Effects of initial microstructure on the grain boundary network during grain boundary engineering in Hastelloy N alloy

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Abstract:

Grain boundary engineering (GBE) was carried out on Hastelloy N alloy which is an important structural material used for molten salt reactor. The proportion of low Σ coincidence site lattice (CSL) grain boundaries of the Hastelloy N alloy can be enhanced to more than 70% with the formation of large-size highly-twinned grain-cluster microstructure which was formed through extensive multiple twinning events during recrystallization. The effects of cold deformation amounts and subsequent annealing on the grain boundary character distribution (GBCD) were investigated. The effects of initial grain size and the primary carbide distribution which was affected by the content of silicon on the grain boundary network evolution were discussed. It was determined that the initial grain size and primary carbide distribution will affect the recrystallization kinetics and hence influence the formation of highly twinned grain-cluster microstructure and the GBCD. The particle stimulated nucleation (PSN) caused by the primary carbides has a detrimental effect on the promotion of low Σ CSL grain boundaries.

Key words: Hastelloy N; grain boundary engineering; primary carbide particles; grain boundary network distribution; particle stimulated nucleation

1 Introduction

In recent years, the nuclear power has been playing a more and more important role due to its great advantage in many aspects such as safety, environment protecting and cost saving. Among the six new generation *IV* reactors, the Molten Salt Reactor (MSR) is the only liquid fueled reactor which could use thorium-based molten salts as liquid fuel to realize the thorium-uranium fuel cycle. The MSR uses fuel-contained molten fluoride salts as both the coolant and reactant, which brings it superiorities in inherent safety, strong negative feedback coefficients, higher power generation efficiency, and so on [1-3].

The concept of MSR originated in the Aircraft Reactor Experiments (ARE) in 1950s. Then, a small MSR was designed and constructed by Oak Ridge National Laboratory (ORNL) and it became critical in 1965. In order to resist the high temperature, chemically aggressive fluoride molten salts and intense radiation fluxes, a polycrystalline Ni-Mo-Cr superalloy, Hastelloy N, was invented by ORNL to be used as the main structural material for MSR [4]. After being operated successfully for 4 years, the reactor was shut down and its components had been examined systematically. Hastelloy N presented some deficiencies during this examination, and one of them was that the grain boundaries (GBs) were embrittled to depth of 50-250 μ m resulting from being attacked by fission product tellurium (Te) [5]. According to the research conducted by Liu [6] and Všíanská [7], Te favours substituting Ni in the GB plane and forming strong bonds with neighboring Ni atoms, and the GB expansion is induced by the large atomic size of Te which is the source of the Te-induced GB

decohesion. The Te induced intergranular cracking of Hastelloy N can deteriorate the mechanical properties of the structural components of the MSR and further shorten their service life. Therefore, it's of great importance to suppress the intergranular embrittlement caused by Te. Meanwhile, it has been revealed that Te diffused into Hastelloy N mainly along GBs [8].

The idea of Grain Boundary Engineering (GBE) was originated from the concept of “Grain boundary design” proposed by Watanabe [9]. The main aim of GBE is to enhance the grain-boundary-related properties such as corrosion resistance, intergranular cracking resistance and suppression of the intergranular diffusion of materials which have face centered cubic (FCC) structure with low stacking fault energy (SFE) by changing the grain boundary character distribution (GBCD) and the grain boundary connectivity. Despite some researches had opened the possibility of GBE via hot deformation [10], cold work with the subsequent annealing is often used to realize the GBE by promoting the multiple twinning events and increase the fraction of low- Σ coincident site lattice (CSL) grain boundaries ($\Sigma \leq 29$) [11-13]. The Σ value is the reciprocal density of coincident sites between two adjoining grains. According to the results given by Bechtel [14], GBE could markedly reduce the susceptibility to intergranular hydrogen embrittlement in metallic materials. The results of Kobayashi [15] showed that the polycrystalline nickel specimen with higher fraction of low- Σ CSL GBs exhibited higher resistance to sulfur segregation-induced intergranular fracture. Our previous work [16, 17] showed that GBE can enhance intergranular corrosion resistance of Ni based Alloy 690 and 304 stainless steel. The GBE is expected to increase the resistance to Te-induced intergranular cracking of Hastelloy N by increasing the proportion of the low- Σ CSL GBs and suppressing Te diffusion along the GBs.

Gehlbach and McCoy [18] found that the microstructure of Hastelloy N was featured by the

strings consisting of massive primary M_6C (Ni_3Mo_3C) type carbide particles in matrix. Meanwhile, according to the results given by Xu et al [19], the content of Silicon played an important role in the amount, distribution, and structure of the primary carbide. The addition of silicon would increase the amount of M_6C carbides and reduce the lattice parameter of M_6C carbide in Ni-Mo-Cr superalloy. Since the primary carbides do not decompose until 1335°C [19], which is much higher than the thermal-mechanical processing (TMP) temperature of Hastelloy N, it will be of great importance and meaning to investigate how the content of Silicon, i. e. the amount and distribution of primary carbides, will act in the GBE process of Hastelloy N. One vacuum-melted standard specimen with normal silicon content and one low-silicon specimen are used to study the influences of the primary carbides on the GBCD changes during GBE. In this paper, the effects of initial microstructure including both the grain size and the carbide particle distribution in the matrix on the microstructural evolution during TMP of grain boundary engineering are investigated.

2. Experimental details

The compositions of the two Hastelloy N alloy heats with different silicon contents used in this investigation are shown in Table 1. The starting condition of the materials are in solution annealed (SA) state with the annealing temperature of 1177 °C. Then the two kinds of original samples with different contents of silicon were cut into strips of 15 mm × 10 mm in square cross-section. After being cold rolled with the reduction of 50% and subsequently solution annealed under three conditions: at 1100 °C × 10 min, 1177 °C × 10 min, and 1177 °C × 40 min, those three specimens with different initial grain sizes designated as specimens S, M and L were obtained correspondingly. The TMPs of GBE were carried out on these samples with low-strain room temperature tensile deformation prior to short-duration annealing at an adequately high temperature [20, 21]. For the

standard sample, specimens with different initial grain sizes (specimens S, M and L) were deformed with tensile strains of 3%, 5%, 7%, and 10% respectively. Meanwhile, all the three low-silicon specimens (specimens LS, LM, and LL) were deformed with tensile strains of 5% and 7%. Then, all of those eighteen tensile-strained strips were annealed at 1177 °C for 10 minutes and subsequently quenched into water. Thereafter, all the GBE specimens were obtained. The GBE specimens obtained from standard sample with normal silicon content were designated as S3, S5, S7, S10, M3, M5, M7, M10 and L3, L5, L7, L10 corresponding to starting sample S, M, and L. Meanwhile the GBE specimens obtained from low-silicon sample were designated as LS5, LS7, LM5, LM7 and LL5, LL7 correspondingly. The specific TMP procedures are shown in Table 2. Metallographic samples were grounded using SiC sandpapers in the order of 400, 600, 800, 1000, 1500 and 2000 grits and then mechanically polished. Then the polished specimens were electro-etched in a solution containing 10% oxalic acid—90% H₂O (wt. %) at room temperature with 20 V direct current for 90 s. After that, the metallographic samples were observed and recorded by KEYENCE VH-Z100 optical microscopy (OM). Prior to scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) experiments, all the specimens were grounded using SiC papers and then electro-polished in an electrolyte containing 20% HClO₄—80% CH₃COOH at room temperature with 30 V current for 60 s. EBSD was employed for the determination of grain boundary misorientations using the HKL-Channel 5 EBSD system attached to a CamScan Apollo 300 thermal field emission gun SEM. The operation conditions are: 20 kV accelerating voltage, 30 mm working distance, 70° beam incidence angle. The scans were carried out on a rectangular area of 1200 μm×800 μm, with each orientation point being represented as a square cell using a 4 μm step size. The misorientation angle used as threshold for defining a grain is 2°. Moreover, grain boundaries with misorientation angle

larger than 2° but less than 15° are defined as low angle grain boundaries, and grain boundaries with misorientation angle larger than 15° are defined as the high angle grain boundaries which can be divided into random grain boundary and special structure grain boundary categories. Grain boundary characters were defined by CSL model according to the Palumbo-Aust' criterion ($\Delta\theta_{max} = 15^\circ \Sigma^{-5/6}$) [22]. In this paper, the grain is defined as a crystal with a unique orientation. Therefore, all types of boundaries are included as defining individual grain, which means that annealing twins are also regarded as grains. All the data collected from EBSD was processed by the software Channel 5. The mean grain size of the tested specimens was calculated by both the line intercept method (LI) and equivalent circle diameter (ECD) in the Channel-5.

3. Results and discussion

3.1 Microstructure of the pre-processing specimens

The microstructure of the initial solution annealed Hastelloy N specimens are shown in Fig. 1. For the standard specimen with normal silicon content, many strings along the rolling direction consisting of primary carbide particles can be observed as shown in Fig. 1a. While the strings cannot be observed in the low-silicon specimen and the carbide particles are smaller and more dispersed, as shown in Fig. 1b. Both intergranular and transgranular primary carbides can be observed in the two specimens.

The grain size of pre-processed specimens was intentionally manipulated to three sizes and designated as: S, M, and L through TMPs as mentioned in the previous section. The optical microstructure and grain boundary networks (GBNs) of those pre-processed specimens are displayed in Fig. 2 and Fig. 3 respectively. As shown in Fig. 2, the primary carbide particles did not decompose upon the samples being deformed and subsequently heat treated at high temperatures (1100°C or

1177°C). Therefore even after the deformation and heat treatments, the standard specimen with normal silicon contents still has intensively distributed large size carbides, even though the distribution of strings along the rolling direction can no longer be seen.

Although the grain size and the morphology of the carbide particles are different in those six samples, there are some features in common among all the specimens as can be seen from Fig. 2 and Fig. 3. First, the mean grain size increased with the increase of annealing temperature and duration. Meanwhile, in all the six microstructures, the $\Sigma 3$ boundaries appear in the shape of straight single line or parallel line pairs, either grain spinning or terminated within a single grain, i.e., all the annealing twins are isolated within a single grain. The mean grain size of the pre-processed standard sample S, M, L and low-silicon sample LS, LM, LL, as well as the proportion of low- Σ CSL boundaries of the six samples were shown in Table 3. Comparing the change trend of the mean grain size between the standard samples and the low-silicon samples, it might be found out that the annealing temperature made more differences than annealing time in grain growth during annealing process for Hastelloy N, considering the annealing conditions between the S ($1100\text{ }^{\circ}\text{C} \times 10\text{ min}$), M ($1177\text{ }^{\circ}\text{C} \times 10\text{ min}$) and L ($1177\text{ }^{\circ}\text{C} \times 40\text{ min}$) samples.

The grain boundary character distributions (GBCDs) of all the six samples show that the proportion of $\Sigma 3$ boundaries are all around 50% and it accounts for about 95% of all the low- Σ CSL boundaries. Table 3 shows that the proportions of $\Sigma 3$ boundaries of S and SL specimens are smaller than that of other specimens. A $4\mu\text{m}$ was chosen as the step size for all the specimens for a consistent parameter between all the specimens, while some small annealing twins in S and SL specimens can't be distinguished with a $4\mu\text{m}$ step size.

3.2. The effect of initial grain size on the GBN during GBE process

The GBNs of all the GBE-processed standard specimens are shown in Fig. 4. Different colors were used to show the different type grain boundaries in Fig. 4, including $\Sigma 1$ (grey, low-angle boundaries, misorientation angle range: $2-15^\circ$), $\Sigma 3$ (red), $\Sigma 9$ (blue), $\Sigma 27$ (green) and random boundaries (black). The $\Sigma 3^n$ ($n = 1, 2, 3 \dots$) grain boundaries connected with each other forming many triple junctions, such as $\Sigma 3$ - $\Sigma 3$ - $\Sigma 9$, $\Sigma 3$ - $\Sigma 9$ - $\Sigma 27$, inside the area encircled by random grain boundaries [23]. The highly twinned microstructures featured by clustering of $\Sigma 3^n$ ($n=1, 2, 3 \dots$) type boundaries could be observed after full recrystallization. The formation of highly twinned large grain-cluster through multiple twinning starting from a single nucleus during recrystallization is one of the marked features of the GBE microstructure, as shown in Fig. 5. Some black lines delineated random grain boundaries inside the grain-cluster are actually high order twin boundaries, such as $\Sigma 3^4$ ($\Sigma 81$), $\Sigma 3^5$ ($\Sigma 243$)..., which are arbitrarily defined as random ones by the channel 5 system due to their Σ values are larger than 29 [21]. The smaller grains as circled in Fig. 4b and g are the indication of the positions where the primary carbide particles presented.

As can be seen from Fig. 4, the GBN maps of the specimens with different origin grain sizes and GBE TMPs showed a marked difference with each other. It can be expected that a larger grain-cluster with smaller inner grains could have higher proportion of $\Sigma 3$ and related boundaries. The grain size and grain-cluster size together with the proportions of low- Σ CSL grain boundaries are therefore been used to describe the grain boundary network in this work and the results are shown in Fig. 7. Comparing the grain sizes among the specimens S3, S5, S7 and S10, generally, both the grain size and grain-cluster size decrease as the pre-strains increases from 3% to 10%. A higher deformation amount will provide a higher nucleation density during recrystallization and hence a smaller final grain-cluster size and more random grain boundaries. Whereas, different tendencies can

be observed on the effects of pre-strain on the recrystallized grain size between S series specimens and M, L series specimens. The M, L series specimens represent a peak grain size and grain-cluster size at the tensile strain of 5%.

As shown in Fig. 4a, the grain sizes of the S3 specimen are much larger than the initial grain sizes shown in Fig. 3a, and most of the twin grains are gathered in each grain-cluster, as can be seen in Fig. 5. While in specimen M3, a grain-cluster surrounded by many smaller grains with the same grain size of the initial specimen were observed, as shown in Fig. 4b. The grain size of the L3 specimen is nearly the same as the initial grain size shown in Fig. 4c. The local misorientation maps corresponding to specimens S3, M3 and L3 were shown in Fig. 6. As shown in Fig. 6d, most areas of the S3 specimen have the low local-misorientation values indicating an almost fully recrystallized microstructure. A part of area of the M3 specimen has low local-misorientation value while other area has higher misorientation value as shown in Fig. 6e. Almost all the grain boundaries have high local-misorientation value in the L3 specimen as shown in Fig. 6f. Judging from both the GBN and the local-misorientation map, the S3 specimen is fully recrystallized and M3 is in the partial recrystallized state, while the L3 specimen is still in the deformed state. The maximum of the pre-strain is 10% for all the specimens in this work, and all the pre-strains applied in this work can be classified as low strains. According to previous researches [24-26], the specimen with a larger grain size will gain less stored energy during low-strain deformation process. This will contribute to the increase of the recrystallization temperature. On the other hand, grain boundaries are preferential sites for nucleation of recrystallization, and therefore a larger initial grain size provides fewer nucleation sites. So the recrystallization in the M and L series specimens are slower than the smaller grain sized S series specimens.

The GBCDs of the GBE-processed standard specimens are shown in Fig. 8. The GBCD of S3 (proportion of overall low- Σ CSL GBs, 71.24%), M3 (proportion of overall low- Σ CSL GBs, 52.96%), L3 (proportion of overall low- Σ CSL GBs, 54.97%) can be explained by previous results about the recrystallization states of those three specimens. Comparing the specimens with a same initial grain size, while their pre-strains varies from 3% to 10%, the proportions of overall low- Σ CSL GBs increased at first and gained the maximum at the pre-strain of 5% and then began to decrease as the pre-strains continued to increase. As mentioned before, the recrystallized grain-cluster size will be smaller with a larger pre-strain due to a higher nucleation density. As a consequence, the smaller grain-cluster size will increase the amount of random grain boundaries, which will contribute to the decrease of the proportion of overall low- Σ CSL GBs.

The recrystallization temperature decreases as strain increases. The stored energy, which provides the driving force for recrystallization, increases with pre-strain increasing. Therefore, both the nucleation and grain growth are more rapid or occur at a lower temperature in a more highly deformed specimen. For the specimens with a larger pre-strain, the recrystallization was already finished before the annealing finished. Then the grain began to grow during the rest time, and the proportion of the overall low- Σ CSL GBs began to decrease due to being swept away by the migration of general high angle grain boundaries. According to the research results of Li [27] and Bozzolo [28], a higher rate of grain boundary migration was more favorable to promote the generation of annealing twins. Compared with recrystallization, the lower driving forces in grain growth resulted in much slower grain boundary migration. Moreover, Jin [29] proposed that some large grains will consume small grains and their twins without producing many new twin boundaries in the grain growth regime.

It could be seen that all those three series (S, M, L) specimens gained their max proportion of overall low- Σ CSL GBs at the pre-strain of 5%, as shown in Fig. 8. However, the proportion of overall low- Σ CSL GBs decreased much faster when the pre-strain continued to increase in S series specimens. Because the recrystallization completed earlier in the S series specimens, the grains had much more time to grow after the full recrystallization, then the proportion of overall low- Σ CSL GBs would decrease to a lower extent after the annealing.

As can be seen from Fig. 4 and Fig. 6, a larger grain-cluster size usually but not necessarily suggests a higher proportion of overall low- Σ CSL GBs. During the research of applying GBE TMP to alloy 690, Liu [30] had proposed that the ratio of the grain-cluster size over the grain size governed the proportion of overall low- Σ CSL GBs. GBE-processing is a recrystallization process, in which each grain-cluster was formed by “multiple twinning” starting from a single recrystallization nucleus. In the GBE-processed microstructure, both the grain-cluster size and the twin boundary density worked together to determine the proportion of overall low- Σ CSL GBs. Therefore, the GBE-processed microstructure with a larger grain-cluster size and a smaller grain size (which indicated the higher twin boundary density) would have higher proportion of overall low- Σ CSL GBs.

3.3 The effect of primary carbides on the GBN during the GBE process

The GBN maps of the GBE-processed low-silicon specimens are displayed in Fig. 9. According to the existence of the large size grain-cluster and the large amounts of the $\Sigma 3^n$ ($n=1, 2, 3$) type GBs, it can be seen that all those six specimens were fully recrystallized. Fig. 10 and Fig. 11 presents the grain size, grain-cluster size and the grain boundary character distribution of all the low-silicon specimens.

As shown in Fig. 9b and Fig. 11, the LM5 specimen have the highest proportion of overall

low- Σ CSL GBs (79.88%), which is higher than that of the M5 specimen (75.8%) with the same GBE TMP. Both the M and L series low silicon content specimens have the higher proportion of low- Σ CSL GBs than that of the corresponding standard specimens, whereas the S series specimens have the lower proportion of overall low- Σ CSL GBs. It is deduced that for LS5 specimen the recrystallization had already completed before the annealing finished so that grain growth occurred to swept away the already formed low- Σ CSL GBs during the rest time resulting in the decrease of the proportion of the overall low- Σ CSL GBs. The main difference between specimens M5 and LM5 was that M5 specimens have more intensive distributed primary carbide particles. Therefore, it can be deduced that the primary carbide would hinder the immigration of the grain boundaries, thus hinder the growth of the nucleuses of recrystallization during the GBE TMP of Hastelloy N.

As shown in Fig. 4b and Fig. 4g, grains are surrounded by many much smaller grains, where is consistent with the distribution characteristic of the primary carbides. The primary carbides would not decompose during the GBE-processing since the primary carbides do not decomposed until 1335°C [19]. The results of the SEM and EDS tests conducted on M3 specimen are displayed in Fig. 12. The SEM images and the corresponding EDS results in Fig. 12 reveal that small particles in the matrix are the primary carbides. Although the shape of the primary carbides may be different with each other, the chemical compositions are quite identical, as can be seen from Fig. 12.

In the 1970s, Particle Stimulated Nucleation (PSN) has been studied in many alloys by Hansen [31] and Herbst [32]. A necessary criterion for the formation of a nucleus is that the maximum misorientation within the deformation zone is sufficient to form a high angle boundary within the matrix, and therefore the conditions for nucleation depend on both the particle size and the strain. For this reason, PSN is usually found to occur at particles of diameter greater than a certain size

(normally around $1\mu\text{m}$) [33]. For the grains formed by PSN, the grain may stop growing when the deformation zone is consumed. Therefore, it has become a common feature that the PSN grain does not grow largely and eventually will be surrounded by other grains, which is just consistent with what can be seen in the circled areas in Fig. 4b and Fig. 4g.

In order to figure out the influence of primary carbide particles during the annealing process, six standard specimens were selected with the same grain size (which was the same as the M specimen) and the same pre-strain of 3%. The six specimens were annealed at 1177°C for 0, 2, 4, 6, 8, and 10 minutes respectively. Then all the six specimens were examined by SEM and the results are displayed in Fig. 13. As was revealed by the SEM images in Fig. 13, before the annealing, the grain size near the primary carbide particles are nearly the same as that of the surrounding grains. Then, as the annealing began, there were many relatively smaller grains formed near the primary carbide particles as shown in Fig. 13b. When the annealing time continued to increase, the surrounding grains gradually grew while the grains near the primary carbide particles stayed the same.

All the results being discussed before suggest that the PSN had played an important role in the microstructure evolution during the GBE-process of the Hastelloy N. Therefore, the standard specimen, which have more primary carbide particles, would be affected more seriously by PSN. In the meantime, the nucleation occurs preferentially where the particles are clustering [32, 34]. This will also result in the fact that the standard specimens are influenced more pronouncedly by PSN. Thus, there will be more concentrated smaller grains in the standard specimens, as shown in Fig. 4b and Fig. 4g. Most importantly, the majority of the boundaries of the PSN grains are random grain boundaries. Both the facts will decrease the grain-cluster size and increase the amounts of the random grain boundaries, resulting in the decline of the proportion of overall low- Σ CSL GBs.

Generally speaking, the increase of the content of the silicon will decrease the proportion of overall low- Σ CSL GBs, i.e. it will weaken the effect of the GBE-process.

4. Summary

The effects of initial grain size and the primary carbide distribution which was affected by the content of silicon on GBE microstructures were focused on in this paper. Under the same low-strain tensile-deformation and annealing conditions, the larger initial grain size will delay the recrystallization during the TMP of GBE. For the larger initial grain size sample, a higher pre-strain was needed to achieve GBE. For the smaller initial grain size sample the nucleation density is higher and hence yield a smaller grain-cluster size and lower proportion of low- Σ CSL GBs after recrystallization. For the medium initial grain size sample, a highest low- Σ CSL GBs can be obtained, around 75% for the standard sample and almost 80% for the low silicon content sample respectively. The low silicon content samples have smaller and more dispersed primary carbides and have higher proportion of low- Σ CSL GBs. While, in the standard silicon content samples, the particle simulated nucleation (PSN) caused by the bigger primary carbides increases the random boundary density and hence has a detrimental effect on the enhancement of low Σ CSL grain boundary proportions.

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Tables

Table 1 Chemical composition of two investigated specimens of Hastelloy N. The bold values indicate the amounts of the silicon are the main difference between two specimens

Alloy specimens	Ni	Mo	Cr	Fe	Mn	Si	C
Standard specimen	balance	16.6	7.09	3.83	0.52	0.46	0.04
Low-silicon specimen	balance	16.7	7.35	4.19	0.44	0.06	0.053

Table 2 Thermo-mechanical treatment of the alloy HASTELLOY N specimens.

Pre-processing			GBE processing		
Cold Rolling (%)	Annealing	Sample ID	Elongation (%)	Annealing	Sample ID
50%	1100°C×10min	S	3	1177°C×10min	S3
			5×2		S5/LS5
			7×2		S7/LS7
			10		S10
	1177°C×10min	M	3		M3
			5×2		M5/LM5
			7×2		M7/LM7
			10		M10
	1177°C×40min	L	3		L3
			5×2		L5/LL5
			7×2		L7/LL7
			10		L10

Table 3 Mean grain size of the pre-processed standard sample S, M, L and low-silicon sample S, M, L calculated by line intercept method (LI) and equivalent circle diameter (ECD), and the proportion of low- Σ CSL boundaries of the six samples.

		Mean grain size(μm)		proportion of	proportion of	proportion of
		LI	ECD	$\Sigma 3$ GBs,%	low- Σ CSL GBs,%	$\Sigma 3$ in Low- Σ CSL, %
Standard Sample	S	10.5	11.2	36.9	39.3	93.9
	M	25.2	22.6	52.6	53.7	98.0
	L	28.0	24.5	51.7	53.1	97.2
Low-Silicon Sample	LS	13.3	13.7	43.0	45.1	95.4
	LM	19.0	17.3	50.3	51.9	96.9
	LL	22.2	18.6	54.2	55.7	97.4

Figure Captions

Fig. 1 Microstructure of (a) the standard specimen with normal silicon content and (b) the low-silicon specimen

Fig. 2 The microstructure of the pre-processed specimens:(a), (b) and (c) correspond to S (1100°C×10min), M (1177°C×10min) and L (1177°C×40min) of the standard specimens with normal silicon content; (d), (e) and (f) correspond to LS, LM and LL of the low-silicon specimens.

Fig. 3 GBNs of the pre-processed specimens: (a), (b) and (c) correspond to S (1100°C×10min), M (1177°C×10min) and L (1177°C×40min) of the standard specimens with normal silicon content; (d), (e) and (f) correspond to LS, LM and LL of the low-silicon specimens. Random boundaries, $\Sigma 3$, $\Sigma 9$, $\Sigma 27$ and other low- Σ CSL boundaries, and low-angle grain boundaries are black, red, blue, green, yellow, and gray respectively. (The same below)

Fig. 4 GBN maps of the GBE-processed standard sample, (a), (d), (g), (j) correspond to S3, S5, S7, S10; (b), (e), (h), (k) correspond to M3, M5, M7, M10; (c), (f), (i), (l) correspond to L3, L5, L7, L10.

Fig. 5 The analysis of the grain-cluster in Fig. 4(a). (a)OIM maps of different grain boundaries; (b) Orientation distribution of the grains, contrasted by colour of inverse pole figure; (c) inverse pole figure for colour code.

Fig. 6 OIM map of S3 (a), M3 (b), L3(c), and the corresponding local-misorientation map, different color were used to represent different level of local-misorientation.

Fig. 7 Grain size and grain-cluster size of all the GBE-processed standard samples; the grain size (black), the grain-cluster size (grey).

Fig. 8 Grain boundary character distribution (GBCD) of all the GBE-processed standard samples. $\Sigma 3$ (grey), $\Sigma 9+\Sigma 27$ (black) and other low- Σ CSL GBs (red).

Fig. 9 GBN maps of the GBE-processed low-silicon samples (a), (d) correspond to LS5 and LS7; (b), (e) correspond to LM5 and LM7; (c), (f) correspond to LL5, LL7.

Fig. 10 the grain size and grain-cluster size of all the GBE-processed low-silicon samples; the grain size (black), the grain-cluster size (grey).

Fig. 11 Grain boundary character distribution (GBCD) of all the GBE-processed low-silicon samples; $\Sigma 3$ (grey), $\Sigma 9 + \Sigma 27$ (black) and other low- Σ CSL GBs (red).

Fig. 12 EDS result of the small particles in the matrix of M3 specimen.

Fig. 13 SEM photos of the specimens with the elongation of 3% and the annealing time of 0, 2, 4, 6, 8, 10 minutes.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13