J.of Metastable and Nanocrystalline Materials Vols.15-16 (2003) pp193-198.

# COMPARISON OF NANOCRYSTALLIZATION IN STEELS BY BALL MILLING AND BALL DROP TEST

M. Umemoto, Y.Todaka, T.Yasuda and K. Tsuchiya

Department of Production Systems Engineering, Toyohashi University of Technology

Tempaku-cho, Toyohashi 441-8580, Japan

**Keywords**: Nanocrystallization, Steels, Ball Milling, Ball Drop, Eutectoid

**Abstract** Nanocrystallization of steels by ball milling and by a ball drop test was compared using specimens with different carbon content and starting microstructures. The nanocrystalline structure produced by ball milling and ball drop test has essentially the same characteristics; nano-sized ferrite grains, dissolution of cementite, high hardness (about 10 GPa), and absence of recrystallization and slow grain growth by annealing. The present ball drop test confirmed that nanocrystallization by ball milling is due to severe plastic deformation and not due to contamination. Low test temperature and pre-strain enhanced the nanocrystallization in a ball drop test. The amount of true strain necessary to obtain nanocrystalline regions was estimated to be larger than 3 using the shear band produced by one time of ball drop.

## Introduction

Nanocrystallization by severe plastic deformation in steels has been a subject of many researches [1-5] in the last decade. Among the various severe plastic deformation processes, extensive work has been performed on ball milling (BM) due to its simplicity, low cost, and applicability to essentially all classes of materials. From our previous BM experiments on the nanocrystallization in steels [6-11], the nanocrystalline regions formed by BM were found to have the following characteristics; 1) homogeneous and featureless structure under optical microscope or SEM with sharp boundaries between the work hardened regions, 2) fine-grained structures with less than 100 nm and almost no dislocations, 3) extremely high hardness (8 ~ 14 GPa depending on carbon content), 4) no cementite (complete dissolution of pre-existed cementite), and 5) no recrystallization but slow grain growth upon annealing. Although BM is a powerful method to produce nanocrystalline structures, it is not suitable to study the nanocrystallization mechanism since the deformation mode of powder is extremely complicated and contamination is hard to be avoided. To make the deformation mode to produce nanocrystalline structure simple, we developed a ball drop test in which a ball with weight was dropped onto a bulk specimen [12,13]. With this method, similar microstructure and hardness as those of nanocrystalline structure observed in the BMed powder could be produced.

The purpose of the present study is to compare in detail the microstructural evolution to nanocrystalline structure by BM and a ball drop test. The deformation conditions and nanocrystallization mechanism in these processes are compared. The annealing behavior of the obtained nanocrystalline regions in steels was studied.

## Experimental Procedures

The materials used in this study were eutectoid carbon steels and a fine-grained low carbon steel. Eutectoid steels of Fe-0.80C (Fe-0.80C-0.20Si-1.33Mn in mass%) and Fe-0.89C (Fe-0.89C-0.25Si -0.50Mn in mass%) were heat treated to obtain either pearlite or spheroidite structure [11]. A low carbon steel of Fe-0.15C (Fe-0.15C-0.35Si-1.24Mn in mass%) with grain size about 1 μm was

produced by heavy hot rolling [14]. For ball milling, the chips cut from alloy blocks were loaded into a stainless steel pot with bearing steel balls. 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 specimens with flat surface. The details of the ball milling [10] and the ball drop test [13] were described in our previous paper. To study the effect of pre-strain on the formation of nanocrystalline structure, specimens were rolled to various reductions by multipass rolling (with 10 % or 20 % reduction per pass). Annealing of nanocrystallized specimens was carried out at 873 K for 3.6 ks by sealing in quartz tubes with pure Ar protective atmosphere. Specimens were characterized by SEM, TEM and Vickers microhardness tester (load of 0.98 N for 10 s). Specimens for SEM were etched by 5 % Nital.

## Results and Discussion

Figure 1 shows a SEM micrograph of the cross section of Fe-0.89C powder with pearlite structure ball milled for 360 ks. Two types of regions can be seen. One is a dark smooth contrast region without pearlite structure near the surface of the powder. This region was confirmed by TEM as nanocrystalline structure [11]. Another is a bright contrast region with deformed structure in the interior of the powder. This region is a conventional work-hardened region as proved by TEM. A drastic difference in hardness between these two structures exists as is shown by the indentation marks in Fig. 1 (b). The boundary between the nanocrystalline and work-hardened regions is sharp. Figure 2 shows a SEM micrograph of the cross section of Fe-0.89C powder with spheroidite structure ball milled for 360 ks. Two types of regions can be also seen. A drastic difference in hardness between these two types of structures is shown in Fig. 2 (a). In some places curved bands with a thickness of 0.1 to 0.3 mm are observed between the work-hardened and nanocrystalline regions parallel to the boundary (Fig. 2 (b)). Such bands were observed only in the specimens with spheroidite structure and not in pearlite, martensite or ferrite structures. By further milling the number of bands increases and results in a uniform nanocrystalline structure. Thus these bands are considered to be highly deformed small nanocrystalline regions and not deformed cementite particles.

Figure 3 is a SEM micrograph of the cross section of Fe-0.89C specimen with pearlite structure after a ball

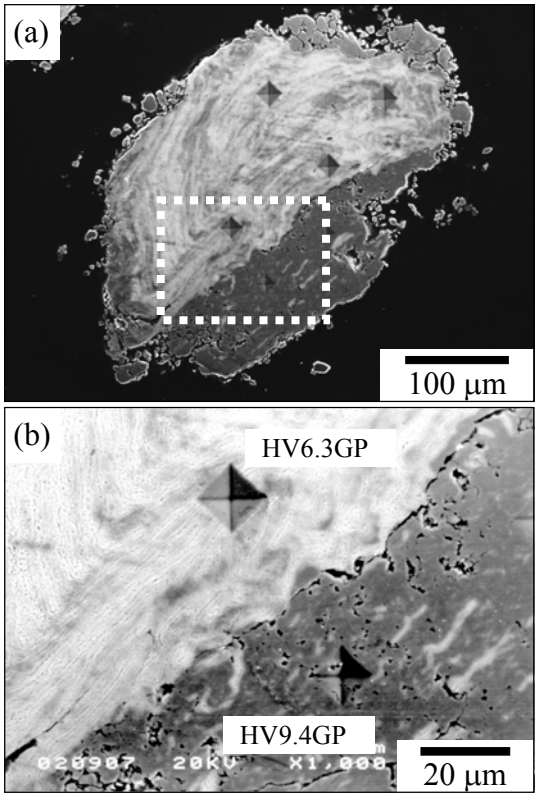


Fig. 1 SEM micrographs of Fe-0.89C powder with pearlite structure ball milled for 360 ks.

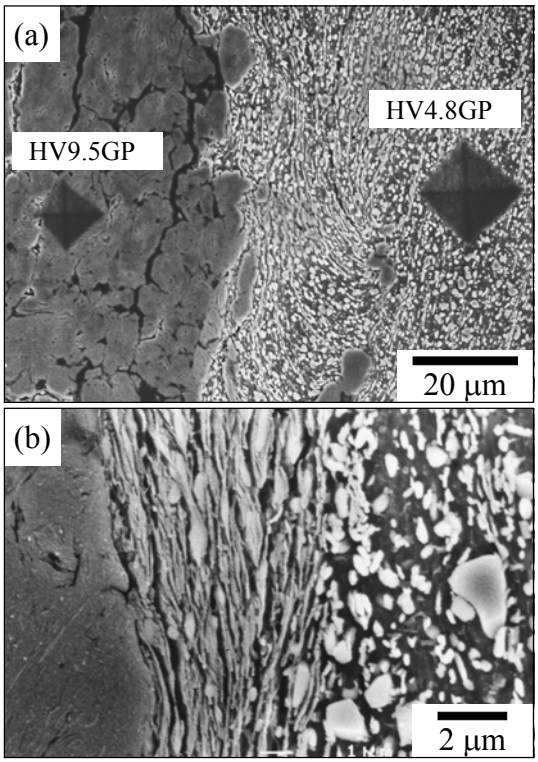


Fig. 2 SEM micrographs of boundary between nanocrystalline and work-hardened regions in Fe-0.89C powder of spheroidite structure ball milled for 360 ks.

drop test (8 times, 4 kg in weight, 1 m in height) at room temperature. A dark smooth contrast region without pearlite structure is seen near the surface of the specimen. The microhardness of this region is as high as 11.7 GPa. TEM observation of this region revealed that the crystal size is less than 100 nm [12]. It is noted that the microhardness and microstructure of the dark contrast region produced by a ball drop test are similar to those observed in ball milled Fe-0.89C powder shown in Fig. 1. Figure 4 shows a SEM micrograph of the cross section of Fe-0.89C powder with spheroidite structure after a ball drop test (50 times, 2 kg, 1 m). The microhardness of the dark contrast layer produced by the coalescence of bands (9.0 GPa) is similar to that observed in the ball milled sample. As is seen in Fig. 4 (b), thin bands locate not only with direct contact to cementite particles but apart from cementite particles. This indicates that these bands form at the places where the strain is accumulated. Cementite particles observed in the band structure did not fracture but dissolved during the coalescence of bands. These microstructural evolution in spheroidite by heavy deformation is quite similar to that observed in ball milling [10]. The nanocrystallization by ball milling was observed in various steels irrespective of the carbon content (0.004 ~ 0.89 mass%C) or starting microstructure (ferrite, martensite, pearlite and spheroidite) [6]. However, nanocrystallization by ball drop test was observed in fine-grained low carbon steels but not observed in coarse grained low carbon steels with ferrite + pearlite structure even after the maximum possible number of ball drop of 50. Figure 5 shows a cross sectional SEM micrograph of fine-grained (grain size of about 1 μm) Fe-0.15C specimen after a ball drop test (8 times, 5 kg, 1 m). The hardness of the specimen before the test was 2.4 GPa which is comparable with that of Fe-0.89C with pearlite structure (3.1 GPa) or spheroidite structure (2.0 GPa). A dark region similar to that observed in the pearlite (Fig. 3) is seen. A drastic difference in hardness is also confirmed between these regions. This result showed that nanocrystallization by a ball drop test occurs even in low carbon steels when the starting grain size is sufficiently small. To obtain nanocrystalline regions by a drop test, it is considered that the initial hardness of the specimen should be high.

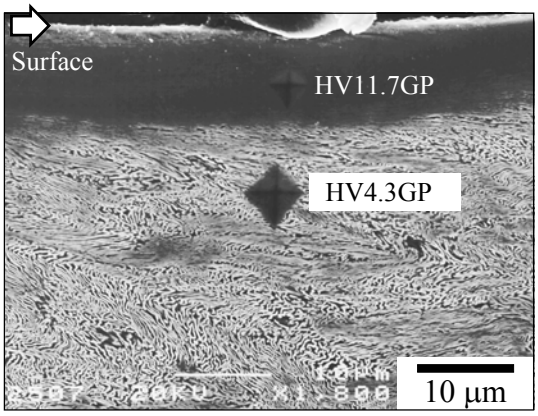


Fig. 3 SEM micrograph of Fe-0.89C specimen with pearlite structure after 8 times of ball drop (4 kg weight, 1 m height).

The present ball drop test showed that nanocrystalline regions form even completely inside samples where there is no chance for contamination. From this result, it is concluded that nanocrystallization in ball milling is not due to contamination but due to purely severe plastic deformation. During ball milling of soft materials, powder particles are flattened, fractured and cold-welded repeatedly and result in crystal grain refinement to sub-micron grain size. Thus nanocrystallization occurs even in soft materials by ball milling. On the other hand, in a ball drop test, there is no cold-welding process and thus nanocrystallization is

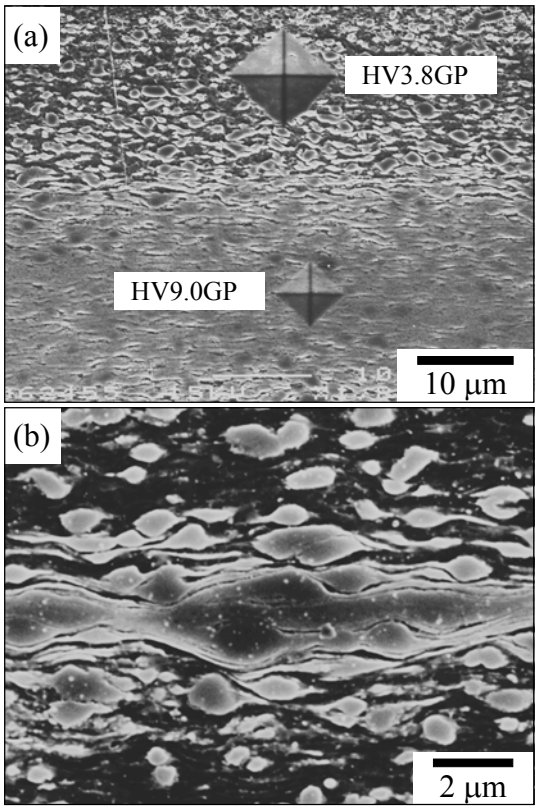


Fig. 4 SEM micrographs of boundary between nanocrystalline and work-hardened regions in Fe-0.89C specimen with spheroidite structure after 50 times of ball drop (2 kg weigh, 1 m height).

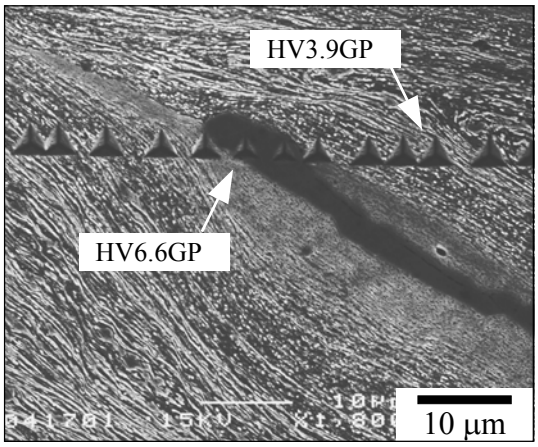


Fig. 5 SEM micrograph of cross section of Fe-0.15C specimen after 8 times of ball drop (5 kg weight, 1 m height).

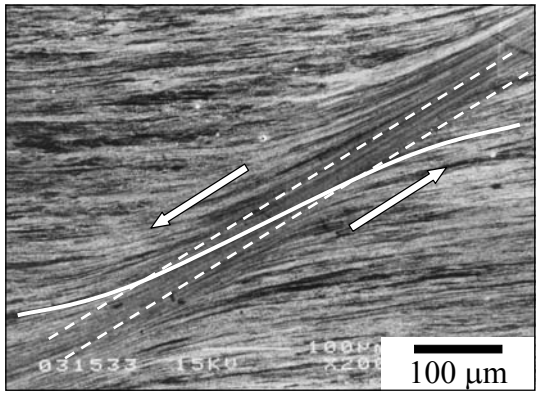


Fig. 6 Shear deformation in Fe-0.80C specimen with pearlite structure after prior cold rolling to 80 % reduction (10 % reduction per pass) and one time of ball drop (5 kg weight, 1 m height).

hard to occur in soft materials.

The number of ball drops necessary to produce a nanocrystalline layer depends on the chemical composition, microstructure and temperature of specimens and the ball drop conditions (weight and height). The number is less for harder sample and higher energy drop conditions (larger weight and height). Pre-strain of specimens also reduces the necessary number of ball drops. In an extreme case, nanocrystallization by one time of ball drop (5 kg, 1 m) was achieved for a pre-strained pearlitic specimen. In such a specimen, a dark contrast shear band with extremely high hardness was observed as is shown in Fig. 6. From the contrast and harness, this shear band is considered to be a nanocrystalline region. Using the stripes morphology crossing the shear band, the amount of shear strain in the nanocrystalline shear band was estimated to be 8.1. Adding the pre-strain of 80 % rolling (1.9 in true strain) and the observed shear strain of 8.1 (1.2 in true strain), the total true strain necessary to produce nanocrystalline layer is estimated to be 3.1.

Deformation of nanocrystalline regions has been observed in the ball drop test specimens. When a sample receives a further ball drop after the formation of the nanocrystalline region, the nanocrystalline region deforms. Figure 7 shows SEM micrographs of Fe-0.89C specimen with pearlite structure after a ball drop test (10 times, 5 kg, 1 m) showing a deformed nanocrystalline region. The nanocrystalline layer with a thickness of about 10 μm is completely separated by a large shear deformation (Fig.7(a)). Micro-shear bands are also observed in the nanocrystalline layer as is shown in Fig. 7 (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. Cracks in a deformed nanocrystalline layer were also observed

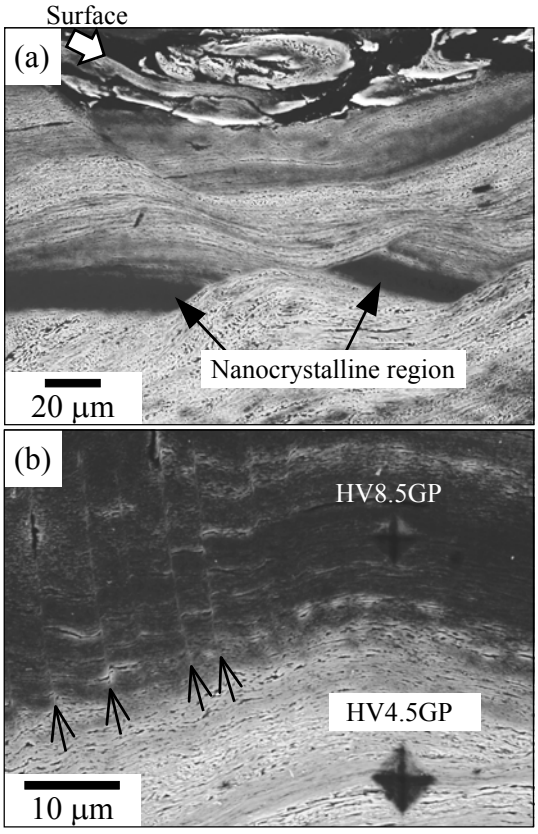


Fig. 7 Typical SEM micrographs of deformed nanocrystalline region in Fe-0.89C specimen with pearlite structure after 10 times of ball drop (5 kg weight, 1 m height).

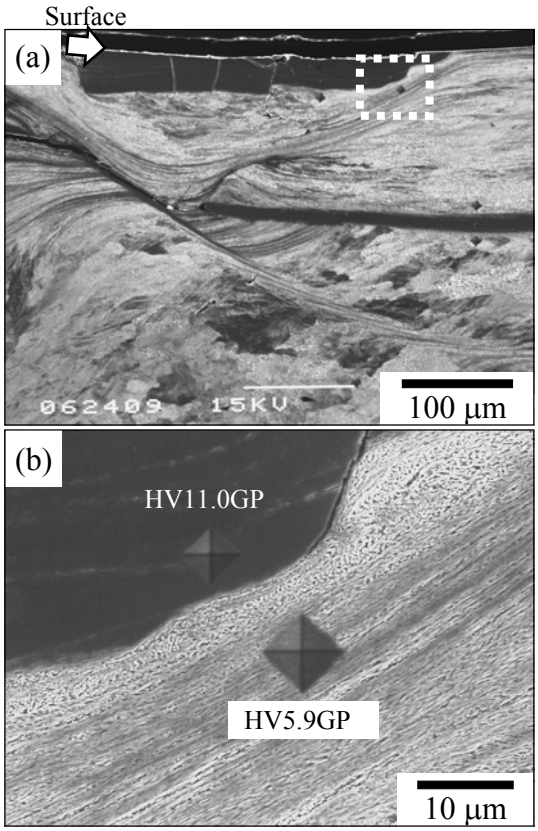


Fig. 8 SEM micrographs of Fe-0.80C specimen with pearlite structure after 8 times of ball drop (5 kg weight, 1 m height) at liquid nitrogen temperature.

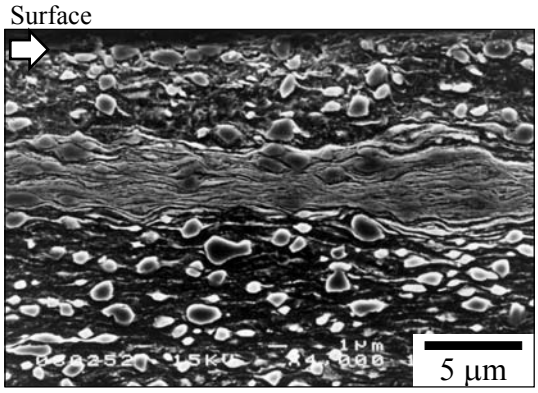


Fig. 9 SEM micrographs of Fe-0.80C specimen with spheroidite structure after 8 times of ball drop (5 kg weight, 1 m height) at liquid nitrogen temperature.

especially at the specimen surface (Fig. 8 (a)).

It was observed that at low deformation temperature a larger volume of nanocrystalline region forms under the same ball drop condition. Figure 8 is a SEM micrograph of a cross section of a pearlitic specimen after a ball drop test (8 times, 5 kg, 1 m) at liquid nitrogen temperature. The microhardness of the nanocrystalline layer is 11.0 GPa which corresponds to a ferrite grain size of about 30 nm [15]. Figure 9 shows a specimen with spheroidite structure after a ball drop test (8 times, 5 kg, 1 m) at liquid nitrogen temperature. Curved thin bands similar to those observed in ball milled powders or 50 times ball dropped specimens at room temperature are seen. This band structure could not be produced by 8 times of ball drops at room temperature.

**Annealing behavior of nanocrystalline regions**

Figure 10 shows typical SEM micrographs of ball milled (a) and ball dropped (b) Fe-0.89C specimens with spheroidite 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 clear. In the prior

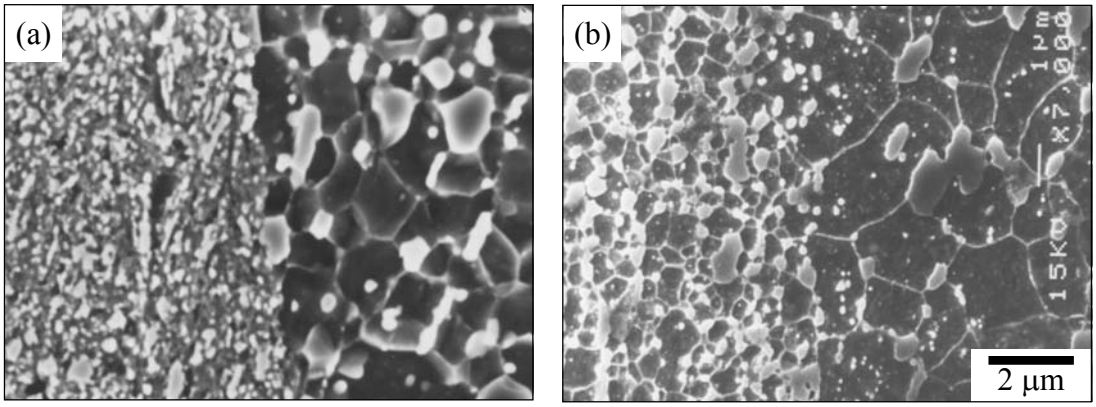


Fig. 10 SEM micrographs of Fe-0.89C specimen with spheroidite structure annealed at 873 K for 3.6 ks after (a) ball milling for 360 ks and (b) 50 times of ball drop (5 kg weight, 1 m height).

work-hardened region, the recrystallization and grain growth of ferrite took place, leading to relatively large ferrite grains of about 1 μm. In the prior nanocrystalline region, fine cementite particles are reprecipitated and ferrite grains are still submicron range. Comparing ball milled and ball dropped samples, the annealed structure in the prior nanocrystalline region of a ball drop test sample is coarser than that of ball milled sample. This may be due to the more severe deformation and more complete dissolution of cementite that occurred in the ball milled sample compared to the ball dropped sample.

## Summary

Nanocrystallization in steels by ball milling and by a ball drop test were compared using samples with different carbon content and different initial microstructures. The main results obtained are as follows.

1) The nanocrystalline structure produced by ball milling and ball drop test has essentially the same characteristics; nano-sized ferrite grains, sharp boundaries with work-hardened regions, no cementite and extremely high hardness (about 10 GPa).
2) In a ball drop test pre-strain and low temperature enhances the formation of nanocrystalline region.
3) Nanocrystalline region deforms with shear mode.
4) Upon annealing nanocrystalline regions do not recrystallize but grains grow slowly.

## Acknowledgment

This study is financially supported in part by the Grant-in-Aid by the Japan Society for the Promotion of Science. Authors are grateful to Kobe Steel Ltd. for supplying Fe-0.15C steel developed in the Super Metal Project.

## References

[1] J.S.C.Jang and C.C.Koch: Sripta Metal. Vol.24 (1990), p.1599.
[2] H.J.Fecht, E.Hellstern, Z.Fu and W.L.Johnson: Met. Trans. Vol.21A (1990), p.2333.
[3] A.V.Korznikov, Y.V.Ivanisenko, D.V.Laptionok, I.M.Safarov, V.P.Pilyugin and R.Z.Valiev: NanoStructured Mater. Vol.4 (1994), p.159.
[4] N.R.Tao, M.L.Sui, J.Lu and K.Lu: NanoStructured Mater. Vol.11 (1999), p.433.
[5] D.H.Shin, B.C.Kim, Y.S.Kim and K.T.Park: Acta Mater. Vol.48 (2000), p.2247.
[6] M.Umemoto, Z.G.Liu, K.Masuyama, X.J.Hao and K.Tsuchiya: Scripta Mater. Vol.44 (2001), p.1741.
[7] Z.G.Liu, X.J.Hao, K.Masuyama, K.Tsuchiya, M.Umemoto and S.M.Hao: Scripta Mater. Vol.44 (2001), p.1775.
[8] M.Umemoto, Z.G.Liu, X.J.Hao, K.Masuyama and K.Tsuchiya: Mater. Sci. Forum Vols.360-362 (2001), p.167.
[9] J.Yin, M.Umemoto, Z.G.Liu and K.Tsuchiya: ISIJ Int. Vol.41 (2001), p.1389.
[10] Y.Xu, Z.G.Liu, M.Umemoto and K.Tsuchiya: Metall. Mater. Trans. Vol.33A (2002), p.2195.
[11] Y.Xu, M.Umemoto and K.Tsuchiya: Mater. Trans. Vol.43 (2002) p.2205.
[12] M.Umemoto, B.Huang , K.Tsuchiya and N.Suzuki: Scripta Mater. Vol.46 (2002), p.383.
[13] M.Umemoto, X.J.Hao, T.Yasuda and K.Tsuchiya: Mater. Trans. Vol.43 (2002) p.2536.
[14] Y.Todaka, M.Umemoto and K.Tsuchiya: ISIJ Int. Vol.42, No.12 (2002) in press.
[15] H.Hidaka, T.Suzuki, Y.Kimura and S.Takaki: Mater. Sci. Forum Vols.304-306 (1999), p.115.