INTERFACE CLASSIFICATION FOR GRAIN BOUNDARY ENGINEERING OF POLYCRYSTALS

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Abstract

Grain Boundary Engineering is a prospective, recently proposed technology for processing of polycrystalline materials with optimum properties via controlled arrangement of individual (types of) grain boundaries. To fabricate a polycrystal in this way, it is ultimately necessary (i) to design the distribution and positions of individual grain boundaries in material on the basis of knowledge of the structure/property relationship, and (ii) to process this polycrystal. In the present contribution, the attention will be focussed on the first step of Grain Boundary Engineering – the classification of grain boundaries. Structural dependence of grain boundary segregation as measured at individual interfaces in model bicrystals of a silicon steel will be referred: These properties are decisive for both the process of polycrystal fabrication and the mechanical properties of the final product. Individual grain boundaries will be classified onto special, vicinal and general, and their role in the process of Grain Boundary Engineering will be discussed.

1. INTRODUCTION

Polycrystalline materials consist of a large number of small grains characterized by different orientations. They are separated by grain boundaries possessing higher energy as compared to the grain interior. Due to worse physical, mechanical and chemical properties, grain boundaries creating a three-dimensional net throughout the whole material, represent the weakest link of the material structure. This can be documented by a tendency of material to brittle intergranular fracture under mechanical loading at low temperatures that can completely destroy the polycrystal [1]. However, grain boundary properties exhibit a strong structural dependence. Therefore, the distribution of individual types of grain boundaries in a polycrystal will control how easily the material will crack under loading. If brittle general boundaries form a continuous path in the polycrystal, the material will crack under low stress. On the other hand, a specific arrangement of special grain boundaries can prevent the crack propagation along the grain boundaries in polycrystal in such an extent that the material cracking becomes comparable with transgranular fracture. Based on this idea, Watanabe proposed the concept of Grain Boundary Engineering of polycrystals (GBE) [2]. GBE is expected to produce polycrystalline material with grain boundaries of that character and distribution suppressing “detrimental effects” of the grain boundaries and, in contrast, enhancing their “beneficial effects” to a maximum extent. In this case, the properties of a polycrystal could be significantly improved [3].

Production of a polycrystals with optimum properties by GBE requires two fundamental steps to be realized [1]:

(i) a proposal of the character and distribution of the grain boundaries for required application of the material;

(ii) processing of the predicted grain boundary character and distribution leading to the proposed structural material.

Each step of this concept itself represents a complex problem. The proposal of a polycrystal requires to consider numerous parameters of a large spectrum of grain boundaries such as boundary area, junctions, grain size and shape, faceting, precipitation, grain boundary width,
type, character and structure of grain boundaries, segregation, energy, electronic charge, magnetic state etc. [4]. To produce a polycrystal, various kinds of thermomechanical treatment (incl. classical strain–anneal techniques) will be used that can increase the population of special grain boundaries interrupting frequently the network of general interfaces in a new microstructure. In this way, the resistivity of the material against intergranular brittle fracture is enhanced [5]. Increased population of special grain boundaries may originate from their faster movement during recrystallization as compared to general ones [6]. Recently proposed processes of GBE use, for example, a magnetic–field annealing of a material that retards recrystallization and substantially increases the population of special grain boundaries in an Fe–9%Co alloy [7].

In any respect, the knowledge of the structure/property relationships is the basic ultimate step for successful GBE of polycrystals. Therefore, the study of the properties of individual grain boundaries and their anisotropy is absolutely necessary for this concept. In the present contribution, a new approach to classification of grain boundaries of α-iron into special, vicinal and general [8] according to their segregation behavior is presented. Based on this classification, a new approach to the design of a polycrystal in the concept of GBE.

2. ANISOTROPY OF GRAIN BOUNDARY SEGREGATION

In the past decade, we performed a series of systematic measurements of solute segregation at well-characterized symmetrical and asymmetrical tilt grain boundaries by Auger electron spectroscopy (AES) (for review, see e.g., Ref. [3]). For these measurements, oriented bicrystals (13 mm in diameter, 60 mm long with the boundary parallel to the growth axis) of an Fe–3.55at.%Si (0.014at.%C and 0.0089at.%P) were prepared by floating-zone-melting technique. Cylindrical bicrystalline seeds of required misorientations and boundary plane orientations were used for this purpose [9]. Grain boundary composition was investigated at temperatures between 773 K and 1173 K by means of high-resolution scanning AES (SAM PHI 600). These measurements were performed on fracture surfaces of in-situ intergranularly broken samples. Ar+ ion sputtering of the fracture surface was done to check the thickness of the segregated layer. The details of both the sample preparation and the AES measurements are given elsewhere [10].

The AES spectra were transformed into composition of a monatomic layer at the grain boundary by means of a standardless method [10]. The temperature dependence of grain boundary composition was correlated according to the Guttmann model of grain boundary segregation in multicomponent systems [11]

\[
\frac{X_{GB}^I}{1 - \sum_j X_{GB}^j} = \frac{X_I}{1 - \sum_j X_j} \exp \left( \frac{-\Delta G_I}{RT} \right)
\]

with

\[
\Delta G_I = \Delta H_I^0 - T\Delta S_I^0 - 2\alpha_{MI} (X_{GB}^I - X_I) + \sum_{J=1}^{M-1} \alpha_{IJ} (X_{GB}^J - X_J)
\]

In eqs. (1) and (2), \(X_I\) and \(X_{GB}^I\) are the bulk and grain boundary concentrations of element \(I\), \(\Delta H_I^0\) and \(\Delta S_I^0\) are standard molar enthalpy and entropy of segregation of the element \(I\) in dilute binary alloy with the matrix \(M\). \(\alpha_{MI}\) and \(\alpha_{IJ}\) are the coefficients of binary \(I-I\) interaction and ternary \(I-J\) interaction in matrix \(M\), respectively. Using this correlation, the thermodynamic parameters of segregation of phosphorus, silicon and carbon in α-iron were determined from measurements in a complex multicomponent Fe–Si–P–C system. The values
of segregation enthalpy and entropy for considered segregants at individual grain boundaries are listed in Table 1.

Table 1.

Enthalpy $\Delta H^0_i$ (in kJ/mol) and entropy $\Delta S^0_i$ (in J/(mol.K)), of segregation of Si, P, and C at individual grain boundaries in $\alpha$-iron [3,12] (N = not measured). The values of reciprocal density of CSL sites $\Sigma$ and interplanar spacing $d_{eff}$ normalized by the lattice parameter $a$, and grain boundary type (S – special, V – vicinal, and G – general) for each interface are also given.

<table>
<thead>
<tr>
<th>Grain boundary</th>
<th>$\Delta H^0_{\text{Si}}$</th>
<th>$\Delta S^0_{\text{Si}}$</th>
<th>$\Delta H^0_{\text{P}}$</th>
<th>$\Delta S^0_{\text{P}}$</th>
<th>$\Delta H^0_{\text{C}}$</th>
<th>$\Delta S^0_{\text{C}}$</th>
<th>$\Sigma$</th>
<th>$d_{\text{eff}}/a$</th>
<th>type</th>
</tr>
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<tr>
<td>70.5°[110], {112}</td>
<td>-3</td>
<td>-3.8</td>
<td>-7.9</td>
<td>+42.7</td>
<td>N</td>
<td>N</td>
<td>3</td>
<td>0.408</td>
<td>S</td>
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<tr>
<td>90°[110], (001)/(011)</td>
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<td>+2</td>
<td>-14</td>
<td>+25</td>
<td>-33</td>
<td>+8</td>
<td>$\infty$</td>
<td>0.604</td>
<td>S</td>
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<tr>
<td>18.9°[100], {016}</td>
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<td>-15</td>
<td>-31</td>
<td>+17</td>
<td>-49</td>
<td>+1</td>
<td>37</td>
<td>0.082</td>
<td>G</td>
</tr>
<tr>
<td>22.6°[100], {015}</td>
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<td>-9</td>
<td>-16</td>
<td>+38</td>
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<td>-7</td>
<td>13</td>
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<tr>
<td>28.1°[100], {014}</td>
<td>-14</td>
<td>-9</td>
<td>-35</td>
<td>+19</td>
<td>-50</td>
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<td>17</td>
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<td>36.9°[100], {013}</td>
<td>-8.5</td>
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<td>-13.3</td>
<td>+45.2</td>
<td>-40</td>
<td>+12</td>
<td>5</td>
<td>0.316</td>
<td>S</td>
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<td>36.9°[100], (018)/(047)</td>
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<td>-8</td>
<td>-32</td>
<td>+19</td>
<td>-50</td>
<td>+3</td>
<td>5</td>
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<td>G</td>
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<tr>
<td>36.9°[100], (001)/(034)</td>
<td>-9</td>
<td>-3</td>
<td>-25</td>
<td>+29</td>
<td>-44</td>
<td>+6</td>
<td>5</td>
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<tr>
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<td>-22</td>
<td>-14.5</td>
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<td>5</td>
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<td>36.9°[100], (0 3 11)/(097)</td>
<td>-11</td>
<td>-5</td>
<td>-32</td>
<td>+21</td>
<td>-48</td>
<td>+3</td>
<td>5</td>
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<tr>
<td>45°[100], [0kl]</td>
<td>-17</td>
<td>-13</td>
<td>-37</td>
<td>+18</td>
<td>-51</td>
<td>+6</td>
<td>$\infty$</td>
<td>0</td>
<td>G</td>
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<tr>
<td>45°[100], (001)/(011)</td>
<td>-6</td>
<td>+2</td>
<td>-19</td>
<td>+38</td>
<td>-39</td>
<td>+11</td>
<td>$\infty$</td>
<td>0.604</td>
<td>S</td>
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<td>50°[100], {0 7 15}</td>
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<td>-3</td>
<td>-31</td>
<td>+25</td>
<td>-45</td>
<td>+6</td>
<td>87</td>
<td>0.06</td>
<td>G</td>
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<tr>
<td>53.1°[100], {012}</td>
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<td>+0.2</td>
<td>-10.9</td>
<td>+42.5</td>
<td>-35.0</td>
<td>+12</td>
<td>5</td>
<td>0.224</td>
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<tr>
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<td>-5</td>
<td>-34</td>
<td>+20</td>
<td>-48</td>
<td>+4</td>
<td>53</td>
<td>0.097</td>
<td>G</td>
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<tr>
<td>64.0°[100], {058}</td>
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<td>-11</td>
<td>-37</td>
<td>+16</td>
<td>-53</td>
<td>-1</td>
<td>89</td>
<td>0.053</td>
<td>G</td>
</tr>
<tr>
<td>113°[100], (001)/(015)</td>
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<td>-3</td>
<td>-22</td>
<td>+32</td>
<td>-41</td>
<td>+10</td>
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<td>V</td>
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<td>18.4°[100], (001)/(013)</td>
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<td>-2</td>
<td>-19</td>
<td>+35</td>
<td>-38</td>
<td>+14</td>
<td>$\infty$</td>
<td>0.408</td>
<td>S</td>
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<tr>
<td>26.1°[100], (001)/(012)</td>
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<td>-5</td>
<td>-26</td>
<td>+28</td>
<td>-47</td>
<td>+4</td>
<td>$\infty$</td>
<td>0.362</td>
<td>V</td>
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<tr>
<td>33.7°[100], (011)/(015)</td>
<td>-7</td>
<td>-2</td>
<td>-18</td>
<td>+37</td>
<td>-40</td>
<td>+9</td>
<td>$\infty$</td>
<td>0.452</td>
<td>S</td>
</tr>
<tr>
<td>27.0°[100], (011)/(013)</td>
<td>-6</td>
<td>-1</td>
<td>-17</td>
<td>+37</td>
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<td>+14</td>
<td>$\infty$</td>
<td>0.512</td>
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<tr>
<td>18.5°[100], (011)/(012)</td>
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<td>-2</td>
<td>-17</td>
<td>+36</td>
<td>-34</td>
<td>+16</td>
<td>$\infty$</td>
<td>0.465</td>
<td>S</td>
</tr>
</tbody>
</table>

A comparison of the data listed in Table 1 shows that segregation behavior as characterized by the segregation enthalpy differs substantially from boundary to boundary. Minima of $|\Delta H^0_i|$ exist at {015}, {013} and {012} [100] symmetrical tilt grain boundaries that are close to corresponding values of $\Delta H^0_i$ for the {112} coherent twin boundary. In the case of asymmetrical boundaries, comparable values of $\Delta H^0_i$ with those of above mentioned special symmetrical interfaces, were found at the (013)(001) boundary as well as at all grain boundaries formed on one side by the (011) plane which is the most dense plane in the bcc structure. Grain boundaries formed by the (001) plane on one side are characterized by intermediate values of $\Delta H^0_i$. Based on these results, individual [100] high-angle grain boundaries can be classified according to their segregation tendency in the following way [12]:

- **special grain boundaries**: {015}, {013} and {012} symmetrical, and (001)/(013) as well as all (011)/(0kl) asymmetrical interfaces,
- **vicinal grain boundaries**: the boundaries in the vicinity of special grain boundaries and all (001)/(0kl) interfaces,
- **general grain boundaries**: all other grain boundaries.

- 3 -
This classification which is in a good correlation with geometric classification of grain boundary planes [13,14] is schematically depicted in Fig. 1.

![Figure 1: Map of character of [100] tilt grain boundaries in α-iron, as indicated by different shadings and symbols. All boundaries in white area are general [12].](image)

**3. PROPOSALS FOR GRAIN BOUNDARY ENGINEERING**

In many studies published in literature (for review, e.g., Refs. [1,3]), the classification of grain boundaries is accepted that is based on the simplest coincidence site lattice (CSL) concept. The CSL is a tetragonal superlattice that is constructed for a given misorientation of two adjacent crystals by coinciding atom positions of the crystal lattices of both grains when they are extrapolated across the boundary to interpenetrate each other [3]. As a “characteristics” of the boundary, the reciprocal density $\Sigma$ of coincidence sites has been used. For example, $\Sigma=5$ means that one fifth of the (volume) lattice sites of each grain are the coincidence sites. Although $\Sigma$ characterizes the misorientation of both grains only and is not sensitive to the position of the boundary between them, i.e., to the actual grain boundary plane orientation, it is widely accepted that low values of $\Sigma$ indicate special grain boundaries (see Ref. [8] for critical assessment). This approach is practically exclusively used for characterization of interfaces in the concept of GBE [2,4–7].

Let us compare the CSL model with the above presented classification of the grain boundaries. We can find that the special $\{012\}$, $\{013\}$ and $\{015\}$ symmetrical tilt grain boundaries possess low values of $\Sigma$ being 5, 5 and 13, respectively. This is in agreement with the CSL approach. However, the asymmetrical interfaces do not fit with this idea. For example, the non-coincidence ($\Sigma\to\infty$) incommensurate 45°[100], (001)/(011) asymmetrical
tilt grain boundary is special. On the other hand, its corresponding symmetrical $45^\circ[100]$, \(\{0kl\}\) tilt grain boundary is general. It is also apparent from Table 1 and Fig. 1 that the \(\Sigma=5\), $36.9^\circ[100]$ misorientation covers all types of grain boundaries, special \(\{013\}, (011)/(017),\) and \(\{012\}\), vicinal \((001)/(034)\) and general, e.g., \((018)/(047)\) and \((0 3 11)/(097)\) [12]. From this point of view, the automatic acceptance of \(\Sigma\) as the criterion of specialty is misleading.

Instead of \(\Sigma\), another geometric criteria characterizing grain boundaries can be used to characterize special grain boundaries. One of them is the interplanar spacing, \(d\), defined as the distance between two crystal planes parallel to the boundary plane (\(d_{\text{eff}}\) in the case of an asymmetrical grain boundary represents the arithmetic average of \(d\) as measured on both sides of the boundary). As it is apparent from Table 1, high values of \(d\) (or \(d_{\text{eff}}\)) are joined with special interfaces (or to vicinal ones in the case of interfaces formed by low-index planes on one side) despite of the symmetry of the interface. From this point of view, the interplanar spacing is better characteristics of the grain boundaries than \(\Sigma\). Nevertheless, neither \(d\) is universal parameter applicable as the criterion to find special grain boundaries: it fails completely in the case of twist grain boundaries [3]. For technological use, it is necessary to choose a simple but more realistic criterion for characterizing special grain boundaries or to use a combination of the simple ones.

Figure 2: Model ensemble of four grains, A, B, C and D, with mutual orientation relationships A–B: $45^\circ[100]$, B–C: $22.6^\circ[100]$, and C–D: $36.9^\circ[100]$. Two alternative interfacial paths are formed by (a) 1–2–3, general interfaces \(\{0kl\}, (023)/(015)\) and \((0 1 1 4)/(0 2 0 2 3)\) (dashed-line path), and (b) 1'–2'–3' special grain boundaries \((001)/(011), \{015\}\) and \(\{013\}\) (full-line path). Both configurations are declined by $22.5^\circ[100]$.
In fact, the real existence of special asymmetrical interfaces broadens the spectrum of grain boundaries suitable for GBE and consequently, it may qualitatively change the approach to the concept. Let us document it for the following example. Let us have a model polycrystal containing grains A, B, C and D as depicted in Fig. 2. Orientation relationships between individual grains are $45^\circ[100]$ for A–B, $22.6^\circ[100]$ for B–C, and $36.9^\circ[100]$ for C–D with respective values of $\Sigma$, being $\infty$, 13 and 5 (cf. Table 1). These grains, can be separated with a path 1–2–3 of general boundaries $\{0kl\}$, (023)/(015) and (0 1 14)/(0 20 23) (dashed-line path in Fig. 2). If we only rotate the orientation of this path by $22.5^\circ[100]$, however, we obtain another path constructed from special grain boundaries (001)/(011), {015} and {013} (full-line path 1'–2'–3' in Fig. 2). It is clear that the path 1'–2'–3' consisting of special grain boundaries is much stronger and we will need much higher load $\sigma$ to crack the material than the path 1–2–3 of general grain boundaries. Using this example, however, it is clear that it is not necessary to use only twin interfaces as "good" grain boundaries in the concept of GBE but also other special grain boundaries. To reach the more suitable latter arrangement, one does not need to develop any complicated technology since grain boundary migration during thermal treatment should support stabilization of low-energy special interfaces instead of high-energy general ones. As mentioned above, the change of the boundary orientation from high-energy to low-energy configuration was observed during high temperature annealing of as-grown parts of $36.9^\circ[100]$ bicrystal of an Fe–Si alloy with originally (0 1 14)/(0 20 23) grain boundary. Just after start of its growth by the floating-zone-melting technique, it regularly inclined to either (001)/(034) vicinal or (011)/(017) special orientations. From this point of view, a more important task of the technology consists in providing suitable orientation relationships between individual grains that offer existence of special interfaces. However, the adjustment of grain boundaries into low-energy orientations depends not only on their migration ability but also on other parameters as listed in Introduction. This complex process resulted in formation of a sharp (001) or (011) textures with decreased amount of the general grain boundaries by 30% in an Fe–6.5mass%Si alloy strips and thus, in reduction of “intrinsic brittleness” of a conventional polycrystal. [16].

4. CONCLUSIONS

The knowledge of both the structure/property relationship for grain boundaries and their classification is absolutely needed to start successful design of polycrystals in the concept of Grain Boundary Engineering. In this contribution, we present the results of experimental study of solute segregation at individual grain boundaries and a consequent classification of grain boundaries onto special, vicinal and general in $\alpha$-iron and other materials such as steels, molybdenum and other refractory bcc based metals. It was shown that this classification does not fit with the most frequently used concept of the reciprocal density of CSL sites. It is also proposed that the path formed by brittle general boundaries could be simply transformed into the path formed by special (vicinal) interfaces by suitable heat treatment. Such configuration should strengthen the polycrystal, however, it is necessary to take into account other structural, energetic and morphologic parameters of the actual polycrystalline structure to realize such transformations.

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