Effects of Pre-exsisting Boundaries on Microstructure Obtained by Plasma-nitriding of Fe–18%Cr Alloy

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The present authors have studied the plasma-nitriding behavior of Fe–high Cr alloys and reported that ferrite grains are newly formed by holding the strict Σ9 coincidence site lattice (CSL) relation with respect to the original ferrite grain [G. Miyamoto et al., Acta Mater. 54 (2006), 4771]. In this study, effects of pre-existing grain boundaries on the growth behavior of the newly formed ferrite grains in the plasma-nitriding of an Fe–18mass%Cr alloy is investigated by means of electron backscatter diffraction analysis. The growth of newly formed ferrite grains is mostly stopped at pre-existing boundaries misoriented larger than 5 degrees because of losing the Σ9 CSL relation at the boundaries. Instead, ferrite grains nucleate at such boundaries by holding the Σ9 CSL relationships with respect to the ferrite grain in front. By two-step nitriding, it is confirmed that ferrite grains can nucleate even inside of grains without a presence of grain boundaries or the free specimen surface.

KEY WORDS: nitriding; EBSD; orientation relationship; coincidence site lattice; recrystallization.

1. Introduction

During nitriding of steels containing strong nitride forming element, such as Ti, V, Cr and Al etc., fine alloy nitrides are precipitated in matrix.1–6 This phenomenon is called as internal nitriding and can lead to a pronounced increase in surface hardness. Among those alloying elements, microstructure change and kinetics in nitriding of Cr-added steels have been studied extensively in wide composition and temperature ranges due to its engineering importance.6–14 The present authors13,14 recently reported that columnar-shaped ferrite (α) grains containing lamellar CrN are newly formed in the nitrided zone of an Fe–18mass%Cr alloy plasma-nitrided at 843 K instead of ordinary continuous precipitation of disk-shaped CrN in the original α grains as shown in Fig. 1. The lamellae tend to align nearly perpendicular to the growth front (Fig. 1(b)). It was also clarified that the interlamellar spacing of (α+CrN) lamellae increases with depth from the specimen surface or with raising the nitriding temperature.14 It was supposed that recrystallization of α matrix is induced by a large volumetric mismatch between CrN and α matrix as proposed by Sennoir et al.11 and subsequent discontinuous precipitation of CrN at the boundary between recrystallized and the original α grains forms (α+CrN) lamellar structure. It was also clarified that most of these columnar α grains hold the Σ9 coincidence site lattice (CSL) relationship, represented by 38.9° rotation around (110)α, with the original α grains within a deviation of 5 degrees. However, only coarse-grained α specimens, of which grain size is larger than the thickness of the nitrided zone as shown in Fig. 1(a), were used in the previous study.13,14 Thus strict orientation relationship between the columnar and original α grains raises

Fig. 1. (a) SEM image of a cross-section in the Fe–18mass%Cr specimen nitrided at 843 K for 18 ks, (b) enlarged image near the growth front of the nitrided zone in (a).
the question how pre-existing grain boundaries affect the growth of columnar $\alpha$ grains. The present study aims to clarify the effect of grain boundaries in the initial microstructure on nitriding behaviors of the Fe–18mass%Cr ferritic alloy by nitriding of fine-grained or cold-deformed specimens.

2. Experimental Procedure

An Fe–18.4mass%Cr alloy was prepared by vacuum melting. After homogenization treatment at 1453 K for 86.4 ks, the specimen was water-quenched. The average $\alpha$ grain size of the specimen is 683 $\mu$m and this specimen will be denoted as the coarse-$\alpha$ specimen hereafter. Cold-rolled (CR) specimens were obtained by cold-rolling of the coarse-$\alpha$ specimen by 75% reduction. Fine-$\alpha$ specimens consisting equi-axed $\alpha$ structure with an average $\alpha$ grain size of 52 $\mu$m were obtained by annealing of the CR specimen at 1173 K for 180 s and subsequently quenched into water. Plasma nitriding treatments were carried out at 843 K for various periods of time with a gas mixture of 20%N$_2$–80%H$_2$ at a total pressure of 700 Pa. Sample preparation and conditions of plasma nitriding were described in detail previously.13)

Microstructure observations were performed with a field-emission scanning electron microscope (SEM: JSM-6500F operated at 15 kV) equipped with electron backscatter diffraction analyzing system and a field-emission transmission electron microscope (TEM: CM-200FEG operated at 200 kV). Sample preparation for SEM and TEM observations and EBSD measurements were also described in the previous study.13) Dislocation substructures of unnitrided zone in the CR specimen after nitriding were characterized by measuring misorientation using the convergent beam Kikuchi diffraction method.

3. Results and Discussion

Figure 2 shows an $\alpha$ orientation map and the corresponding grain boundary map in the fine-$\alpha$ specimen nitrided at 843 K for 72 ks. It is observed that columnar-shaped $\alpha$ grains of which orientations are different from the original $\alpha$ grains are newly formed, even in the grains that are not exposed to the specimen surface (Fig. 2(a)). Figure 2(a) also indicates that the original $\alpha$ grain boundary is preserved during nitriding. When a $\alpha$ grain is transformed into newly formed $\alpha$ grains completely, orientation relationships between the original and newly formed $\alpha$ grains cannot be analyzed directly. Therefore, orientation relationships between the newly formed $\alpha$ grains themselves are compared with the relationships of intervariants of $\Sigma 9$ CSL relationships here. An $\alpha$ grain boundary map of Fig. 2(b) displays intervariant boundaries of $\Sigma 9$ CSL relationships as red lines and other high-angle boundaries as black lines. In contrasting that original $\alpha$ grain boundaries in the initial microstructure are ordinary high angle boundaries in general, most of columnar $\alpha$ grains hold near $\Sigma 9$ CSL orientation relationships with respect to the original $\alpha$ grains in the whole nitrided zone. Noting that since some of the intervariants of the $\Sigma 9$ CSL relationships are identical to the $\Sigma 9$ CSL relationship, boundaries between the nitrided and unnitrided zones are also illustrated as red line. Although gradual orientation change and low angle boundaries of which misorientation is about 10 degrees were observed in some $\alpha$ grains in the nitrided zone in Fig. 2(a), most bound-
aries between nitrided and unnitrided zones hold $\Sigma 9$ CSL relations within a deviation of 5 degrees. Hence, it is clear that the growth of columnar $\alpha$ is stopped at pre-existing $\alpha$ boundaries, and then, new $\alpha$ grains holding the $\Sigma 9$ CSL relationships with respect to the original $\alpha$ grain in front are nucleated at the $\alpha$ grain boundaries.

Figure 3 shows an orientation map viewed along TD direction of the CR specimen nitrided at 843 K for 18 ks. The unnitrided zone, with a small fraction of recrystallization taking place at nitriding temperature as indicated by white arrows, contains low angle boundaries and a small amount of high angle boundaries. In the nitrided zone, $\alpha$ grains are newly formed as in the fine-$\alpha$ specimen whereas these $\alpha$ grains are much finer than those in the fine-$\alpha$ specimen. Figure 4 shows distributions of deviation angles from exact $\Sigma 9$ CSL relationship between $\alpha$ grains across the boundary at the growth front. Dashed lines in the figures indicate the distribution of deviation angles from $\Sigma 9$ CSL relationship for randomly oriented grains that is obtained by numerical calculation. In the fine-$\alpha$ specimen shown in Fig. 4(a), most of columnar $\alpha$ grains satisfy $\Sigma 9$ CSL relationships within a deviation of 5 degrees, which is the maximum permissible deviation angle for $\Sigma 9$ CSL relationships in the Brandon’s criterion.\(^{15}\) In the CR specimen shown in Fig. 4(b), newly formed $\alpha$ grains still tend to hold the orientation relationship around $\Sigma 9$ CSL relationship with respect to the original $\alpha$ grains by comparing with the random distribution. However, the deviation in the CR specimen is larger than that in the fine-$\alpha$ because higher dislocation density in the original $\alpha$ grains may cause deviation from the $\Sigma 9$ CSL relationship between the nitried and unnitrided zones during growth of the $\alpha$ grains.

Figure 5(a) shows enlarged image of orientation map in Fig. 3 near the boundary between the nitried and unnitrided zones, in which low angle boundaries misoriented larger than 5 degrees are illustrated by thin lines as well as high angle boundaries as thick lines. In the unnitrided zone, a density of low angle boundaries is higher than that of high angle boundaries. The spacing of low angle boundaries is 2 to 5 $\mu$m and nearly the same as the $\alpha$ grain size in the nitried zone. TEM micrograph and corresponding grain boundary map of Figs. 5(b) and 5(c) show dislocation substructure in the unnitrided zone. They show that subgrain boundaries misoriented less than 5 degrees is dominant. The size of such subgrains is less than 1 $\mu$m and much smaller than that of $\alpha$ grains in nitried zone. Those facts indicate that growth of columnar $\alpha$ grains is not inhibited by pre-existing boundaries of which misorientation angle is less than 5 degrees, but stopped at a large part of the boundaries misoriented larger than 5 degrees. According to the Brandon’s criterion,\(^{15}\) permissible deviation angle for the $\Sigma 9$ CSL relation is 5 degrees. Hence, it can be reasonably concluded that growth of columnar $\alpha$ grains is inhibited at boundaries misoriented larger than 5 degrees due to loss of the $\Sigma 9$ CSL orientation relationships between the columnar and the original $\alpha$ grains, and then, new $\alpha$ grains holding the $\Sigma 9$ orientation relationships with respect to the original $\alpha$ grain in front nucleate at the $\alpha$ grain boundaries in some cases. This results in much finer $\alpha$ grains in the nitried zone in the CR specimen than annealed one (fine-$\alpha$ specimen).

It was proposed that recrystallization of $\alpha$ matrix is in-
duced by a large volumetric mismatch between CrN and α matrix and subsequently discontinuous precipitation of CrN occurs at the grain boundaries between recrystallized and the original α grains.11,13) Based on the fact that spontaneous migration of α grain boundary without CrN precipitation is not observed in this study, a mechanism assuming precipitation on migrating boundary for discontinuous precipitation16) can be ruled out. Instead, precipitation-induced boundary migration, called as the pucker mechanism, was proposed for discontinuous precipitation.17) In the pucker model, migration of the boundary is driven by the reduction of interfacial energy of the precipitate. In the nitriding of the Fe–18mass%Cr alloy, it was clarified that the Baker–Nutting orientation relationship exists between CrN and α in the lamellar structure and their habit plane is \((001)_{\text{CrN}}/(001)_{\alpha}\).13) This orientation relationship and the habit plane have been frequently observed in the ordinary continuous precipitation of CrN in α matrix11) and considered to be highly coherent. Therefore, the migration of the boundary between newly formed and the original α grains can be induced by precipitation of CrN as in the pucker mechanism. Nakashima et al.18,19) reported that mobility of \(\Sigma 9\) boundary in an Fe–3mass%Si alloy is larger than those of low-angle and high-angle random boundaries at relatively low temperatures because Si atoms interact with the \(\Sigma 9\) CSL boundary weaker than random grain boundaries. Similarly, \(\Sigma 9\) CSL boundary would have higher mobility than that of the random boundaries in the nitriding of high Cr steels due to smaller drag effect by Cr atoms. Hence preferential growth due to the high growth rate of \(\Sigma 9\) boundaries would result in the preferential formation of the \(\Sigma 9\) α grains. According to such preferential growth mechanism, growth inhibition by losing \(\Sigma 9\) CSL relationship at the high angle boundaries or subgrain boundaries misoriented larger than 5 degrees can be explained well.

We carried out two additional experiments to investigate nucleation and growth behavior of the α grain holding the \(\Sigma 9\) relationship with the original α grain; one is nitriding for short periods to observe the nucleation stage of the recrystallized α grain, the other is two-step nitriding at different temperatures. Figure 6 shows optical microstructure and corresponding α orientation map taken along the surface normal in the coarse-α specimen nitrided at 843 K for 180 s, then subsequently water-quenched. \(\Sigma 9\) CSL boundaries are drawn by black lines in Fig. 6(b). The specimen was electropolished before nitriding to remove a deformed layer introduced by mechanical polishing at the surface. It is clearly seen that α grains, whose orientations are different from the original one, nucleate at the surface and grow radially along the specimen surface. Furthermore, the grain boundary between these newly formed α and original α grains are mostly \(\Sigma 9\) CSL relationship. However, whether the α grains hold \(\Sigma 9\) relationship from the nucleation stage or not cannot be clarified because newly formed α grains already grow larger than 20 μm in spite of the quite short nitriding period.

The two-step nitriding was performed as follows; a specimen was first nitrided at 943 K for 3.6 ks where the columnar α is not formed during the one-step nitriding,13,14) and subsequently cooled to 843 K where columnar α is formed, and then nitrided for 36 ks. Figure 7 shows a SEM image

![Fig. 6](image_url)  
**Fig. 6.** (a) Optical microstructure observed along the surface normal in the coarse-α specimen nitrided at 843 K for 180 s, (b) the corresponding α orientation image map to (a), in which \(\Sigma 9\) CSL boundaries within a deviation of 5 degrees from the exact \(\Sigma 9\) CSL relationship are drawn by black lines.

![Fig. 7](image_url)  
**Fig. 7.** (a) SEM micrograph of a cross section of the coarse-α specimen nitrided by two steps, (b) corresponding α orientation map. Two steps nitriding is carried out at 943 K for 3.6 ks followed by 843 K for 36 ks. (c) shows deviation in orientation relationships from the exact \(\Sigma 9\) CSL relation between the newly formed and original α grains in the area A and B in (b).
and the corresponding $\alpha$ orientation map of the coarse-$\alpha$ specimen nitried by two steps. In Fig. 7(a), the nitried zone consists of two regions. $\alpha$ in the region 1 (formed during the first step) remains the original $\alpha$ structure as shown in Fig. 7(b) whereas the columnar $\alpha$ is formed within the original $\alpha$ grains in the region 2 (the second step). Clearly, columnar grains are formed without a presence of pre-existing boundaries or the free surface. Figure 7(c) shows orientation relationships between newly formed $\alpha$ grains and the original $\alpha$ grain in the area where the formation of columnar $\alpha$ grains initiates (area A) and the growth front (area B). Although $\alpha$ grains in both areas hold near $\Sigma 9$ CSL relationship, deviation angles from exact $\Sigma 9$ CSL relation in the initial stage of the formation of $\alpha$ grains in the area A are relatively larger than those at the growth front in the area B, where orientations of most of the $\alpha$ grains are within a deviation of 5 degrees from the exact $\Sigma 9$ CSL relationships. Larger deviation from $\Sigma 9$ CSL relation in the initial stage in the area A, partly more than 10 degrees, than that in later stage in the area B shown in Fig. 7(c) strongly supports the preferential growth mechanism of $\Sigma 9$ CSL grains. However the mechanism how the newly formed $\alpha$ grains hold orientation relationship rather close to the $\Sigma 9$ CSL relation with original $\alpha$ grains even in the initial stage in the area A is still not clear. It should be worthwhile to investigate evolution of deformation structure and subsequent nucleation of $\alpha$ grains during recrystallization induced by precipitation of CrN.11,13)

4. Summary

Growth behavior of newly formed $\alpha$ grains across initial high angle grain boundaries and subgrain boundaries in the Fe-18mass%Cr specimens plasma-nitried at 843 K is investigated by means of EBSD. The results obtained are summarized as follows:

(1) Growth of newly formed $\alpha$ grains is stopped at pre-existing $\alpha$ grain boundaries and partly by subgrain boundaries misoriented larger than 5 degrees due to loss of $\Sigma 9$ CSL orientation relationships between the newly formed and the original $\alpha$ grains. Then, new $\alpha$ grains holding $\Sigma 9$ CSL orientation relationships with respect to the original $\alpha$ grain in front nucleate at the $\alpha$ grain boundaries.

(2) $\alpha$ grains can nucleate inside $\alpha$ grains even without the presence of initial $\alpha$ grain and subgrain boundaries or the specimen surface. It is suggested that preferential growth of $\Sigma 9$ oriented grains results in the characteristic columnar grains structure.

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REFERENCES

1) D. H. Jack: *Acta Metall.*, 24 (1976), 137.
2) D. S. Rickerby, S. Henderson, A. Hendry and K. H. Jack: *Acta Metall.*, 34 (1986), 1687.
3) D. S. Rickerby, A. Hendry and K. H. Jack: *Acta Metall.*, 34 (1986), 1925.
4) H. H. Podgurski and H. E. Knechtel: *Trans. Metall. Soc. AIME*, 245 (1969), 1595.
5) G. Miyamoto, Y. Tomio, T. Furuhara and T. Maki: *Mater. Sci. Forum*, 492–493 (2005), 539.
6) B. Mortimer, P. Grieveson and K. H. Jack: *Scand. J. Met.*, 1 (1972), 203.
7) E. J. Mittemeijer, A. B. P. Vogels and P. J. Van Der Schaaf: *J. Mater. Sci.*, 15 (1980), 3129.
8) P. M. Hekker, H. C. F. Rozendaal and E. J. Mittemeijer: *J. Mater. Sci.*, 20 (1985), 718.
9) R. E. Schacherl, P. C. J. Graat and E. J. Mittemeijer: *Z. Metallkd.*, 93 (2002), 468.
10) R. E. Schacherl, P. C. J. Graat and E. J. Mittemeijer: *Mater. Trans. A*, 35A (2004), 3387.
11) M. Sennour, P. H. Jouneau and C. Esnouf: *J. Mater. Sci.*, 39 (2004), 4521.
12) S. S. Hosmani, R. E. Schacherl and E. J. Mittemeijer: *Mater. Sci. Technol.*, 21 (2005), 113.
13) G. Miyamoto, A. Yonemoto, Y. Tanaka, T. Furuhara and T. Maki: *Acta Mater.*, 54 (2006), 4771.
14) G. Miyamoto, A. Yonemoto, Y. Tanaka, T. Maki and T. Furuhara: *ISIJ Int.*, 47 (2007), 1491.
15) D. G. Brandon: *Acta Metall.*, 14 (1966), 1479.
16) R. A. Fournelle and J. B. Clark: *Metall. Trans.*, 3 (1972), 2757.
17) K. N. Tu and D. Turnbull: *Acta Metall.*, 15 (1967), 369.
18) H. Nakashima, T. Ueda, S. Tsukakawa, K. Ichikawa and H. Yoshihaga: *Testu-to-Haganë*, 82 (1996), 238.
19) M. Uehara, H. Toshida and H. Nakashima: *Tetsu-to-Haganë*, 84 (1998), 212.