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ATOMISTIC STUDIES OF GRAIN BOUNDARIES
WITH SEGREGATED IMPURITIES

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286

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1. Introduction

The aim of this research project is to carry out atomistic studies of grain boundaries with impurities. The emphasis of the investigation is on the effect of segregation upon the structure of grain boundaries and their properties. Since the necessary precursor of any atomistic study is a description of interatomic interactions an empirical scheme for the construction of interatomic potentials was first developed. In this scheme which was summarized in a previous report, the interatomic interactions are described by pair potentials together with a volume dependent term which represents a major contribution to the overall energy of the studied system. This is a physically realistic description of interatomic forces in metals since it is known that in these materials the bulk of the cohesive energy is well described by the volume dependent term. A new relaxation method had to be developed that includes the volume dependent term into the calculations which are then carried out at constant pressure rather than at constant volume. Furthermore, this method also includes the possibility of dealing with spatially varying concentration of impurities. It is described in more detail in the present report.

Another important task was to develop a method of interpretation of the results and of the description of the boundary structure and of the corresponding structural changes in physically meaningful terms. This has been achieved by developing the concept of atomic level stresses which describe the local stress field in an immediate vicinity of the boundary.

The calculations were then carried out for systems of Cu-Ag and Cu-Bi. First isolated impurities in an otherwise perfect

lattice were studied. This revealed that in order to achieve consistency in reproduction of the enthalpy of mixing, the potentials have to be self-consistently readjusted to take into account local atom rearrangement near the impurity. This modification of the potentials is now in progress.

The effect of a low concentration of alloying elements on grain boundaries has been calculated for two boundaries in copper. The first is a favored boundary which does not contain any secondary grain boundary dislocations and the second a more general boundary which may be described as a favored boundary with a network of the corresponding dislocations. The results of this study are also described in this report.

A limited effort was also devoted to further development of the theory of intergranular fracture in which a relationship between the plastic work and cohesive energy is sought (see enclosed reprints). The present emphasis is on taking into account the dynamic effects which is essential for development of a more quantitative theory which when combined with the measurements of the local fracture stress⁽¹⁾ could provide a method for the direct measuring of boundary cohesion.

2. Method of Calculation

The grain boundary can always be assumed to be periodic. In the case of pure metals the two dimensional repeat cell is the corresponding largest planar Wigner-Seitz (WS) cell of the crystal planes parallel to the boundary⁽²⁾. When impurities are considered they may be introduced as periodically distributed in the boundary. The corresponding repeat cell will now be

either the same or a multiple of the repeat cell of the boundary in the pure metal. This repeat cell has to be taken as the basic cell in the calculations and periodic boundary conditions can be applied. Because of this periodicity there can be no area change of the WS cell parallel to the boundary and thus the only volume change which can occur is an expansion or compression perpendicular to the boundary.

Whether the calculation is carried out at constant total volume or at constant total pressure the resulting configuration must be such that forces on all atoms are zero. However, in the latter case the requirement of constant total pressure, which can be set to zero, leads to an auxiliary condition which can be written as

$$\sum_{\ell} p_{\ell} = 0 \quad (1)$$

where the summation extends over all the layers parallel to the boundary and p_{ℓ} is the average local hydrostatic pressure at the layer ℓ . This pressure can be written as

$$p_{\ell} = p_{\ell}^{\phi} + p_{\ell}^{\nu} \quad (2)$$

where

$$p_{\ell}^{\phi} = \frac{1}{N_p} \sum_k \frac{1}{6v_{ak}} \sum_j \frac{\partial \phi^{kj}}{\partial r_{kj}} r_{kj} \quad (3)$$

is the contribution from the central forces and

$$p_{\ell}^{\nu} = \frac{1}{N_p} \sum_k \left(\frac{\partial u_k^{\nu}}{\partial v_a} \right)_{v_a = v_{ak}} \quad (4)$$

is the contribution from the density dependent part of the energy. In each layer ℓ the summation over k extends over all

the atoms in the WS cell of the boundary and the summation over j extends over all the atoms interacting with the atom k ; N_p is number of atoms in the WS cell. ϕ^{kj} is either ϕ^{AA} , ϕ^{BB} or ϕ^{AB} and, similarly, U_v^j is either U_v^A or U_v^B , depending on whether atoms k and j are elements A or B. Although both p and p^v are evaluated as average values over all the atoms N_c in the WS cell, both the interatomic potentials and the density dependent parts of the energy used in this calculation are those corresponding to the local alloy concentration and to the local atomic volume v_{ak} .

The relaxation which results in zero force on every atom has been carried out in the same way as in our previous studies of grain boundaries in pure metals and it has been described in detail in the reference(2). This method allows for relative rigid body translations of the two grains parallel to the boundary, relative displacements both parallel and perpendicular to the boundary of any atomic layers parallel to the boundary, as well as complete individual relaxation of all the atoms within the WS cell of the boundary. When evaluating forces on atoms, the potentials corresponding to the local alloy concentrations were used. However, the condition of zero forces on all the atoms does not imply that equation (1) is also satisfied. Hence, the above calculation has to be combined with an additional relaxation which allows for an overall expansion and/or contraction of the relaxed block and leads to satisfaction of the condition (1). This expansion (contraction) is perpendicular to the boundary and occurs principally in the vicinity

of the boundary while atomic layers remote from the boundary experience a rigid body displacement perpendicular to the boundary. This type of relaxation has not been used in any previous calculations and it is, therefore, described in more detail.

When equation (1) is not satisfied there is a net hydrostatic pressure in the block which must be relieved by a corresponding expansion and/or contraction. This can be achieved by displacing every layer k , by a Δy_k perpendicularly to the boundary. To find these displacements every iteration (n) of the relaxation procedure leading to zero forces on all atoms has been followed by displacing the corresponding layer k by

$$\Delta y_k^{(n)} = \sum_l \Delta y_{k,l}^{(n)} \quad (5)$$

where $\Delta y_{k,l}^{(n)}$ is the displacement of the layer k due to the pressure $p_l^{(n)}$ at layer l (given by equations (3) and (4)) in the n^{th} iteration. $\Delta y_{k,l}^{(n)}$ has been evaluated as follows:

$$\Delta y_{k,l}^{(n)} = p_l^{(n)} f(y_k^{(n)} - y_l^{(n)}) \quad (6)$$

where $y_j^{(n)}$ is the average y coordinate (perpendicular to the boundary) of atoms in the layer j in the n^{th} iteration. f is a function defined as:

$$\begin{aligned} f(x) &= x \exp(-|x|/r_c) \text{ for } |x| < r_c \\ &= r_c/e \text{ for } x \geq r_c \\ &= -r_c/e \text{ for } x \leq -r_c \end{aligned} \quad (7)$$

where r_c is the cut-off radius of the pair potential of the host material and e is the base of natural logarithms. This means that the displacement $\Delta y_{k,l}^{(n)}$ is always proportional to $p_l^{(n)}$; a non-zero strain is imposed on the layers within the distance from layer 1 equal to the cut-off radius of the potential of the host material while beyond this radius layers are rigidly displaced. The choice of f ensures continuous transition between the displacement and strains in these two regions. If this relaxation procedure converges $\Delta y_{k,l}^{(n)} \rightarrow 0$ as $n \rightarrow \infty$ and equation (1) is satisfied. This method was tested for several previously calculated boundary structures in pure metals and complete agreement with the known results was obtained.

3. Atomic level stresses

In any system of N atoms in equilibrium there may exist internal stresses, e.g. those due to defects. These can be "measured" by applying a small homogeneous strain e_{ij} and observing the corresponding change in the energy due to the atomic interactions. This energy change is at the same time equal to

$$\frac{1}{2} \sum_{k=1}^N \Omega_k \sigma_{ij}^k e_{ij} \quad (8)$$

where Ω_k is the atomic volume and σ_{ij}^k is the atomic level stress at atom k . It can be shown^(4,5) that

$$\sigma_{ij}^k = \frac{1}{2\Omega_k} \sum_{l=1}^N \frac{\partial \phi}{\partial r_{kl}} r_{kl}^i r_{kl}^j \quad (9)$$

where ϕ the central force potential and U_v the volume dependent part of the energy, r_{kl}^i is the i^{th} component of the vector r_{kl} . In the ideal lattice all $\sigma_{ij}^k = 0$. However, the stress is non-zero in the vicinity of defects and it can be used conveniently for their characterization. We employed the hydrostatic stress $p = 1/3 \sigma_{ii}$ to analyze the stress distribution in the vicinity of tilt grain boundaries. The maps of the hydrostatic stress for $\Sigma 5$ (210) and $\Sigma 17$ (530) boundaries are shown in Figs. 1 and 2, respectively. The arrows pointing to the right represent hydrostatic compression and those pointing to the left tension. These maps clearly reveal non-uniform stress distribution in the $\Sigma 17$ boundary where the centers of large compressive stresses are positioned above the cores of d.s.c. dislocations. At the same time in the case of $\Sigma 5$ boundary the stress map shows contiguous array of primary dislocation cores showing thus that this boundary is favored⁽³⁾. Both these boundaries were employed in segregation studies.

4. Computer Simulation Studies

4.1 Impurities in the ideal lattice

A rectangular array of impurity atoms (Ag and Bi) was introduced substitutionally into a (2 $\bar{2}$ 0) plane of an ideal f.c.c. lattice of copper. The impurities were located at the corners of rectangles defined by vector $8/2[110]$ and $6[001]$. There were, therefore, 48 atoms in each periodic cell, 47 of which were host copper atoms. The impurities were thus sufficiently spaced so that any interaction between them can be neglected. The block was then relaxed using the method

described in section 2.

The stress field maps for Ag and Bi are shown in Figs. 3 and 4, respectively. In both cases a hydrostatic tensile stress field arises near the impurity. However, in the case of Bi this is appreciably stronger than in the case of Ag. Also in the case of Bi the relaxation of surrounding Cu atoms is much more extensive than in the case of Ag. The first nearest neighbors move outwards while the second nearest neighbors move inwards. The energies of Ag and Bi as impurities in Cu calculated after the relaxation are 2.4eV and 12.7eV, respectively. These values are too high and lead to too large enthalpies of mixing which we attempt to match when constructing the potentials. For this reason a self-consistent readjustment of the potentials is needed and this is being carried out at present.

4.2 Impurities in Grain Boundaries

Two symmetrical [001] tilt boundaries in copper were selected for this study: $\Sigma 5(210)$, 36.87° and $\Sigma 17(530)$, 28.07° . The reason for this choice is that $\Sigma 17(530)$ boundary is an unfavoured boundary composed of two units of the $\Sigma 5(210)$ and one unit from the ideal crystal. The latter unit always represents the core of a d.s.c. dislocation of the $\Sigma 5$ system. In the case of $\Sigma 5$ boundary the impurity was introduced into two non-equivalent sites. The first (C) is in the pure case associated with high hydrostatic compression and the other (T) with tension. In the case of $\Sigma 17$ boundary impurities were introduced only into the T sites in the cores of dsc dislocations.

The changes in the hydrostatic stress field when Ag or Bi atoms are introduced into T sites in the $\Sigma 5$ boundary are shown in Figs. 5 and 6, respectively. In both cases the change of the stress is tensile. However, in the case of Bi it is spread much further from the boundary which leads to significant changes in atom separation relatively far from the boundary. The calculated energies of segregation are both negative (-0.25 eV for Ag and -3.8 eV for Bi) so that T sites are suitable for segregation. On the other hand in the case of C sites both Ag and Bi lead to high positive segregation energies and thus both species are repelled from these sites.

The changes in the hydrostatic stress field when Ag or Bi atoms are introduced into T sites in the $\Sigma 17$ boundary are shown in Figs. 7 and 8. Again the stress is in both cases tensile but spreads much further in the case of Bi. The segregation energy for Ag is now positive but small ($+0.01$ eV). However, it is strongly negative for Bi (-3.1 eV). Thus, Bi shows again a strong tendency to segregation while Ag is practically neutral.

In all cases studied the grain boundary energy measured with respect to the pure material always increased when impurities were introduced. At the same time, however, the driving force for segregation exists since the energy of the block decreases if impurity is removed from the lattice and placed into the boundary. This suggests that basically "unfavourable" changes occur in the boundary even when segregation is energetically favourable.

5. Summary

- 1). A method for computer modelling of grain boundaries (and planar defects in general) at constant pressure has been developed. This method can be used for both boundaries in

pure metals and boundaries containing impurities.

ii). The method of relaxation was first tested for several boundaries in pure Cu the structure of which was calculated previously by a different method, and thus validity of the new method has been confirmed. A calculation of an array of noninteracting impurities in otherwise ideal lattice was then performed. In this study it has been found that a self-consistent readjustment of the empirical potentials has to be made to achieve matching of the enthalpy of mixing.

iii). There does not seem to be any strong preference for segregation to unfavored boundaries when compared with the favored ones. The preferential sites for segregation are in both cases those sites which in the pure case possess large hydrostatic tension. This is likely to be true generally for impurity atoms which are larger than the host atoms. It is thus possible that a rather general picture of conditions for segregation and of changes in the boundary structure can be achieved by detailed studies of only favored boundaries.

This requires, however, further investigation.

iv). In all cases studied the grain boundary energy increased when impurities were introduced to the boundary although the segregation is energetically favourable. The changes which occurred at the boundary were rather small in the case of Ag but quite significant in the case of Bi. In both cases an expansion occurred but in the latter case this is spread to at least four layers parallel to the boundary indicating thus a substantial weakening of bonding across the boundary. This shows that while segregation is an energetically favourable

process as far as the whole block of material is concerned, it is an unfavourable process when considering the boundary structure only. This suggests that significant structural changes can be expected when increasing the density of the segregating species in the boundary, which can then lead to substantial alterations of boundary properties. Study of these effects will be the principal aim of our future investigation.

REFERENCES

1. J. Kameda, C. J. McMahon, Jr., Met. Trans. 11A, 91, 1980.
2. V. Vitek, A. P. Sutton, D. A. Smith and R. C. Pond, Grain Boundary Structure and Kinetics, ASM, p. 115, 1980.
3. A. P. Sutton and V. Vitek, Scripta Metall. 14, 129, 1980.
4. N. Born and K. Huang: Dynamical Theory of Crystal Lattices (Oxford, Clarendon Press), 1954.
5. T. Egami, K. Maeda and V. Vitek, Phil. Mag. 41, 883, 1983.

Figure 1. Map of the hydrostatic stress field of the $\Sigma 5(210)$ boundary in Cu.

Figure 2. Map of the hydrostatic stress field of the $\Sigma 17(530)$ boundary in Cu. Unit corresponding to the ideal crystal is marked by dashed rectangle. In between these units the boundary consists of units of $\Sigma 5(210)$ boundary.

Figure 3. Hydrostatic stress field map for Ag impurities in the ideal Cu lattice.

Figure 4. Hydrostatic stress field map for Bi impurities in the ideal Cu lattice.

Figure 5. Change of the hydrostatic stress field of $\Sigma 5(210)$ boundary in Cu caused by Ag atoms at T sites.

Figure 6. Change of the hydrostatic stress field of $\Sigma 5(210)$ boundary in Cu caused by Bi atoms at T sites.

Figure 7. Change of the hydrostatic stress field of $\Sigma 17(530)$ boundary in Cu caused by Ag atoms at T sites.

Figure 8. Change of the hydrostatic stress field of $\Sigma 17(530)$ boundary in Cu caused by Bi atoms at T sites.