobile dislocations caused by dragging solute atmosphere increases with decreasing the velocity of dislocation.5 However, in a Fe-high Cr alloy there is no report about the relationship between strain rate relating to dislocation velocity and stress-strain curves visually representing plastic deformation. On the other hand, there are also few reports that deformation twinning occurs at elevated temperature. Anglada et al. reported that in Fe–28Cr–Mo–Ni alloys deformation twinning appearing at elevated temperatures is related to dynamic strain aging caused by substitutional atoms,6 and that the twinning disappears at room temperature as the strain rate is lowered. Magnin and Moret have reported that in Fe–25Cr–Mo–Ni–Cu alloys deformation twinning at elevated temperatures is caused by an intrinsic effect of nickel and by the spinodal decomposition.7 However there is no report about the relationship between the strain rate and the formation of deformation twins at elevated temperatures. Furthermore there is no report about the effect of the aging treatment controlling the state of interstitial atoms on the serration of Fe-high Cr alloys at elevated temperature.

In this work, thus we investigate the effects of strain rate and aging on the tensile properties of high-purity Fe–50 mass%Cr alloys at elevated temperatures, by tensile tests and microstructural observations, using two kinds of specimens with two different grain sizes.

2. Experimental Procedure

An Fe–50 mass%Cr alloy (Fe–50Cr) ingot and an Fe–50 mass%Cr–166 mass ppm C alloy (Fe–50Cr–166C) ingot were made from high-purity electrolytic iron (99.995%), high-purity chromium (99.98%) and high-purity white cast iron by induction melting in a copper-cold-crucible under a high-purity Ar atmosphere. These ingots were hot-forged and hot-rolled to rods 12 mm in diameter after heating at 1373 K under a high-purity Ar atmosphere. These rods were machined to 10 mm in diameter to remove the scale. A high-purity Fe–50Cr alloy was prepared from the rod by floating-zone melting under a dry hydrogen atmosphere to reduce non-metallic impurities (C, N, O and S). The work coil was passed up and down twice (4 zone-leveling passes) at a speed of 0.067 mm/s. The compositional details are given in Table 1.

These rods of a high-purity alloy and a carbon-doped alloy were rolled to sheets 1 mm in thickness at 573 K. Tensile test specimens with the gauges 20 mm in length and 3 mm in width were machined from these sheets. We prepared two kinds of specimens with two different grain sizes, because deformation mode relates to the grain size in a high-purity Fe–50 mass%Cr alloy.3 Thus every specimen was annealed in a vacuum of better than $2 \times 10^{-2}$ Pa at 1123 or 1323 K for 1.8 ks (0.5 h) for recrystallization and growth, and then quenched into oil cooled to 273 K.

A high-purity and a carbon-doped Fe–50Cr alloys heated at 1123 K for recrystallization were aged at 573 K for 36 to 360 ks (10 to 100 h) or at 773 K for 1.8 to 36 ks (0.5 to 10 h), to study the effect of the aging treatment. Some specimens heated at 1123 K were deformed up to the end of Lüders de-
formation and then aged at 573 K for 36 ks to study the static strain aging in Fe–Cr alloys. Some specimens of Fe–50Cr (–166C) alloys heated at 1323 K for recrystallization were aged at 1123 K for 1.8 ks (0.5 h) to study the aging treatment on the formation of deformation twin.

Tensile tests for investigating the effect of strain rate were performed at an initial strain rate between $4.2 \times 10^{-5}$ and $1.7 \times 10^{-2}$ s$^{-1}$ at 773 K in a vacuum of better than $6 \times 10^{-4}$ Pa. Tensile tests for investigating the effect of the aging treatment at 573 and 773 K were carried out at 293 K at an initial strain rate of $4.2 \times 10^{-4}$ s$^{-1}$. Tensile tests for investigating the effect of the aging treatment at 1123 K were carried out at 773 K at an initial strain rate of $4.2 \times 10^{-2}$ s$^{-1}$.

Optical microstructural observation was performed on such specimens. Thin foils were prepared as follows: electrolytically polished on 45 V in 90% acetic acid and 10% perchloric acid at 290 K. Elemental composition of precipitates was measured by energy dispersive X-ray spectrometry (EDX) attached to HF3000.

Table 1 Chemical compositions of high-purity Fe–50Cr(–166C) alloys.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>Al</th>
<th>Cu</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>Si</th>
<th>Ti</th>
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<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
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<tr>
<td>mass%</td>
<td></td>
<td>Bal.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe–50Cr</td>
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<td>Bal.</td>
<td>3.2</td>
<td>2.5</td>
<td>1.0</td>
<td>8.6</td>
<td>3.2</td>
<td>19</td>
<td>2.1</td>
<td>0.40</td>
<td>0.31</td>
<td>8.6</td>
<td>7.5</td>
<td>2.5</td>
<td>5.6</td>
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<tr>
<td>Fe–50Cr–166C</td>
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<td>Bal.</td>
<td>2.8</td>
<td>3.1</td>
<td>2.4</td>
<td>—</td>
<td>7.7</td>
<td>7</td>
<td>15</td>
<td>2.5</td>
<td>0.86</td>
<td>166</td>
<td>7.0</td>
<td>50.1</td>
<td>2.5</td>
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</table>

Table 2 Grain size of high-purity Fe–50Cr(–166C) alloys after heat treatment.

<table>
<thead>
<tr>
<th></th>
<th>Annoaling temperature $T/K$</th>
<th>Annoaling time $t/ks$</th>
<th>Grain diameter $d/\mu$</th>
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</thead>
<tbody>
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<td>Fe–50Cr</td>
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<td>1.8</td>
<td>29</td>
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<tr>
<td></td>
<td>1323</td>
<td>1.8</td>
<td>108</td>
</tr>
<tr>
<td>Fe–50Cr–166C</td>
<td>1123</td>
<td>1.8</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1323</td>
<td>1.8</td>
<td>114</td>
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</tbody>
</table>

3. Experimental Results

3.1 Effect of strain rate on the tensile properties of a high-purity Fe–50Cr alloy

Tensile tests were carried out on two kinds of specimens with different grain sizes as shown in Table 2. Figure 1 shows the stress-strain curves of Fe–50Cr with the grain size of 29 μm at 773 K. The serration due to P-L mechanism during Lüders deformation were seen in the curves at the strain rates of $4.2 \times 10^{-4}$ and $4.2 \times 10^{-3}$ s$^{-1}$. The serration due to P-L mechanism during strain hardening were seen in the curves at the strain rates of $4.2 \times 10^{-3}$ and $1.7 \times 10^{-2}$ s$^{-1}$. The yield stresses in the curves at strain rates of $4.2 \times 10^{-5}$, $4.2 \times 10^{-4}$, $4.2 \times 10^{-3}$ and $1.7 \times 10^{-2}$ s$^{-1}$ were 557, 535, 494 and 456 MPa, respectively; the ultimate tensile strength 654, 627, 578 and 578 MPa, respectively and the elongation 13.9, 15.7, 16.8 and 17.1%, respectively.

Figure 2 shows the stress-strain curves of Fe–50Cr with the grain size of 108 μm at 773 K. The stress drops with audible sound caused by twinning were seen in all curves. The amplitude of stress drops increased with decreasing strain rate. The stress after the first stress drop in the specimens due to deformation twinning was defined as the lower yield stress. The yield stresses in the curves at strain rates of $4.2 \times 10^{-5}$, $4.2 \times 10^{-4}$, $4.2 \times 10^{-3}$ and $1.7 \times 10^{-2}$ s$^{-1}$ were 454, 452, 459 and 456 MPa, respectively; the ultimate tensile strength 623, 582, 556 and 541 MPa, respectively and the elongation 20.4, 17.0, 13.3 and 13.8%, respectively. The deformation twinning occurred at the similar stress of 480 MPa at 773 K, independently of strain rate.
3.2 Effect of aging at 573 K on the tensile properties of high-purity Fe–50Cr(–166C) alloys

Fe–50Cr(–166C) with small grains were aged at 573 K. Figure 3 shows the TEM micrographs after the aging treatment at 573 K for 360 ks. This aging treatment formed a few small precipitates in matrix of Fe–50Cr, which had not been observed after recrystallization treatment. On the other hand, carbides were observed in Fe–50Cr–166C, which had carbides in the same state after recrystallization treatment. Figure 4 shows the stress-strain curves of Fe–50Cr and Fe–50Cr–166C aged at 573 K. The aging treatment at 573 K had little influence on the stress-strain curves, irrespective of carbon doping.

We have carried out the aging treatment for pre-strained specimens to examine whether the static strain aging occurs or not, as shown in Fig. 5. At first, Fe–50Cr was strained up to the end of Lüders deformation, the plastic strain of 5.3%, and then aged at 573 K for 36 ks. The pre-strained and aged specimen was strained again. The pre-strained and aged specimen yielded again at a higher stress than the yield point of the specimen after recrystallization treatment. The specimen strained up to the end of Lüders deformation was further heated at 573 K for 36 ks and then strained once more up to fracture. This result means that static strain aging occurs in Fe–50Cr containing only 16 mass ppm interstitials (C + N). The total elongation was 20.4%. The lower yield stresses at the first, second and last yielding were 594, 657 and 757 MPa, respectively. Figure 6 shows TEM micrographs of a pre-strained and aged specimen of Fe–50Cr–166C. A grain-boundary and dislocations were observed in bright field images. Carbides were observed on the grain-boundary and dislocations in a dark field image. This result means that the aging treatment at 573 K caused the precipitation of carbides on grain-boundary and dislocations.

3.3 Effect of aging at 773 K on the tensile properties of high-purity Fe–50Cr(–166C) alloys

Figure 7 shows TEM micrographs after the aging treatment at 773 K. The aging treatment formed small precipitates on grain-boundary of Fe–50Cr, which had no obvious precipitate after recrystallization treatment. On the other hand, carbides were observed in Fe–50Cr–166C, which had carbides in the same state after recrystallization treatment. Figure 8 shows the stress-strain curves of Fe–50Cr and Fe–50Cr–166C aged at 773 K. The yield stress of Fe–50Cr aged for 0, 1.8, 3.6 and 36 ks were 594, 710, 746 and 785 MPa, respectively, and the elongation 25.8, 22.3, 20.9 and 13.7%, respectively. The yield stress of Fe–50Cr–166C aged for 0 and 3.6 ks were 633 and 744 MPa, respectively, and the elongation 29.7 and 24.4%, respectively. Aging treatments at 773 K caused an increase in yield stress and a decrease in elongation. Aging treatment at 773 K for 3.6 ks and over caused stress drops with audible sound in Fe–50Cr. Owing to the aging treatment for
36 ks, yield point disappeared and the strain hardening became remarkably intensive. Figure 9 shows optical micrographs after tensile tests. Deformation twins were observed in Fe–50Cr aged for 3.6 ks and over where the stress-strain curves showed stress drops with audible sounds. On the other hand, no twin was observed in Fe–50Cr–166C aged at 773 K for 3.6 ks. Thus the carbon doping restrains the formation of deformation twin.

3.4 Effect of aging at 1123 K on the tensile properties of Fe–50Cr(–166C) alloys

We have carried out the aging treatment at 1123 K in Fe–50Cr and Fe–50Cr–166C, which were heated at 1323 K for recrystallization treatment, and then performed tensile tests at 773 K. Figure 10 shows the stress-strain curves of Fe–50Cr as recrystallized, Fe–50Cr–166C as recrystallized and Fe–50Cr–166C aged at 1123 K for 1.8 ks. The stress-strain curves of the alloys as recrystallized had stress drops with audible sound due to deformation twinning. The frequency of stress drops of Fe–50Cr–166C was fewer than that of Fe–50Cr. The serration without audible sound due to P-L mechanism appeared during strain hardening in the curves of Fe–50Cr–166C aged at 1123 K. The yield stresses of Fe–50Cr as recrystallized, Fe–50Cr–166C as recrystallized and Fe–50Cr–166C aged at 1123 K were 452, 511 and 491 MPa, respectively, and the elongation 17.0, 19.3 and 15.1%, respectively.

Figure 11 shows TEM microstructure in the non-deformed part of the specimens tensile tested at 773 K (see Fig. 10). Figures 11(a), (b) and (c) show the microstructures tensile tested at 773 K on Fe–50Cr as recrystallized at 1323 K, Fe–50Cr–166C as recrystallized at 1323 K and Fe–50Cr–166C recrystallized at 1323 K and then aged at 1123 K, respectively. Any precipitate was not observed in Fe–50Cr as shown in Fig. 11(a). On the other hand many precipitates were observed on a grain-boundary and in matrix of Fe–50Cr–166C as shown in Fig. 11(b), although the specimens had no precipitate after recrystallization treatment. Denuded zone of precipitates was observed in the vicinity of the grain-boundary and the width of the zone was about 15 µm. The precipitates on the grain-boundary observed in Fe–50Cr–166C were identified as M23C6 type of carbide containing 80 mass%Cr by electron diffraction patterns and EDX analysis as shown in Fig. 12.

The precipitates in the matrix observed in Fe–50Cr–166C were very small and disc-like. It seemed to lie on (100) plane. They were not identified because of the small size, but it may be carbides, judging from the shape. The carbide lie on the same plane as carbides in Fe-0.013%C alloy. In Fe–50Cr–166C aged at 1123 K, large precipitates were observed on grain-boundary as shown in Fig. 11(c). Figure 13 shows precipitates in the matrix of Fe–50Cr–166C aged at 1123 K. The precipitates in the matrix were identified as M23C6 type carbides containing about 80%Cr. Microstructural observation revealed that the heat added during tensile tests at 773 K caused precipitation of carbides in the matrix of Fe–50Cr–166C as recrystallized. On the other hand the heating during
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4. Discussion

4.1 Effect of strain rate on the tensile properties of high-purity Fe–50Cr alloys

The serration due to P-L mechanism during Lüders deformation was seen in the curves at the strain rates of $4.2 \times 10^{-4}$ and $4.2 \times 10^{-3} \text{ s}^{-1}$. The serration due to P-L mechanism during strain hardening was seen in the curves at the strain rates of $4.2 \times 10^{-3}$ and $1.7 \times 10^{-2} \text{ s}^{-1}$. This difference in the strain rates for the serration between Lüders deformation and strain hardening can be explained as follows. This tendency should be caused by the difference in mobile dislocation densities. In case of Lüders deformation, plastic deformation is concentrated in the narrow region called as the Lüders front. A sum of mobile dislocations during Lüders deformation is thus fewer than that during strain hardening. Consequently the velocity of mobile dislocations during Lüders deformation becomes higher than that during strain hardening, to balance the strain rate given by tensile testing machine. Considering that P-L mechanism works in the range of some dislocation velocity, the serration during Lüders deformation occurs at lower strain rate than that during strain hardening.

The result of tensile tests showed that the yield stress of Fe–50Cr with the grain size of 29 µm decreased with increasing strain rate. Yoshinaga and Morozumi reported that the friction stress of mobile dislocations caused by dragging solute atmosphere increases with decreasing the velocity of dislocation. The tendency of experimental results is consistent with their theory. The tensile tests of Fe–50Cr with the grain size of 108 µm showed that the deformation twins occurred at the same stress of 480 MPa independently of strain rate at 773 K. Marcinkowski and Lipsitt have reported that the stress for deformation twinning depends on the grain size, irrespective of strain rate, under room temperature. The result in this study is consistent with their results, though there is no report about the stress for deformation twinning at elevated temperatures.

4.2 Effect of carbides on the tensile properties of high-purity Fe–50Cr alloys

The addition of carbon to Fe–50Cr decreased the frequency of the stress drop caused by twinning as seen from tensile tests at 773 K did not form new precipitates in matrix of Fe–50Cr–166C aged at 1123 K and seemed only to grow the carbides formed by aging treatment at 1123 K.
tests of the alloys heated at 1323 K, and the aging treatment at 1123 K restrains the formation of deformation twins. Microstructural observation revealed that M\(_{23}C_6\) type of carbides precipitated in matrix during tensile tests at 773 K and that the aging treatment at 1123 K formed large carbides on grain-boundary. Arai and Takeda proposed a formulation of carbon’s solubility limit in Fe–Cr alloys, on the basis of the
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Fig. 12 $\text{M}_2\text{C}_6$ type of carbide on the grain-boundary in the matrix of Fe–50Cr–166C.

Fig. 13 $\text{M}_2\text{C}_6$ type of carbide in the matrix of Fe–50Cr–166C.

thermodynamic data from the experimental evaluations, using steels containing various contents of chromium. Ohta et al. have reported that Arai’s formulation is suitable to high-purity Fe–50Cr alloys. According to Arai’s formulation, solubility limits of carbon in Fe–50Cr alloys at 773, 1123 and 1323 K are < 1, 45 and 204 mass ppm, respectively. For the heat treatments at 773, 1123 and 1323 K, the concentrations of carbon precipitating as carbides in Fe–50Cr–166C are calculated as 166, 121 and 0 mass ppm, respectively. During tensile tests at 773 K, supersaturated carbon in Fe–50Cr, Fe–50Cr–166C and Fe–50Cr–166C aged at 1123 K are 9, 166 and 45 mass ppm, respectively. The amount of precipitation on grain-boundaries during tensile tests at 773 K will show the following tendency, Fe–50Cr < Fe–50Cr–166C < Fe–50Cr–166C aged at 1123 K, because the amount of precipitates on grain-boundaries in Fe–50Cr–166C is fewer than that in Fe–50Cr–166C aged at 1123 K by the degree of precipitates in matrix. The formation of deformation twins in the present work can be related not to the content of solute carbon but to carbides on grain boundary. Kako et al. have reported that one cause for the formation of deformation twins may be the shortage of dislocation sources. Inclusions on grain boundaries act as dislocation sources. Thus the restraint of twinning in Fe–50Cr–166C aged at 1123 K might be caused by increases in dislocation sources.

4.3 Effect of aging at 573 and 773 K on the tensile properties of high-purity Fe–50Cr(–166C) alloys

Tensile test and microstructural observation of Fe–50Cr–166C aged at 573 K showed that the aging treatment at 573 K caused the precipitation of carbides on grain-boundaries and dislocations, and then caused the static strain aging in Fe–50Cr–166C. This result means that the aging treatment at temperatures above 573 K caused the precipitation of carbides and dislocations firmly pinned by solute atmosphere. On the other hand, the restraint of deformation twinning in Fe–50Cr–166C aged at 773 K for 3.6 ks is similar to the inhibitory effect of carbides on grain-boundary in Fe–50Cr–166C aged at 1123 K, as mentioned in Section 4.2. However the aging treatment at 773 K for Fe–50Cr caused an increase in yield stress and promoted the formation of deformation twins by the aging treatment for 3.6 ks and over. Effects of aging at 573 and 773 K are the followings. Firstly the aging treatment at 773 K causes an increase in yield stress with increasing aging time up to 3.6 ks. Secondly the aging treatment at 573 K promotes the formation of deformation twins at the aging time for 3.6 ks. Thirdly the aging treatment at 573 K for 36 ks changes the deformation mode from Lüders deformation with yield point to the deformation without yield point and let the strain hardening rate remarkably intensive. There are two reasons for the promotion of deformation twins by the aging treatment at 773 K. One is that spinodal decomposition promotes the formation of deformation twins. Another is that the precipitation or solute atmosphere in matrix promotes the formation of deformation twins. Cortie and Pollak reported that in Fe–38Cr alloy dislocation locking by carbon and nitrogen clusters appears faster than spinodal decomposition and causes the rapid deterioration in toughness. In this study the formation of deformation twin occurs in too early time of 3.6 ks for spinodal decomposition. More study is required to confirm which of spinodal decomposition, solute atmosphere and the others promotes the formation of deformation twin.

5. Conclusions

The effect of strain rate and aging treatment on the tensile properties of high-purity Fe–50Cr(–166C) alloys was investigated by tensile tests and microstructural observations.

(1) The serration on the stress-strain curves in a high-purity Fe–50Cr alloy with the grain size of 29 µm at 773 K disappears in the strain rate under $4.2 \times 10^{-5} \text{ s}^{-1}$ and over $1.7 \times 10^{-2} \text{ s}^{-1}$.

(2) The deformation twinning in a high-purity Fe–50Cr alloy with the grain size of 108 µm at 773 K occurs at the
same stress of 480 MPa, independently of strain rate.

(3) The pre-strained specimen of high-purity Fe–50Cr alloys shows the static strain aging by the aging treatment at 573 K.

(4) The aging treatment at 773 K causes the precipitation of carbides and promotes the formation of deformation twins.

(5) In a high-purity Fe–50Cr–166C alloy, the heat treatment for precipitating carbides on grain-boundaries restrains the formation of deformation twin at 773 K.

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