Microstructural Changes during Annealing of Work-Hardened Mechanically Milled Metallic Powders (Overview)

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The behavior of work-hardening which occurs during mechanical milling (MM) treatment in metallic powders, and the process of recovery and recrystallization which occurs during annealing in the MM powders were over-viewed showing the results obtained by the authors using an industrial pure iron powder. Through the MM treatment, metallic powders stores extremely large strain energy, and this results in the marked work-hardening and the formation of a fine structure with nanocrystalline grains. In the case of iron, the hardness of powder can be increased to DPH1024 in practice, and the crystalline grain size is to be reduced to the limiting value of 3.4 nm in principle. The polycrystallization of dislocation cells and subgrains also proceeds on the grain refining process. When the MM powders are annealed, the powders undergo different microstructural changes depending on the degree of work-hardening subjected by the prior MM treatment. In the case that powders are not work-hardened so much, usual recovery and recrystallization occur with raising annealing temperature. However, when powders are extremely work-hardened to the level where crystalline grain size nearly reaches the limiting value, only the process of normal grain growth occurs during annealing and this results in the softening of MM powders. Under the usual milling conditions, the degree of work-hardening of powders is in the middle stage, so that both of the above two processes are possible with overlapping each other. It was confirmed in both of MM iron powders and annealed iron powders that the relation between hardness and polycrystalline grain size gives a good fit to the Hall-Petch relationship in a wide grain size range up to 6 nm. In addition, some examples are introduced at the end, in order to excellent properties of materials produced from MM powders.

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I. Introduction

Mechanism of strengthening in metallic materials is classified to work-hardening, solid-solution strengthening, dispersion strengthening (including precipitation hardening) and grain refining strengthening. Of these mechanisms, grain refining is most useful technique for the strengthening of steels, because the ductility and toughness of steels are not reduced so much and the grain size of steels can easily be controlled through a simple heat-treatment and thermo-mechanical heat treatment. Steels are characterized by having many kinds of phase transformation, and the combination of deformation and phase transformation makes a more effective grain refining possible. For instance, the reversion of martensite induced by cold-working in metastable austenite results in the formation of very fine austenite grains of under $1\text{ }\mu\text{m}$.⁽¹⁾ The value of 0.2% proof stress of austenitic steels increases with grain refining to $0.5\text{ }\mu\text{m}$ on the Hall-Petch relationship, as shown in Fig. 1.⁽²⁾ In the grain size range below $0.5\text{ }\mu\text{m}$, 0.2% proof stress deviates from the Hall-Petch relationship probably due to the presence of subgrains⁽²⁾, and it has already pointed out that the low-angle boundaries such as subgrain boundaries does not contribute so much to the strengthening in terms of grain refining strengthening⁽³⁾⁽⁴⁾. The grain size obtained by the reversion treatment of deformation induced martensite

becomes smaller with increasing the amount of cold-working subjected to metastable austenitic steels⁽¹⁾, but grain refining in bulk materials is limited to the scale of submicrons because of the limitation of cold-working given by conventional rolling.

In the technique of mechanical milling (MM) of powder, however, extremely large strain can be stored within powder particles by the MM treatment. In many metallic powders like a plain iron⁽⁵⁾⁻⁽⁷⁾, Fe-Cu alloy⁽⁸⁾ and Fe-C

Fig. 1 Relation between 0.2% proof stress and crystalline grain size in a metastable austenitic stainless steel. Fine grains of $0.2\sim 0.5\text{ }\mu\text{m}$ was obtained by the reversion of deformation induced martensite, and grain size is controlled by annealing at elevated temperatures.

Fig. 2 Illustration of the consolidation process of mechanically milled powders and heat treatment of compacted materials.

alloy⁽⁹⁾, it has already been known that large strain stored during milling makes possible the formation of not micron-sized but nano-sized grains through the process of forging, fracture and agglomeration of powder particles. For example, in supersaturated Fe-Cu alloys produced by mechanical alloying from elemental crystalline powders, the deformation by milling reduces the grain size of alloys to 6–20 nm⁽⁸⁾. The energy stored in powder was estimated at 14 kJ/mol in an Fe-40 at% Cu alloy⁽⁸⁾. This value is extremely larger than the strain energy stored by conventional cold-rolling (~ 0.1 kJ/mol)⁽¹⁰⁾. The use of this large energy will surely enable a marked development in the strengthening of steels and lead to a breakthrough of the strength limitation which could not be surmounted in bulk materials produced by the conventional melt-casting process.

On the powder metallurgy, however, there is a troublesome problem on the consolidation of powder. Especially, the powder with MM treatment are too hard to get green compacts by the usual die-compaction, therefore, a special technique such as extrusion and hot-press is required for the consolidation of MM powder. An example of the treatment process of MM powder is given in Fig. 2. The application of superplasticity to the consolidation⁽¹¹⁾ of MM powder is one of the most interesting subjects, although the subject is not discussed here. In this paper, the behavior of work-hardening during milling and the process of recovery and recrystallization was over-viewed for many kinds of metallic MM powders, with showing the data obtained by author *et al.* in an industrial pure iron powder.

II. Microstructure of Metallic Powders Work-Hardened by Mechanical Milling

The behavior of work-hardening of metals is generally explained by the decrease in mobility of dislocations attributed to the formation of dislocation cells, and in a fine wire steel, work-hardening is confirmed to proceed through the refining of dislocation cells even in the range of heavy cold-working above 90% reduction in area⁽¹²⁾. In the process of mechanical milling of powder, however, it is found that extremely large work-hardening

can take place^{(13)–(15)} and that nanometer-sized grains (not dislocation cells) are formed after a long milling treatment with a high energy ball-mill⁽¹⁶⁾. Figure 3 represents a relation between milling time and Vickers hardness in a industrial pure iron powder milled with a high energy planetary ball-mill. In the figure, the degree of work-hardening achieved by conventional cold-rolling is also illustrated for a 98% cold-rolled bulk iron. The value of 98% reduction in area was the maximum achieved by the rolling-machine used, and the amount of cold-working surely falls under the category of heavy cold-working in the field of bulk materials, nevertheless hardness of the heavily cold-rolled bulk iron is as small as HV280. On the other hand, hardness of the iron powder with MM treatment increases greatly with elongated milling time, and finally reaches the level of around HV950, which would not be achieved by the conventional rolling technique. The contamination from balls and pots was so small even after a long MM treatment that the influence of contamination on hardness of MM powder was thought to be negligibly small. This figure means that the category of heavy cold-working in bulk materials is just corresponding to the initial stage of work-hardening in the MM process of powder.

It is experimentally known that heavy cold-working of metals causes a broadening of X-ray diffraction peaks, and the X-ray peak broadening is thought to arise mainly from the effective size of crystalline grains (including dislocation cells and subgrains) and local strain (localized elastic strain in the matrix)⁽¹⁷⁾. Hall *et al.* suggest that, in a plot of $(\sin \theta / \lambda)$ vs $(\beta \cos \theta / \lambda)$ for X-ray diffraction peaks, the slope of the straight line plot gives the local strain while the intercept gives the contribution of the crystalline grain size to the peak broadening⁽¹⁸⁾. In practice, this Hall's method is tried in a couple of MM powders, and the crystalline grain size and the amount of local strain are adequately estimated in the MM powders used⁽¹⁹⁾. The results obtained by the Hall's method for an

Fig. 3 Change in hardness of iron powder with mechanical milling using a high-energy planetary ball mill. The increment of hardness by 98% cold-rolling is shown in the figure for a bulk iron produced by the conventional melt-casting process.

MM iron powder are shown in Fig. 4, as a function of Vickers hardness of the powder. As hardness of the MM powder is increased, the amount of local strain also increases and the crystalline grain size is reduced to around 20 nm. It should be noted here that local strain tends to be decreased again in the range of very high hardness of HV800~1000. Such a curious change in the amount of local strain has already been reported in other MM powders; an Fe-Cu system alloy⁽⁸⁾ and an AlRu intermetallic compound⁽²⁰⁾. By means of transmission electron microscopy (TEM) and X-ray diffraction analysis for an MM iron powder, Jang and Koch⁽⁵⁾ investigated the evolution of a dislocation cell structure into a nanocrystalline grain structure, and indicated that the dislocation cell structure becomes finer with longer milling time and that the size of dislocation cell was finally reduced to 10 nm. However, the boundaries of dislocation cells is still of low angle. After further milling treatment, the cell structure exhibits a marked change in the misorientation angles between cells, although the change in cell size is just a little. Bodart *et al.*⁽²¹⁾ examined the change in the TEM microstructure of a Fe-Cr-Ti-Mo ferritic alloy powder with MM treatment, and indicates that the microcrystallization accompanied by the change in diffraction pattern from dispersed spots to ring spots proceeds with the morphological change from elongated grains to equiaxed grains in the latter milling stage. This suggests the possibility of grain boundary sliding in the latter milling stage, where the size of dislocation cells and subgrains is nearly reduced to a limiting value which depends on the kind of materials.⁽¹⁶⁾⁽²²⁾ In iron, the size of crystalline grains is to be refined to 3.4 nm in principle⁽²²⁾. The use of a very strong high-energy ball mill makes the ultra grain refining up to 6 nm possible, and the hardness of the iron powder is increased to HV1900 (converted by author *et al.* from the DPH hardness number 1024), in practice⁽⁵⁾. When the size of crystalline grains is refined to the limiting value, it is supposed that there will be no dislocation pile-up within a grain, and that the Hall-Petch relationship will break down⁽²²⁾. Therefore, the grain size of 6 nm and the hardness of HV1900 are thought to reach almost the limiting value obtained in pure iron by cold-working.

Although the mechanism of above microcrystallization (referred as “polycrystallization” in the present paper) should be discussed furthermore, it is sure that crystalline grains bounded by low-angle boundaries (dislocation cells and subgrains) changes to polycrystalline grains bounded by high-angle boundaries. The amount of local strain seems to be gradually reduced with the progress of polycrystallization. Figure 5 is a TEM photograph of an MM iron powder hardened to HV950. Milling time is not long enough to complete the full polycrystallization, but very small particles of 20~50 nm are found in the TEM image. Although most of these particles may be subgrains or dislocation cells, a diffraction pattern taken from the observed area indicates that there are some polycrystallized grains with different crystallographic orientation within the MM iron powder. The grain size obtained by the Hall’s method in X-ray diffraction analysis is

Fig. 4 Changes in local strain and crystalline grain size obtained by the Hall’s method in X-ray diffraction analysis, as a function of Vickers hardness of iron powders with mechanically milling treatment.

Fig. 5 Transmission electron micrograph of a iron powder work-hardened to HV950 by mechanical milling treatment. The diffraction pattern was taken from the observed area.

around 30 nm, so that the result of TEM observation demonstrates the reasonableness of the Hall’s method for the measurement of small crystalline grains.

III. Evaluation of Strain Stored in Mechanically Milled Powder

Wire drawing is the most effective technique for giving

large strain into bulk materials. In wire materials drawn up to around 99% reduction in area, there is a good linear relationship between the strength of materials and true strain⁽²³⁾⁽²⁴⁾. For instance, Langford and Cohen⁽²⁴⁾ report the value of 15.6 kg/mm² (153 MPa) per unit strain as the strain-hardening rate between 1 and 7 in true strain (63.2% and 99.91% reduction in area) for iron wires. Vickers hardness number of iron and steel materials is given by a three times large value as the tensile strength (kg/mm²)⁽²⁵⁾, so that the strain-hardening rate is estimated at HV45 per unit strain in terms of Vickers hardness. The estimation of strain from the hardness of MM iron powders is not accurate strictly, but the strain subjected to an MM iron powder with the hardness of HV950 is roughly estimated at about 20 in true strain. When an iron powder is cold-worked to the level of HV1900⁽⁵⁾, the true strain is estimated at about 40 (99.999999999999% reduction in area). Shingu⁽²⁶⁾ demonstrates in experiment that mechanical alloying of metallic powders can take place by the method of repeated cold-rolling and bending, as well as the technique of high energy ball milling. When the reduction of 50% in area is subjected to a material at one time, the repetition of 25 times and 50 times results in the accumulation of extreme large strain of 20 and 40 in true strain, respectively. This means that, when the process of forging, fracture and agglomeration of powder particles are repeated only several-tens times in a milling pot, powder is easily work-hardened up to the hardness level of HV1000~1900.

IV. Recovery and Recrystallization of Mechanically Milled Powder

The annealing process of work-hardened metals is divided to four stages of recovery, recrystallization (first recrystallization), normal grain growth and secondary recrystallization in order from lower temperature side. Recovery is accompanied by the relief of local strain and the decrease in dislocation density. Recrystallization proceeds through the nucleation and growth of fresh grains without strain which are bounded by high-angle (high-energy) boundaries. After the full recrystallization, normal grain growth arises in order to reduce the total grain boundary energy in a unit volume. Secondary recrystallization is also one kind of grain growth in polycrystalline grains, but it is distinguished from the normal grain growth in terms that only a few grains with a nature of easy grain growth undergo an abnormal growth with making inroads into the other small grains. In metallic powders with MM treatment, the crystallization process of amorphous is frequently discussed in relation to the chemical free energy change⁽²⁷⁾⁽²⁸⁾, but the process of recovery and recrystallization in extremely work-hardened metals is not cleared enough yet. Heavy cold-working to bulk metal is not so easy that a metallic powder produced by filing has often been used for the research on recovery and recrystallization of extremely work-hardened metals. For instance, the results obtained by Averbach *et al.*⁽²⁹⁾ is as follows: By means of X-ray diffrac-

tion analysis, calorimetric analysis and hardness measurement in a filed Au-25 mass%Ag alloy, they suggest that most of stored energy is associated with the presence of low-energy (low-angle) boundaries introduced during the deformation and that the contribution of elastic energy arising from local strain is a little. When the powder with heavy cold-working is annealed, a substantial relief of the local strain and a slow growth of crystalline grains occur during the recovery process, and then low-energy boundaries are eliminated during the following recrystallization process. Figure 6 represents the variations of hardness with annealing in MM iron powders with the different initial hardness of HV340 through HV950. The data of a heavily cold-rolled bulk iron (initial hardness; HV280) is shown in the figure for reference. In the cold-rolled bulk iron, the softening at around 800 K was confirmed to be due to recrystallization. Since the iron powder of HV340 is work-hardened to the same hardness level by MM treatment, softening of the powder almost follows the same way as the cold-rolled bulk iron. In the iron powder of HV470, no hardness change occurs from room temperature to 700 K and then two softening stages appear: One is the softening between 700 and 900 K, and the other is above 900 K. With the increase in the initial hardness of MM iron powders, the step in hardness change at around 900 K tends to disappear. The softening of extremely work-hardened iron powder (HV950) is characterized by the continuous decreasing in hardness in the wide temperature range from 600 K to 1200 K. Figure 7 shows the changes in crystalline grain size and local strain of an MM iron powder (initial hardness; HV470), as a function of annealing temperature. Below 700 K, there is no change in the size of crystalline grains but local strain is almost eliminated before reaching 700 K. The comparison of the change in local strain with the hardness variation in the Fig. 6 makes it clear that local strain does not affect the hardness of iron powder so much. Above 700 K, an abrupt grain growth is caused by

Fig. 6 Changes in hardness of iron powders hardened to several hardness levels by mechanical milling, as a function of annealing temperature. The hardness change of a bulk iron with 98% cold-rolling is also shown for reference.

Fig. 7 Changes in local strain and crystalline grain size obtained by the Hall's method in X-ray diffraction analysis, as a function of annealing temperature in a mechanically milled iron powder (HV470).

Fig. 8 Changes in local strain and crystalline grain size obtained by the Hall's method in X-ray diffraction analysis, as a function of annealing temperature in a mechanically milled iron powder (HV950).

recrystallization, and this probably leads to the first softening between 700 and 900 K in the hardness change. The following softening above 900 K is supposed due to the normal grain growth. The mechanism of grain growth is apparently different between recrystallization and normal grain growth, so that it is not strange that two steps of hardness change are found in the softening behavior. While, on the extremely work-hardened iron powder (initial hardness; 950), the changes in crystalline grain size and local strain are also shown in Fig. 8, as a function of annealing temperature. This figure indicates that crystalline grains gradually grow even in the low temperature range below 700 K where local strain is relieved. Since the presence of local strain scarcely affect the hardness of iron powder, the slow softening in the temperature range below 700 K is concluded due to the growth of crystalline grains (dislocation cells and subgrains). The abrupt decrease in local strain at around 800 K is likely caused by recrystallization. After the complete relief of local strain, crystalline grains make a rapid growth, but it

Fig. 9 Transmission electron micrographs of a bulk material produced from mechanically milled iron powder. Bright field (a) and dark field (b) images, and diffraction pattern (c) taken from the observed area. Iron powder was work-hardened to HV950 by mechanical milling treatment and compacted to a bulk at the pressure of 4 GPa, and then sintered at 823 K for 1.8 ks. The specimen used was prepared from the sintered bulk material.

should be noted that the grain size vs annealing temperature curve shifts toward higher temperature side in comparison with the Fig. 7. Figure 9 represents TEM images of a bulk material produced from an MM iron powder: The MM iron powder work-hardened to HV950 was compacted at the pressure of 4 GPa, and then the green compact was sintered at 823 K for 1.8 ks in hydrogen gas atmosphere. Specimens for TEM observation was prepared from this sintered bulk material. Bright (a) and dark field (b) images show the existence of very small grains of 20~100 nm. Average grain size measured by the Hall's method was about 50 nm. Diffraction pattern (c) indicates that a lot of grains with different crystallographic orientations are formed at random. Although a small amount of local strain retained under the annealing condition of 823 K-1.8 ks, we could frequently find

Fig. 10 Illustration showing the microstructural changes of metallic powders during mechanical milling and of the mechanically milled powders during annealing.

fresh grains without dislocation. Therefore, it is sure that recrystallization starts before completing the elimination of local strain and that the relief of local strain is accelerated owing to recrystallization.

Figure 10 illustrates the change of microstructure during mechanical milling and annealing of MM powders. At the initial stage of MM treatment, iron powder is work-hardened by the formation of dislocation cells. Further MM treatment arises an extreme work-hardening through the ultra refining of dislocation cells, and this process accompanies a great increase in the amount of local strain. On the process, dislocation cells might gradually change to subgrains. When the size of dislocation cells and subgrains reaches a critical size (around 20 nm for iron) and grain refining becomes harder, polycrystallization by grain boundary sliding starts. At this point, local strain will be saturated at all. During a further MM treatment, grain size is gradually reduce to the limiting value (3.4 nm for iron), and full polycrystallization will be achieved finally. Local strain will be decreased again during the process of polycrystallization. While, on the annealing of MM powders, the changes of microstructure are different depending on the degree of work-hardening. When the microstructure is of dislocation cells, recovery accompanied by the relief of local strain takes place at the beginning of annealing. There is no change in hardness and crystalline grain size at this stage, but most of dislocation cells change to subgrains. At the second stage, recrystallization proceeds by forming fresh grains bounded by high-energy boundaries while low-energy boundaries are eliminated on the process. Rapid

grain growth is caused through recrystallization and this results in an abrupt softening. Polycrystalline grains formed after the full recrystallization undergo a normal grain growth, and this leads to a slow softening. On the other hand, in the case that iron powder is sufficiently mechanically-milled to have the limiting grain size, only normal grain growth occurs from beginning because crystalline grains have already been polycrystallized during the prior MM treatment. In general, the milling condition of MM powders is between above two stages, both of these two processes will take place with overlapping each other.

V. Discussion on the Hall-Petch Relationship

Strength of polycrystalline materials is known to obey the Hall-Petch relationship in terms of grain refining strengthening. The grain size d discussed in bulk materials is usually in the range of $100 \sim 10 \mu\text{m}$ ($3 \sim 10$ in d (mm) $^{-1/2}$; root- d number). Recently, grain refining up to $0.2 \mu\text{m}$ has been achieved in metastable austenitic steels, and it is demonstrated that there is the Hall-Petch relationship up to the grain size of $0.5 \mu\text{m}$ (45 in root- d number) to 0.2% proof stress⁽²⁾. In the grain size range below $0.5 \mu\text{m}$, the Hall-Petch relationship is broken down owing to the presence of many subgrains. Further grain refining is not so easy in bulk materials, but by the technique of powder metallurgy using a ultra fine iron powder, Hayashi and Kihara⁽³⁰⁾ indicates that there is a clear Hall-Petch relationship up to the grain size of about $0.15 \mu\text{m}$ (82 in root- d number) to Vickers hardness. Jang and

Fig. 11 Relation between Vickers hardness and crystalline grain size in iron. The data obtained by author *et al.* and the other researchers are summarized.

Koch⁽⁵⁾ point out that the hardness vs grain size data gives a good fit to the Hall-Petch relationship in the grain size range of 8.5 ~ 6 nm (350 ~ 400 in root-d number), when the nanocrystalline grains are clearly random in the crystallography. The data of Vickers hardness vs root-d number are summarized in Fig. 11. Data of Jang are converted to Vickers hardness from the DPH hardness number, and the data obtained by author *et al.* are also plotted in the figure. It is very interesting that all of data (excepting subgrains and dislocation cells) are almost on the same linear line in the wide grain size range, although samples are prepared in various ways and the data are obtained by different researchers. Consequently, it is probably that the strengthening of polycrystalline materials by grain refining is substantially possible to the limiting grain size on the basis of the Hall-Petch relationship, as far as specimens are composed of only polycrystalline grains bounded by high-energy boundaries.

VI. Conclusion

Refining of microstructure is one of the most attractive points in MM treatment, and the practical use of MM powder is expected in the both fields of functional and structural materials. A lot of problems are still remained for the consolidation process, but there are great possibility for the use of MM powders. Figure 12 displays the microstructure of Fe-25 mass%Cu alloy consolidated from MM powder (a) and the mixed elemental powder of iron and copper (b). Although the conditions of compacting and sintering is same in both samples, the bulk material produced from MM powder has a finer microstructure and a higher density without pores. When metallic powders are subjected to MM treatment with fine dispersoid like oxide powders, fine grained structure can be kept after the consolidation at high temperature. The fine

Fig. 12 Optical microstructures of a Fe-25 mass%Cu alloy produced from a mechanically milled powder (a) and the mixed powder of elemental iron and copper (b). Powders were compacted to a bulk at the pressure of 588 MPa and then sintered at 1373 K for 3.6 ks.

microstructure contributes to superplastic deformation of bulk materials⁽³¹⁾⁽³²⁾ and improvement of high temperature creep property by using an abnormal secondary grain growth⁽³³⁾⁽³⁴⁾. Ultra grain refining by MM treatment affects the phase transformation itself due to the increase of physical driving force and the change in behaviors of elemental diffusion. In practice, it has been shown that the phase transformation from the two phases of Fe_2Si_5 and FeSi to the FeSi_2 single phase is promoted in Fe-Si alloys by MM treatment prior to annealing⁽³⁵⁾, and that the reversed massive transformation from ferrite to austenite is induced in a two-phase stainless steel powder with MM treatment⁽¹³⁾. On the property against high temperature oxidation in stainless steels, it is reported that the steel produced from MM powder has a markedly improved nature in comparison with the steels produced by the conventional melt-casting process, because the formation of excellent oxide layer (Cr_2O_3) becomes possible owing to the rapid Cr diffusion accelerated by the prior MM treatment⁽³⁶⁾. The application of MM powders to practical materials has just started recently, so that much effort should be done on the consolidation process as well as the powder making process, in order to enlarge the use of MM powders.

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