Electron Microscopic Study of Deformation Behavior of Iron-Chromium Alloy Aged at 470°C*

By Genjiro Mima** and Masaharu Yamaguchi**

The deformation behavior of an aged iron-chromium alloy at 470°C has been investigated by means of electrical resistivity measurements and electron microscopic observations, in order to make clear the embrittlement of the iron-chromium alloy aged at 475°C. The electrical resistivity of the aged iron-40wt% chromium alloy which was measured at the liquid nitrogen temperature increased with the aging time. The deformation substructure of the slightly deformed brittle specimens remarkably differs from the slightly deformed ductile specimens. In the former deformation twins were directly observed by transmission electron microscopy, and dislocations were found to be almost straight. In the latter the dislocations showed a rather irregular form and irregular tangles were observed sporadically.

The specimens aged for a long time at 470°C were mostly, fractured by cleavages with a few isolated regions of intergranular fractures, and many traces of twins were observed on the fracture surface. The deformation twins observed in the aged and slightly deformed specimens seem to be closely related to the embrittlement of the aged iron-chromium alloy.

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I. Introduction

The embrittlement occurs after heating between 400° and 550°C in the high chromium steel. The phenomenon has been termed the 475°C embrittlement because of the most remarkable temperature effect.

During the past decade many investigators have probed into this phenomenon, and there have been developed two contradictory views of it. The first theory ascribes the 475°C embrittlement phenomenon to the formation of superlattices⁽¹⁾⁽²⁾⁽³⁾. However, all at-

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** Department of Metallurgy, Faculty of Engineering, Osaka University, Osaka, Japan.

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tempts to observe superlattices in iron-chromium alloys by neutron diffraction techniques have been unsuccessful⁽⁴⁾⁽⁵⁾. The second most popular theory is that the embrittlement phenomenon is due to the formation of coherent precipitates due to the occurrence of a miscibility gap in the iron-chromium system below about 550°C. By making use of extraction replica and electron diffraction methods, Fisher, Dulis, and Carroll⁽⁶⁾ have shown the existence of the coherent precipitates of chromium-rich body centered cubic phase.

Recently Marcinkowski, Fisher and Szirmai⁽⁷⁾ have investigated the deformation behavior of this alloy by observation of deformation markings around hardness impressions and made clear that twinning becomes more important as a mode of deformation than slip deformation as the aging time increases.

Three different models have been proposed for the dislocation mechanism of twinning in body centered cubic metals (i) by Cottrell and Bilby⁽⁸⁾, (ii) by Mueller and Parker⁽⁹⁾ and (iii) by Sleswyk⁽¹⁰⁾.

In any of these models the critical stage of twinning seems to be the process of dissociation of slip dislocation in the {112} plane into the twinning dislocation and this dissociation depends upon the stacking fault energy on the {112} plane.

For the iron-chromium alloy, twinning cannot be observed in the unaged one⁽⁷⁾. Therefore it may be predicted that the occurrence of twinning in the aged alloy is closely related to the deformation substructure which may produce a stress concentration sufficient to nucleate twins rather than the effect of chromium on the stacking fault energy. Direct observation of deformation twins in the aged alloy and the increase of electrical resistivity at the liquid nitrogen temperature have been briefly reported by the authors⁽¹¹⁾.

The present research was aimed to investigate the structures and deformation behaviors of aged and unaged iron-chromium alloys by means of direct observations of deformation substructures of the unaged and aged alloys and measurements of electrical resistivity during isothermal aging.

II. Experimental Procedure

The material used throughout this investigation was a vacuum-melted iron-chromium alloy with the following chemical composition: Cr 40.19, C 0.042, N 0.011 Al 0.15, Si 0.31, Mn 0.02, P 0.016, S 0.009 wt%.

The alloy was cast in the iron mold. The ingot was annealed at 1350°C, hot forged, hot rolled and finally cold rolled to the strip of 0.15 mm in thickness, from which specimens for resistivity measurements and elec-

tron transmission microscopic observations were prepared. All the specimens were annealed for 15 hr at 950°C in the evacuated quartz tube and quenched in ice brine and then aged at 470°C in the evacuated quartz tube for various periods of time.

As a ductility criterion a simple bending test (cantilever type) was carried out at room temperature and after the bending test, the side-views of specimens were observed by optical microscopy. The electrical resistivity was measured at the liquid nitrogen temperature. To prepare the thin foils for transmission electron microscopic observation the specimens thus heat treated were thinned by electropolishing.

The Electrolyte used was a perchloric acid-glacial acetic acid (1 : 8) solution. As the electron microscope used was the Hitachi HU-10, operated at 75 kV.

III. Experimental Results

The effect of aging at 470°C on the electrical resistivity at low temperature of the 40 wt% chromium alloy was determined by measurements of the electrical resistivity at the liquid nitrogen temperature.

When measured at the aging temperature the resistivity decreases continuously with the lapse of the aging time. It has been known that the decrease in resistivity at elevated temperature is greater than that at low temperature, from which it can be supposed that there is a rather large increase in resistivity at lower temperature⁽¹²⁾.

As reported previously, a large increase of resistivity has been found at the liquid nitrogen temperature⁽¹¹⁾.

As shown in Fig. 1, there is a slight initial increase

Fig. 1 Increase of resistivity versus aging time at 470°C ρ_0 corresponds to resistivity of the as-quenched specimen.

which is considered not to be associated with the embrittlement in view of the results of simple bending tests, following which the resistivity begins to increase markedly as observed in the 30 wt% chromium alloy.

Observations of side views of specimens after simple bending were carried out as a criterion of the ductility. The results are shown in Photo.1: (a) corresponds to the end of the first stage of the resistivity vs. aging time curve and the ductility of this specimen is not different

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from the as-quenched specimens ; (b) corresponds to the beginning of the second stage of the resistivity curve ; (c) shows that the specimens which were aged for 20 days fractured without any noticeable deformation. Several kinds of precipitates were observed during aging at

Photo. 1 Side views of specimens after the bending test at room temperature.

- (a) Aged for 3.7×10^2 min at 470°C . ($\times 110$)
 (b) Aged for 3.3×10^3 min at 470°C . ($\times 110$)
 (c) Aged for 3.0×10^4 min at 470°C . ($\times 170$)

470°C . Photo. 2 shows a structure of the as-quenched specimen. In Photo. 3 are shown two kinds of precipitates, the larger ones and the smaller ones, which were most frequently observed. In the first stage of the resistivity curve only the larger precipitates were observed and the precipitates seem to be ordinary carbides observed in chromium steel. The smaller precipitates were observed in the second stage of the resistivity curve and their habit-plane may be $\{100\}_\alpha$ in view of the results of the trace analysis. Despite of many attempts, no identifiable electron diffraction patterns have been obtained from the small precipitates in the foils.

A typical structure of the specimens aged for 20 days is shown in Photo. 4, in which numbers of the small precipitates are observed. Chromium rich particles due to the occurrence of the miscibility gap were not observed in the specimens which were aged for 20 days, presumably because the chromium rich precipitates are too small to be observed by transmission electron microscopy. However, the marked increase of electrical resistivity may suggest the precipitation of very fine chromium-rich

Photo. 2 Structure of the as-quenched iron-40 wt% chromium alloy.

Photo. 3 Structure of the iron-40 wt% chromium alloy aged for 3.0×10^4 min at 470°C .

Photo. 4 Structure of the iron-40% chromium alloy aged for 3.0×10^4 min at 470°C .

precipitates in the brittle specimen.

In an attempt to study the interaction between dislocations and precipitates and the difference in deformation substructure between as-quenched and aged specimens, both specimens were slightly deformed and investigated

were not observed.

The transmission micrographs in Photo.8 (a) and Photo. 9 indicate a typical configuration of dislocations in the specimens which were aged for 20 days and lightly compressed at room temperature. Most of the disloca-

(a)

(b)

Photo. 5 (a) (b) Dislocation structure of the as-quenched iron-40wt% chromium alloy after 6.6% cold rolling.

by transmission electron microscopy. The transmission micrograph in Photo. 5 shows a structure of the quenched and 6.6% cold rolled specimens in which dislocations exist in irregular tangles and form a cell structure. Deformation twins were not observed in these specimens (?).

Deformation of the aged specimen was undertaken by compression at room temperature (the reduction in thickness was very small). Deformation substructures of the specimen aged for a period of 6 hr which corresponds to the first stage of the resistivity curve are shown in Photo. 6 and Photo. 7. In the photographs are shown a rather irregular form of dislocations and a sporadic distribution of irregular tangles. Deformation twins

Photo. 6 Dislocation structure of the iron-40wt% chromium alloy aged for 3.7×10^2 min at 470°C and deformed slightly.

Photo. 7 Dislocation structure of the iron-40wt% chromium alloy aged for 3.7×10^2 min at 470°C and deformed slightly.

tions are almost straight and exist in a regular form. Photo. 8 (b) shows the selected area diffraction pattern taken from the area in which parallel dislocations are observed in Photo. 8 (a). In Photo. 8 (a), assuming that the straight dislocations are parallel to the foil plane which is (001) and using a method of trace analysis⁽¹³⁾, it is turned out that the dislocations, which lie in the direction nearly perpendicular to the $\langle 111 \rangle$ direction, are nearly edges probably moving in the (112) planes with an inclination of 35° to the foil plane. Although the dislocations observed in Photo. 8 (a) are known to be

(13) G. Thomas : *Transmission Electron Microscopy of Metals*, p. 269, John Wiley & Sons Inc. 1962.

Photo. 8 (a) Dislocation structure of the iron-40wt% chromium alloy aged for 3.0×10^4 min at 470°C and deformed slightly.

Photo. 10 (a) Twinning observed in the iron-40wt% chromium alloy aged for 3.0×10^4 min at 470°C and deformed slightly.

Photo. 8 (b) Selected area diffraction pattern taken from the area where the parallel dislocations are observed in Photo. 8 (a).

Photo. 10 (b) Selected area diffraction pattern taken from the twinned area in Photo. 10 (a), twin reflection at t .

Photo. 9 Dislocation structure of the iron-40wt% chromium alloy aged for 3.0×10^4 min at 470°C and deformed slightly.

Photo. 11 Twinning observed in the iron-40wt% chromium alloy aged for 3.0×10^4 min at 470° and deformed slightly.

of the edge type, it is not certain whether the dislocations in Photo. 9 are of the same type. Most of the dislocations observed in these specimens seem to be of the screw type rather than the edge type as well known in iron alloys. The micrographs in Photo. 10 (a), Photo. 11 and Photo. 12 show deformation twins which were

Photo. 12 Twinning observed in the iron-40wt% chromium alloy aged for 3.0×10^4 min at 470°C and deformed slightly.

Photo. 13 Fractograph showing cleavage in the iron-30 wt% chromium alloy aged for 3.0×10^4 min at 470°C, with twin traces. ($\times 250$)

frequently observed in these specimens. Photo. 10 (b) shows the selected area diffraction pattern taken from the twinned area in Photo. 10 (a). A remarkably high stress concentration seems to arise from the intersection of twins as observed in Photo. 12. In effect it has been reported that cleavage cracks are observed at such an intersection of twins in silicon iron⁽¹⁴⁾.

The specimens aged for a long time are usually fractured by cleavages with a few isolated regions of intergranular fractures and many twin traces were observed on the fracture surface. The fractograph in Photo. 13 shows such twin traces.

IV. Discussion of Experimental Results

It has been reported that the changes in electrical resistivity⁽¹⁵⁾ and hardness⁽¹⁶⁾ take place before their changes by which the embrittlement itself is charac-

terized.

In the measurement of electrical resistivity at room temperature the increase of resistivity has been observed before its decrease which is associated with the embrittlement. On the other hand, in the measurement of hardness a peak which may be associated with the precipitation of chromium carbides has been observed prior to the increase of hardness corresponding to the embrittlement.

In the present investigation the resistivity at the liquid nitrogen temperature increases in two stages with the aging time. It seems to be very unlikely that the slight initial increase of resistivity is due to the large precipitates observed in the first stage. This slight increase of resistivity cannot be explained clearly at present.

The marked increase of resistivity in the second stage which is associated with the embrittlement seems to be attributable to the chromium-rich precipitates, which would be too small to be observed, rather than to the small precipitates observed in the second stage, in view of the size and interdistance of the small precipitates. The precipitation of the chromium-rich precipitates which are presumed to take place from the remarkable increase of resistivity and the small precipitates seem to have influence on the deformation behavior and hardening of the aged alloy.

In the as-quenched specimens the dislocations showed irregular tangles, forming deformation cells. This implies that since the dislocations can easily cause cross slip and are rearranged form to a cell structure, they prevent the occurrence of local stress concentrations. For this reason, twinning was not observed in these specimens.

In the specimens which were aged for a period of 6 hr that corresponds to the first stage of the resistivity curve and then slightly compressed, dislocation tangles and any structure liable to cause the local stress concentrations were not observed. When these specimens are deformed more than 5%, a cell structure seems to be formed without twinings as observed in the as-quenched specimens.

In the specimens aged for 20 days twinings were frequently observed by a slight degree of deformation. In these specimens dislocation tangles were scarcely observed and most of the dislocations lay in one crystallographic plane or narrow band in a certain crystallographic direction. Such a dislocation configuration shows that a small number of the dislocation sources generate a cause large number of dislocations and these dislocations cannot easily cause cross slip during the activation of the sources. The groups of these dislocations confined to one crystallographic plane or narrow band in the crystal may build up a stress concentration sufficient to nucleate twins⁽¹⁷⁾ which seem to be closely related to the embrittlement.

As reported on numbers of body centered cubic metals by many investigators, it is most likely that cleavage cracks are initiated at twin-twin or twin-grain boundary intersections^{(14) (18) (19)}. In the present investigation

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twin traces were frequently observed on the fracture surfaces. Remarkable interactions between dislocations and small precipitates having the $\{100\}_\alpha$ habit plane were not observed. Therefore, it is reasonable to consider that the small precipitates do not make a great contribution to the hardening of the aged alloy. The great difference in the hardness and deformation substructure between ductile and brittle specimens seems to be due to the difference in the facility of cross slip and in the frictional stress against the movement of slip dislocations.

The large increase of frictional stress seems to be sufficiently inducible by chromium-rich precipitates produced during aging, and it can also be predicted from the microstructural observation that the dislocations cannot easily cause cross slip in the brittle specimens.

It is necessary to make a further investigation of the deformation behavior of the aged alloy, in order to explain more clearly the embrittlement of high chromium ferrite aged at about 500°C.

V. Summary and Conclusion

(1) The electrical resistivity at the liquid nitrogen temperature increases in two stages with the aging time and the embrittlement is observed in the second stage.

The increase of resistivity in the second stage seems to be due to the precipitation of the chromium-rich precipitates which were too small to be observed in the present investigation.

(2) In the second stage of the resistivity curve, a large number of the small precipitates which show the $\{100\}_\alpha$ habit plane are observed.

(3) In the quenched and cold rolled specimens the dislocations exist in irregular tangles and form deformation cells, and twinning is not observed.

(4) In the specimens which were aged for 20 days and slightly compressed, the dislocations mostly lie in one crystallographic plane or narrow band and in one crystallographic direction. Moreover many deformation twins are observed. Such a dislocation configuration may build up the stress concentration to nucleate twins. In these specimens cross slip of dislocations seems to be more difficult than that case of the ductile specimens.

(5) Twin traces are frequently observed on the fracture surfaces.

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