1. Introduction

Nanocrystalline materials have attracted considerable scientific interests in the past decade. Nanocrystalline materials possess fundamentally different properties and behaviors from their conventional coarse-grained polycrystalline counterparts due to the high density of grain boundaries. Various severe plastic deformation methods have been proposed to produce nanocrystalline materials, such as ball milling, severe plastic torsion straining, equal channel angular pressing and accumulative roll-bonding. Among these, extensive works have been performed on the formation of nanocrystalline structures by ball milling due to its simplicity, low cost, and applicability to essentially all classes of materials.

In our previous papers, we have reported the microstructural evolution and nanocrystallization in the carbon steels by ball milling and ball drop test. The deformation mode in a ball milling process is substantially complicated, and thus the deformation conditions to induce nanocrystallization have been unknown. The morphologies such as pearlite lamellar, spheroidite cementite, ferrite grain boundary disappeared by nanocrystallization. The hardness of the nanocrystalline region is about two times higher than that of work-hardened region. The annealing of nanocrystalline region shows substantially slow grain growth and re-precipitation of fine cementite. From the present study, it was confirmed that the deformation mode applied is substantially different.

KEY WORDS: nanostructure; nanocrystalline ferrite; carbon steel; ball milling; severe deformation.

2. Experimental Procedures

The materials used in the ball milling were Fe–0.89C (Fe–0.89C–0.25Si–0.50Mn in mass%) chips (thickness: <1 mm, length: several mm) with pearlite and spheroidite structures. Ball milling was performed using a conventional horizontal ball mill under the protection of pure Ar atmosphere with a weight ratio of ball to powder of 100:1. In the ball drop test, the bulk specimens (thickness: several mm, diameter: 15 mm) of Fe–0.89C (Fe–0.15C–0.35Si–1.24Mn in mass%, ferrite + cementite) were used. Fe–0.15C specimen with grain size about 1 μm was produced by heavy rolling (1 123 K–50%, 1 073 K–50% and 1 023 K–80%) after austenitized at 1 223 K. The production process of this ultrafine grained steel was developed in the Super Metal Project in Japan. In the ball drop test, the weight with a ball attached on its bottom was dropped from a height of 1 or 2 m onto bulk specimen with flat surface. The ball of 6 mm in diameter and the weight of 2, 4 or 5 kg were used. All tests were carried out produced by ball milling and ball drop test. The sharpness of the nanocrystalline region, deformation mode and number of deformation to produce nanocrystalline structure was discussed.
at room temperature in air. The details of the ball drop test were described in our previous paper. 15) To obtain nanocrystalline structure by one time of ball drop, specimens were cold-rolled to various reductions by multipass rolling with 20% or 25% reduction per pass before ball drop test. Ball milled powders and specimens after ball drop test were annealed at 873 K for 3.6 ks to study annealing behavior. Microstructures of ball milled and ball dropped specimens were investigated using scanning electron microscope (SEM, JEOL JSM-6300) operated at 15 kV or 20 kV and transmission electron microscope (TEM, HITACHI H-800) operated at 200 kV. Specimens for SEM observations were etched by 5% Nital. Microhardness measurement was carried out using AKASHI MVK-G1 Vicker’s hardness tester with an applied load of 0.98 N for 10 s and SHIMADZU DUH-W201S dynamic microhardness tester with an applied load of 29.4 mN for 10 s.

3. Experimental Results

3.1. Microstructural Evolution of Specimen with Pearlite Structure by Ball Milling and Ball Drop Test

Figure 1 is a SEM micrograph of the cross section of Fe–0.89C powder with pearlite structure ball milled for 360 ks. Two types of region can be seen; a dark smooth contrast region without pearlite structure near the surface of the powder and a bright contrast region with deformed structure in the interior of the powder (referred to as work-hardened region). Figure 2 shows the microstructural evolution of Fe–0.89C powder with pearlite structure by ball milling. In the early stage of ball milling (Fig. 2(a)), above two types of structures can be seen in most of powder. In the middle stage of ball milling (Fig. 2(b)), the dark smooth contrast region brakes into small pieces and the fine particles with dark smooth contrast increases. In the final stage of ball milling, all the powder becomes fine with dark smooth contrast (Fig. 2(c)). Such microstructural evolution was observed in the milled powders irrespective of the carbon content (0.004–0.89 mass% C) or starting microstructure (ferrite, martensite, pearlite or spheroidite). 11–14) It should be noted that there is a drastic difference in hardness between these two types of structures as is shown in Fig. 2(a). The microhardness of the dark contrast region near the powder surface (10.8 GPa) is almost double of that of the work-hardened region (6.5 GPa). A boundary between the dark contrast region and the work-hardened region is clearly seen. This suggesting that the hardness increase occurs discontinuously. Figure 3 is a typical TEM (bright filed (BF)) image showing the dark contrast region near the surface of Fe–0.89C powder with pearlite structure ball milled for 360 ks. Equiaxed nanocrystalline grains with average size around 20 nm are observed. (The dark contrast region is hereafter referred to as nanocrystalline region.) The selected area diffraction (SAD) rings correspond to those of α-Fe, indicates that cementite has dissolved into the nanocrystalline ferrite.

Figure 4 is a typical SEM micrograph of the cross section of Fe–0.89C specimen with pearlite structure after 8 times of ball drop with a weigh of 4 kg from 1 m height. Two types region can be seen; a dark contrast layer without pearlite structure near the surface of the specimen and a bright contrast region with deformed structure (referred to as work-hardened region) in the interior of the specimen. The dark contrast layer with a thickness of several tens micrometers is seen along the surface near the edge and bottom of the ball indentation. Figure 5 is a SEM micrograph of the cross section of Fe–0.89C specimen showing the dark contrast layer near the surface produced by ball drop test. The microhardness of the dark contrast layer is as high as 11.7 GPa, which is much higher than that of the work-hardened region (4.3 GPa). It is noted that the observed microhardness and microstructure after the ball drop test are similar to those observed in ball milled Fe–0.89C powder shown in Fig. 2(a). The microhardness of the dark contrast region in the ball milled powder (10.8 GPa) is almost same with that in ball dropped specimen. The dark contrast layer
formed by ball drop test was observed by TEM. 

**Figure 6** is TEM dark field (DF) image and SAD pattern of the specimen with pearlite structure after ball drop test. The DF image shows that the grain size is of the order of 100 nm. (The dark contrast layer in a ball dropped specimen is hereafter referred to as nanocrystalline region.) In the SAD pattern, nearly continuous rings are seen, indicating the random orientations of ferrite grains. All the diffraction rings correspond to those of the bcc ferrite and rings corresponding to cementite are hardly detected. This indicates that the cementite is mostly dissolved into the nanocrystalline ferrite. By applying prior cold rolling, the formation of nanocrystalline layer is observed even by one time of ball drop. **Figure 7** shows such an example where the specimen was cold rolled to 82% reduction and then ball dropped one time (5 kg weight, 2 m height). It is seen that nanocrystalline layer (dark contrast layer) formed symmetrically along the ball falling axis in the Fe–0.80C (Fe–0.80C–0.20Si–1.33Mn in mass%) specimen with pearlite structure.
The layer appeared along the surface of the edge of ball indentation and penetrated to the bottom surface of the specimen. Figure 8 shows a layer structure in the Fe–0.80C specimen with pearlite structure after prior cold rolling to 80% reduction and one time of ball drop (5 kg weight, 1 m height). The amount of shear strain in the layer was estimated through the equation

$$\gamma = \frac{1}{\tan(\theta)}$$

in which $\gamma$ is shear strain and $\theta$ is the angle between the directions of lamellae and layer. From the angle $\theta$ of 7°, the shear strain was calculated to be 8.1. This indicates that by ball drop test adiabatic shear bands with localized heavy shear form especially when specimens are properly predeformed. Such region become nanocrystalline structure when the degree of deformation is large enough. Figure 9 is typical SEM micrographs showing deformed nanocrystalline region in Fe–0.89C specimen with pearlite structure after 10 times of ball drop (5 kg weight, 1 m height). Figure 9(a) shows that the nanocrystalline layer with a thickness of about 10 µm is completely separated by a large shear deformation. Micro-shear bands are also observed in the nanocrystalline layer as is shown in Fig. 9(b). The distance of each micro-shear band is about 5 µm, and the nanocrystalline layer is sheared about a few micrometers at these micro-shear bands. From these observations, it is clear that nanocrystalline layer can deform by shear mode without cracks. Occasionally, cracks were observed in a deformed nanocrystalline layer, especially at specimen surface.

3.2. Microstructural Evolution of Specimen with Spheroidite Structure by Ball Milling and Ball Drop Test

Figure 10 shows typical micrographs of Fe–0.89C powder with spheroidite structure observed after ball milling for 360 ks. In Fig. 10(a), two types of structures are seen, a dark smooth contrast region (left hand side) and a deformed structure (work-hardened) region (right hand side). In a dark smooth contrast region, spheroidal cementite is hardly observed. Occasionally, three types of structures were observed as is shown in Fig. 10(b). Besides the dark smooth contrast region and deformed structure region, a region containing wavy bands is observed. The wavy band structure is observed either surface of powder or between the dark contrast region and the work-hardened region as is shown in Fig. 10(b). In the final stage of ball milling, the dark smooth contrast region breaks into small pieces and all the powders become fine (less than 10 µm) with dark smooth contrast structure. Figure 11 shows the TEM (BF) image of the boundary between the dark contrast region and work-hardened region in Fe–0.89C powder with spheroidite structure after ball milling for 360 ks. In the upper part of the picture, the layered nanocrystalline ferrite with average thickness of 10–50 nm is seen. In the lower part of the picture, some deformed grains with diameter larger than 100 nm are seen. Dislocations in the grains and some subgrain boundaries are clearly visible. The boundary between the layered nanocrystalline ferrite and the work-hardened region is sharp. The detail TEM observations on microstructural evolution of Fe–0.89C powder with spheroidite structure by ball milling were reported in our previous papers.14,16) It was found that in the early stage of ball milling
dislocation density increases and cellular structure is formed. In the middle stage of ball milling, the cellular structure changes to granular nanocrystalline structure by further deformation. Degree of deformation in nanocrystalline region might be much larger than that in work-hardened region. Together with the nanocrystalline ferrite, the dissolution of cementite was observed. In the final stage of ball milling, equiaxed nanocrystalline ferrite forms from layered nanocrystalline ferrite by increasing the local misorientation.

The typical microstructure produced by ball drop test is shown in Fig. 12. Pictures were taken from Fe–0.89C specimen with spheroidite structure after 50 times of ball drop (2 kg weight, 1 m height). The uniform structured layer is seen along the specimen surface in Fig. 12(a). The microhardness of this region is 8.8 GPa which is much higher than interior work-hardened region (5.5 GPa). The highest microhardness of the uniform structure layer in the ball-dropped specimen (after 8 times drops) was 9.6 GPa, which well correspond with that measured in the ball-milled powder in Fig. 10(b) (9.5 GPa). It should be noted that cementite particles are hardly observed in the uniform structure layer but remain undeformed in the work-hardened region. The uniform structured layer was also observed in the interior of the ball-dropped specimen as shown in Fig. 12(b). Many wavy bands parallel to each other are seen together with spheroidal cementite. The density of wavy bands near the center is higher and it looks like they coalesce with each other. The observed microstructures are quite similar to those in ball milled powder (Fig. 10(a)).

### 3.3. Nanocrystallization of Fe–0.15C Specimen by Ball Drop Test

It has been confirmed that nanocrystallization by ball milling occurs in various steels irrespective of the carbon content (0.004–0.89 mass% C) or starting microstructure (ferrite, martensite, pearlite and spheroidite). However, nanocrystallization by ball drop test is limited in high carbon steels (Fe–0.89C with pearlite or spheroidite structure). This reason is considered as follows. During ball milling of pure iron, powder particles are deformed and cold welded repeatedly. These processes produce fine grained structures (sub-micron grain size). The increase in hardness by grain refinement and reduction of particle size increases the effective strain rate during ball milling. Thus nanocrystallization occurs even in low carbon steels by ball milling. On the other hand, in a ball drop test, the plastic deformation of low carbon steels occurs in relatively large volume because of low strength and low work-hardening rate. As a result, deformation occurs under low strain rate, and the stress achieved is low since the ball-specimen contact area is large. Thus nanocrystallization is hard to occur in low carbon steels. To obtain nanocrystalline regions by a ball drop test, the initial strength of specimen is considered to be important rather than carbon content. A fine grained low carbon steel sample was chosen to examine this aspect. The specimen was Fe–0.15C specimen with about 1 μm grain size prepared by a special thermomechanical processing developed by the Super Metal Project. The initial hardenness of the specimen is 2.4 GPa which is comparable with Fe–0.89C specimen with pearlite structure (3.1 GPa) or spheroidite structure (2.0 GPa), and is much higher than Fe–0.03C steel (1.1 GPa). Figure 13 shows a cross sectional SEM micrograph of Fe–0.15C specimen after 8 times of ball drop (5 kg weight, 1 m height).
seen; dark smooth contrast area without structure and bright contrast area with deformed structure. These structures are similar to those observed in ball dropped specimens in eutectoid steels, shown in Fig. 5 (Fe–0.89C, pearlite) and Fig. 12 (Fe–0.89C, spheroidite). A drastic difference in hardness is seen between these regions. The microhardness of the dark contrast region (6.6 GPa) is almost double of that of the deformed structure region (3.9 GPa) although these values are not accurate because the indentations are too close to each other. Thus it is confirmed that nanocrystallization occurs even in low carbon steels by ball drop test when a specimen has a high strength and high work hardening rate.

3.4. Annealing Behavior of Specimen with Pearlite and Spheroidite Structure after Ball Milling and Ball Drop Test

Figure 14 shows typical SEM micrographs of ball milled (a) and ball dropped (b) Fe–0.89C specimens with pearlite structure after annealing at 873 K for 3.6 ks. It is seen that after annealing, the microstructures of work-hardened region (right hand side) and nanocrystalline region (left hand side) are still quite different and the boundary between these two regions is clearly seen. In the work-hardened region, the recrystallization and grain growth of ferrite took place, leading to recrystallized ferrite grains with an average size of about 0.5 μm. Simultaneously, the spheroidization of lamellar cementite resulted in spherical cementite particles with an average size of about 0.2 μm. In contrast, a much fine microstructure is seen in the prior nanocrystalline region, in which fine cementite particles re-precipitated and the ferrite grains are less than 0.2 μm.

Figure 15 shows the annealing (873 K for 3.6 ks) behavior in spheroidite structure (Fe–0.89C), (a) ball milled (360 ks) powder and (b) specimen after the case of ball drop test (5 kg weight, 1 m height, 50 times). The work-hardened region (right hand side) and nanocrystalline region (left hand side) are distinguishable and the boundary between these two regions is clearly seen. In the work-hardened region, similar recrystallization and grain growth (to about 0.5 μm) of ferrite is realized in both specimens. The annealed microstructures in the nanocrystalline region in the two speci-
mens are similar but there is some difference. In the ball milling specimen only re-precipitated fine cementite particles (<0.2 μm) are seen. While in the specimen of ball drop test, two kinds of cementite particles are seen, re-precipitated fine cementite particles (<0.2 μm) and bigger particles (>0.5 μm) which are remained as undissolved by ball drop test. The ferrite grains around bigger cementite particles are larger (about 0.5 μm) than those around fine cementite particles. This observation suggests that dissolution of cementite by ball drop test is less complete than that of ball milling.

It was noticed that the microstructure of the initial spheroidite structure is coarser than that of pearlite structure. The microstructure change from work-hardened state to nanocrystalline requires higher strain (longer milling time) in spheroidite specimen than that of pearlite. By ball milling, the nanocrystallization completed after 720 ks in the specimen with pearlite structure, while it requires about 1800 ks in the specimen with spheroidite structure.[14]

4. Discussion

4.1. Sharpness of Boundary between Nanocrystalline and Work-hardened Regions

The boundary between nanocrystalline and work-hardened regions in the ball-milled powders (Fig. 2 and Fig. 10(a)) is generally sharper than that in the ball-dropped specimens (Fig. 5 and Fig. 12(a)). The boundary in the specimen of ball drop test becomes sharper with increasing the times of drop. This reason is considered as follows. The specimen has uniform strength before ball drop test. Adiabatic shear bands form by ball drop test. The temperature at the shear band becomes higher than the surrounding matrix, and the strain concentrates at shear bands. In the subsequent ball drop, the strength (hardness) of the shear band region is much higher by nanocrystallization than that of the matrix. Thus, in the further ball drop, the strain of the matrix in the vicinity of the boundary between shear band and matrix will become large. This makes the boundary of nanocrystalline structure and matrix sharp like observed in the ball milled powder.

4.2. Deformation Mode and Strain Rate to Produce Nanocrystalline Structure

A high degree (about 8 in nominal shear strain) of shear deformation was observed in the nanocrystalline region in the specimen served for ball drop test (Fig. 8). Valiev et al.[9] reported the formation of nanocrystalline structure by torsion straining under high pressure. This suggesting that shear deformation plays important role in the formation of nanocrystalline structure. However, shear deformation was not always observed at the nanocrystalline region formed in specimens with ball drop test. For instance, nanocrystalline layer is observed several tens of micrometers beneath the surface at the bottom of the ball indentation (Fig. 4). The deformation mode of such region is not a simple shear rather uniaxial compression. In the ball milled powder, shear deformation was not observed around the nanocrystalline structure. The mode of deformation to obtain nanocrystalline structure should be studied further.

High strain rate is considered to be an important factor to produce nanocrystalline structure. The strain rate in ball milling and ball drop test is estimated to be $10^2 - 10^4$ s$^{-1}$.[15] When the sample used in the ball drop test was compressed slowly (strain rate of about 1 s$^{-1}$) with the same ball to a similar degree of deformation, nanocrystalline structure was hardly observed.[16] This confirms that high strain rate is an essential factor to form nanocrystalline structure. The high strain rate deformation has two major effects. One is induce highly localized large strain due to adiabatic deformation as is shown in Fig. 7. High degree of deformation can be obtained locally even the macroscopic degree of deformation is low. Second is that a higher strain rate deformation results in a higher dislocation density at a given degree of deformation. An increase in flow stress (equivalently dislocation density) with strain rate is reported by Chiem et al.[17] in aluminum and Lee et al.[18] in steel. Thus high strain rate deformation makes it possible to reach a critical dislocation density at which work-hardened structure changes into nanocrystalline structure.

4.3. Number of Deformation to Produce Nanocrystalline Structure

In the present ball milling experiment, the formation of nanocrystalline structure requires more than 180 ks of milling (about 285,000 rotation of vial with 1,000 pieces of ball). The numbers of ball collision to a given powder is considered to be more than several thousands times. In ball drop test, nanocrystalline structure forms even by one single drop when the specimen is properly pre-deformed. It was suggested that there is a critical dislocation density at which cellular structure changes to granular nanocrystalline structure. When the dislocation density increases, the rate of recovery increases at the same time. Thus, to reach a critical dislocation density, a high strain rate is required. In the ball milling, a large number of high degrees of deformation are occurred under high strain rate. While, in ball drop test, a small number of high degree of localized strain occurred under high strain rate.

5. Conclusions

Nanocrystallization by ball milling and ball drop test was studied. In ball milling, nanocrystalline structure can be obtained irrespective of the carbon content (up to 0.9 mass% C) and starting microstructure (ferrite, martensite, pearlite and spheroidite) although there is a difference in the required milling time. In ball drop test, nanocrystalline structure was obtained only in high strength steels such as high carbon steels or fine grained steels. The nanocrystalline structure produced by ball milling and ball drop test has essentially the same characteristics; nano-sized ferrite grains, dissolution of cementite, substantial high hardness (about 10 GPa), and without recrystallization and slow grain growth by annealing. It was expected that a large strain with high strain rate is a common deformation condition required to produce nanocrystalline structure by ball milling and ball drop test. The mode of deformation preferable for nanocrystallization is unknown although large shear deformation was observed in the nanocrystalline region produced by ball drop test.
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