Low-Temperature Fracture of High Purity Iron and Its Relationship to the Grain Boundary Character

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The mode of fracture and the ductile-to-brittle transition temperature (DBTT) of high purity iron ($\geq 99.999\%$) have been investigated with two sets of specimens of different grain boundary character. Wire specimens of 0.4 mm diameter were tested in tension at a strain rate of $8.33 \times 10^{-5}/s$.

The grain structure of one set of specimens is of bamboo-type with high angle boundaries, which are nearly parallel to the $\{100\}$ or $\{110\}$ planes of the grains separated by the boundary and nearly normal to the specimen axis. As expected, these specimens fracture in the intergranular mode and DBTT is between 110 and 125 K. Specimens of the other set have coarse grain structure. Most of the boundaries are of small angle or near-twin type with random boundary plane orientation. These specimens fracture in the transgranular mode at and below 50 K; DBTT for the intergranular fracture, if any, is below 4.2 K. This is in contrast to the occurrence of intergranular fracture even at 77 K for less pure iron specimens (99.99% or below) with the grain boundary character of the second type.

Thus, DBTT for the intergranular fracture, which is the common fracture mode in pure iron, depends strongly on the purity and on the grain boundary character of iron specimens. If the grain boundary character is unfavorable to the intergranular fracture, DBTT decreases from above 77 K to below 4.2 K by increasing the purity from 99.99% to 99.999%. In specimens favorable to the intergranular fracture, DBTT is about 120 K even in 99.999% pure iron.

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I. Introduction

Iron is usually brittle at low temperatures, *e.g.*, 77 K and below, and fracture occurs mainly in the intergranular manner. It has been a long asked question whether the intergranular fracture (IGF) is caused by impurities or not. This question appeared to have been answered by Matsui, Moriya, Takaki and Kimura⁽¹⁾. They prepared iron much purer than iron so far used in the study of mechanical properties, and showed that coarse-grain specimens of iron of about 99.999% and higher purity did not exhibit IGF even at 4.2 K by tensile tests at a strain rate of $8.33 \times 10^{-5}/s$. They also showed that iron of about 99.99% purity fractured in the IGF mode. Hence, they have concluded that IGF is not an inherent properties of iron, but caused by impurities. (In the Matsui *et al.* paper, the purity of specimens is not explicitly given. Rather, the residual resistivity ratio, which will be explained in the last paragraph of this section, is given as a measure of the purity.)

Since some years after the report by Matsui *et al.*, the structure of grain boundaries and its effects on the properties of polycrystalline materials have attracted much at-

tention and the effect of the character of grain boundaries on IGF has gradually been clarified. Thus, a question has been raised that the iron specimens used by Matsui *et al.* might contain no grain boundary susceptible to IGF⁽²⁾. The purpose of the present research is to answer this question. The specimens used by Matsui *et al.* were subjected to the γ to α transformation during the final stage of specimen preparation; they were cooled from 1203 to 1073 K and kept there for the hydrogen treatment. In the present research, the final treatment was done in two manners; in one manner specimens were subjected to the same γ to α transformation as those used by Matsui *et al.*, and in the other they were hydrogen treated only in the α -phase region, *i.e.*, at 1073 K. The grain boundary character is completely different between the two groups of specimens, and hence we have been able to investigate the dependence of the fracture mode on the grain boundary character. We have also investigated the ductile-to-brittle transition temperature (DBTT) for IGF and for transgranular fracture (TGF).

As done by Matsui *et al.*, the purity of specimens in the present research is represented with the residual resistivity ratio (RRR). RRR is the ratio of the electrical resistivity of a metal measured at a fixed temperature near 273 K (298 K in the present research) to that measured at 4.2 K. For iron it is abbreviated to RRR_H , since the 4.2 K resistivity is measured under a magnetic field, H , of 64 kA/m, to minimize the resistivity of a magnetic origin. The larger RRR_H values correspond to the higher purity. RRR_H of 5000 for iron is considered to be equivalent to 99.999% purity; if the resistivity contribution of metallic impurities of 1 ppm is reasonably assumed to be

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$2 \times 10^{-10} \Omega\text{-cm}$.

II. Experimental Procedure

1. Specimen preparation

The high purity iron was prepared from a commercial high purity iron with electron-beam floating-zone melting under ultrahigh-vacuum with the same technique as that used by Matsui *et al.*⁽³⁾ In the present research, the iron has been further purified with floating-zone leveling under purified dry hydrogen flow. Although the concentration of interstitial impurities is reduced by the ultrahigh-vacuum melting below the limit of detection of the chemical analysis⁽⁴⁾, the melting under hydrogen was applied to enable direct comparison of the present results with those of Matsui *et al.*

The purified iron rod was cold-drawn to wire of 0.55 mm diameter with caution to prevent the wire from contamination. The following two heating processes were applied to obtain specimens with different grain boundary structures; (a) 40 min at 1203 K under dry hydrogen, 24 h at 1073 K under wet hydrogen and finally 20 h at 1073 K under dry hydrogen, and (b) 24 h at 1073 K under wet hydrogen and then 24 h at 1073 K under dry hydrogen. The first process is the same as that adopted by Matsui *et al.* Since specimens were subjected to the γ to α transformation, this process will be referred to as the γ -treatment in the present paper. In the second treatment, specimens were heated only in the α -phase region and the treatment will be called the α -treatment. The recrystallization fiber texture was significantly reduced by the γ -treatment but reserved by the α -treatment. Thereby specimens with different grain boundary characters were obtained. Possible contamination mainly with carbon during the wire drawing was also removed with the hydrogen treatment. Purified and annealed specimens were chemically polished⁽⁵⁾, and the final diameter of specimens became 0.4 mm. The residual resistivity ratio of the specimens was more than 5000, and hence the purity was 99.999% or better.

2. Analysis of the grain boundary character

Since coarse-grain specimens with one or a few grains in the cross-section were obtained, the orientation of each grain was determined by the X-ray Laue method, and the grain boundary character was identified by a computer program.

Firstly, metallographic observation was made on each specimen and then each grain was oriented three-dimensionally with respect to the specimen axis, the orientation of the incident X-ray beam and the orientation perpendicular to these two orientations. The X-ray beam was 0.5 mm in diameter and directed to one grain at a time. The angle of rotation between two neighboring grains and the crystallographic orientation of the rotation axis were determined. There are 24 possible sets of a rotation angle and a rotation axis for each pair of grains. Among them, the set with the minimum rotation angle was

selected to define the rotation angle and the rotation axis of the boundary. Boundaries with the rotation angles 15° and smaller were classified as small angle boundaries. Coincidence boundaries were defined with the Brandon criterion⁽⁶⁾. The overall accuracy of the rotation angle determination was $\pm 1^\circ$. The main source of the inaccuracy was in the specimen setting. When a grain boundary was sufficiently flat, the orientation of the boundary was determined by optical microscopy.

Figure 1 shows an example of the analysis of the boundary orientation. The center pole of the stereographic projection ($\times$) coincides with the specimen axis. Solid and broken lines are the projection of the $\{100\}$ and $\{110\}$ planes of the two neighboring grains. The traces of the grain boundary are shown by small solid circles and the pole of the boundary is shown by a large solid circle. Also shown here with an open double circle is the rotation axis. The angle between the rotation axis and the pole of the boundary is denoted by χ . The magnitude of χ gives the nature of the boundary; a pure twist boundary for $\chi=0^\circ$ and a pure tilt boundary for $\chi=90^\circ$. The example in Fig. 1 is of a random boundary; no low index plane of one grain coincides with that of the other. For a small angle boundary, the projections of low index planes of both grains almost coincide with each other, and for $\Sigma 3$ boundaries, $\langle 111 \rangle$ poles of both grains coincide with each other. Thus, we can easily distinguish random boundaries from small angle and $\Sigma 3$ boundaries.

3. Tensile tests

Tensile tests were performed at temperatures between 4.2 K and 130 K. The gauge length of specimens was 10 mm, and the strain rate was $8.33 \times 10^{-5}/\text{s}$. The test temperature was controlled within ± 0.5 K at all temperatures. When specimens were fractured in a brittle manner, the fractured surface was investigated by scanning electron microscopy (SEM).

Fig. 1 An example of the analysis of grain boundary orientation.

III. Experimental Results and Discussion

1. Character of grain boundaries

Figure 2 shows the orientation of the specimen axis in each grain of α -treated (a) and γ -treated (b) specimens together with the illustration of the grain structure of each specimen. The α -treated specimen has a fiber structure with (100) oriented grains and few (110) oriented ones. On the other hand, the γ -treated specimen has no clear fiber structure.

Analysis of the relative orientation between two neighboring grains has shown that about 90% of the boundaries in the α -treated specimens are high angle boundaries and 75 to 80% of those in the γ -treated specimens are small angle or $\Sigma 3$ boundaries. Harase, Shimizu, Tomimasu and Takahashi have also found $\Sigma 3$ boundaries with high frequency after the α to γ transformation in iron single crystals of 99.8% purity⁽⁷⁾.

Thus, the α -treated specimens have a bamboo structure with high angle boundaries nearly perpendicular to the specimen axis, i.e., most of the boundaries are nearly parallel to the {100} or {110} planes of the mated grains.

Fig. 2 Orientation of grains and the schematic illustrations of grain structure of (a) α -treated specimens and (b) γ -treated specimens.

The cleavage plane in iron is a {100} plane; the atomic cohesion across a {100} plane is expected to be weaker than that across other planes. The tensile stress acts almost perpendicular to the grain boundaries. Hence, we expect the α -treated specimens to be susceptible to IGF. On the contrary, in the γ -treated specimens, most of the boundaries are small angle or twin boundaries, and not perpendicular to the specimen axis. Moreover, the boundary planes are not flat. Hence we expect the γ -treated specimens do not show IGF.

2. Tensile tests at 77 K

Figure 3 shows some of the stress-strain curves measured at 77 K. All of the α -treated specimens fracture after slight plastic deformation. Twinning is also observed as shown by sharp drops in the flow stress. The flow stress at 0.1% plastic strain $\sigma_{0.1}$ is 356 ± 22 MPa. The γ -treated specimens do not fracture but show full ductility, i.e., 100% reduction of the cross-section. (One of ten specimens, however, fractured in a brittle manner. The fractured surface was almost perpendicular to the specimen axis and not far from the {100} plane; this particular specimen has a similar grain boundary character to that in the α -treated specimens.) $\sigma_{0.1}$ of the γ -treated specimens is 372 ± 24 MPa.

Most fractured surfaces in the α -treated specimens are flat and smooth, and nearly perpendicular to the specimen axis. The only feature, if any, observed on the surface is the trace of deformation twins. No feature showing precipitate particles is observed. We have also observed that the crystallographic orientation of two mated crystals separated by the fracture is different from each other. These observations clearly show that the fracture mode in the α -treated specimens is intergranular. In a few cases, mixture of IGF and cleavage is observed. Even in these cases the appearance of the fracture surface indicates that the fracture is initiated at a grain boundary.

3. The ductile-to-brittle transition temperatures for intergranular fracture and transgranular fracture

The α -treated specimens were tested at temperatures from 100 K to 130 K to determine DBTT for IGF. Figure

Fig. 3 Stress-strain curves at 77 K of α - and γ -treated specimens.

Fig. 4 Ductile-to-brittle transition of α -treated specimens obtained by the reduction-of-area in tensile test.

4 shows the reduction of area against the test temperature. The ductile-to-brittle transition occurs in a temperature range from 125 K to 110 K. The rather wide temperature range likely reflects the variety of grain boundary character. Although all the α -treated specimens have grain boundaries of similar character, slight differences in the character may give different DBTT.

Figure 5 shows the temperature dependence of the fracture stress of the α -treated specimens below DBTT. The fracture stress, like the yield stress, increases with decreasing temperature. Moreover, a small amount of plastic deformation is observed before IGF. These results suggest that the fracture is controlled by the motion of dislocations; dislocations piled up at grain boundaries initiate IGF.

Figure 6 shows the stress-strain curves of γ -treated specimens at 50, 55 and 60 K. Cleavage fracture occurred at 50 K and specimens were ductile above 55 K. Two specimens were tested at 4.2 K; one showed cleavage fracture and the other IGF with no plastic deformation. The fracture stress for IGF is much lower than the cleavage stress. Although more specimens should be tested to determine DBTT for the cleavage more accurately, we consider it to be near 50 K in the present test conditions. These results imply that DBTT for IGF, if any, is near or below 4.2 K in the γ -treated specimens. It has been already shown by Matsui *et al.* that γ -treated specimens of higher purity do not show IGF even at 4.2 K. It should be noted here that no difference in mechanical properties has been found between the specimens used by Matsui *et al.* ($RRR_H \geq 5000$) and the present γ -treated specimens.

Thus, DBTT for IGF is between 125 and 110 K in the α -treated specimens and below 4.2 K in the γ -treated specimens; DBTT for IGF strongly depends on the grain boundary character. As commented by McMahon⁽²⁾, the specimens used by Matsui *et al.* and the γ -treated specimens in the present research are not susceptible to IGF because of their grain boundary character.

The above conclusion, however, does not mean that impurities play no role in IGF. Actually, IGF is promoted by impurities as already shown by Matsui *et al.* They have shown that γ -treated specimens of lower puri-

Fig. 5 Temperature dependence of the fracture stress for IGF of α -treated specimens.

Fig. 6 Stress-strain curves of γ -treated specimens at 50, 55 and 60 K.

ty, i.e., about 99.99%, fracture by IGF at 77 K. Since γ -treated specimens of higher purity do not show IGF even at 4.2 K, IGF observed in polycrystalline specimens of so-called pure iron, i.e., of about 99.9 to 99.99% purity, is concluded to be promoted by impurities. Although they did not identify the impurities responsible for IGF, they always observed precipitate-like particles on the fractured surface of specimens of lower purity. Since no such a feature is observed in high purity specimens, they have concluded that those particles are responsible for IGF in the γ -treated specimens of lower purity. Matsui and Kimura⁽⁸⁾ doped γ -treated specimens with oxygen and investigated the effect of oxygen segregated at grain boundaries. The doped specimens showed IGF at and below 15 K, while undoped specimens were ductile at 4.2 K. The concentration of oxygen was so small that no oxide particle was formed at grain boundaries. Hence, it was concluded that the oxygen segregated at grain boundaries promoted IGF.

It should be noted here that the results described above, especially those with the α -treated specimens, are for wire specimens. If specimens are prepared by rolling and annealing in the α -phase region, the recrystallization

texture will be different from that in the present α -treated specimens, and different results will be expected. One more note should be made. Although it is difficult, if we prepare high purity fine-grain bulky specimens by the α -treatment, they may not be as susceptible as the present α -treated specimens to IGF.

IV. Conclusions

(1) The ductile-to-brittle transition temperature under tensile tests of high purity iron (about 99.999% or better) strongly depends on the grain boundary character. It ranges from 125 to 4.2 K or below. Without specifying the grain boundary character, it is meaningless to discuss whether iron shows intergranular fracture or not at low temperatures.

(2) The purity also affects the intergranular fracture. Specimens of 99.99% purity are more susceptible to IGF than those of 99.999% purity.

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REFERENCES

- (1) H. Matsui, S. Moriya, S. Takaki and H. Kimura: *Trans. JIM*, **19** (1978), 163.
- (2) C. J. McMahon, Jr.: private communication.
- (3) S. Takaki and H. Kimura: *Scripta Met.*, **10** (1976), 1095.
- (4) R. Onodera, S. Takaki, K. Abiko and H. Kimura: *Mat. Sci. Eng.*, **A141** (1991), 261.
- (5) S. Takaki and H. Kimura: *Scripta Met.*, **10** (1976), 701.
- (6) D. G. Brandon: *Acta Met.*, **14** (1966), 1072.
- (7) J. Harase, R. Shimizu, K. Tomimasu and N. Takahashi: *J. Japan Inst. Metals*, **54** (1990), 509.
- (8) H. Matsui and H. Kimura: *J. Japan Inst. Metals*, **47** (1983), 294; *Trans. JIM*, **24** (1983), 539.