THE EFFECT OF GRAIN BOUNDARY MISORIENTATION ON THE GRAIN
BOUNDARY ENERGY IN A HIGHLY TWINNED ALLOY 690

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ABSTRACT
Grain boundary engineering (GBE) was applied to Alloy 690, in the microstructure of which the proportion of low Σ coincidence site lattice (CSL) grain boundaries was increased to more than 70%, most of them being Σ3n (n=1,2,3) types. Recent research showed that even in the low Σ CSL grain boundary regime, the boundaries with different Σ values showed different susceptibility to element segregation, precipitation and sensitization. Not all of the interfaces with low Σ CSL character have better properties than random grain boundaries. In the current work, thermal grooving was used to measure the grain boundary energy of Alloy 690. The misorientations of different types of GBs were identified with the electron backscatter diffraction (EBSD) technique. The morphology profile, dihedral angle etc. of thermal grooves were measured with atomic force microscopy (AFM). The ratio of interface energy over surface energy was calculated according to the shape of thermal grooves of different GB characters. Random and Σ 27 GBs have similar energies. The incoherent twin boundary (Σ3i) has a similar energy with that of the Σ9. Both of them have one half of the random GB energy. The energy of Σ1GB varied with the misorientation angle. The coherent twin boundary (Σ3c) has the lowest GB energy of the investigated GBs.

Keywords: Alloy 690, grain boundary energy, CSL grain boundary.

1.0 INTRODUCTION
Most metallic materials used in industry are polycrystalline materials. Grain boundaries play an important role in many properties. The concept of grain boundary design was proposed by Watanabe [1], and later on was refined to be grain boundary engineering (GBE) [2]. By exercising control over the population of low Σ (Σ≤29) coincidence site lattice (CSL) grain boundaries, the resistance to grain boundary degradations can be greatly enhanced, such as intergranular corrosion (IGC) [3], intergranular stress corrosion cracking (IGSCC) [4], and creep [5]. Σ refers to the reciprocal density of the coincidence site lattice on both sides of the GB [6]. The lower the Σ value is, the higher the proportion of the coincidence sites in the lattice.

Nickel-based Alloy 690 has been used as a substitute for Alloy 600 as a steam generator tube material in pressurized water reactors because of its excellent corrosion resistance in a broad range of aqueous environments [7]. However, further improvement of Alloy 690 corrosion resistance and other properties is a subject worthy of study [8]. Alloy 690 is a face-centered cubic metal material with low stacking fault energy. The proportion of low Σ CSL grain boundaries can be increased to more than 70% by thermal-mechanical processing, and most of the low Σ CSL grain boundaries are of Σ3n type [9].

Recent research showed that even in the low Σ CSL grain boundary regime, the boundaries with different Σ values showed different susceptibility to element segregation [10], precipitation [11], corrosion [12], and cracking [13]. Not all of the low Σ CSL GBs have better properties than random grain boundaries. West and Was [14] showed that the cracking frequency of Σ3 boundary was much less than that of other type of low Σ CSL boundaries (Σ9 and Σ27) and random grain boundaries when they studied the intergranular stress corrosion cracking susceptibility of Type 316L stainless steel and nickel-based Alloy 690 in supercritical water. Furthermore, it is more generally accepted that only the coherent twin boundary (Σ3c)
is special because of the perfect grain boundary atoms arrangement [13]. The micro tensile tests at room
temperature demonstrated that the $\Sigma 3$ $(1 1 1)$ boundary was the strongest of all the CSL boundaries
examined, and CSL boundaries with larger $\Sigma$ numbers typically showed grain boundary fracture [15]. The
coherent $\Sigma 3$ boundaries showed the smallest Cr depletion after irradiation [10]. Even the different low
$\Sigma$ CSL GBs showed remarkable anisotropy properties. Hence it is necessary to compare the GB energy of
different character GBs.

It is known that the general trends of grain boundary energy as a function of misorientation angle are
obeying the Ready-Shockley relationship for low angle boundaries and exhibiting cusps for low $\Sigma$ CSL
misorientations [16]. So it is necessary to compare the free energy in between different low $\Sigma$ CSL grain
boundaries. Thermal grooving has been recognized as a useful method to measure the grain boundary
energy in many metallic materials and ceramic materials [17-20]. A developed groove can reflect the
equilibrium between the GB and the free surface. By measuring the groove profile and the groove
dihedral angle, the ratio of grain boundary energy over the free surface energy can be calculated, with the
assumption of isotropic free surface energy [17].

In the current work, a grain-boundary-engineered Alloy 690 was heat treated under high vacuum to get
thermal grooves of grain boundaries. The misorientation of different grain boundaries are identified with
the electron backscatter diffraction, (EBSD) technique. The morphology profile, dihedral angle and etc. of
thermal grooves were obtained with atomic force microscopy (AFM). The ratio of interfaces energy to
surfaces energy could be calculated for comparing the energy of different type of interfaces. Thus, the
relationships between grain boundary misorientation and energy are established.

2.0 EXPERIMENTAL PROCEDURE

The composition of Alloy 690 used in this study is (w.t. %): 30.39 Cr, 8.88 Fe, 0.023 C, 0.002 S, 0.006 P,
0.07 Si, 0.23 Mn, 0.22 Al, 0.26 Ti, 0.02 Cu, and the balance Ni. The Alloy 690 plate sample was vacuum
sealed in quartz capsule. The quartz capsule with sample inside was annealed at 1100°C for 15 min, then
quenched into water and broken quartz capsules simultaneously, for the starting sample (solution
annealed, SA). Then the samples were cold rolled 10% and subsequently annealed at 1100 ºC for 5 min
then quenched into water. This combination of cold working and annealing is the thermal-mechanical
processing of the GBE sample for obtaining a high proportion of low $\Sigma$ CSL grain boundaries. The sample
was then cut into strips with dimension of $8\text{mm} \times 5\text{mm} \times 1\text{mm}$. The samples were prepared with a final
polish with 1200-grit SiC and then electro-polished in an electrolyte containing 2.5 mol/L HClO$_4$ +
10mol/L CH$_3$COOH at room temperature with 36V direct current for 30 s. The samples were sealed
together with Zr flakes under a vacuum of $5 \times 10^{-3}$ Pa into a quartz capsule. The quartz capsules containing
samples and Zr flakes for absorbing the residual oxygen was annealed at 1100 ºC for 5 min. After that the
quartz capsule was quenched into water. It took about 10 seconds for the inside samples to cool down to
the ambient temperature. The samples were taken out of the quartz capsules after the cool down. All of
the annealing were carried out at 1100 ºC (equal to the solution annealing temperature), and therefore the
carbides would not re-precipitate at the grain boundaries.

Several areas were marked by micro hardness indentations for positioning. Thus, the same grain
boundaries can be characterized by electron backscatter diffraction (EBSD) and atomic force microscopy
(AFAM). 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 scanning electron
microscopy (SEM). Operating conditions were: 20 kV accelerating voltage, 170 $\mu$ A emission current and
about 10 nA incident current as measured with a Faraday cup, 30 mm working distance, 70° beam
incidence angle. The scans were carried out on the marked areas, with each orientation point being
represented as a square cell using a 1.5 $\mu$m step size. Values of the proportion of grain boundaries defined
by the CSL model were expressed as a length fraction by dividing the number of data point cells of a
particular boundary type with that of the entire grain boundaries. Any adjacent point pair with
misorientation exceeding 2° is considered to be a boundary. The Brandon criterion ($\Delta \theta_{\text{max}} = 15^\circ \Sigma^{-1/2}$) was
used to define the CSL misorientations [21]. AFM was employed for obtaining the three-dimensional morphologies and the profiles of the grain boundaries. AFM is operated in contact mode with the tip being dragged across the surface of the sample. The areas with 10 μm×10μm were being scanned each time. Focus ion beam (FIB) was employed for obtaining the GB cross-section which is perpendicular to the surface and also perpendicular to the grain boundaries for measuring the angle between the grain boundary plane and surface.

3.0 RESULTS AND DISCUSSION

The grain boundary network (GBN) of the GBE sample consisted of different types of GBs is shown in Fig.1a. There are many Σ3 (red), Σ9 (blue), and Σ27 (green) grain boundaries and they are clustering together in the GBE sample, as shown in Fig.1a. The large size twin-induced grain-clusters are easily identified in Fig 1a, such as the gray area. Within the grain-clusters, all the grains have Σ3n mutual misorientations, and all these category boundaries connected with each other, forming many triple junctions of Σ3n-type boundaries, such as Σ3-Σ3-Σ9 and Σ3-Σ9-Σ27, inside of the area encircled by random grain boundaries (black). The GBE sample contains about 72% low Σ CSL GBs, most of which are Σ3n grain boundaries. Σ3 boundaries mentioned here can be classified as coherent twin boundary (Σ3c) and incoherent twin boundary (Σ3i). Σ3c boundaries possess very low interface energy because of the perfect GB atoms arrangement. Σ3c boundary is featured by a straight line morphology, while the incoherent twin boundary appeared as small steps or at the terminal of the coherent twin boundaries. Most of the Σ3n GBs are annealing twins and its variants, such as Σ9 and Σ27 GBs, which are formed in the process of multiple twinning [22,23]. So their proportions are dominantly high.

After being thermally etched under a vacuum at 1100ºC, the GB thermal grooves were established, and the morphology of the sample surface is shown in Fig. 2. It’s obvious that the width and depth of the GBs are different from one another. By correlating the GBs’ groove morphologies with their misorientations obtained by EBSD, it can be roughly distinguished that the random GBs and Σ27GBs have much wider and deeper grooves than that of the Σ3c boundaries, and that of the Σ1, Σ3i and the Σ9 GBs are in-between them.

It should be noted that, except for the Σ3c boundaries, all other type boundaries have a curved shape, for example the Σ9 GB in (e), Σ27 GB in (f) and random GB in (g) of Fig. 2. Many other GB grooves were also observed and had the similar trend. GBs seldom have a straight shape except the coherent twin boundary which lie on the (111) plane. This means that the grain boundary does not have an identical GB crystal-graphical plane; rather the GB plane is always changing along the grain boundary. Step segments can sometimes be observed on the grain boundaries. For example, in the Fig 2(e), the observed Σ27 GB have steps, and the groove of steps have different depth and width than that of other part of this grain boundary. This indicates that each step has a different GB plane inclinations from other parts of the GB, and hence each has different energies. Many articles have pointed out the significant influence of GB plane inclination on the GB energy and properties [24, 25]. However, a curved GB or GB with steps should be divided into small segments with each segments have an identical GB plane so that each part can be fully defined by the five parameters. When considering the correlation between the GB properties and GB structure, it’s better to analyze the GB segment by segment rather than by just the whole GB. But this kind of work is labor-intense, and technically unfeasible. So it is common to use the misorientation between the adjoining grains to describe the structure of the GBs by ignoring the grain boundary plane inclination.

The AFM was used to scan the GBs with known CSL misorientations. At least 10 GBs for each character were selected to be scanned by the AFM. The three-dimensional morphologies were obtained and one for each character is shown in Fig. 3. The depth profile perpendicular to the GB was extracted from the 3D morphology of the grooves, and shown in Fig. 3. The depth profile of the grooves can be used to extract the dihedral angle $\beta$, depth $d$, and width of the grooves $w$. 


In the 1960s, Mullins [17] presented a model to measure the grain boundary energy. But the GB in Mullins’s model was symmetrical, with a GB perpendicular to the free surface. However, the geometrical shape of GBs differ from material-to-material. Many modified models were made based on the model of Mullins [26]. The morphology and the groove profiles were obtained by the AFM examinations and shown in Fig. 3. The tangent lines on both side of the groove root were made to measure $\alpha_+$ and $\alpha_-$ which are the angles formed by the right and left tangent lines of the groove root with the x-axis, as shown in Fig. 4. $\theta$ is the angle between the assumed grain boundary plane position and the vertical direction.

$$\alpha_+ = \frac{\sigma}{2} - \theta$$  \hfill (1)  
$$\alpha_- = \frac{\sigma}{2} + \theta$$  \hfill (2)  
$$\sigma = \alpha_+ + \alpha_-$$  \hfill (3)  
$$\beta = 180^\circ - (\alpha_+ + \alpha_-)$$  \hfill (4)  

In this paper the $\gamma_b/\gamma_s$ value was used to describe the relative energy of the GBs, where $\gamma_b$ and $\gamma_s$ are the GB and surface energy, respectively. The ratio of $\gamma_b/\gamma_s$ can be determined by a simple Young-type equation:

$$\gamma_b = 2 \gamma_s \sin \frac{\sigma}{2}$$  \hfill (5)  

$\frac{\sigma}{2}$ is the angle after being corrected between tangent line and free surface at the triple line. The $\gamma_b/\gamma_s$ value could be calculated based on the parameters of the groove. The assumption in Mullins’s model [17] is still obeyed when calculating the $\gamma_b/\gamma_s$ value in this paper. It is assumed that the free surface is considered to be isotropic [17]. The result of Mullins showed that once the thermal groove established, the groove profile was shown to have a time-independent shape, in another word, the dihedral angle at the root of a GB groove is kept constant all the time.

At least 10 GBs for each character were chosen to be measured to yield the average value, and the results are shown in Fig. 5 (a) and (b). The average depths of different types of GBs were shown in Fig. 5 (c). The depth refers to the vertical distance of the lowest point to the highest point of the lower side of the groove. The depth has the same trend as that of the $\gamma_b/\gamma_s$. In Fig. 5, the relative GB energy (the ration of $\gamma_b/\gamma_s$) of $\Sigma 1$, $\Sigma 3c$, $\Sigma 3i$, $\Sigma 9$, $\Sigma 27$ and RGB GBs were 0.2481, 0.0582, 0.2238, 0.2597, 0.3761 and 0.4532, respectively. The GB energy of $\Sigma 3c$, $\Sigma 3i$, and $\Sigma 9$ GBs were almost one tenth, one half, and two thirds of that of the RGBs, respectively. The $\Sigma 27$ GBs have a similar average value of $\gamma_b/\gamma_s$ with that of RGBs. $\Sigma 1$ has a GB energy between that of $\Sigma 3i$ and $\Sigma 9$ GBs. The relative energy of GBs increased as the $\Sigma$ increase, except for RGB and $\Sigma 1$ GBs. Thus, it could be concluded that the property of $\Sigma 3c$ GBs were much better than that of the others. Also, $\Sigma 27$ GBs were not superior to RGBs. Fig. 6 shows that the GB energy of the $\Sigma 1$ boundary (low angle grain boundary with a misorientation angle smaller than 15°) increases with increasing misorientation angles.

Three factors affect the calculated GB relative energy ($\gamma_b/\gamma_s$): 1) the character (or misorientation) of the GB; 2) the grain boundary plane of the GB; and, 3) the angle between the GB and the free surface. In the previous paragraphs, the dependence of GB energy on the GB character was presented. Most of the grain boundaries have a curved shape so that it is not possible to use an identical GB plane to define a whole GB. Therefore in the current study, the effect of the GB crystallographic plane on the GB energy is not being focused on. However, the angle between the grain boundary plane and the free surface was measured in this study, and the results are shown in Fig. 7. Three special types of GBs were chosen in this paper: $\Sigma 3c$, $\Sigma 9$ and $\Sigma 27$. The angle between the GB and the surface was measured by means of focus ion beam (FIB). The results show that the closer the GB is to being perpendicular to the free surface, the higher of the measured GB energy will be.
CONCLUSION

In the current work, thermal grooving was used to measure the grain boundary energy of Alloy 690. The ratio of interface energy over surface energy was calculated according to the shape of thermal grooves of different character GBs. The Random GBs and $\Sigma 27$ GB have similar GB energies. The incoherent twin boundary ($\Sigma 3i$) has a similar GB energy with that of the $\Sigma 9$ GBs, both of which are one half of that of random GBs. The GB energy of $\Sigma 1$ GBs varied with the misorientation angle. The coherent twin boundary ($\Sigma 3c$) has the lowest GB energy among all the investigated GBs. Even in the low $\Sigma$ CSL grain boundary regime, the boundaries with different $\Sigma$ values have different GB energies, and not all the low $\Sigma$ CSL have special properties.

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Fig. 1 Orientation image microscope (OIM) map (a) and grain boundary character distribution (GBCD) (b) of the sample with high proportional (72%, Brandon criterion) low ΣCSL boundaries (the samples were cold-rolled 10% and recrystallization annealed at 1100°C for 5 min).
Fig. 2 The morphology of all types of interfaces after GBE and thermal-etching; the SEM images (a, c, d, e, f, g) of all types of interfaces.
Fig. 3 The morphology ($a_1, b_1, c_1, d_1, e_1, f_1$) and the depth profile along the black lines ($a_2, b_2, c_2, d_2, e_2, f_2$) of all types of interfaces as measured with AFM.
Fig. 4 The model for calculating the relative grain boundary energy.

Fig. 5 (a) The scatter of the energy for different type grain boundaries; (b) The average value of the relative energy of different type grain boundaries; (c) The average depth of grooves of different type grain boundaries.
Fig. 6 The relative GB energy ($\gamma_b/\gamma_s$) value v.s. misorientation angle ($\theta$) of $\Sigma 1$

Fig. 7 The angle $\theta$ (a, b, c) between grain boundary plane and vertical direction for $\Sigma 3c$ (a), $\Sigma 9$ (b), $\Sigma 27$ (c) GBs as examples, (d) the $\theta$ values vs relative GB energy.