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Nano-Crystallization of Steel Powders with Mechanical Milling Treatment

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It is well known that severe plastic deformation of metals causes grain refinement of the matrix without special heat treatments. In this study, the difference in grain refinement behavior through severe plastic deformation was compared between conventional cold rolling of pure iron sheet and Mechanical Milling (MM) treatment of pure iron powder. And then the importance of carbon addition for the grain refinement was discussed in Fe-(0-0.8)mass%C alloy powders.

The hardness of the pure iron sheet increases with increasing the amount of strain, but levels off at the hardness level of 2GPa after 90% cold rolling (ε_{eq}=2.65). The hardness of the cold-rolled iron sheet is explained by the dislocation strengthening with Bailey-Hirsh equation. On the other hand, the hardness of the pure iron powder easily exceeds 2GPa and it reaches 6GPa after 360ks MM treatment. Microstructure of the MM-treated pure iron powder is characterized by fine grained structure formed through Dynamic Continuous Recrystallization (DCR). In the Fe-C alloy powders with the MM treatment of 360ks, the grain size and subgrain size decrease with increasing carbon content. The MM-treated Fe-0.8mass%C alloy powder has nano-structure with grain size of about 10nm. And no subgrain is observed in the grain.

After a discussion of grain refinement mechanism, it was concluded that multi-directional deformation is indispensable for DCR and the carbon addition promotes DCR in iron during severe plastic deformation.

Key words: iron-carbon alloy, sever plastic deformation, mechanical milling, hardness, nano-crystallization

1. INTRODUCTION

Severe plastic deformation is an useful technique for direct grain refinement of metallic materials without special heat treatment. Many researchers have reported various kinds of severe plastic deformation technique such as Accumulative Roll Bonding (ARB)[1], Equal Channel Angular Pressing (ECAP)[2,3], High Pressure Torsion Straining (HTS)[4-6], Mechanical Milling (MM)[7] and so on. Recently, it is reported that multi-directional deformation is important as well as the amount of strain for grain refinement through severe plastic deformation. For example, in the ECAP treatment, the specimen should be rotated with the longitudinal axis by 90 degree in positive between each pressing [8]. From the point of view, MM treatment is a suitable technique for grain refinement because the powders are homogeneously deformed through the collisions between powder and ball from random directions [7]. For instance, ultra grain refinement to 20-30nm has been already achieved by mechanical milling in commercial pure iron [9]. On the other hand, grain refinement behavior through MM treatment depends on alloying elements. We found that Y_2O_3 addition promotes grain refinement in high Cr stainless steel and the grain size is of about 10nm after long MM treatment [10]. In the case of carbon steel, we have already gotten nanocrystalline ferritic structure with the grain size of about 10nm in Fe-0.8mass%C alloy [11]. However, the effect of the content of such alloying elements on grain refinement behavior has not been sufficiently clarified.

In this study, the effect of multi-directional deformation on the grain refinement behavior in iron was investigated by comparing the microstructural change of iron powder in MM treatment with that of iron sheet in cold rolling. The effect of carbon content on grain refinement behavior was also discussed in the MM-treated Fe-(0-0.8)mass%C alloy powders.

2. EXPERIMENTAL PROCEDURE

A commercial pure iron bulk sheet, an IF steel sheet, electrolytic pure iron powder and cementite powder were used in this study. Table 1 shows chemical compositions of the specimens. Carbon content of commercial pure iron is of about 80ppm, and IF steel contains a small amount of Ti to reduce soluble carbon in ferrite matrix.

The pure iron sheets were recrystallized by annealing at 1023K to decrease dislocation density, and then they were cold-rolled up to 90% reduction in thickness (ε_{eq}=2.65). On the other hand, MM treatment was performed as follows: The electrolytic pure iron powder was mixed with cementite powder. Chemical composition of the powder mixture is Fe-(0-0.8)mass%C. The mixed powder was put into stainless steel pot with steel balls and then subjected to mechanical milling treatment in an Ar gas atmosphere up to 360ks. The weight ratio of ball/powder is 20.

The cold rolled pure iron sheets and MM-treated powders are subjected to X-ray diffractometry, TEM observation and hardness testing. Crystallite size and local strain are measured by Hall-Williamsons method (Eq.1) using X-ray diffractometry [12].

$$\beta\cos\theta/\lambda=2\varepsilon_{hkl}\sin\theta/\lambda+0.9/D_{hkl} \quad \text{Eq.(1)}$$

Where β is half-peak width, λ is wavelength of CoKα (0.1788965nm), D_{hkl} is crystallite size and ε_{hkl} is local strain (%). It is known that the crystallite size given by this equation corresponds to the minimum crystalline size in microstructure such as grain size, sometimes dislocation cell size or subgrain size. The local strain is originated from the elastic strain due to defects such as dislocation and grain boundary.

On the other hand, dislocation density (ρ) can be estimated from the obtained local strain (ε_{hkl}) with an equation expressed as follows [13].

$$\rho=(K\times\varepsilon_{hkl}^2)/b^2 \quad \text{Eq.(2)}$$

Where K is a constant (=14.4) [13].

Table 1 Chemical composition of bulk and powder materials used in this study. (mass%)

Bulk materials	C	Si	Mn	Ti
Commercial pure iron	0.008	<0.01	0.005	-
IF steel	0.0016	<0.01	0.13	0.08
Powder materials				-
Pure iron powder	0.0009	0.0043	0.0008	-
Cementite powder	6.3	-	-	-

3. RESUTS AND DISCUSSIONS

3.1 Microstructural development of pure iron through cold rolling and mechanical milling treatment

Fig. 1 shows change in hardness of the commercial pure iron and the IF steel sheets during cold rolling. The hardness of the pure iron sheets increases with increasing strain and it levels off at around 2GPa. Fig. 2 shows relation between hardness and square root of dislocation density of the pure iron sheets shown in Fig.1.

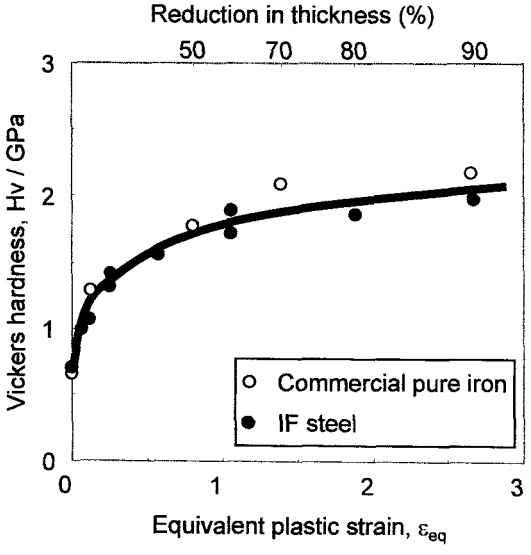

Fig. 1 Change of hardness in pure iron bulk sheet during cold rolling.

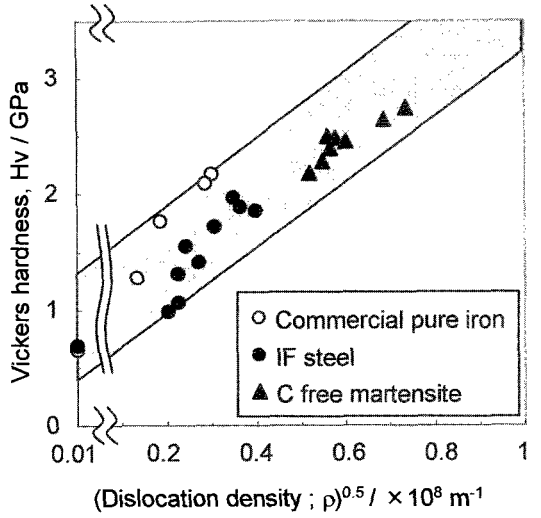

Fig. 2 Relation between hardness and square root of dislocation density; $\rho^{0.5}$ in the pure iron sheet shown in fig.2. The data of carbon free martensite is also plotted in the figure for references.

The result in carbon free martensite, whose strengthening mechanism is explained by dislocation strengthening [14], is also shown in the figure. According to Bailey-Hirsh equation, strength is proportional to square root of dislocation density [15], hardness of the pure iron sheets is in proportion to $\rho^{0.5}$ as well as the carbon free martensite. This means that the hardness of the cold rolled pure iron and carbon free martensite is described by the same Bailey-Hirsh equation.

On the other hand, Fig. 3 shows change in hardness of the pure iron powder during MM treatment. Hardness of the pure iron powder rapidly increases in the initial stage of MM treatment and it reaches about 3GPa in the 10.8ks MM powder. But it levels off at about 5.5GPa, after MM treatment for 36ks. Fig. 4 shows changes in

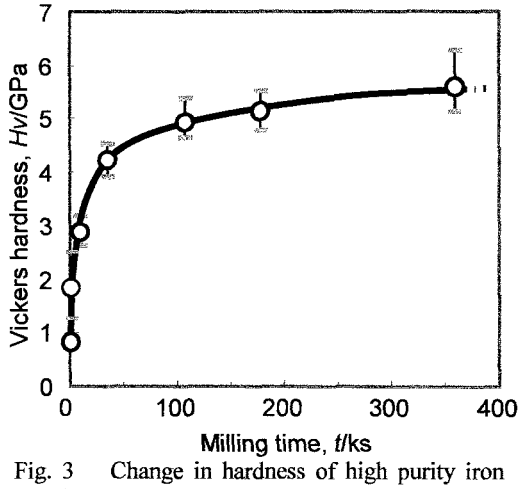

Fig. 3 Change in hardness of high purity iron powder during MM treatment.

crystallite size and local strain during MM treatment in the pure iron powder. The crystallite size is of around 80nm in the initial stage of MM treatment. The size gradually decreases with increasing MM time to the size of 60nm. With decreasing of the crystallite size, the local strain increases and levels off at 0.6% in the latter stage of the treatment.

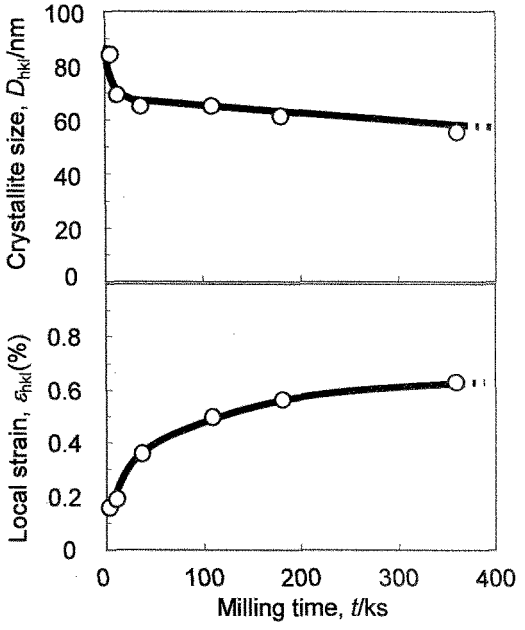

Fig. 4 Change in crystallite size and local strain in pure iron powder during MM treatment.

Fig. 5 shows relation between the MM time and the dislocation density obtained from the Eq(2) in the pure iron powder. The dislocation density of annealed specimen is presumed to be $10^{12}(m^{-2})$. The dislocation density of the MM-treated pure iron powder rapidly increases in the initial stage of MM treatment, which corresponds to the change in local strain (fig4), and then saturates after the long time MM treatment. In the 360ks MM-treated powder, the dislocation density reaches at about 10^{16} (m^{-2}). Assuming that the dislocations arrange

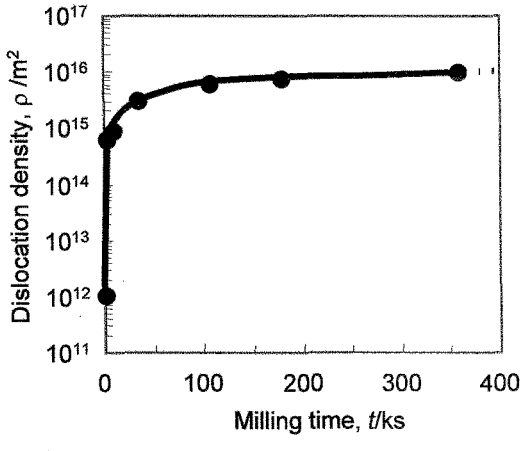

Fig. 5 Relation between MM time and dislocation density in the pure iron powder during MM treatment. The dislocation density is estimated from local strain shown in Fig.4.

at even intervals, the mean distance between dislocations becomes of about 10nm.

Fig.6 summarizes relation between hardness and $\rho^{0.5}$ in the pure iron powder MM-treated for various times. The data shown in fig.2 is also plotted in the figure. Hardness of the pure iron powder MM-treated for 3.6ks is in the band corresponding to dislocation strengthening, but hardness of the powder with longer MM treatment shifts to higher hardness side from the band. This suggests that strengthening mechanism of MM-treated powder switches from dislocation strengthening to grain refinement strengthening.

In order to clarify the difference between cold rolling and MM treatment in microstructural development, Fig.7 represents TEM images of the cold rolled pure iron sheet and the MM-treated pure iron powders. The diffraction patterns were taken from selected areas of 1.5μm in diameter and the dark field images were taken from the ferrite (110) diffraction spots. The microstructure of pure iron sheet cold-rolled by 90% (1), is characterized by high dislocation density as clearly observed in the dark field image (1-c). Its diffraction pattern (1-b), however, indicates that most of misorientations between adjacent grains is small in this area, namely, it is subgrain structure. Similarly, the 3.6ks MM powder (2) also has a subgrain structure, which is formed with small angle boundaries, although the subgrain size is rather small compared with cold-rolled iron sheet. The misorientation becomes larger with increasing MM treatment time. In the specimens MM-treated for 10.8ks (3-b), isolated fine ferrite grains with the size of about 500nm are formed (3-c). The grains have been formed by the repeated multi-directional deformation through MM treatment without annealing. This means that the grain refinement is caused by so-called Dynamic Continuous Recrystallization (DCR) [16-18]. It should be noted that the grain refinement does not occur in the cold-rolled sheet but does in the MM-treated powder, although

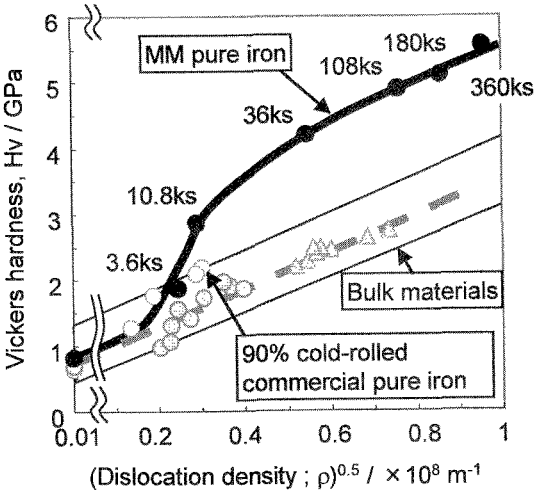

Fig. 6 Relation between hardness and square root of dislocation density; $\rho^{0.5}$ in the pure iron powder (●)MM-treated for various times. MM time is shown in the figure and the data of bulk materials (Commercial pure iron;○, IF steel; ◍, and C free martensite; ◭) is also plotted in the figure.

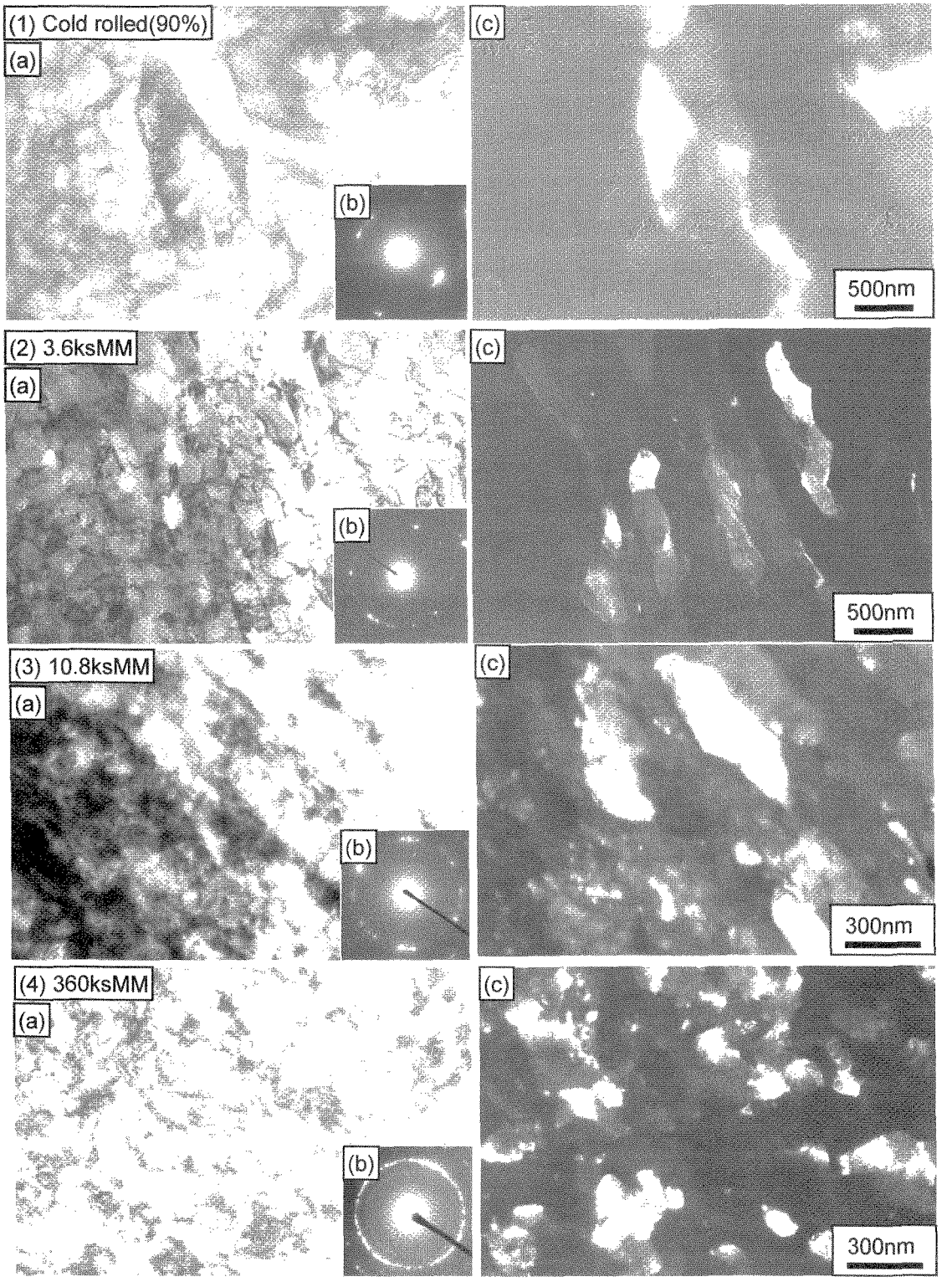

Fig. 7 TEM images of bulk pure iron cold-rolled by 90% (1)and pure iron powder MM-treated for various times; 3.6ks MM (2), 10.8ks MM (3) and 360ks MM (4) treatment. Bright field image (a), diffraction pattern taken from the area of 1.5μm in diameter (b) and dark field image (c) from ferrite (110) diffraction spots.

dislocation density of 90% cold-rolled sheet and 10.8ks MM powder are almost the same. This suggests that the multi-directional deformation is indispensable for DCR.

After 360ks MM treatment, Debye-Scherrer rings are observed in the diffraction pattern (4-b), indicating that a lot of DCR grains are formed in this area. The dark field image (4-c) shows that the microstructure is consisted of fine ferrite grains with the size of about 200nm. It was confirmed that the grain refinement does not proceed in the latter stage of MM treatment (<36ks). Such microstructural evolution well corresponds to the hardening behavior shown in Fig. 3. It was also found that the grain size obtained by MM treatment is limited to the submicron order even though the MM treatment is further prolonged in the case of high purity iron.

3.2 Effect of carbon content on microstructural development through MM treatment

Fig. 8 shows changes in hardness during MM treatment in Fe-C alloy powders with different carbon content. The hardening behavior of the Fe-C alloy powders is similar to that of the pure iron powder, and the saturated hardness increases with increasing carbon content. Authors confirmed that all of cementite decomposes into ferrite matrix as solute carbon atoms after 360ks MM treatment in Fe-C alloy with the carbon content of less than 2.5mass% [19]. In order to clarify the effect of carbon content on microstructural development, Fig. 9 shows TEM dark field images of the Fe-C alloy powders MM-treated for 360ks. These images were taken from the (110) ferrite Debye-Scherrer ring. In the pure iron, lots of subgrains and dislocation cells with the size of 100nm are observed within ferrite grains. The crystallite size measured by X-ray diffractometry (fig.4) corresponds to the substructure size. With increasing carbon content, the subgrain size is gradually reduced and fine isolated grains, whose grain boundary has large misorientation, appears in the Fe-C alloys. The number of isolated grain markedly increases, and microstructure becomes homogeneous in the Fe-0.8mass%C alloy.

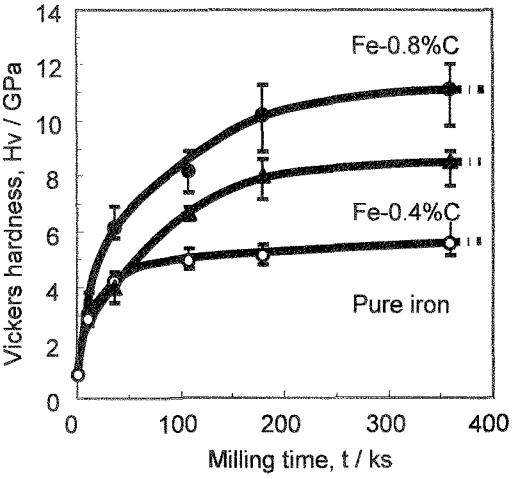

Fig. 8 Changes in hardness during MM treatment in Fe-C alloys with different carbon content.

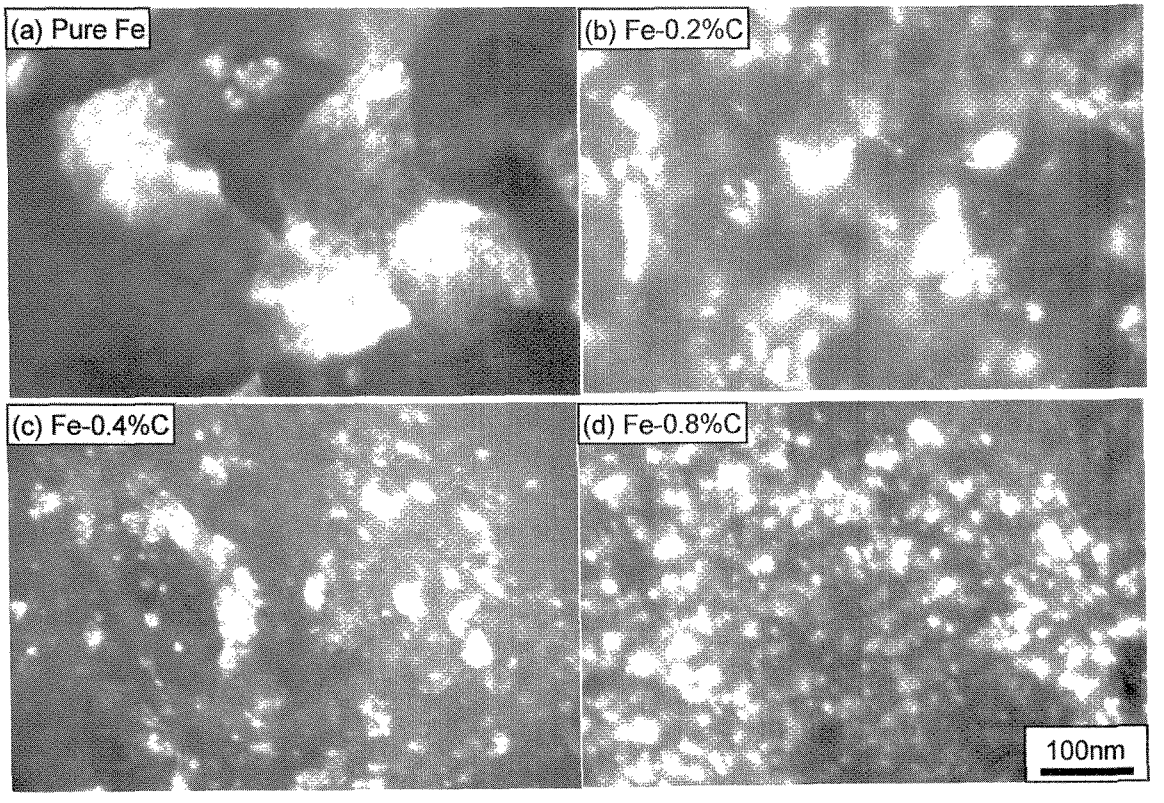

Fig. 9 Dark field images of Fe-C alloys MM-treated for 360ks; pure iron (a), Fe-0.2mass%C (b), Fe-0.4mass%C (c) and Fe-0.8mass%C (d).

The ferrite grain size of the alloy is about 10nm and it corresponds to crystallite size measured by X-ray diffractometry. This means there is no substructure within grains in the MM-treated Fe-0.8mass%C alloy. Such a grain refinement behavior is very similar to that of Fe-0.8mass%C alloy during MM treatment [11], and effect of carbon addition in pure iron is thought to be effect of prolonging MM time in the Fe-0.8mass%C alloy. It could be concluded that carbon promotes DCR during MM treatment at room temperature. Detail mechanism of promotion of DCR due to carbon addition has not been clarified, but it is possible that dragging effect causes increment of stored dislocation and this result in decreasing grain size in Fe-C alloy.

5 CONCLUSIONS

1. Multi-directional deformation is indispensable for Dynamic Continuous Recrystallization through severe plastic deformation in the pure iron. Therefore, MM treatment, multi-directional deformation is very effective for grain refinement.

2. Carbon addition results in grain refinement due to promotion of DCR, and nano-crystalline structure with the grain size of about 10nm is obtained in Fe-0.8mass%C alloy.

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