Formation of Surface Nanocrystalline Structure in Steels by Shot Peening and Role of Strain Gradient on Grain Refinement by Deformation

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The amount of strain provided by shot peening (SP) was estimated by comparing the shot-peened surface structure to the cold-rolled structure. The grain size of recrystallized structure beneath the shot-peened nanocrystalline (NC) surface after annealing was similar to that of the specimen after cold-rolling (equivalent strain \( \varepsilon_{eq} = \text{ca.} 6 \)) and annealing. The \( \varepsilon_{eq} \) larger than 6 seems to be given to the surface region by SP. This strain amount is consistent with the necessary condition \( \varepsilon_{eq} \geq 7 \) to produce NC structure proposed in the previous study. The large strain gradient is also generated at the shot-peened surface. The strain gradient has been suggested as one of important factors on strengthening and on grain refinement. The deformation by SP is complex; the role of strain gradient was investigated by using high-pressure torsion (HPT) process. The maximum hardness (Hv = 5 GPa) in the Fe–0.03mass% C disk after HPT-straining was twice higher than the hardness (2.4 GPa) obtained by cold-rolling. At the center of HPT-processed disk, where shear strain is nominally zero, the hardness increased up to a saturation value of 3.3 GPa. These results in the HPT experiment show that strain gradient contributes to strengthening and to grain refinement. However, the grain refinement was saturated with around 200 nm in layered grain thickness although the HPT-processed disk was applied large strain and strain gradient. This suggests that not only strain gradient and strain but also other deformation conditions are necessary to form NC structure.

KEY WORDS: nanocrystalline structure; strain; strain gradient; severe plastic deformation (SPD); shot peening; high-pressure torsion (HPT).

1. Introduction

In the last few decades, severe plastic deformation (SPD) technique\(^1\) has been applied widely to design ultrafine-grained materials, especially nanocrystalline (NC, grain size smaller than 100 nm) materials, with improved properties due to its simplicity and applicability for all class of materials. Submicron-grained materials can be successfully produced by most SPD processes. However, NC structure can not be formed by equal channel-angular pressing (ECAP)\(^2,3\) or accumulative roll bonding (ARB)\(^4,5\) which are homogeneous deformations with large amounts of strain (equivalent strain \( \geq 5 \)). While, NC materials are obtained by non-homogeneous deformation processes with large strain gradients, such as high-pressure torsion (HPT)\(^6\), ball milling (BM)\(^7-9\) and shot peening (SP)\(^10-18\). J. G. Sevillano explained that high density of geometrically necessary dislocations is generated by applying large strain gradient and these dislocations contribute to the formation of NC structure and to the extra strengthening.\(^19\)

Shot peening, which is one of the non-homogeneous deformation process, has attracted to produce bulk materials with surface NC layer,\(^10-19\) since failure of engineering materials is strongly affected by its surface structure and properties. G. Liu \( \text{et al.} \) reported that the surface nanocrystallization by SP led to improve the tensile yield strength of Fe–0.11mass% C plates with a minimum degradation of ductility and toughness.\(^11\) It was found by Z. B. Wang \( \text{et al.} \) that the surface NC Fe–0.11mass% C steel exhibited greatly improved wear and friction properties.\(^12\) Moreover, X. Y. Wang \( \text{et al.} \) showed that the surface NC stainless steel revealed the considerably high resistance to corrosion, wear and corrosive wear.\(^13\) In our previous SP experiments in steels,\(^14-18\) it was found that NC regions with several microns thick are formed irrespective of carbon content (up to 0.8 mass% C) and initial microstructure (ferrite, martensite, pearlite or spheroidite) under appropriate conditions. In this regard, however the NC structure forms when specimen hardness is lower than shot hardness. In addition, it was found by using Fe–3.3mass% Si (Fe–3.3Si) steel that the
formation of NC structure by SP is unconcerned to phase transformation, because in the Fe–3.3Si steel bcc structure is stable up to its melting point. The necessary condition to form NC structure by deformation was proposed to apply an equivalent strain larger than about 7.15) However, it is not clear how much amount strain provided by SP is because the deformation mechanism by SP is complex.

In the present study, the amount of strain given by SP is estimated by comparing the shot-peened surface structure to the cold-rolled structure. The strain gradient, which generates at the shot-peened surface, is conjectured as one of important factors to form NC structure. The role of strain gradient on grain refinement by deformation is discussed from the investigations of microhardness and structural evolution by HPT process.

2. Experimental Procedures

The chemical compositions of specimens used in the present study are listed in Table 1. To obtain martensite structure in Fe–0.10C, the specimen was austenitized at 1 273 K for 3.6 ks and quenched into ice water. (All annealing processes excluding quenching were carried out under pure Ar atmosphere by sealing specimen in a quartz tube.) Spheroidite structure in S20C was obtained by austenitized at 1 1 73 K for 3.6 ks and quenched into oil, and then tempered at 983 K for 79.2 ks.

SP was carried out at ambient temperature using air blast SP equipment in which shots were projected by compressed air. The SP conditions are shown in Table 2. Coverage, which is one of important parameters in SP process, is the area fraction of indentations formed by shot bombardment. The indentation area was measured using a substance microscope. The coverage higher than 50% is estimated by multiplying SP time required at the state of 50% coverage. The annealing of shot-peened specimens was carried out at 873 K for 3.6 ks. Fe–3.3Si steel was cold-rolled to various final reductions (maximum reduction: 99.4%, (equivalent strain: 5.9)) at ambient temperature and subsequently annealed at 873 K for 3.6 ks. Recrystalline grain size in the annealed specimens was measured perpendicularly to the reduction axis at the cross-section by a linear intercept method. HPT experiment was performed at ambient temperature by using anvils with a depression of 0.85 mm and a diameter of 10 mm was held between the two anvils opposed vertically and was torsion-strained by rotating the lower anvil at a rotation speed of 5 rpm under a pressure of 5 GPa. The disk flowed to the radial direction during HPT due to the lack of side constraint, resulting in the reduction of thickness to about 0.6 mm. Specimens were characterized by optical microscope (OM, NIKON OPTIPHOT-100S), scanning electron microscope (SEM, JEOL JSM-6500F), transmission electron microscope (TEM, HITACHI H-800 operated at 200 kV) and Vicker’s microhardness tester (AKASHI MVK-G1). The specimens etched by 5% Nital were observed by OM and SEM. TEM samples in the SP experiment were prepared parallel to the shot-peened surface of specimens. In the HPT-processed disks, the regions about 3.2 mm away from the disk center were observed by TEM.

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<thead>
<tr>
<th>Table 1. Chemical compositions of specimens.</th>
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<td>Structure</td>
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<tr>
<td>Fe-3.3Si ferrite</td>
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<td>Fe-0.01C ferrite</td>
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<tr>
<td>Fe-0.10C martensite</td>
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<td>S20C spheroidite</td>
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<th>Table 2. Conditions of shot peening.</th>
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<td>Condition</td>
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<tr>
<td>Shot velocity [m/s]</td>
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<tr>
<td>(Blasting pressure [MPa])</td>
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<tr>
<td>Shot diameter [mm]</td>
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<td>Shot material (mass%)</td>
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<td>Vicker’s microhardness of shot [GPa]</td>
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Fig. 1. SEM micrograph at the surface region of S20C spheroidite steel after SP (Condition-1 in Table 2, 3 000% in coverage).

3. Results

3.1. Formation of Surface Nanocrystalline Structure by Shot Peening

Figure 1 shows a typical nanocrystalline (NC) regions formed in the S20C steel with spheroidite structure by SP (Condition-1 in Table 2, Coverage: 3 000%). The NC regions with around 20 µm thick were seen at the top surface of specimen, and were separated from an adjacent deformed structure region with sharp boundary. Cementite particles in the NC regions were invisible, indicating the dissolution of cementite. These structures are similar to those observed in the eutectoid steel powders after BM.8,9) To characterize the structure of NC regions formed by SP, TEM observations were performed. Figure 2 shows TEM dark field (DF) images and corresponding selected area diffraction (SAD) rings taken from the top surface regions in the Fe–3.3Si ferrite and Fe–0.01C martensite steels after SP (Condition-1, 6 000%). These images show that the structure of NC regions consisted of randomly oriented grains with around 20 nm in size. In the both steels, the similar structure was observed irrespective of composition and initial structure. The SAD rings in these steels corresponded to those of bcc-ferrite (which could not be distinct from martensite phase), and also in the SAD rings of Fe–0.10C steel Fe3O4 phase was detected as the innermost ring (Fig. 2(b)). It is not clear when the Fe3O4 phase formed in the Fe–0.10C steel (during SP and/or TEM sample preparation process). The existence of such precipitates and/or impurities is favorable to form NC structure because dislocation
motion is prevented and recovery is suppressed consequently. However, Fe$_3$O$_4$ phase is not observed in Fe–3.3Si steel (Fig. 2(a)) and NC structure formed in pure Fe by wire drawing$^{20}$ and BM.$^{21}$ The existence of precipitates and/or impurities seems to be not necessary condition to form NC structure.

Figure 3 shows the microstructure of Fe–3.3Si steel after SP (Condition-2) with different coverage and subsequent annealing at 873 K for 3.6 ks. The NC regions kept finer structure even after annealing at 873 K than that of deformed structure regions where recrystallization occurred. The observed maximum thickness of NC region and the grain size of recrystalline (RC) structure as a function of coverage were summarized in Fig. 4. The RC grain size in the specimens annealed at 873 K for 3.6 ks was measured by a linear intercept method at the 10 $\mu$m inner position from NC region. The maximum thickness of NC region increased with coverage and finally tends to saturate. After the maximum thickness was saturated, the area fraction of NC region increased with coverage and NC region became consequently layer-like (Fig. 3(c)). The RC grain size decreased from 6.5 $\mu$m (3 000% in coverage) to 4.3 $\mu$m (30 000%), indicates that the strain in RC region was accumulated with coverage. Since RC grain size has close relation to strain amount (dislocation density) in cold-deformation processes, the relationship of strain amount and RC grain size was investigated in the cold-rolled specimen to estimate the amount of strain after SP. Figure 5 shows the RC grain size in the Fe–3.3Si steel after cold-rolling and annealing at 873 K for 3.6 ks as a function of equivalent strain, $\varepsilon_{eq}$. From Fig. 5, the $\varepsilon_{eq}$ at the RC regions after SP with the coverage of 3 000 and 30 000% were estimated around 3 and 6 respectively. The structure at the surface region was the mixed structure of NC and RC, and the grain size of such RC structure was much smaller than the measured grain size at the inner RC region. It is suggested that SP can apply the strain larger than 6 to the sample surface, although this estimation is rough because deformation mechanism is different between SP and cold-rolling. This amount of strain is consistent with the necessary condition ($\varepsilon_{eq}$$>$ ca. 7) to form NC structure by deformation which was proposed in our previous study.$^{15}$

Thus, the extremely large strain is given at the surface region by SP and also leading to generation of large strain.
gradient. In Fig. 3, the amount of strain in the inner region at around 100 μm in depth from the surface seems to be approximately zero because no recrystallization occurred, indicating that the large strain gradient generated after SP. It is difficult to investigate the effect of strain gradient on formation of NC structure because the deformation by SP is complex. HPT experiment was performed, therefore, to understand the role of strain gradient on grain refinement as follows.

3.2. Hardness and Structure Evolution by HPT

Figure 6 shows the radial distributions of microhardness, Hv, in the Fe–0.03C disks processed by HPT for varying turns (1/4–300 turns). Vicker's microhardness measurement was carried out with an applied load of 4.9 N for 10 s. The Hv of undeformed specimen was 0.9 GPa, and the Hv of disk compressed at an applied pressure of 5 GPa in HPT dies without torsion-straining was 1.8 GPa. After smaller number of turns (N<1), Hv increased linearly with distance from the disk center, since the shear strain, γ, is proportional to the distance, r, according to the following equation: 

\[ \gamma = 2\pi Nr/\ell \]

where \( \ell \) is disk thickness during torsion-straining (0.6 mm) and N is number of turns. Although Hv increased with the number of turns (N>1), the rate of increase near the outer edge decreased. For N>10, therefore, the distribution of Hv became homogeneous in the outer region (r>0.5 mm). Finally, the Hv in the whole disk showed the approximate values of 4–5 GPa, and the Hv hardly increased with more HPT turns (N>50). At the disk edge (r=5 mm) after N=50, the amount of equivalent strain, \( e_{eq} \), is 9.1, which is calculated by the following equation:

\[ e_{eq} = 2/3^{1/2} \ln(1 + (\gamma^2/4)^{1/2} + \gamma/2) \]

It is interesting to note that the Hv at the center of disk increased with number of turns although here shear strain is theoretically zero (\( \gamma = 0 \)). To measure precisely the Hv at the center of disk, the center region was detected from the microstructure. The microstructure near the center region in the HPT-processed disk for N=10 is shown in Fig. 7. It can be seen grain boundary structure within the area of about 300 μm in diameter at the center region and concentric plastic flow in the region away from the center. Hv around the detected center region (400×500 μm²) was measured in 50 μm interval with an applied load of 98 mN for 10 s (in this measured condition, the indent size in the specimen with Hv 2 GPa is less than 10 μm). Figure 8 shows the variation of Hv in the HPT-processed disk for N=10. The lowest Hv measured was taken as the Hv of the specimen cen-
ter since \( Hv \) increased concentrically with distance from the center. The \( Hv \) at the center of disk processed by HPT as a function of number of turns are shown in **Fig. 9**. The \( Hv \) in Fig. 9 is smaller than that in Fig. 6 in the same number of turns (\( e.c. \) \( Hv \) 3.3 GPa in Fig. 9 and 4.0 GPa in Fig. 6 in the condition of \( N \)=100). This is attributed to the fact that the \( Hv \) measured area in Fig. 6 included the strain hardened area not only the center region since the \( Hv \) in Fig. 6 was measured with the larger applied load. The \( Hv \) at the center increased rapidly with the number of turns for smaller number of turns (\( N \)<10), and increased gradually to a saturation value of 3.3 GPa. The saturation value is 1.5 GPa higher than the \( Hv \) in the compressed disk before torsion-straining. Since here shear strain is nominally zero, the obtained extra hardening at the center by torsion-straining is considered to be a strain gradient hardening, as will be discussed below.

The evolution of microstructure during torsion-straining was investigated by TEM. In the bright and dark field images of the disk subjected to \( N \)=1 (**Figs. 10(a), 10(b)**), the layered structure in sub-micrometer scale with high dislocation density was observed. The corresponding SAD pattern (**Fig. 10(c)**) shows elongated and clustered diffraction spots, which suggests that the layered microstructure consisted of low angle sub-boundaries. The boundaries of layered microstructure became sharp and the thickness of layer decreased with increase in the number of turns. In the disk processed for 50 turns in which the \( Hv \) value saturated, the layered grains with clear boundary and about 200 nm thick was observed.

4. Discussion

In the results of HPT experiments, it is noteworthy that the \( Hv \) at the center of HPT-processed disk increased with number of turns (Fig. 9). Other researchers\(^{24-26} \) reported similar results in the HPT experiments. A. Vorhauer et al.\(^{25} \) suggested that a possible reason for the disappearance of the undeformed center region of disk is the misalignment of anvil rotation axis or other deviations from the idealized HPT deformation. However, their suggestions can not explain that the saturation values of \( Hv \) at the center region (\( Hv \) 3.3 GPa) and at the outer region (5 GPa) are much higher than the \( Hv \) of the cold-rolled Fe–0.03C plate (2.4 GPa at reduction of 97.6\% (\( e_{eq} \)=4.3)\(^{27} \)). Thus, such hardening by HPT deformation is considered to be associated with strain gradient.

In the torsion-straining of a disk, the strain is finite at the edge and zero at the twist axis, resulting in appearance of strain gradient.\(^{19,28} \) The strain gradient requires the storage of geometrically necessary (GN) dislocations. The GN dislocation density, \( \rho_{GN} \), induced by torsion-straining is expressed as \( \rho_{GN} = 2/h \cdot 1/r = 4 \pi N/b \cdot 1/t \), where \( h \) is screw dislocation spacing (\( b \): magnitude of Burger’s vector (0.248 nm in pure Fe), \( \theta \): rotation angle). If hardening is governed by the sum of statistically stored (SS) dislocation density, \( \rho_{SSD} \), and \( \rho_{GN} \) is assumed, the simplest possible relationship between flow stress \( \sigma \) and total dislocation density is given by the following equation:

\[
\sigma = \frac{G b}{2 \pi} \left( \frac{1}{r} \right)^{1/2} \left( \frac{N}{b} \right) \rho_{SSD} + \rho_{GN}
\]

where \( G \) is the shear modulus. The hardening by torsion-straining is considered to be associated with strain gradient.

**Fig. 9.** The \( Hv \) at the center region of Fe–0.03C disks processed by HPT for varying turns.

**Fig. 10.** TEM images ((a), (d) bright and (b), (e) dark field images) and corresponding (c), (f) SAD rings taken from the areas of around 3.2 mm from the center of Fe–0.03C disks processed by HPT for (a)–(c) 1 turn and (d)–(f) 50 turns. (In SAD patterns, the spots from Fe\(_2\)O\(_4\) phase are seen.)
density is expressed as $\sigma = a \mu b^{1/2}(\rho_{\text{SSD}} + \rho_{\text{GND}})^{1/2}$, where $\alpha$ is a constant (1) and $\mu$ is shear modulus (80 GPa in pure Fe).\(^{26}\) Accepting the approximate relation between hardness, HV, and $\sigma$ as $HV = 3 \sigma$, the dislocation density in the compressed disk before torsion-straining is estimated to be $2.5 \times 10^{14}$. Thus, the HV at the center region of HPT-processed disk can be expressed as $HV = 3a \mu b^{1/2}(\rho_{\text{SSD}} + \rho_{\text{GND}})^{1/2} = 3a \mu b^{1/2}(2.5 \times 10^{14} + 4\pi N / b / \eta)^{1/2}$.

The calculated values of HV at the center region correspond well to the measured values for $N > 10$ (Fig. 9). For large number of turns ($N > 10$), however, the deviation increased since the measured HV became a constant at about 3.3 GPa. This tendency of HV saturation was observed in the whole HPT-processed disk. It appears that the HV saturation is correlated to microstructural equilibrium caused by the balance of deformation and recovery. Furthermore, it is considered that the major strengthening mechanism probably changed from dislocation hardening ($N < 10$) to grain refinement hardening ($N > 10$) since grain refinement and formation of high-angle grain boundaries formed by accumulation of GN dislocations. The saturation HV value (3.3 GPa) at the center of disk was much higher than that (2.4 GPa) of the specimen after cold-rolling which is homogeneous deformation. This indicates that the strain gradient has the marked effect on both hardenings of dislocation and grain refinement.

As described above, strain gradient as well as strain contributes significantly to strengthening and grain refinement. In the present HPT experiment, however, the grain refinement was saturated with around 200 nm in layer grain thickness in the Fe-0.03C disk although the HPT-processed disk was applied large strain and strain gradient. This suggests that not only strain gradient and strain but also other deformation conditions are necessary to form NC structure. From comparison of the deformation condition of SP and HPT, strain rate\(^{15}\) and multi-directional deformation\(^{17}\) are suggested as the other necessary conditions. Further studies about the necessary conditions to form NC structure by deformation are in progress.

5. Conclusions

(1) The surface NC structure with equiaxed grains of around 20 nm were formed in various steels by SP. The NC layer with around 40 μm thick formed under appropriate SP condition.

(2) The recrystallized grains beneath the shot-peened surface after annealing were similar size to those of the specimen after cold-rolling ($\varepsilon_{eq} = ca. 6$) and annealing. The $\varepsilon_{eq}$ larger than 6 seems to be given to the surface region by SP. This also indicates that large strain gradient is generated at the shot-peened surface.

(3) The maximum hardness (HV 5 GPa) of HPT-processed Fe-0.03C disk was twice higher than that (2.4 GPa) obtained by cold-rolling.

(4) The hardness at the disk center increased up to a saturation value of 3.3 GPa without any strain.

(5) The results of HPT experiment indicated that strain gradient contributes to strengthening and to grain refinement. To form NC structure, however, it seems that not only strain gradient and strain but also other deformation conditions, such as strain rate and multi-directional deformation, are necessary.

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