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MULTIPLICITY OF GRAIN BOUNDARY STRUCTURES: VACANCIES IN BOUNDARIES AND TRANSFORMATIONS OF THE BOUNDARY STRUCTURE

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Résumé.- Un nombre de structures non-équivalentes ont été trouvées dans les études atomistiques des joints de grains périodiques. Ces structures peuvent se transformer mutuellement en ôtant, ou en ajoutant des lamelles d'atomes qui sont parallèles aux joints [19]. Cette multiplicité résultante des structures est très extensive pour des joints de grains généraux avec de longues périodes. On montre ici que les configurations de lacune d'énergie plus basse dans les joints de grain correspondent à la présence locale des unités de structures alternatives, alors que l'absorption ou l'émission des lacunes à un joint peuvent être regardées comme des transformations structurelles locales. Alors, quand la température monte et la concentration équilibre des lacunes monte, on augmente le désordre correspondant à la présence de diverses unités alternatives dans le joint. Ceci peut arriver ou graduellement, ou par une transformation du type ordre-désordre. On montre aussi que l'accumulation de lacunes ou d'impuretés dans le joint peut provoquer des transformations de glissement entre des structures de joint alternatives, conduisant en même temps à la migration des joints. Nous abordons ici l'importance de ces divers genres de transformations structurelles pour les phénomènes qui se produisent dans les joints de grain.

Abstract.—A number of non-equivalent structures have been found in the atomistic studies of periodic grain boundaries. These can transform into each other by removal or insertion of layers of atoms parallel to the boundary [19]. The ensuing multiplicity of structures is very extensive for long period, general, boundaries. We show here that low energy configurations of vacancies in grain boundaries correspond to the local presence of units of alternative structures so that absorption or emission of vacancies at a boundary can be regarded as local structural transformations. Hence, as the temperature rises and the equilibrium concentration of vacancies increases the disorder corresponding to occurrence of various alternative units in the boundary increases. This may happen either gradually or through an order–disorder transformation. It is further shown that accumulation of vacancies or impurities in the boundary may induce shear transformations between the alternative boundary structures which leads at the same time to the migration of the boundary. The significance of these different structural transformations for various grain boundary phenomena is discussed.

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1. Introduction

The atomic structure of grain boundaries has been the object of research ever since the existence of these interfaces was recognized (see e.g. [1]). The reason is that most of the grain boundary phenomena occur in the cores of the boundaries where no other than fully atomistic descriptions are applicable. On the other hand, most observations of the boundary structures, for example, by electron microscopy, relate to long range strain fields associated with the boundaries. These fields are then usually interpreted in terms of linear elastic fields of networks of grain boundary dislocations (primary or secondary). While the strain field of a boundary is determined uniquely by the atomic structure of this boundary, the atomic structure of a boundary cannot be deduced unambiguously from the knowledge of its strain field, i.e. from the knowledge of the dislocation content of the boundary [2-5]. Similarly, the coincidence site lattice (csl) and the 0-lattice do not provide means for finding the atomic structure of interfaces, though they are of paramount importance since they provide a crystallographic framework for the study of periodic boundary structures. Recently, some direct observations of the atomic structure of grain boundaries have been made using the high resolution electron microscopy (see [6]) but these results are still very limited. Hence, our present understanding of the atomic structure of grain boundaries is to a great extent the result of atomistic computer simulation studies which have been carried out extensively in the last decade [4,5,7-9].

All the atomistic studies of grain boundaries have employed pair potentials to describe forces between the atoms. This approximation is known to be good in simple metals (e.g. [10]). However, it is much less certain in noble and transition metals although recent theoretical studies [11,12] suggest that pair potentials are applicable in transition metals if the density of the material is kept fixed. In general, we cannot expect to obtain exact numerical values of parameters such as grain boundary energy, diffusivity, cohesion etc., for specific materials, particularly if empirical potentials are employed. However, we can follow general structural features and trends which are not sensitively dependent on the interatomic forces used. This was the rationale for the recent studies of Sutton and Vitek [13,14] who calculated structures of very long period symmetrical and asymmetrical tilt boundaries with the aim to seek the relationship between structures of grain boundaries throughout a misorientation range for a particular rotation axis and inclination of the boundary plane. In general, structures of all these boundaries are composed of mixtures of two structural elements. These elements are the 'units' of the boundaries delimiting the misorientation range. Each delimiting boundary is composed of a contiguous sequence of one of these units. The sequence which appears in any intervening periodic boundary is unique and determined by the condition that the minority units are as widely separated as possible. Short period, low E* boundaries can always be chosen as the delimiting boundaries so that structures of a very large number of boundaries are described in terms of the structural units of only a small number of boundaries. This structural unit model was first established for tilt boundaries in f.c.c. metals [13,14] but more recently it has been shown that it also applies to (001) twist boundaries in these materials [15,16] as well as to tilt boundaries in b.c.c. metals [17]. Hence, it is very likely that this model is appli-

* E is the reciprocal density of coincidence sites.
cable generally for mixed boundaries in various cubic lattices.

The structural unit model appears to determine uniquely the structure of a general long period (high \( E \)) boundary in terms of units of short period delimiting boundaries. However, it has been shown \([18,19]\) that an extensive multiplicity of boundary structures arises if there are more than one possible structure of the delimiting boundaries. These structures may then transform into each other when a layer of atoms is either removed from or inserted to the boundary. This suggests that the structural multiplicity may play an important role in any processes involving absorption or emission of vacancies at grain boundaries.

In this paper we first review briefly the main features of the structural multiplicity. We then concentrate on \( C = 5 \) symmetrical tilt boundaries in f.c.c. and b.c.c. crystals and discuss further the possible extent of multiplicity if the assumption of boundary periodicity is relaxed. In particular, this is possible at high temperatures where a more disordered state of the boundary structure can be attained either gradually, or by a structural transformation. The investigation of the structure of vacancies and vacancy clusters is then presented and the relationship between their structures and structural multiplicity of boundaries discussed. Finally, shear transformations between different multiple structures, induced by vacancy clustering or by segregation of impurities, usually associated with the boundary migration, are discussed.

2. Periodic multiple structures of grain boundaries.

It has been found in a number of atomistic studies \([8,9,16-20]\) that more than one metastable structure of a boundary defined by its geometrical parameters, may exist. In some special cases these different structures are related by a symmetry operation of the holosymmetric interfacial structure \([21,22]\) and possess then the same energy. But more commonly the different structures are not symmetry related and their energies differ. This is not surprising since the energy of a boundary is a very complicated function of the coordinates of all the atoms and such a function is likely to have more than one minimum.

A systematic study of the structural multiplicity which reveals its large extent and establishes a relationship between alternative structures, has recently been made using the structural unit model \([18,19]\). Let us consider symmetrical tilt boundaries with [001] rotation axis in f.c.c. and b.c.c. metals. In both cases all these boundaries can be regarded as composed of units of ideal crystal and \( E = 5 \) boundaries \([17,19]\). In the atomistic studies which employed a large variety of starting configurations and always assumed the shortest possible period of the boundary, it was found that each of the \( E = 5 \) boundaries possesses two different structures. As examples we discuss structures of the \( E = 5 \) (210) 36.87° boundary in an f.c.c. lattice, shown in Fig. 1, and of the \( E = 5 \) (310) 36.87° boundary in a b.c.c. lattice, shown in Fig. 2. (The cases of the \( E = 5 \) (310) 53.13° boundary in an f.c.c. lattice and the \( E = 5 \) (210) 53.13° boundary in a b.c.c. lattice are entirely analogous.) Their structures were calculated using the potentials for Cu and Fe, respectively, which were constructed in refs. \([23,24]\); the potential for Fe is very similar to the Johnson's potential \([25]\). The triangles and crosses represent atoms projected onto the (001) plane and they distinguish between the two (002) planes in each crystal period along the tilt axis. Both of these boundaries are centred \([14]\) so that the atomic structure of the first half period is identical to the second, with atoms represented by triangles in one half corresponding to atoms represented by crosses in the other half and vice versa. The lines
(full and broken) drawn in these figures indicate suitable units of these boundaries. These units contain sufficient number of atoms to typify the boundary structure but more atoms can always be included if necessary. In the following we shall mark the units of the (210) boundary shown in Figs. 1a and b, B and B', and units of the (310) boundary shown in Figs. 2a and b, B₁ and B₁'. The two alternative structures of these boundaries differ in their translation states by

\[ \Sigma = 5(210) \] in an f.c.c. lattice. (a) B structure (b) B' structure.

\[ \Sigma = 5(310) \] in a b.c.c. lattice. (a) B₁ structure (b) B₁' structure.

the removal of a (420) and (310) plane, respectively, from the upper or lower grains. This means that transformations between different structures can be accomplished by removal or insertion of the appropriate planes of atoms followed by a collapse or expansion of the bicrystal by one interplanar spacing of these planes and a local relaxation. In particular, such transformations between structures shown in Figs. 1 and 2, respectively, are realized if the planes of circled atoms are removed and the above procedure followed. Removal of a layer of atoms parallel to the boundary is equivalent to the
addition of a vacancy to each repeat unit of the boundary. Hence, the multiplicity of structures may play a role in annihilation or creation of vacancies at boundaries and, generally, in any phenomenon involving point defects. This is discussed in more detail below.

The energies of the B and B' structures of the (210) boundary were found to be 1449 mJ/m² and 1507 mJ/m², respectively, and of the B₁ and B₁ structures of the (310) boundary 1379 mJ/m² and 1580 mJ/m², respectively. The importance of these numbers is not that they represent exact values of the energies of the corresponding grain boundaries in Cu and Fe. This cannot be expected in the framework of the empirical potentials. However, they show that the energies of different structures of the same boundary may be similar so that the lowest energy structure is not necessarily the only one which is physically significant.

A very extensive multiplicity of structures may occur in general, long period boundaries the structures of which are, according to the structural unit model, composed of units of two different delimiting boundaries. If either of the delimiting boundaries has more than one metastable configuration various combinations of these configurations may occur in intervening boundaries. Suppose that the delimiting boundaries have i and j different structures. Then a periodic intervening boundary with a period which is composed of m units of the first delimiting boundary and n units of the second, may have \( i^m j^n \) alternative structures. This represents an upper limit since these structures are not necessarily all metastable but the calculations in ref. [19] show that a very large number of these structures, indeed, exist. They frequently differ only slightly in energy and the lowest energy structures do not necessarily comprise units of the lowest energy delimiting boundaries.

The number of alternative structures increases as the size of the repeat cell of the boundary increases. In ref. [19] the smallest possible repeat cells, i.e. the csl cells, or their fractions in the case of the centred boundaries, were always assumed. If this condition is relaxed the number of possible different structures is much larger and it becomes infinite if there is no periodicity. The latter is possible at high temperatures when a disordered "solution" of alternative structural units may be present in the boundaries. This is discussed in more detail in section 4. However, even at 0°K structures in which every smallest possible repeat cell has the same structure, are not necessarily energetically the most favourable. Longer period structures of the \( \Sigma = 5 \) symmetrical tilt boundaries have been studied and it was found that the structures consisting of the checker board pattern of the two alternative structural units, are always metastable.

![Fig. 3 The [001] projection of two (002) planes of the \( \Sigma = 5(210) \) boundary with the checker board pattern of B and B' units.](image)
In the case of the $\Sigma = 5$ (210) boundary in an f.c.c. lattice the repeat cell is now $[\overline{1}20] \times [002]$ comprising two csl cells. The structure of this boundary calculated using the potential for Cu, is shown in Fig. 3. Its energy is 1303 mJm$^{-2}$, lower than that of either of the short period structures. In the case of the $\Sigma = 5$ (310) boundary in a b.c.c. lattice the repeat cell $[\overline{1}30] \times [002]$ also comprises two csl cells. The energy calculated using the potential for Fe is 1959 mJm$^{-2}$ which is higher than that of the short period structures.

3. Vacancies in grain boundaries.

It is generally assumed that vacancies exist in grain boundaries as well defined point defects and play in the diffusional processes a similar role as in the bulk of the crystals (for reviews see [26-28]). Several atomistic studies of vacancies in grain boundaries have been made recently and they, indeed, confirm their localization though the details of the structure of vacancies are sensitively dependent on the local atomic environment [29-31]. Here we present atomistic studies of vacancies in the $\Sigma = 5$ symmetrical tilt boundaries in the b.c.c. lattice. These calculations were carried out using the pair potential for Fe [24] and for low energy structures, e.g. $B_1$ structure in the case of the (310) boundary. A two dimensional periodic array of vacancies was always introduced into the boundary starting with such a separation of vacancies that they can be regarded as noninteracting, isolated defects. In the case of the (310) boundary the cell containing one vacancy was bounded by vectors $2[110]$ and $3[001]$, containing thus six repeat cells of the boundary; in the case of the (210) boundary the cell containing one vacancy was bounded by vectors $3[120]$ and $4[001]$, containing thus twelve repeat cells of the boundary.

![Fig. 4 Vacancy in the $\Sigma = 5(310)$ boundary formed by removal of the atom marked $\alpha$ in Fig. 2a.](image1)

![Fig. 5 Vacancy in the $\Sigma = 5(310)$ boundary formed by removal of the atom marked $\beta$ in Fig. 2a.](image2)

When the vacancy was created in the (310) boundary by removing the atom marked $\alpha$ in Fig. 2a the relaxed structure shown in Fig. 4 resulted. It is seen that only minor relaxation took place and the vacancy is very localized. The vacancy formation energy (evaluated using
the pair potential only) is 1.48 eV which is higher than that of the unrelaxed vacancy in the bulk (1.24 eV). However, a rather different situation arises when the atom marked $\beta$ in Fig. 2a has been removed, as shown in Fig. 5. The atom $\beta$ is from the layer of atoms the removal of which leads to the transformation from $B_1$ to $B_1$ structure. The structure of the vacancy clearly corresponds to the formation of the $B_1$ unit within the boundary. Examination of the atom positions in the atomic layers adjacent to the vacancy show little deviation from the $B_1$ structure and thus the vacancy is still well localized. The formation energy of this vacancy is 0.38 eV, well below that in the bulk. Hence, although the removal of the atom $\alpha$ leads to a metastable configuration the configuration of the vacancy corresponding to the local transformation to the alternate structure is the energetically favoured one. This position of the vacancy was also found to be most favourable in refs. [30,31]. Furthermore, in the calculations of Brokman et al [30] an analogous situation arises in the case of the most favoured vacancy position in the $\Sigma = 5$ (310) boundary in copper. It can be seen from Fig. 4c of ref. [30] that after the removal of an atom, a neighbouring atom moved so as to form locally the alternate structure of this boundary.

In the case of the (210) boundary in the b.c.c. iron only very small relaxation near the vacancy occurred and the lowest formation energy found was 0.7 eV. The vacancy configuration which would correspond to the local formation of the alternate structure has not been found. This is, perhaps, not surprising because of the large difference in the energies of the alternate structures of the (210) boundary (50%) when compared with that of the (310) boundary (20%).

When another vacancy has been added to the (310) boundary by removing the atom marked $\gamma$ in Fig. 2a the two adjacent vacancies both assume the configurations corresponding to the local formation of the $B_1$ structure. These two vacancies are strongly bound with the binding energy 0.27 eV. Thus there is a tendency for vacancies to coalesce and produce locally regions of alternate, higher energy, structures. These regions are separated from the rest of the boundary by partial grain boundary dislocations. In the case of the region composed of the $B_1$ units in the (310) boundary such dislocation has the Burgers vector 1/10 [310]. As will be shown below the higher energy regions may then transform by shear to the lower energy ones and these transformations are accompanied by the migration of the boundary.

4. Multiplicity and transformations of grain boundary structures at non-zero temperatures.

At a temperature $T>0$ every grain boundary contains an equilibrium concentration of vacancies. The calculations presented in the previous section suggest that the low energy structures of vacancies in grain boundaries correspond to units of alternate structures of the delimiting boundaries. Hence, structure of a boundary with vacancies may be regarded as a structure in which certain fraction of the units of delimiting boundaries found at $0^\circ$ K were replaced by the alternate units. Let us consider, for simplicity, a delimiting boundary which possesses two alternate structures and employ the regular solution model to study possible changes of its structure with temperature. At a finite temperature the structure of this boundary consists of $n_1$ units of the first type and $n_2$ units of the second type. The total number of units $n = n_1 + n_2$ is constant. The self energy of a unit may be identified with the energy of the boundary composed of units of only one type per area of the unit. The interaction energy between the units is in general different when the units meet along
the directions perpendicular and parallel to the tilt axis, respectively. We mark these energies $\epsilon_{1}^2$ and $\epsilon_{12}^1$ and the self-energies $\epsilon_1$ and $\epsilon_2$, respectively. The internal energy of the structure with a random distribution of the alternate units is then

$$E = n_1 \epsilon_1 + n_2 \epsilon_2 + 2n_1 n_2 \left( \epsilon_{12}^1 + \epsilon_{12}^2 \right)$$  \hspace{1cm} (1)

The corresponding configuration entropy $S = k \ln(n! / n_1 n_2 !)$. Minimization of the free energy determines the concentration of the units of the second type, $c_2 = n_2 / n$:

$$\ln(c_2/(1-c_2)) = -(1 + 4 \kappa (1-2c_2)) \Delta e / kT$$  \hspace{1cm} (2)

where $\Delta e = \epsilon_2 - \epsilon_1$ and $\kappa$ is the parameter which measures the interaction between different units defined by the relation $\kappa \Delta e = 1/2(\epsilon_{12}^1 + \epsilon_{12}^2)$. This parameter can be determined if the metastable structure composed of equal number of the two types of units distributed in the checker board pattern exists. The energy per one repeat unit of this boundary is in this model: $\Delta e_1 + \Delta e_2 = 2(\epsilon_1 + \epsilon_2) + 4(\epsilon_{12}^1 + \epsilon_{12}^2)$. Hence, knowing $\epsilon_1 + \epsilon_2$ $\kappa$ can be easily evaluated.

Clearly, $c_2$ depends principally on the difference between the energies of alternate units, $\Delta e$, and for a given $\Delta e$ it decreases with increasing $\kappa$. However, if $\kappa$ is negative an ordered distribution of alternate units in the boundary will be favoured energetically. In this case the internal energy is

$$E = n_1 \epsilon_1 + n_2 \epsilon_2 + 2n_1 n_2 \left( \epsilon_{12}^1 + \epsilon_{12}^2 \right).$$  \hspace{1cm} (3)

Furthermore, at least half of the units are the lower energy units of the first type and we may assume that in the ordered case they form a checker board pattern comprising half of all the available boundary cells. $n_2$ of the units of the second type are then distributed randomly in $n/2$ of empty cells and the remaining cells are again occupied by the units of the first type. The configuration entropy is then

$$S = k \ln[(n/2)!/(n/2-n_2)!n_2!]$$  \hspace{1cm} (4)

and in equilibrium

$$c_2 = 1/2 \left[ \exp ((1+4\kappa) \Delta e / kT) + 1 \right]^{-1}$$  \hspace{1cm} (5)

An order-disorder transformation then occurs at a temperature $T_C$ for which the free energies of structures corresponding to the ordered and disordered distributions of alternate units are equal. Using equations (1)-(5) it can be shown that for $\kappa>-0.25$ no ordered distributions exist.

Using the results of section 2 for the $\Sigma = 5$ (210) boundary in Cu we obtain $\Delta e = 0.053$ eV and $\kappa = -1.5$. This gives $T_C = 1392^\circ K$, slightly above the melting temperature ($1356^\circ K$). Hence, in the present model the ordered structure is always favoured but if $\Delta e$ were changed by less than 4% $T_C$ would fall below the melting temperature. Furthermore, the exact value of $T_C$ is also affected by the change in the vibrational entropy which has been neglected here. For the $\Sigma = 5$ (310) boundary in Fe we obtain $\Delta e = 0.24$ eV and $\kappa = 0.71$ so that the ordered structure is not favoured. The study of the structural multiplicity in ref. [19] shows a very wide range of the values of $\Delta e$ for more general longer period boundaries. Thus we can expect that in some boundaries the order-disorder transformations of the type described here will take place at temperatures below the melting point while in other boundaries the disorder will only be increasing gradually as the
temperature increases.

5. Shear transformations of boundary structure.

It has been shown in section 3 that vacancies present in grain boundaries may have a tendency to coalesce forming thus regions of alternative boundary structures. Atomistic studies of boundaries with a large accumulation of vacancies show that their structures may transform spontaneously by shear into lower energy structures. As an example a boundary containing a row of vacancies in every third

repeat cell of the $\Sigma = 5$ (310) boundary in Fe is shown in Fig. 6a. The period of this boundary in the direction perpendicular to the tilt axis, $3/2[130]$, consists of two $B_1$ and one $B'_1$ units. When another row of vacancies was introduced into each period, attempting thus to create a structure containing one $B_1$ and two $B'_1$ units in each period, the transformation into the structure shown in Fig. 6b took place. At the same time the grain boundary moved upwards by one interplanar spacing of the (310) planes and the upper grain was displaced with respect to the lower grain by the vector $1/10 [130]$. This transformation can therefore be regarded as produced by gliding of a partial DSC dislocation with this Burgers vector through the grain boundary. Each period of this boundary in the [130] direction again consists of one $B_1$ unit and two $B'_1$ units. However, the $B_1$ units are now those marked by broken lines in Fig. 2a while $B'_1$ units in Fig. 6a are those marked by full lines in Fig. 2a. Thus the structures before and after transformation are not identical and the latter structure has the energy which is 2% lower.

Similar transformations have been observed in atomistic studies of grain boundaries with segregated impurities [32,33]. An example for the $B'$ structure of the $\Sigma = 5$ (210) boundary in Cu with segregated bismuth atoms is shown in Fig. 7. A Bi atom has been placed substitutionally into the site marked D in Fig. 7a into every second repeat cell of this boundary. It is strongly bound to the boundary and its segregation energy is 1.6 eV. At this stage rather extensive local relaxation occurs. However, when the second Bi atom is placed into the site $D_1$ and thus there is one Bi atom in each repeat cell of the boundary, the structure transforms into the structure B as seen in Fig. 7b. At the same time the boundary moves upwards by one interplanar spacing of (420) planes and the upper grain is displaced...
with respect to the lower grain by the vector $\frac{1}{10}[1\bar{2}0]$. Again the transformation can be regarded as produced by gliding a partial DSC dislocation with this Burgers vector through the boundary. Hence presence of vacancies, segregated impurities and possibly other defects, may lead, at least locally, to a shear transformation of the boundary structure into another energetically more favourable configuration. This process can be visualized as nucleation and gliding of a partial DSC dislocation in the boundary. In general, a step is associated with such a dislocation [34,35] which leads to the displacement of the boundary upwards or downwards.

Fig. 7 The $\Sigma = 5(210)$ boundary, $B'$ structure in Cu. (a) Before transformation. (b) After transformation induced by placing Bi atoms into $D$ and $D_1$ positions.

6. Discussion

The multiplicity of structures of periodic grain boundaries found in our atomistic studies [19] suggests that crystallographically well defined boundary (i.e. with a fixed rotation axis, misorientation of grains and orientation of the boundary plane) may possess a wide variety of different atomic structures. In different structures different types of units of delimiting boundaries occur. However, the sequence of the units of two delimiting boundaries is always the same since minority units are always separated as far as possible. For example, consider the $\Sigma = 97 (1350)$ boundary in an f.c.c. material. Its repeat cell is always composed of two units of the $\Sigma = 5 (210)$ boundary and three units of the $\Sigma = 5 (310)$ boundary. Each of the delimiting boundaries has two alternative structures $B,B'$ and $C,C'$, respectively. There are thirty two possible structures of the repeat cell of the $\Sigma = 97$ boundary of the type $B'C'BCC$, $B'C'BCC$, $B'C'BCC$ etc. However, structures of the type $BBCC$, $BB'C'C$, etc. are forbidden. Since the minority units (B) can be associated with the cores of grain boundary dislocations providing for deviation away from the delimiting boundary composed of the majority units (C) [13,14] the distribution of these dislocations in the boundary is the same for every multiple structure but their cores are different. This conclusion is valid even when the condition of the boundary periodicity is relaxed, for example, when a random distribution of alternative units occurs at a high temperature. In spite of this disorder the sequence of units of, say, type B and C will remain the same and, therefore, the apparent dislocation content of the boundary will be unaffected. Hence, observations of these dislocations, i.e. of the long range strain field of the boundary, will always reveal the same
In periodic boundaries different multiple structures can be transformed into each other by inserting vacancies or interstitials into each period of the boundary. Conversely, as shown in section 3, isolated vacancies in a grain boundary can be regarded as units of alternative, higher energy, structures of the delimiting boundaries. Therefore, a boundary with an equilibrium concentration of vacancies may also be regarded as disordered, containing a certain fraction of higher energy units of delimiting boundaries. In general, the atomic structure of grain boundaries may be expected to vary with temperature. This change of structure may occur either gradually or through a structural transformation at a certain critical temperature. The gradual development of disorder is equivalent to the gradual increase of the concentration of vacancies in the boundary. This may become very high if alternative structures have very similar energies. The transformations may be either of the order-disorder type, as discussed in detail in section 4, or analogous to transformations between different crystal structures. In the former case an ordered structure consisting of different alternative units, must be favoured at low temperature and the transformation is driven by the increase of the configurational entropy when disordering. The latter case will correspond to transformation from a lower energy structure, say B, to a higher energy structure, say B', and it is driven by the possible difference in vibrational entropies of these two structures. Whether such transformations occur and at what temperatures depends on the availability of alternative structures of delimiting boundaries and the differences in their energies. Therefore, the types of transformations and corresponding critical temperatures will depend on the boundary crystallography e.g. on misorientation of grains, orientation of the boundary plane etc. Owing to a wide variability of these parameters and the possibility of extensive structural multiplicity we can expect that such transformations are quite common and that the corresponding critical temperatures may span a wide range of temperatures.

The existence of such transformations was proposed using purely thermodynamics arguments by Hart [36] who argued that they may affect dramatically the non-equilibrium, kinetic properties of grain boundaries. An experimental evidence for sudden changes of these properties at certain temperatures has been provided by Aust [37] who observed sharp changes in the rates of boundary migration in bicrystals of lead and in the rates of grain growth in polycrystals of lead at certain temperatures. Recently, Watanabe et al [38] observed similar sharp changes in the rate of grain boundary sliding for symmetrical {1010} tilt boundaries in zinc bicrystals and the critical temperature was found to be strongly dependent on the misorientation of the grains. On the other hand, Kikuchi and Cahn [39] suggested that a "melting" of the boundary may occur at a temperature lower than the melting temperature of the bulk. While this transformation is very similar to the order-disorder transition proposed here a sudden decrease of the viscosity in the boundary region is expected if the true melting occurred. A structural transformation below the melting temperature of the bulk has recently been observed in the molecular dynamics studies of the Σ = 7 [111] tilt boundary [40] but it was not possible to interpret it in more detail. Further studies of the structural transformations in grain boundaries require investigation of vibrational entropies of the different multiple structures of grain boundaries and molecular dynamics studies the results of which have to be interpreted either in terms of the transformations discussed or in terms of melting. Furthermore, in real
materials another type of transformation involving local changes in the orientation of the boundary plane, i.e. faceting, may occur as recently suggested by Cahn [41].

A different type of transformation, described in section 5, may be provoked by accumulation of vacancies or impurities in grain boundaries. These transformations are shear transformations associated with migration of the boundary and displacement of one grain with respect to another. Hence, they can be regarded as resulting from the motion of, in general, partial DSC dislocations along the grain boundaries. A similar process has been observed in the molecular dynamics studies by Bishop et al [42] although in this case the boundary structure did not change during migration. Obviously, these transformations may play a role during the grain boundary migration which can be regarded then as a process involving various structural changes of the boundary. Consider, for example, again the \( \Gamma = 5(310) \) boundary in a b.c.c. material. Accumulation of vacancies and/or extrinsic dislocations which were absorbed by the boundary may lead to a local transformation from the low energy B\(_1\) structure to a higher energy B\(_2\) structure. This transformed region will be bounded by 1/10 [310] partial dislocation. When this region reaches a critical size another partial dislocation with the Burgers vector 1/10 \([130]\) is nucleated which sweeps this region transforming the structure B\(_1\) back to B\(_2\) with the boundary displaced by one spacing of the \( (310) \) planes upwards. This region of the boundary is now surrounded by the dislocation with the Burgers vector 1/5 \([120]\) which is a DSC dislocation associated in the \( (310) \) boundary with a step of the height equal to the spacing of \( (310) \) planes [35]. This dislocation may then expand further extending thus the migrated region. This is, of course, the mechanism of migration proposed by Smith et al. [43] but it is likely that the DSC dislocations will be dissociated in the present case according to the reaction 1/5[120] = 1/10[310] + 1/10[130] and the migration process will be occurring locally in two steps as described above. Similarly, in the case of the diffusion induced grain boundary migration [28,44] the surplus of vacancies or interstitials which is needed for this phenomenon to occur [44], will lead to local structural transformations and the presence of impurities may enhance the shear transformations which lead to the boundary migration. The shear transformations induced by impurities may also play a role when considering other effects of segregation. For example, structures of vacancies in the transformed structure will be rather different than in the original structure which may affect, for example, the grain boundary diffusion.

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References


