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Ultra Grain Refining of Iron Using Mechanical Milling Technique

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SYNOPSIS

Mechanical milling treatment of iron powder was applied as the technique to charge an extremely large strain into iron matrix. Milling treatment using high energy vibration ball mill enable a significant work hardening of iron to Hv950 after a long time milling, whereas the maximum hardness achieved by conventional cold-rolling process for bulk iron is small as Hv280. For the mechanically milled iron powder with the hardness Hv950, the grain size is refined to several tens nm due to super heavy deformation through mechanical milling. On the annealing of this mechanically milled powder, it was confirmed that softening occurs not through the well-known recrystallization process but through gradual grain growth of such fine grains. The hardness of iron powders yields the Hall-Petch relation to the grain size, in the case they do not have substructures within each grain such as dislocation cells and subgrains. Mechanically milled iron powder can be consolidated to the bulk with full density at the low temperature of 923K and the grain size is kept at about 0.2 μ m due to the grain boundary pinning effect of finely dispersed oxide particles. 0.2% proof stress of this bulk iron is increased to about 1.6GPa by grain refining strengthening. The behavior of grain refining strengthening is identical in both steels of fcc and bcc structure regardless of the crystal structure.

KEY WORDS

iron powder, mechanical milling, work hardening, ultra grain refining, Hall-Petch relation

1 Introduction

Mechanical milling is a useful technique for charging a large strain into metals because there is no dimensional restriction as far as using powders. In many metallic powders; a plain iron¹⁻³⁾, Fe-Cu⁴⁾, Fe-C⁵⁾ and Fe-Y₂O₃⁶⁾ system, microstructural changes have been investigated in relation to the mechanical milling process. The results of these investigation have pointed out marked grain refining to the level of nanosize. For example, mechanical milling of the mixture of iron and copper powders finally results in the formation of nanosized grains of 6~20nm simultaneously with the formation of supersaturated solid solution⁴⁾. The volume energy stored as grain boundary energy is estimated to be several kJ/mol in the case of grain size; 10nm, while the strain energy introduced by conventional rolling process is much smaller than the above grain boundary energy stored⁷⁾. This means the difficulty of ultra grain refining by conventional mechanical heat treatment. In this paper, work hardening behavior during mechanical milling was examined in connection with the microstructural change in mechanically milled iron powders

in order to clarify the mechanism of extreme large work hardening. And softening behaviors of mechanically milled iron powders on annealing have also discussed to make sure the relationship between hardness and grain size in the annealed iron powders. Finally, the mechanical properties of bulk iron which has fabricated from the mechanically milled iron powder, was introduced in terms of Hall-Petch relationship.

2 Experimental Procedure

The material used in this investigation is a commercial reduced iron powder (KIP255M, -100mesh produced in Kawasaki steel Co. Ltd.). The powder (0.75kg) was put into a stainless pot with steel balls (SUS304, 15mm in diameter) and then sealed under Ar gas atmosphere. The ball/powder weight ratio was 12. Mechanical milling treatment was performed with a high energy vibration ball mill up to 720ks (200h). The powder of the particle size under 75 μ m (-200mesh) was separated from the mechanically milled powder and provided further examinations (the collection rate; 80~90%). The chemical

composition of iron powders is shown in Table 1. The as-received iron powder originally contains 0.2% of oxygen as the oxide such as SiO_2 etc. and the oxygen content increases to 0.47% after 720ks milling treatment due to the contamination from atmosphere.

Consolidation of mechanically milled iron powder was performed by hot-rolling for canned powder. First of all, iron powder was put into a stainless steel tube of 16mm diameter and then the steel tube was sealed by electric welding in vacuum after the degassing treatment of 873K–1.8ks. The sealed steel tube was heated to 923K and then rolled to 1.5mm thickness at this temperature to consolidate the iron powder within the steel tube. This process is named as MMC (Mechanical Milling and Consolidation) process. The bulk iron obtained was machined to the tensile test pieces with the gauge dimension of 10mm length and 5mm width. Tensile test was carried out at the crosshead speed of 0.02mm/s at room temperature.

Grain size was measured mainly by X-ray technique based on the Hall's method⁹ for the iron powders with ultra fine grained structure ($<0.1\mu\text{m}$) and partially by transmission electron microscopy (TEM). For specimens with larger grain size, TEM and optical microscopy were applied for the measurement of grain size. The thin foil specimens for TEM observation were prepared by twin-jet polishing method under the following conditions; an electrolytic current of about 90mA in the electrolyte solution of 10% perchloric acid and 90% acetic acid. X-ray diffraction was performed by using cobalt as the target at an acceleration voltage of 45kV and a current of 60mA. Hardness was represented by the average of eight measurement in micro-Vickers hardness test (load; 0.245N). Iron powders buried in an epoxy resin were polished with buff and polishing ceramic paste, and then subjected to hardness testing.

3 Experimental Results and Discussion

3.1 Work hardening during mechanical milling and softening on annealing

Fig.1 shows the change in hardness of iron powder with mechanical milling. The hardness level achieved by conventional cold-rolling for iron sheet was displayed for reference. It should be emphasized that the work hardening achieved by conventional cold-rolling technique just

corresponds to an initial stage of the latent work hardening which iron has, and that iron can be hardened ultimately to Hv950 through severe deformation. It has already confirmed that the hardening to around Hv600 is reasonably explained by the increase in dislocation density based on "dislocation strengthening", while the hardening above Hv600 is achieved through the contribution of "grain refining strengthening"⁸. For instance, the grain size of iron powder with the hardness Hv950 was evaluated at about 25nm from X-ray diffraction analysis⁸. Annealing of these mechanically milled iron powder makes clearer the difference of strengthening mechanism in the early and latter stage of work hardening. Fig.2 displays the softening behavior of mechanically milled iron powders with different initial hardness. The softening behavior of cold-rolled iron sheet is also shown for reference. The abrupt softening at around 800K is due to the recrystallization of deformed ferrite matrix. In the case the initial hardness of mechanically milled iron powder is not so high (Hv470), the softening by recrystallization is also visible at around the same temperature. However, it should be noted that the hardness is kept high enough even after the recrystallization (Hv300 as to 1000K annealing), because the grain size of recrystallized ferrite is kept to be sufficiently small to contribute to the hardness. At the higher temperature above 1000K, normal grain growth occurs and this results in the gradual softening to around Hv100. On the other hand, iron powder hardened to Hv950 undergoes a completely different softening behavior. The softening is characterized with a gradual and continuous curve to annealing temperature. The softening at around

Fig.1 Change in hardness of iron powder with mechanical milling. In order to increase the work hardening efficiency, the ball/powder ratio was set at 20 only in this case.

Table 1 Chemical compositions of iron powders (mass%).

	C	N	Cr	Si	Mn	P	S	O
as-received	0.007	0.001	0.03	0.04	0.24	0.006	0.005	0.20
720ks MM	0.012	0.003	0.05	0.05	0.26	0.006	0.008	0.47

800K is not so significant anymore in the overall softening behavior, if it has occurred on the annealing. This suggests that the softening of iron powder with ultra fine grained structure is simply caused through the normal grain growth. In order to make this issue clear, it was tried to plot the hardness of iron powder to the grain size. Fig.3 represents the Hall-Petch plot for the materials examined in this investigation. The data reported by K.Hayashi et al.⁹⁾ is also drawn in this figure. It is clear that the data of iron powders locate on an identical linear line, in the case they does not have substructures such as subgrains or dislocation cells within the grains, while the data locate under the line in the case of having substructures. This means that substructures does not directly contribute to the strengthening in terms of grain refining strengthening. The boundary of such substructures is essentially of low angle, hence the boundary of substructures should be greatly different from high angle boundary of usual grains in the interaction to piled up dislocations. In the other words, this result points out the importance of high angle boundary on the mechanism of grain refining strengthening. K.Hayashi et al. have fabricated the ultra fine grained bulk materials through the technique of the consolidation of ultra fine powders. In this case, the grain boundary within the bulk materials is substantially of high angle. Here, it should be noted that the data of K.Hayashi et al. also follow the same line obtained in this investigation. This must demonstrate the reliability of the Hall-Petch relationship drawn in this figure.

3.2 Mechanical properties of bulk iron fabricated from mechanically milled iron powder

The result of Fig.2 also suggests that the temperature around 1000K is low enough for keeping ultra fine grained structure in mechanically milled iron powder. Thus, if the iron powder with nanosized grains could be successfully consolidated, bulk iron with ultra fine grained structure ought to be obtained. In fact, bulk iron with full density was fabricated by MMC process using hot-rolling at the temperature above 923K. Fig.4 shows a typical TEM image of the bulk iron consolidated at 923K. The grain size is kept at about $0.2\mu\text{m}$ after the consolidation, and the hardness is also kept at the high level of Hv570, as previously expected. It should be found here that very small particles (10~20nm in diameter) exist in the dark field image (the photograph (b)). These particles were identified as Fe_3O_4 and the volume fraction was estimated at about 3vol%. The size and the volume fraction of the oxide is seemed to be enough for keeping the ferrite grain size; $0.2\mu\text{m}$ through the Zener's pinning effect. It has been confirmed that a lot of Y_2O_3 once decompose during mechanical milling treatment, and then again precipitates on the heating to the consolidation temperature⁹⁾. Thus, it is reasonably expected that the oxide particles; Fe_3O_4 have also been formed in the same way. Without the oxide particles, the nanosized grains within mechanically milled iron powder should undergo very fast grain growth on the heating for consolidation. In this sense, the oxide particles play an important role in the

Fig.2 Change in hardness of mechanically milled iron powder as a function of annealing temperature. Annealed at selected temperatures for 1.8ks and then subjected to hardness testing at room temperature.

Fig.3 Relation between ferrite grain size and hardness in iron powder. On the samples with substructures (subgrains or dislocation cells) within ferrite grains, data are plotted as a function of the size of such substructures. K.Hayashi et al. have obtained the bulk iron by sintering of fine iron powder⁹⁾.

fabrication of ultra fine grained bulk iron, hence the materials with such a microstructure may be called as Ultra Fine-grained Oxide-dispersion steels (UFO steels).

Even in the UFO steels, grain growth gradually proceeds during annealing and resulting in the continuous softening, as shown in Fig.2. The nominal stress-strain curves of UFO steels with different grain sizes are displayed in Fig.5. 0.2% proof stress is increased to about 1.6GPa by the grain refining to 0.18 μm but the material has no uniform elongation anymore. The strength is eight times as large as that of commercial pure iron. With enlarging the grain size, the proof stress is lowered and uniform deformation becomes to appear (See the curve of $D=1\mu\text{m}$). However, extreme grain growth to 10 μm leads to the occurrence of heterogeneous deformation just after yielding. This is likely suggesting that strengthening mechanism changes with the grain growth. Fig.6 is a schematic illustration showing the relationship between the grain size and the dispersion of oxide particles. In the case the grain size is small enough to the oxide dispersion, most of oxide particles are thought

to be on grain boundaries (the model (a)). With increasing the grain size, some oxide particles are taken in the grains (the model (b)) and finally the grain size becomes large

Fig.5 Nominal stress-strain curves of bulk iron with different grain size. Grain size was controlled by the annealing after the consolidation at 923K.

Fig.4 Transmission electron micrographs of the bulk iron (Hv570) fabricated from mechanically milled iron powder: After 720ks mechanical milling, the powder was consolidated at 923K. Bright field (a) and dark field image (b).

Fig.6 Schematic illustration showing the relationship between grain size and the dispersion of oxide particles.

enough in comparison with the dispersion of oxide particles (the model (c)). In the model (a), the strength of materials should depend on the grain size (grain refining strengthening), while in the model (c), it should be determined depending on the dispersion of oxide particles (dispersion strengthening). The model (b) shows a critical situation between the model (a) and (c). For instance, the material ($D=10\mu\text{m}$) in Fig.5 seems to have the microstructure modeled by (c) but the other materials ($D=1\mu\text{m}$ or under) must have that modeled by (a).

Fig.7 shows the Hall-Petch plot of 0.2% proof stress on the bulk iron fabricated by MMC process. The data of an austenitic stainless steel, which has an ultra fine grained structure¹⁰, are also plotted in the figure. It is surprising that both groups of data are on a identical linear line. The hardness of bulk iron is confirmed to be exactly around the Hall-Petch line shown in Fig.3. The direct plot of the proof stress to the grain size is shown in Fig.8. The limit of grain refining achieved by industrial processes is around $5\mu\text{m}$. This graph indicates that further grain refining below $5\mu\text{m}$ is very effective for increasing the strength of steels, especially in the grain size range under $1\mu\text{m}$. But it also suggests the difficulty of ultra grain refining to the range of submicrons by conventional grain refining technique. In this sense, the word of "ultra fine grains" should be defined as the grains under $1\mu\text{m}$.

4 Conclusion

(1) Extreme large strain can be introduced into iron powder

Fig.7 Relation between grain size and 0.2% proof stress in steels with ultra fine grained structure. On the austenitic stainless steel, the ultra grain refining has been realized by using the technique of reversion of deformation induced martensite in a metastable austenitic stainless steel¹⁰.

through mechanical milling treatment and this results in a significant work hardening to Hv950. The work hardening above Hv600 is achieved by the contribution of grain refining to several tens nm.

- (2) Mechanically milled iron powder can be consolidated to the bulk with full density at the low temperature of 923K and the grain size is kept at about $0.2\mu\text{m}$ due to the grain boundary pinning effect of finely dispersed oxide particles. 0.2% proof stress of this bulk iron is increased to about 1.6GPa by grain refining strengthening. This is eight times as large as that of commercial pure iron.
- (3) The behavior of grain refining strengthening is identical in both steels of fcc and bcc structure regardless of the crystal structure.

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Fig.8 Relation between grain size and 0.2% proof stress in the bulk iron fabricated in this study.

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