Effect of Dispersed Particles on Microstructure Evolved in Iron under Mechanical Milling Followed by Consolidating Rolling

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The microstructure and the strength of an iron mechanically milled with various amounts of oxygen (*i.e.*, 0.2, 0.6, and 1.5 mass pct) were studied. The samples were subjected to a mechanical milling in an argon atmosphere for 100 hours followed by consolidating bar rolling to a total reduction of about 86 pct at 700 °C. The microstructure of the steels sensitively changed depending on the oxygen content, *i.e.*, on the volume fraction of the oxide particles. The average grain size decreased from about 0.7 to 0.2 μm with an increase in the amount of oxygen. Moreover, the misorientation distributions of the grain boundaries were different in the samples with various amounts of oxygen. A relatively large fraction of low-angle boundaries arranged crosswise to the rolling axis was registered in the samples with 0.2 and 0.6 pct oxygen, while the near random distribution of the boundary misorientations was obtained in the specimens with 1.5 pct oxygen. The effect of dispersed particles on the structure evolution and the relationship between microstructures and some mechanical properties are discussed.

I. INTRODUCTION

PRODUCTION of metallic materials with ultra-fine-grained microstructures is of particular interest to metallurgical engineers. Such kinds of materials are believed to have a beneficial combination of mechanical properties, *i.e.*, a high strength at ambient temperature and an improved workability during hot working.[1,2] Several methods have been proposed to produce materials with submicron grains, including rapid solidification, vapor condensation, severe plastic deformation, powder metallurgy, *etc.* The powder metallurgy method has some advantages over the other ones. A special feature of this method is that it allows us to make sizeable stocks and that it is applicable to a larger variety of materials. The latter makes it possible to use the special alloys, which are difficult if not impossible to produce by any other processing.

One type of powder metallurgy processing is mechanical milling followed by consolidating plastic working. Recently, this method has been applied to the production of high-strength steels with fine-grained structures, which contain dispersed oxide particles that are homogeneously distributed throughout the matrix.[3,4] In addition to the conventional dispersion strengthening, the fine particles play an important role in the structure formation, which can also affect the mechanical properties of the steels. The uniform dispersion of the fine oxide particles in the matrix is effective for grain refinement and increasing the strength of steels produced by the mechanical milling.[4] However, the microstructural characteristics of ultra-fine-grained materials containing dispersed particles have not been studied in sufficient detail for the mechanical milling followed by hot working. The effect of fine particles (their size and distribution) on some structural parameters such as texture, (sub)grain-boundary misorientations, dislocation arrangements, *etc.* is still unclear.

The aim of the present work is to study the peculiarities of the fine-grained microstructures developed under mechanical milling followed by consolidating hot rolling of iron powder with various amounts of oxide particles. The present study is focused mainly on the effect of dispersed oxide particles on the (sub)grain-boundary characteristics, such as the misorientation distribution of grain boundaries, their mutual alignment, *etc.*

II. EXPERIMENTAL PROCEDURE

Three kinds of iron-oxide powders with different amounts of oxygen, *i.e.*, 0.2, 0.6, and 1.5 mass pct (Table I), were used as the starting materials. Each powder was mechanically milled by a planetary ball mill in an argon atmosphere for about 100 hours using a stainless steel pot (SUS403) and steel balls (SUJ2). After mechanical milling, the worked powders were canned in a steel pipe with an inner diameter of 30 mm and then multiple bar rolled to a total nominal reduction in area of 86 pct at about 700 °C for consolidation. Since the relative density of canned powders was about 60 pct before consolidation, the true reduction in area for the iron powder during consolidation is calculated to be about 77 pct. The preheating time for consolidating rolling was about 3.6 ks and the reduction per pass was about 10 pct.

The structural analysis was carried out on the sections parallel to the rolling direction using a Jeol JEM-2010F transmission electron microscope operating at 200 kV. All clear defined (sub)grain boundaries were taken into account, while grain sizes and grain-boundary misorientations were studied. The average grain size was measured by the linear intercept method in two directions, *i.e.*, the long intercept and the short intercept. The misorientations on the grain boundaries and sub-boundaries were studied by a conventional Kikuchi-line technique.[5] The accuracy of the measurements was about 1 deg. The grain-boundary misorientations were analyzed in typical areas of two thin foils prepared

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Table I. Measured Chemical Composition of Iron Powders (Mass Pct)

Powder	O	N	C	Si	Mn	P	S	Fe
Fe-0.2 pct O	0.18	0.003	0.002	0.010	0.150	0.010	0.010	bal
Fe-0.6 pct O	0.58	0.005	0.010	0.009	0.110	0.009	0.007	bal
Fe-1.5 pct O	1.51	0.008	0.030	0.005	0.003	0.005	0.001	bal

from each specimen. All of the visible (sub)grain boundaries were studied in arbitrarily selected areas, which included about 25 grains. The same boundaries were used for grain size measurements, and a total of about 100 boundaries was analyzed in each sample.

The mechanical properties were studied by tensile tests at a strain rate of about $5 \times 10^{-4}\ s^{-1}$, using an AG-50kNG tester equipped with an extensometer. The tests were carried out on round tensile specimens, which were machined along the rolling direction with a gage diameter of 3.5 mm and a length of 25 mm. In addition to the tensile tests, the hardness measurements were carried out on the sections that were parallel to the rolling direction.

III. RESULTS

A. *Evolved Microstructures*

Typical microstructures developed in samples with different oxygen contents are shown in Figure 1. The average grain size and aspect ratio decrease with increasing amounts of oxygen. Moreover, general features of the microstructures developed in the specimens are also affected strongly by the amount of oxygen. In the samples with 0.2 pct oxygen, the microstructure looks like a lamellar structure, where (sub)grain clusters are highly elongated in the rolling direction (RD). In contrast, the samples containing 1.5 pct oxygen can be characterized by an ultra-fine-grained microstructure, in which the equiaxed fine grains are almost fully developed throughout the specimen (Figure 1(c)). The microstructure of 0.6 pct oxygen samples looks like an intermediate state between 0.2 and 1.5 pct O specimens (Figure 1(b)). This microstructure is composed of much finer grains than that of the 0.2 pct O specimen. However, the fine grains in Figure 1(b) are clearly arranged in rows parallel to the rolling direction.

The effect of oxygen on the resulting microstructure is associated mainly with the variations in the volume fraction of oxide particles. Assuming that most of the oxygen in the samples is Fe_3O_4-type oxides, the volume fractions of the oxide particles are about 1, 3, and 8 pct in the samples containing 0.2, 0.6, and 1.5 mass pct oxygen, respectively.[4] It is interesting to note that the size of the dispersed oxide particles does not depend strongly on the oxygen content. The average oxide particle size increases from about 9 to 12 nm when the amount of oxygen is increased from 0.2 to 1.5 pct. (Note that particle size was measured using dark-field images and particles larger than 100 nm were omitted.) Figure 2 shows the distribution of the size of the oxide particles for the specimens studied. These charts clearly show a single peak in the distribution for all the samples. The maximum in the distribution appears around 10 nm, although these distributions shift slightly toward larger sizes with increasing oxygen content. Since the average oxide particle size is not affected strongly by the oxygen content,

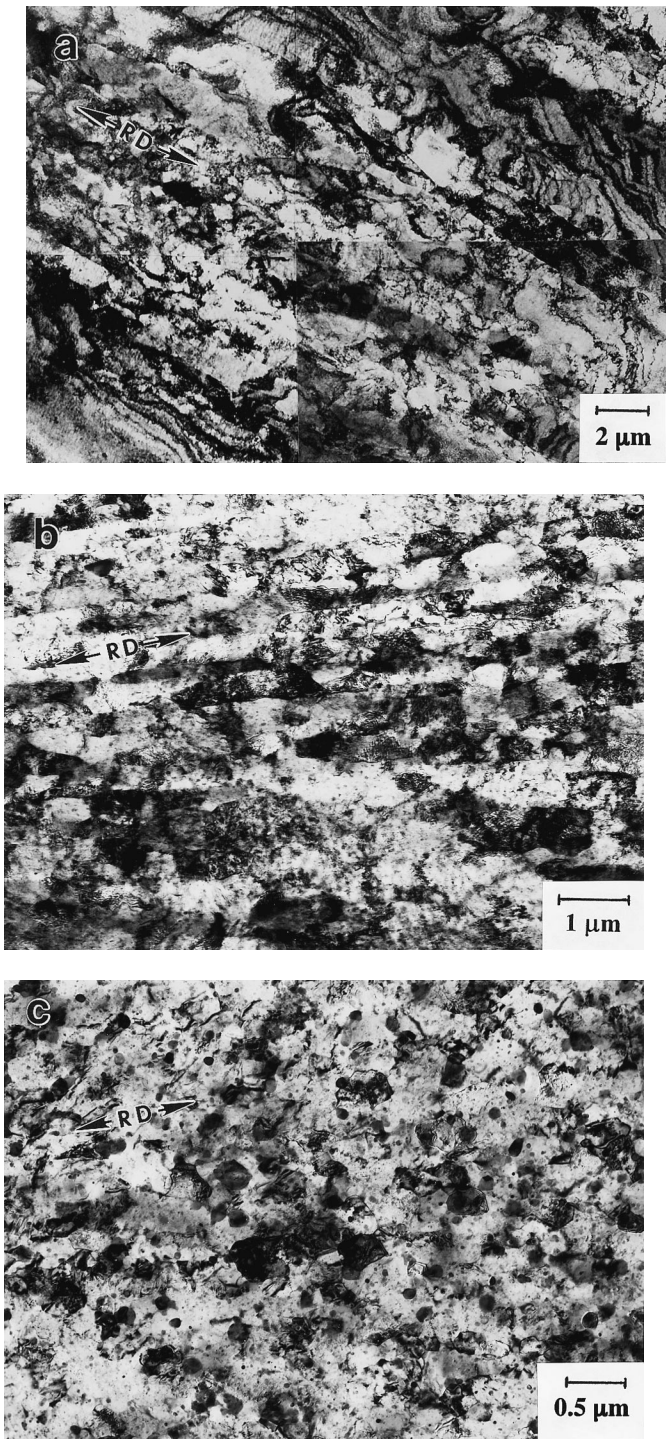

Fig. 1—Typical microstructures developed by mechanical milling followed by hot rolling of iron containing various amounts of oxygen: (*a*) 0.2 pct, (*b*) 0.6 pct, and (*c*) 1.5 pct oxygen.

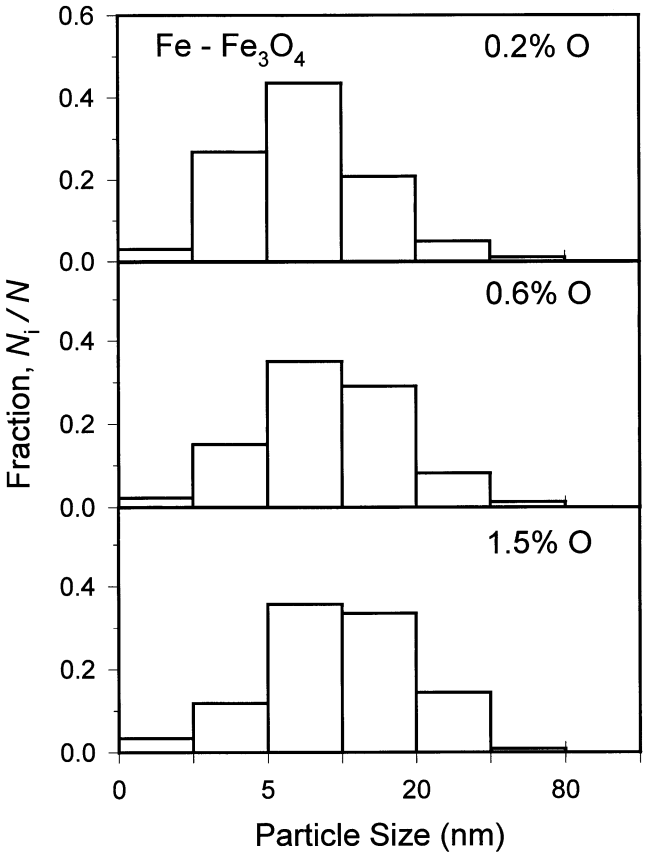

Fig. 2—Effect of oxygen content on the distribution of the size of the oxide particles.

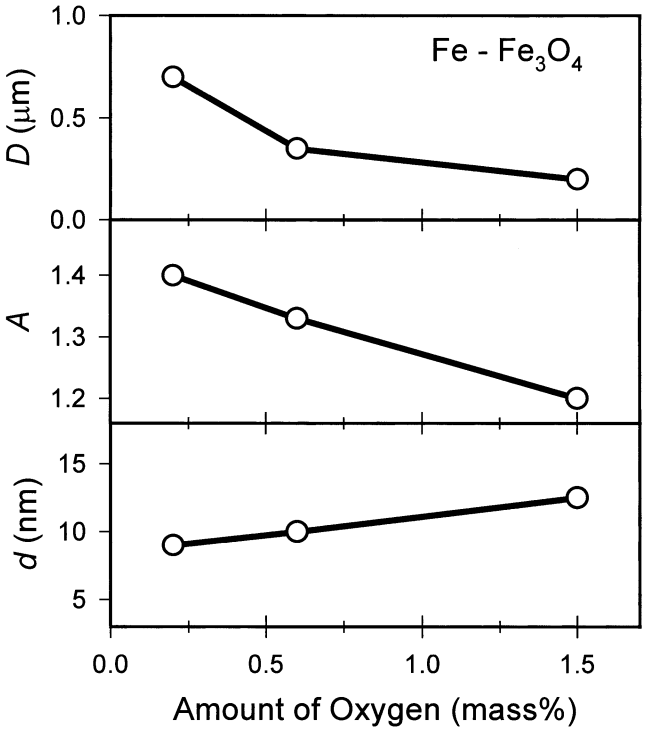

Fig. 3—Effect of oxygen content on the average grain size (*D*), the aspect ratio (*A*), and the oxide particle size (*d*) evolved in iron by mechanical milling followed by hot rolling.

increasing the amount of oxygen leads to a significant increase in the number of oxides. In other words, the specimens studied are quite different in interparticle spacings, which can play an important role in microstructural evolution. The interparticle spacings are calculated as 35, 27, and 23 nm for 0.2, 0.6, and 1.5 pct O samples, respectively, where the sphere in the oxide shape is assumed, and the average particle size is used for the oxide diameter.

Figure 3 summarizes the effect of oxygen on some averaged parameters of the microstructures, *i.e.*, the grain size (*D*), the aspect ratio (*A*), and the oxide particle size (*d*), evolved under the present processing method. The effect of oxygen content on the average grain size correlates to the oxygen dependence for the aspect ratio. The average grain size decreases rapidly from about 0.7 to 0.35 μm when the amount is increased from 0.2 to 0.6 pct. Then the *D* approaches a value of about 0.2 μm as the oxygen content increases to 1.5 pct. The aspect ratio gradually decreases from 1.4 to 1.2 when the oxygen is increased from 0.2 to 1.5 pct. On the other hand, the *d* shows a slight increase with the oxygen content. The size of the oxide particles in mechanically milled samples is mainly affected by the milling time.[4] The finer *d* in specimens with lower oxygen content may result from a difference in the initial size of oxide (larger oxides were used to make the samples with higher oxygen content).

B. *Grain-Boundary Misorientations*

Detailed examination of the orientations of individual grains revealed a difference in the arrangement of the grain boundaries evolved in the samples with various amounts of oxide particles. Figure 4 represents the enlarged micrographs of microstructures developed in the samples corresponding to those in Figure 1. The numbers in Figure 4 indicate the grain-boundary misorientations in degrees. Here, low- and high-angle boundaries are shown by thin and thick lines, respectively. In samples with relatively low amounts of oxygen (Figures 4(a) and (b)), longitudinal boundaries of elongated grains mainly have high-angle misorientations, while those in the transverse direction include a large fraction of low-angle (*i.e.*, sub-boundaries). In contrast, Figure 4(c) shows that an increase in the oxygen content to 1.5 pct leads to a random distribution of the misorientations for the fine grains developed by the present processing method.

Figure 5 represents the quantitative analysis for the effect of oxide particles on the misorientation distribution of grain boundaries. The misorientation distribution for the 0.2 pct O sample can be characterized by a large fraction of low-angle grain boundaries with misorientations (θ) below 10 deg. An increase in the oxygen content in the samples leads to a decrease in the fraction of low-angle boundaries. As a result, the misorientation distribution for the specimen with 0.6 pct O shows two diffuse peaks corresponding to low- and high-angle boundaries. In Figure 5, the fraction of low-angle boundaries drops to near zero for the 1.5 pct O sample; therefore, the majority of grain boundaries are high-angle boundaries. The dashed line in this figure indicates the theoretical misorientation distribution calculated for the random disorientation of grains.[6] The experimental data obtained for the misorientations of grain boundaries evolved in the sample with the highest amount of oxygen are quite close to the theoretical random distribution.

The grain-boundary misorientations resulting from the

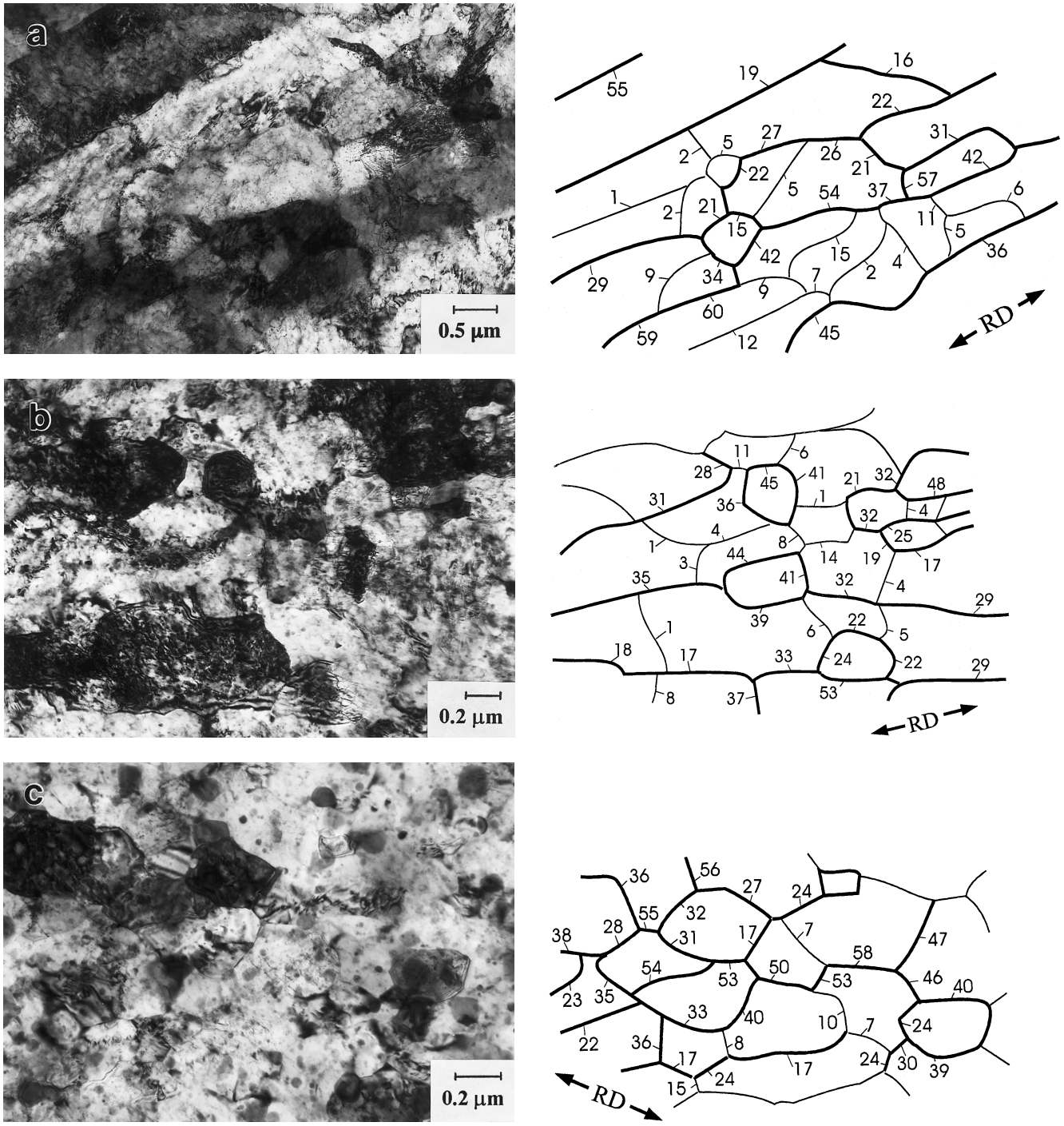

Fig. 4—Effect of oxygen content on the grain boundaries developed in iron under mechanical milling followed by hot rolling: (*a*) 0.2 pct, (*b*) 0.6 pct, and (*c*) 1.5 pct oxygen. Numbers indicate the boundary misorientations in degrees.

orientation of individual grains may be closely connected to the texture evolution. Figure 6 shows inverse pole figures of the rolling direction for the specimens with different amounts of oxygen. The pole figures are similar in appearance for the samples with 0.2 and 0.6 pct oxygen. They clearly show minimums around the ⟨111⟩ direction. This is typical of bcc metals strained by the uniaxial deformation mode, *i.e.*, bar rolling.[7] In contrast, the 1.5 pct O sample shows that the near ⟨111⟩ orientations are along the rolling direction for certain grains. These results are confirmed by X-ray diffraction, as shown in Figure 7. The strong rolling texture for the 0.2 pct O specimen becomes quite weak with increasing the oxygen content. Therefore, the specimen with 1.5 pct oxygen can be characterized by a diffuse texture evolution.

C. *Tensile Strength and Hardness*

Let us consider the effect of the oxygen content on some mechanical properties of the iron samples processed by

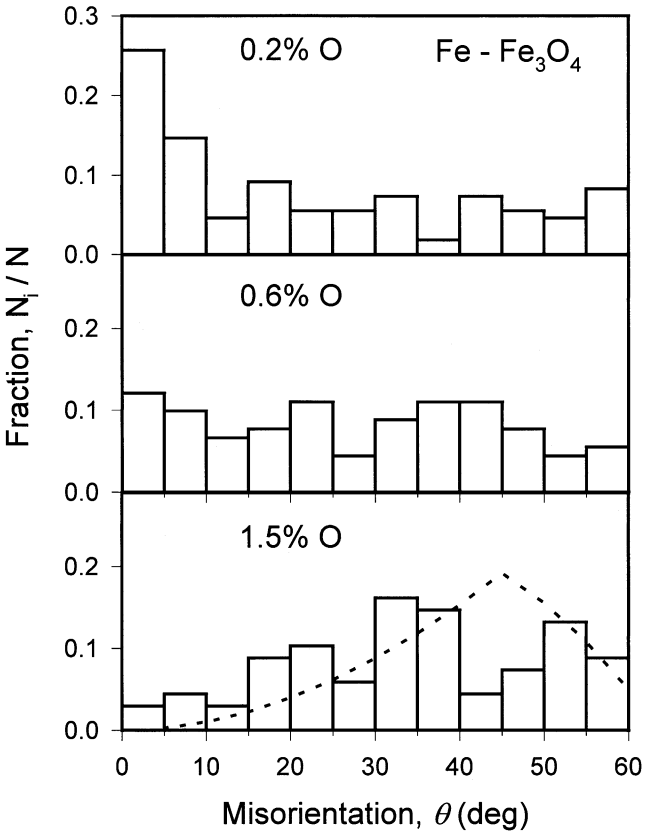

Fig. 5—Misorientation distributions for the grain boundaries evolved in iron with different oxygen contents.

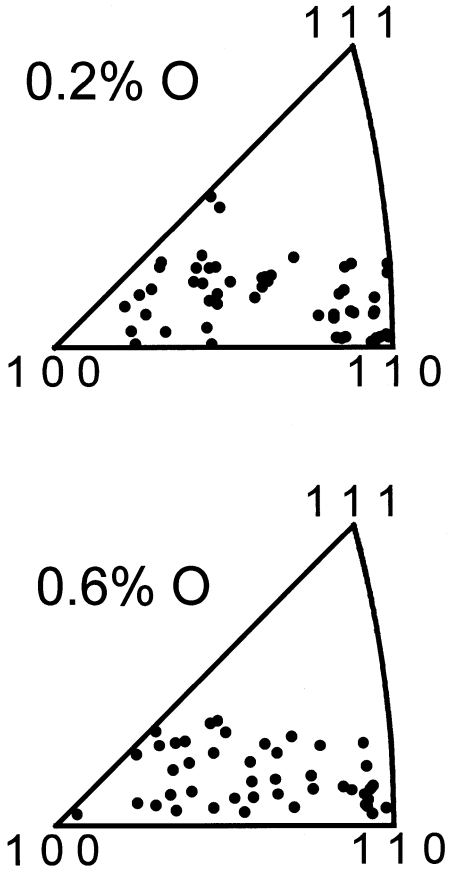

Fig. 6—Inverse pole figures of the rolling direction for the iron specimens with different amounts of oxygen.

mechanical milling followed by hot rolling. Figure 8 shows relationships of the tensile strength (σ_B) and the hardness (H_v) *vs* the oxygen content (X) in a log-log scale. An increase in the oxygen content results in the strengthening of the material. Both σ_B and H_v can be approximated by power-law functions of X with roughly the same exponent of about 0.3. This leads to a linear relationship between the tensile strength and the hardness much similar to the conventional processing of plain carbon steels. Such a relationship is considered to be important for the present material, since powder metallurgy does not always provide the same tensile strength for a given hardness, especially for extremely hard materials.[8]

The strengthening with increasing oxygen percentage is mainly caused by (1) grain refinement (*i.e.*, grain size strengthening) and (2) an increase in the volume fraction of dispersed oxide particles (dispersed strengthening). The H_v-$D^{-0.5}$ relationship for the present material is shown in Figure 9. Open and closed symbols correspond to "average" and "minimal" grain sizes, respectively. The former was averaged over longitudinal and transverse grain sizes, and the latter represents the average grain sizes measured in only the transverse direction. This figure also includes the data for the hardness of mechanically milled and annealed iron containing 0.3 pct O[9] for reference. The H_v obtained in the present study can be expressed by a linear function of the inverse square root of the grain size, similar to the Hall–Petch relationship.[10] It is interesting that the present data obey the Hall–Petch relationship in spite of the differences in grain-boundary characteristics, *i.e.*, a larger fraction of low-angle boundaries in lower oxygen samples. However, longitudinal grain boundaries (*i.e.*, those parallel to the rolling direction) are essentially high-angle grain boundaries for all the specimens studied. Therefore, as shown in Figure 9, for microstructures composed of elongated grains, the transverse grain size may play a dominant role in hardening. It should be noted that the present samples with smaller grains contain larger amounts of oxygen. An increased slope of the H_v-$D^{-0.5}$ plot for these specimens as compared to that for the 0.3 pct O iron[9] can result from an additional strengthening effect of the dispersed oxides.

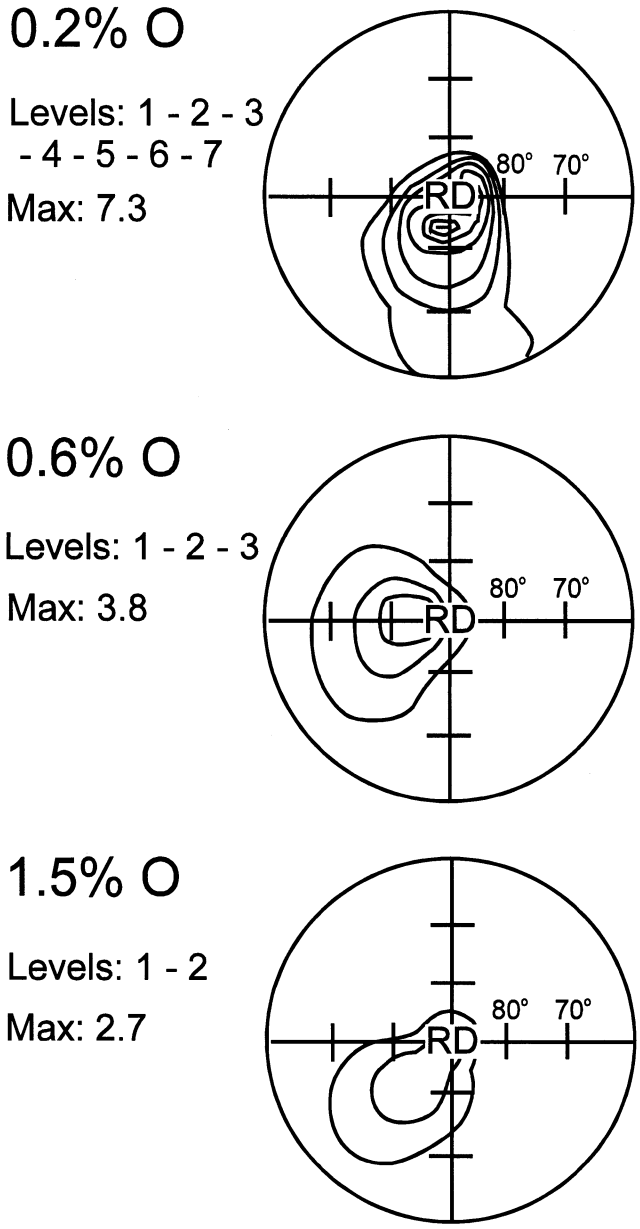

Fig. 7—Fragments of [110] pole figures as related to the RD for the iron specimens with various amounts of oxygen.

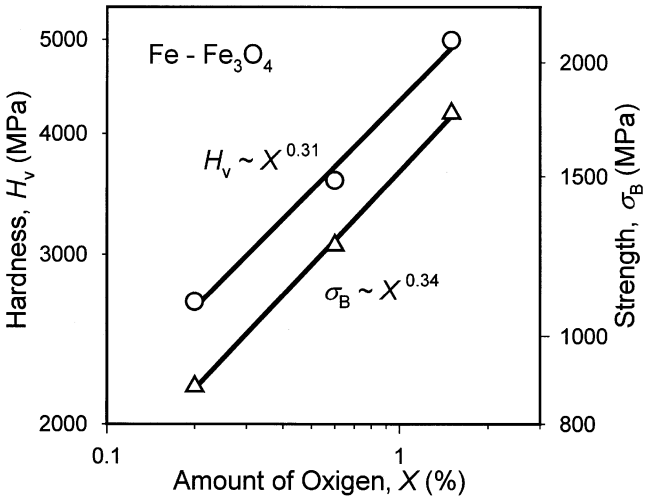

Fig. 8—Effect of the oxygen content on the tensile strength (σ_B) and the hardness (H_v) for the milled and then hot-rolled specimens.

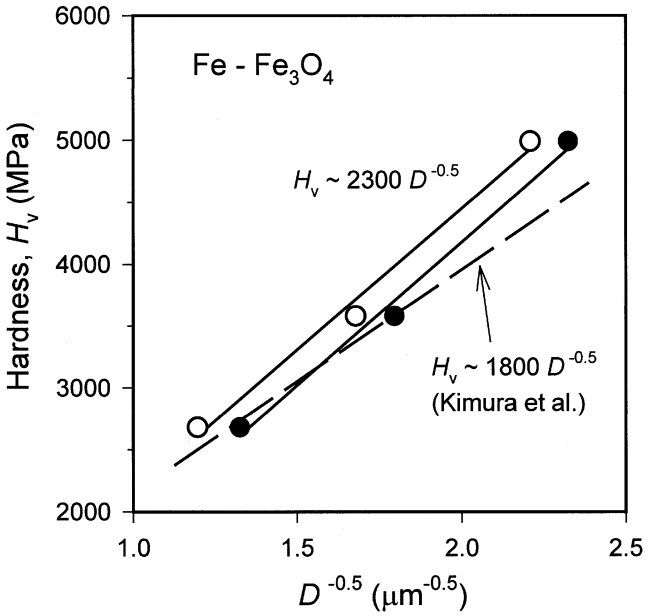

Fig. 9—Relationship between the hardness (H_v) and the grain size. Open and closed symbols correspond to "average" (*i.e.*, longitudinal and transverse) and "minimal" (*i.e.*, transverse) grain sizes for the Fe-Fe_3O_4, respectively. The data for mechanically milled and annealed iron with 0.3 pct O[9] are also plotted with a dashed line for reference.

IV. DISCUSSION

The material in this study has been processed by mechanical milling and then by consolidated hot rolling. Therefore, the microstructure evolution should be affected by both processing methods. As shown in Ref. 9, the mechanical milling of iron powder for about 100 hours led to the development of highly misoriented crystallites within a separate iron powder. The size of such crystallites was below 0.1 μm. However, the results of microstructural observations show that much larger grains evolved in the specimens. This suggests that the microstructures developed during mechanical milling can be significantly changed by further consolidating processing.

Figure 1 shows that the resulting microstructures are quite different from each other. The effect of consolidating working on microstructural changes depends significantly on the amount of oxygen in the samples. Since the solubility of oxygen in iron is very small, the oxygen affects the structural changes through the variation in the volume fraction of dispersed oxides. The most fine-grained microstructure in Figure 1 corresponds to the highest volume fraction of the oxide particles. Therefore, a high fraction of dispersed particles may greatly diminish the effect of consolidating processing on the microstructure that was previously developed under severe plastic working.

An effect of the volume fraction of oxide particles on the microstructure evolution during the processing method, which included mechanical milling and consolidating hot rolling, can be illustrated by a simple schematic drawing,

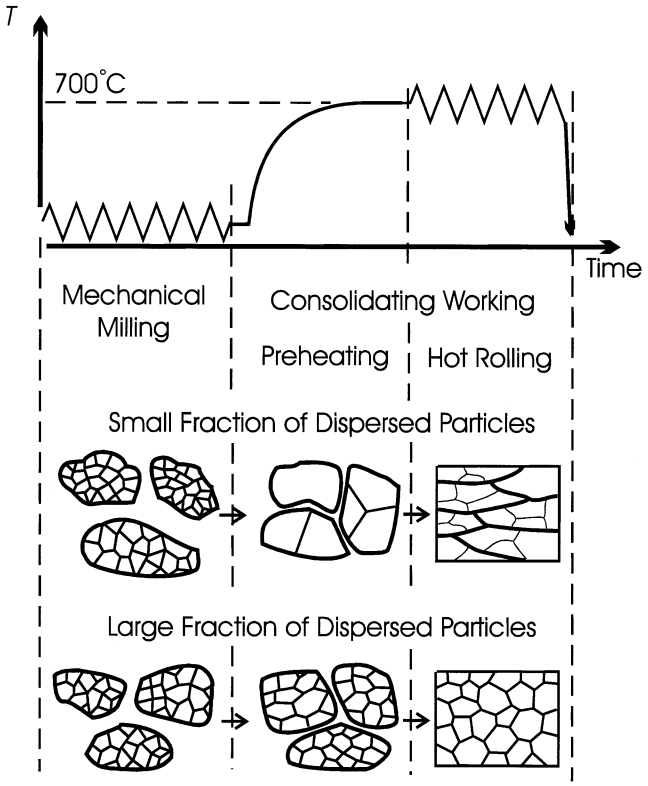

Fig. 10—Schematic drawing of the structural changes taking place in the iron powder during the present processing sequence.

which is shown in Figure 10. The upper part of the figure represents the processing sequence, which includes mechanical milling and consolidating working. The latter can be subdivided into preheating and then hot rolling. Mechanical milling for 100 hours results in the evolution of strain-induced ultrafine grains in the iron powder regardless of the oxide fraction. Then the samples are affected by a static recrystallization, which takes place during preheating time. In the iron powder with a low fraction of dispersed oxides, static recrystallization leads to a rapid grain coarsening. Further hot rolling results in the elongation of such coarse grains in the rolling direction accompanied by the formation of many sub-boundaries. As a result, the misorientation distribution of grain boundaries for the 0.2 pct O sample shows a high fraction of low-angle sub-boundaries and a specific texture (Figures 5 through 7). Similar misorientation distributions have been reported as typical ones for deformation-induced grain boundaries evolved at relatively low strains.[11,12] Therefore, the microstructure developed in the samples with a relatively low volume fraction of the oxide particles is strongly affected by the consolidating working. In other words, it is sensitively dependent on the conditions of plastic deformation following mechanical milling.

The grain growth during preheating time slows with an increasing volume fraction of dispersed particles. This causes the fraction of high-angle boundaries evolved in the final microstructure to increase and the fraction of low-angle sub-boundaries to decrease, as shown in Figure 5 for the 0.6 pct O specimen. Such grain-boundary misorientation distribution can be separated virtually into two portions. One of them is similar to the random distribution, thus it is mainly composed of high-angle boundaries, which originate from high misorientations evolved by mechanical milling. Another part is associated with low-angle sub-boundaries, which are developed during consolidating working. As shown in Figure 10, the grain growth hardly takes place in the iron powder with 1.5 pct oxygen because of the high volume fraction of dispersed oxide particles. In this case, the structural changes during preheating time are mainly associated with the recovery. Such a fine-grained structure does not change significantly under consolidating hot rolling. Similar to superlasticity, these ultrafine grains promote an operation of grain-boundary sliding during hot working.[13] Figures 5 through 7 suggest that in such conditions, the final microstructure is characterized by a random distribution of grain-boundary misorientations, as well as a near random texture evolution.

V. CONCLUSIONS

The microstructure developed by mechanical milling followed by consolidating hot rolling was studied in iron powder with various oxygen contents. The main results can be summarized as follows.

1. An increase in the amount of oxygen from 0.2 to 0.6 mass pct leads to a decrease in the final average grain size from 0.7 to 0.35 μm evolved by the processing. Increasing the oxygen content further to 1.5 pct results in the evolution of ultra-fine-grained microstructure with equiaxed grains of about 0.2-μm size.
2. An average grain-boundary misorientation gradually increases with oxygen content. The grain-boundary misorientations evolved in the sample with 0.2 pct oxygen show a high fraction of low-angle boundaries, which are developed during consolidating processing. The fraction of low-angle boundaries drops rapidly by increasing the oxygen content, leading to a near random distribution of grain-boundary misorientations in the 1.5 pct O sample.
3. The consolidating rolling of mechanically milled iron results in the evolution of a strong crystallographic texture. The ultra-fine-grained microstructure with the high-angle grain boundaries that developed in the 1.5 pct O, however, can be characterized by a randomization of the crystallographic texture.
4. The strengthening of iron by increasing the oxygen content, as obtained under the present processing method, obeys the Hall–Petch relationship regardless of some differences in the grain-boundary characteristics.

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