AMM-1027

Grain boundary engineering of Nickel by iterative recrystallization

Sitthichok Chamnan-Arsa[1], Onuma Santawitee[2] and Panya Kansuwan[1,*]

[1]Department of Mechanical Engineering, Faculty of Engineer, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand 10520

[2]National Metal and Materials Technology Center, Klong Luang, Pathumthani, Thailand 12120

*Corresponding Author: Tel: 02 329 8351, Fax: 02 329 8352, E-mail: kkpanya@kmitl.ac.th

Abstract

The influence of iterative recrystallization process and average grain size was investigated. The fraction of special grain boundary (∑3-∑27) of Ni (99.9%) was altered by thermomechanical process, which included the combination of medium strain and annealing process. Orientation imaging microscopy (OIM) analysis indicated that by using the second recrystallization sample with a 40% thickness reduction followed by annealing at 600^{o}C for 5 min, it is possible to increase the fraction of special grain boundary (f_{SB}) to 52.8%. A large proportion of this f_{SB} was found to be made up of ∑3 and ∑9 boundaries. Grain growth due to prolonging annealing as-2nd recrystallized samples was suggested to relate with the reduction of the special boundaries. On the contrary, after the 3rd recrystallization, f_{SB} approached in the same level when the average grain size was brought to be the same. It is independent of initial grain size and f_{SB} to begin with.

***Keywords**:* Iterative recrystallization, Coincidence site lattices, Grain boundary engineering

1. Introduction

It is well accepted that grain boundary structure has taken significant part in defining how the whole polycrystalline materials behave under various engineering services. When two adjacent grains with different crystallographic orientation meet each other they create a joined open structure layer called Grain boundary (GB) of which the energy varies according to free excess volume and elastic strain energy. The one which possesses lower excess volume exhibits properties approaching that of perfect crystal structure. By any means, if the fraction of the lower energy GBs is increased it is inevitable that some GB controlled phenomena should be enhanced. This concept had brought to light by Watanabe in 1984 [1] and later Grain Boundary Engineering (GBE) represented such the means on the purpose of increasing special boundary fraction (f_{SB}). Since then subsequent study have been performed to test the concept and have verified superior behaviors of GBEed materials to resist intergranular corrosion [2, 3] and creep failure [4]. Nevertheless, the term of special GBs is needed to be clarified and practical criterion is the density of coincident site lattice (CSL). Under the CSL model terminology, sigma number represents the reciprocal density of the CSL with respected to normal lattice. The lower number indicates the less free volume inside the GBs and thus the low energy GBs possess. Typical sigma values between 1 and 37 are considered special. Of our particular attention are twins (∑3) and twins related variants ($\sum 3^n$) boundaries and we define the collective name f_{SB} as the fraction of ∑3 to ∑9.

Grain boundary engineering method utilizes the same procedure as in thermomechanical process, the combination of plastic straining and annealing processes which promote thermodynamics and kinetics optimized for atomic rearrangement at GB until possible high f_{SB} is attained. The favorable thermomechanical routes fall in to two classes (1) single or multiple strain-annealing or (2) single or multiple strain-recrystallization. Strain-annealing uses low levels of deformation, typically at 3-10% which is enough to prevent recrystallization at low temperature but high enough to allow atomic rearrangement at grain boundaries to occur. For instance, 5-6% cold rolled Ni followed by annealing at 900°C for 10 min resulted in an increment of low-∑ CSL fraction from the as-received value of 35% to 65-70% [5, 6].

On the contrary, strain-recrystallization applies medium levels of deformation, typically around 20-50% cold work and high value of aging temperature for a short period of time. Medium level of strain causes partial recovery or recrystallization mechanism upon aging. This process can result in a small grain size and a high fraction of special boundaries of which are mostly twin boundaries generated during recrystallization and grain growth. Such the process route was used by Palumbo [7] consisting of pre-straining in the range of 5-30% and annealing in between 975-1200°C for multiple cycles. He could obtain 80% special boundaries ($\Sigma \leq 29$) from as-received value of 35% for Ni based alloys. Our objective of this paper is to investigate the effect of processing parameters of strain-recrystallization on the proportion enhancement of CSLs (∑3-27) in pure nickel. Grain boundary character distribution (GBCD) is measured by electron backscatter diffraction (EBSD) in scanning Electron Microscope (SEM).

2. Experimental

Specimens of pure nickel (99.9% Ni) of grade N1000 conforming to ASTM 1339-7, which was firstly annealed to 650°C at 10°C/min before immediately quenched in water (WQ), was defined as base materials (BM) of which the samples of 8.8 mm thick were prepared for subsequent cold rolling by 40% thickness reduction (40%TR), annealing at 600°C for 1 h in flowing argon, and then WQ. The processed samples were as-recrystallized (As-ReX) samples which later were subjected to a series of thermomechanical processes as shown schematically in Fig. 1.

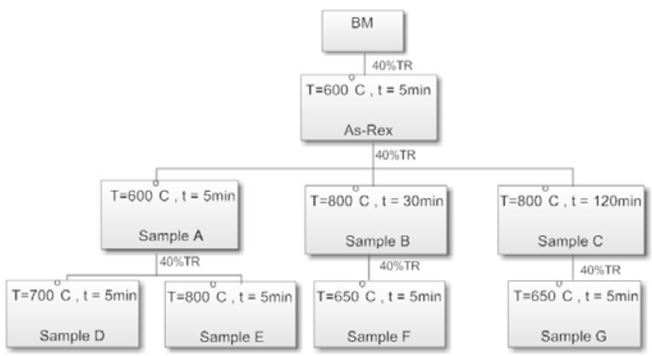


Fig.1 Sequential thermomechanical process

Sample A, B, C were intended to possess fully recrystallized microstructure with three different average grain sizes defined as small (~40 µm), medium (~80 µm) and large (~120 µm) when the last two samples were accomplished by prolonging annealing time of the former one. This set of samples illustrated the effect of grain size while the third recrystallization procedure was conducted to acquire the second set of samples (i.e. D, E, F, G). Sample A, D had the comparable average gain size to sample As-Rex to demonstrate the effect of the re-iterative recrystallization while samples E, F, G were prepared from A, B, C, accordingly, to possess an equivalent grain size about ~60 µm to express the effect of initial grain size and the value of special boundary parameters to the final GBCD results.

During each step, each specimen was metallographically prepared i.e. sectioned, mounted, ground, and finally polished with 1 µm diamond suspension for microstructure examination and finally 0.05 µm colloidal silica for GBCD evaluation at Microscopy Laboratory, MTEC. The SEM of Hitachi model S3400N equipped with TSL/EDAX orientation imaging microscopy and embedded with software version 5.3.2 was used to gather Kikuchi diffraction patterns with step size of 2.5 to 4 µm. The Brandon deviation criterion, $\Delta\theta = 15^{o}\Sigma^{-1/2}$, was chose to classify grain boundaries according to CSL description [8]. The distribution of each grain boundary type (GBCD) based on length fractions. Grain size measurements were performed by optical microscopy using the linear intersection method.

3. Result and Discussion

Fig. 2 shows optical micrographs and their corresponding reconstruction orientation images of the BM and As-ReX samples with average grain size of 23 and 36.6 µm, respectively. The gray lines represent the special grain boundary (3≤∑≤27) while black lines represent the random ones. The grain boundary character distribution (GBCD) of each sample is summarized in Table 1 and Fig. 3 consisting of three categories of boundaries, i.e. low angle boundaries (∑1), special boundaries (3≤∑≤27), and random boundaries. The low angle boundaries are defined by a misorientation angle below 10-15^{o} and special boundaries possess specific misorientation angle θ according to a generating function as follows [9]

$$\sum = x^2 + Ny^2 \quad (1)$$

$$\tan(\frac{\theta}{2}) = \frac{y}{x} N^{\frac{1}{2}} \quad (2)$$

where N = $U^2+V^2+W^2$, x, and y are integers ≥ 0 and [UVW] are the axis of misorientation index when misorientation scheme is used.

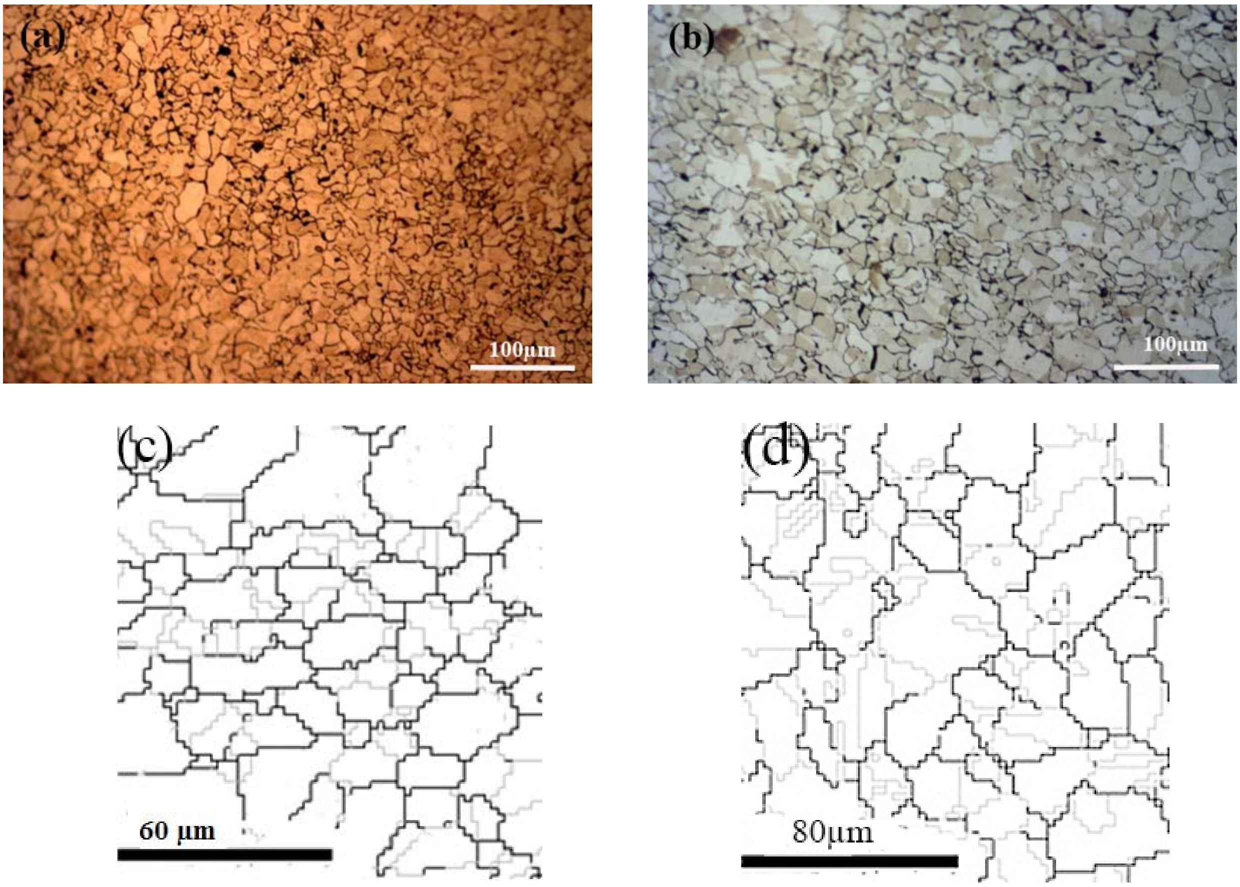


Fig.2. Microstructure and Grain boundary reconstruction images of base metal - BM (a,c) and as-recrystallized – As-ReX (b,d). Grey lines indicate ∑3-29 boundaries and black lines represent ∑>29

Table 1. Grain boundary character distribution statistics of each sample

Sample	grain size (μm)	∑1	∑3	∑9	∑27	∑1-∑27	∑3-∑27
BM	23	30.1	24.5	3.4	0.8	58.8	28.7
As-ReX	37	21.1	37	5.5	8.5	72.1	51
A	44	21.1	39.8	7	3.1	71	49.9
B	76	38.4	29	3.1	1	71.5	33.1
C	115	47.7	22.1	2.1	0.7	72.6	24.9
D	43	24.2	36.4	3.2	0.6	64.4	40.2
E	61	36.4	26.9	1.8	0.8	65.9	29.5
F	62	38.3	25.8	3.6	0.9	68.6	30.3
G	64	46.8	22.8	2.2	0.5	72.3	25.5

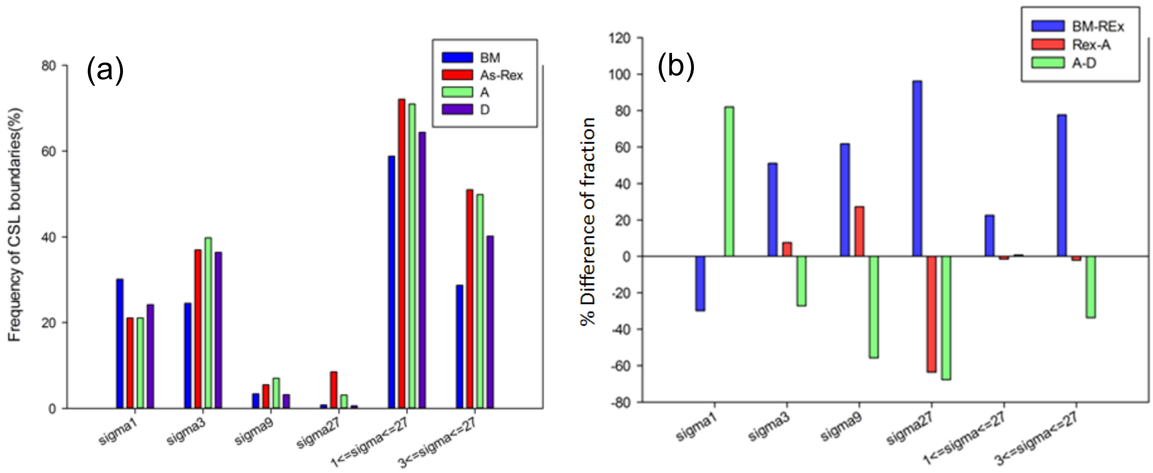


Fig. 3. The Fraction of special boundary of iterative recrystallized sample (a) and % different of fraction of processed samples with respected to former recrystallized samples.

3.1 The effect of iterative recrystallization processing (samples BM, As-ReX, A, D)

In Fig. 3 shows the proportion of ∑3 variants of all the iterative recrystallized samples with controlled average grain size of about 40 μm. Three iterative recrystallizations were performed. BM was first cold rolled and annealed to obtain As-ReX structure. Later re-applying the process to As-ReX samples were sample A for once and D for twice. The result shows that the first recrystallization yields higher fraction of ∑3 and ∑9 than the second-cycle does while the third results in the opposite direction. The lower rate of GBE is perceived as the fraction reaching a presumably equilibrium value when the third cycle could not enhance the low-∑ fraction anymore.

The achievement of GBE relies on the combination of thermomechanical processes i.e. mechanical process, annealing process, and microstructural process. Type and degree of straining like compression and tension including how fast it is applied are grouped into the mechanical category. Annealing process in an atmosphere is the collective name of heating to the pre-selected temperature, aging for a certain time, and finally cooling. All parameters which define the process like temperature, holding time, cooling rate and the atmospheric condition are paramount but less significant for heating rate. In addition, grain size and alloy elements which are regarded as microstructural process can alter twin formation mechanism, as well.

It is well-known that recrystallization required high level of strain (typically > 20% Cold worked) for the recovery and recrystallization to take place. Recovery resorts to dislocation annihilation and polygonization to relief elastic strain energy. Further system energy reduction can be accomplished by recrystallizing strain-free grains. It is this stage that twin boundaries are expected to nucleate by the growth accident of recrystallizing grains or from stacking faults during recovery [10]. The influence of subsequent grain growth by GB migration on the twin boundary fraction is still controversial. For Ni as an example, it was found that the proportion of twins increased in pure commercial Ni while decreased in pure Ni [11].

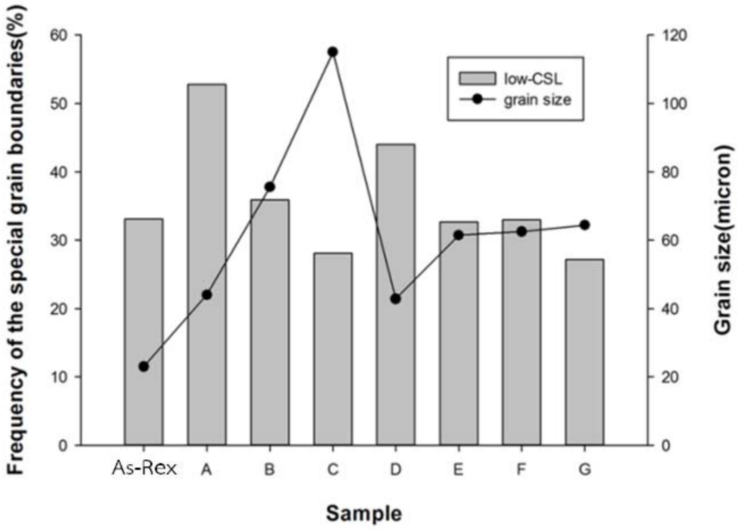


Fig. 4. The fraction of special grain boundary with grain size in each sample

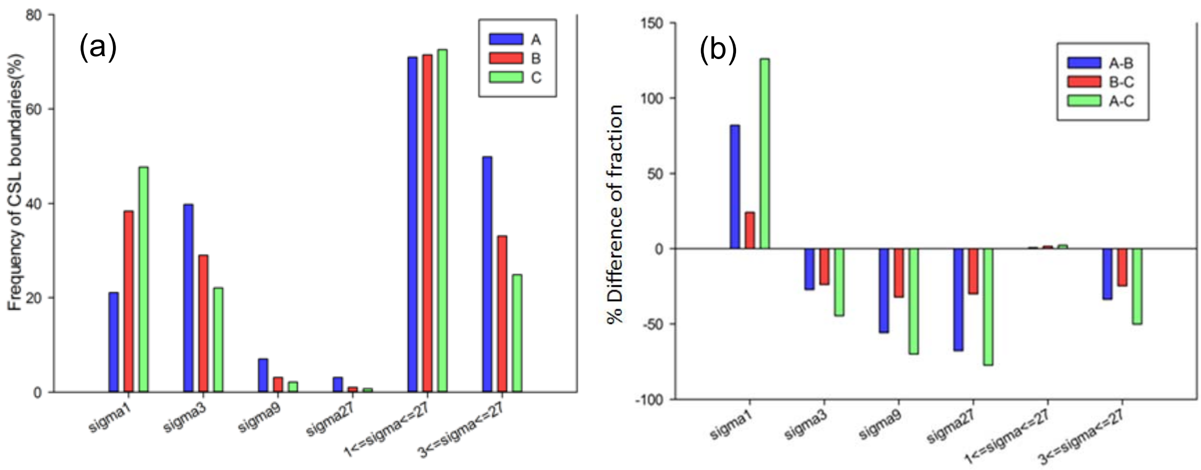


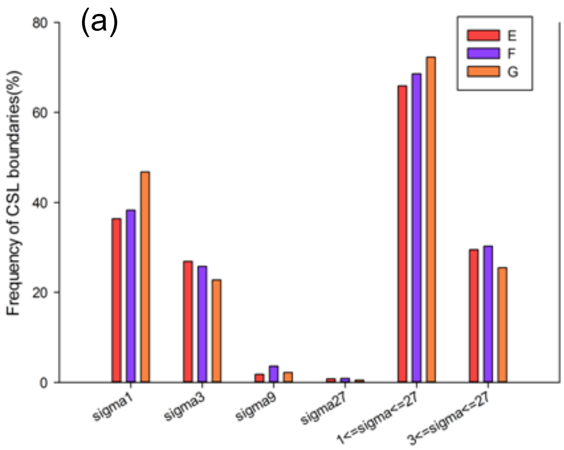
Fig. 5. The Fraction of special boundary of sample A, B, C (a) and % difference of fraction of processed samples with respected to the smaller grain size sample.

3.2 The effect of average grain size and grain growth (A, B, C)

As mentioned above, the effect of twin boundary to the grain growth process is still uncertain. However, our results agree with the work of D. Horton et. al. [11]. The fraction of low CSL decreases as grains grow in relatively pure nickel (Fig. 4, 5). In general, grain boundaries migrate as grain growing which lead to the interaction between each type of grain boundary at the triple junction which can be stated that

$$\sum 3^m + \sum 3^n = \sum 3^{m+n} \ or \ \sum 3^{|m-n|} \qquad (3)$$

in which n and m are positive integers. The later relation is applicable when m>n. This explains the twin increment as grains are growing. But from our result, the fraction of $\sum 1$ boundaries of Sample B, C was increased with average grain size. It is likely that the increase in $\sum 1$ fraction is as a result of the recombination of two like boundaries impinging on each other, such as the $\sum 3+\sum 3=\sum 1$ reaction. This is why $\sum 3$ fraction is dwindling.



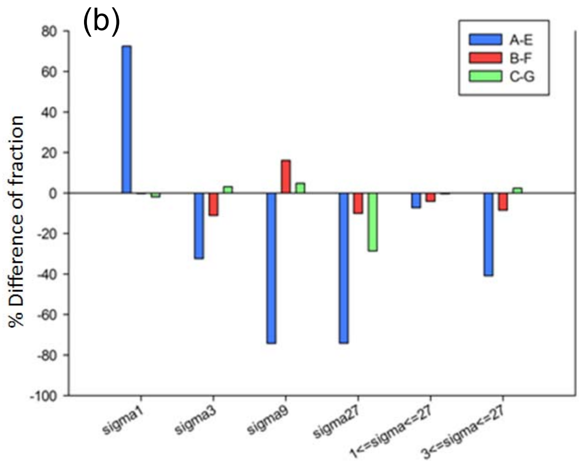


Fig. 5. The Fraction of special boundary of 3rd recrystallized samples (a) and % difference of fraction of each processed sample with respected to its own initial 2nd recrystallized samples.

3.3 The effect of initial grain size (A-E, B-F, C-G)

After the second recrystallization, there is no sign of the success of low-CSL enhancement except the major factor i.e. average grain size as shown in Fig. 5. The initial grain size and low-CSL fraction only influence when the initial value is relative high and their fractions are in the same level when their average grain size are brought about the same value.

4. Conclusion

We aim to alter grain boundary character distribution of electrolyte nickel (99.9%wt Ni) by thermomechanical processing using iterative strain recrystallization. Processing sequence of first recrystallization of 40% strain followed by a 600 ˚C anneal for 5 min, has resulted a special boundary fraction ($3 \leq \Sigma \leq 29$) of 52.8%, compared to the based material of 33.1%. In first recrystallization, the fraction of $\sum 1$ boundaries increased as average grain size is increased. We anticipate that medium straining in combination with high temperature annealing usually resulted in excessive grain growth and low fraction of special grain boundary values while the second recrystallization processing is not enhance the fraction of special boundaries. However when average grain size was equivalent after the third recrystallization, the fraction of low-CSL boundary was at same range independent of the initial value of grain size and the fraction of low-CSL boundaries.

5. Acknowledgement

The authors would like to express our sincere gratitude to the financial funders, Coordinating Center for Thai Government Science and Technology Scholarship Students (CSTS) and National Science and Technology Development Agency (NSTDA) under the project name, A new researcher scholarship of CSTS, MOST. Certainly, this work couldn't be possible without their support.

6. Reference

1. Watanabe, T. (1984). Approach to grain boundary design for strong and ductile polycrystals, *Res Mechanica.*, vol.11(1), January 1984, p. 47.
2. Sinsrok, P. (1999). Effect of recrystallization and grain growth in the formation of annealing twin in the 304 stainless steel, in Nuclear Technology,Chulalongkorn University: Bangkok.
3. Lehockey, E., M., Brennenstuhl ,A. M. and Thompson, I. (2004). On the relationship between grain boundary connectivity, coincident site lattice boundaries, and intergranular stress corrosion cracking, *Corrosion Science*, vol.46, October 2004, p. 2383-2404.
4. Lehockey, E. M. and Palumbo, G. (1997). On the creep behavior of grain boundary engineered nickel, *Materials Science and Engineering*, vol.A237, September 1997, p. 168-172.
5. Guyot, B. M. and Richards, N. L. (2005). A study on the effect of cold rolling and annealing on special grain boundary fractions in commercial-purity nickel, *Materials Science and Engineering A*, vol.395, March 2005 , p. 87-97.
6. Lee, S.-L. and Richards, N. L. (2005). The effect of single-step low strain and annealing of nickel on grain boundary character, *Materials Science and Engineering A*, vol.390, January 2005, p. 81-87.
7. Lin , P. , Palumbo G. and Aust , K. T. (1997). Experimental assessment of the contribution of annealing twins to CSL distributions in FCC materials, *Scripta Materialia*, vol.36, May 1997, p. 1145-1149.
8. Brandon ,D. G. (1966). The structure of high-angle grain boundary, *Acta metallurgica*, vol.14, November 1966: p. 1479-1484.
9. Randle , V. (1993). The Measurement of Grain Boundary Geometry, Bristol and Philadelphia: Institute of Physics Publishing.
10. Mahajan, S., Pande, C.S., Iman, M.A., Rath, B.B. (1997). Formation of annealing twins in FCC crystals, *Acta Metallurgica,* vol. 45(6), June 1997, p. 2633-2638.
11. Horton , D., Thomson ,C. and Randle ,V. (1995). Aspects of twinning and grain growth in high purity and commercially pure nickel, *Materials Science and Engineering A*, vol.203 , November 1995, p. 408-414.