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OXYGEN SEGREGATION IN 32°[001] MOLYBDENUM TILT GRAIN BOUNDARY
I. SEGREGATION SITES DETERMINATION

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Résumé: Les sites de ségrégation de l’oxygène dans le joint de flexion de 32° autour de [001] du molybdène ont été déterminés, d’après des simulations de structures atomiques par une méthode de relaxation statique et des observations de ce joint de grains pur par microscopie électronique de haute résolution. Pour les simulations, on a utilisé des potentiels interatomiques solvant-soluté correspondant à divers rayons du soluté et reproduisant l’enthalpie de mélange de l’oxygène dans le molybdène (2,6 eV).

Abstract: The segregation sites for oxygen in molybdenum 32°[001] tilt grain boundary are determined on the basis of static grain boundary simulations and pure grain boundary high resolution electron microscope observations. Interatomic solute-solvent potentials corresponding to different solute atom radii and reproducing the enthalpy of mixing of oxygen in molybdenum (2.6 eV) are used.

INTRODUCTION
The classic thermodynamic models of intergranular segregation, like the McLean [1] model, are based on the assumption of the existence of unique types of segregation sites in grain boundaries and treat the density of these sites as the same as in perfect crystal. The progress made in the knowledge of grain boundary structure, such as grain boundary structure simulations [2], [3] and electron microscope grain boundary observations with resolution better than 2Å [4], suggests that real grain boundary structure can be taken into account for the description of intergranular segregation.

In this paper, our aim is:
- to compare the 32°[001] Σ53 grain boundary molybdenum structure simulated by molecular statics with that observed by high resolution electron microscopy;
- to determine the oxygen segregation sites by molecular statics simulations, using empirical pair potentials and to discuss the influence of such potentials on the obtained results.

In the second part of this work [5], we will make a comparison between our calculations and measurements of grain boundary segregation and interfacial tension, performed on a molybdenum grain boundary with the same geometry.

I HOST GRAIN BOUNDARY STRUCTURE DETERMINATION

I.1 Grain Boundary Structure Simulation
To determine the segregation sites, one first needs an atomistic grain boundary model. The grain boundary statics simulation method was employed to determine the 32°[001] tilt grain boundary structure. This method consists of the calculating of the atomic positions, corresponding to the energy minimum, by successive displacements of atoms (individual relaxations) and crystals (rigid...
translations), in proportion to the forces to which they are subjected [6]. The forces and energies are calculated using interatomic pair potentials.

To describe the Mo-Mo interaction, a Mie type empirical potential was fitted to the vacancy formation energy (2.4 eV) and the bulk modulus (240 GPA) of Mo. The potential is shown in figure 1. It is well known [7] that potentials fitted to vacancy formation energy reproduce only about 50% of the cohesive energy, but give a reasonable value for the grain boundary energy.

Figure 1. The Mo-Mo potential. (The numbers in the circles correspond to the neighbors positions).

More than 20 different initial structures were used as a starting point for the grain boundary simulation. Two grain boundary structures having much less energy than others were found: the structure G1 presented on the figure 2a (enthalpy of formation $H_B = 842$ mJ/m$^2$) and the structure G2 presented in figure 2b ($H_B = 827$ mJ/m$^2$).

Figure 2. Calculated grain boundary structures: a) G1; b) G2.

1.2 Grain Boundary Structure Observations

In order to test the simulated structures we have performed high resolution electron microscopy observations on molybdenum bicrystal containing a $32^\circ[001]$ tilt grain boundary. A molybdenum bicrystal was grown up, cut into 0.3 mm thick slices and purified as described in [5]. Subsequently 3mm diameter discs with the boundary positioned along the diameter were obtained using an ultrasonic cutter. These discs were mechanically thinned using a dimple grinder and then electrolytically thinned in a double jet cell, until a hole appeared. If the grain boundary did not intersect the hole, a final thinning was performed in sulfuric acid bath, until the boundary could be observed.
A 4000 EX Jeol microscope operating at 400kV was used for the observations. General conditions of imaging are discussed by Penisson [4].

The obtained image is presented in figure 3. One can see that the grain boundary is composed of facets, and that the grain boundary plane is not symmetric. Due to the fact that the [001] tilt axis in the two adjacent grain deviated by 1° from being exactly parallel, the resolution seen in figure 3 is worse than that seen in figure 4 of [4]. Therefore, some filtering has been necessary for correct atomic position determination. The filtered image is presented in figure 4. The fact that some atomic columns produce weak contrast might result from the local presence of an amorphous layer.

Figure 3. Untreated electron micrograph of a 32°[001] tilt grain boundary in purified molybdenum.

Figure 4. Filtered images of two different parts of the grain boundary shown on figure 3. In a) one can see the A units decrease in size along the grain boundary; the center of the first A pattern is empty. In b) one can see the contrasts (marked with the arrows) in the center of A pattern which may result from presence of a supplementary Mo atom.

1.3 Comparison of Observed and Calculated Structures

In both, the observed structure (figure 4a) and simulated structure G-1 (figure 1a), the periods are formed from 4 patterns of 6 atoms (denoted by A in this paper) and one lightly deformed perfect
lattice 4 atoms pattern. The main difference between the observed and calculated structures is that in the observed structure the width $d$ of the $\Delta$ patterns decreases along the grain boundary period while in the simulated structure all the $\Delta$ patterns are almost identical. It is equivalent to say that the secondary structural dislocations in the grain boundary are slightly dissociated perpendicular to the grain boundary in the calculated structure whereas they are not in the observed structure. The phenomenon of greater than observed dislocation core localisation is commonly seen when empirical potential are used (V. Vitek, personal communication).

In the case of the simulated structure G-2, one can see that the $\Delta$ patterns decrease in size as observed in the high resolution electron microscope, but there is a supplementary Mo atom in the center of the first of these patterns. The differences between calculated and observed structure are probably due to the deviation of real bicrystal from the exact $\Sigma 53$ symmetrical tilt orientation. Although the observed grain boundary structures corresponded in the majority of cases to the structure $\text{G1}$, on some facets the $\Delta$ patterns with supplementary atom (the G2 structure) were perhaps observed (figure 4b). Most likely this is a manifestation of the influence of small changes of grain boundary orientation on the grain boundary structure.

II DETERMINATION OF SEGREGATION SITES

In order to determine the segregation sites, we have performed the grain boundary simulation with interstitial atoms placed in different sites. The simulation algorithm was similar to that used for the pure grain boundary calculations, but different interatomic interactions were used: solvent-solvent, solute-solvent and solute-solute. In order to be able to simulate low solute atom grain boundary concentrations, the maximum dimension of the simulated cell was increased to three time the host grain boundary periodicity.

II.1 Choice of Solute-Solvent Potentials

No method exists which can be used for fitting the molybdenum-oxygen, and oxygen-oxygen interatomic potential in solid solution. The method for calculating alloy interatomic potentials on the basis of host element potentials combination [8] requires some similarity between the solvent and solute atoms, which does not exist in the Mo-O case. From a fundamental point of view, little is known about atomic interactions in Mo-O solid solution that could yield an empirical potential. The most valuable data on the Mo-O interaction is the mixing enthalpy, which can be estimated from the solubility of oxygen in molybdenum [5] to be of the order of 2.6 eV per oxygen atom. In an attempt to find solute-solute interactions reproducing this value, we have performed statics simulations of perfect crystal with an interstitial atom in an octahedral site, using different empirical potentials.

For any analytical form of the potential, a choice of minimum energy position and depth allows the enthalpy of mixing to be fixed to any desired value. In the absence of data on the atomic radius of oxygen in solid solution, we have chosen three Morse potentials with different depth and minimum position, corresponding to a mixing enthalpy value of the order of 2.6 eV; these potentials are presented in figure 5. The interatomic potential used for solvent-solvent interactions was the same as that used in the part I.

![Figure 5. Different solute-solvent potentials corresponding to an enthalpy of mixing in a perfect crystal octahedral site in molybdenum equal to 2.6 eV.](image-url)
II.2 Calculation Procedure
In the first part of the calculation, we have performed the simulation using grain boundary structure G-1 with one oxygen atom per calculation cell placed in one of the sites marked by the letters on figure 6, using the selected solvent-solute potentials (figure 5). The enthalpies of mixing $H_K$ and enthalpies of segregation $H_{SK}$ presented on figure 6 were calculated using the formula (3) and (10) from the second part of this publication [5].

Analysis of the results from figure 6 allows these observations:

- The order of the segregation sites (with increasing segregation enthalpy) is the same for all tested potentials (an unimportant exception occurs for site D simulated with potential 3).

- The differences in segregation enthalpy associated with sites of different dimension can be small or large depending on solute-solvent potentials. These differences are more significant for larger atoms.

- The number of segregation sites per period cannot vary continuously, but has to rise with the number of identical sites in the grain boundary period. This means that the number can be 4 (only A sites taken into account) or 5 (4A+B) or 15 (4A+B+10 C) or 25 (4A+B+10 C+10D). In the case of insertion of solute atoms in the sites lying a greater distance from grain boundary than sites D, the enthalpy of segregation found in the case of all tested potentials was close to zero, so it seems that the number of segregation sites cannot exceed 25 atoms per period.

\[
\begin{array}{cccc|cccc}
\text{Sites} & \text{Pot.} & H_K & H_{SK} & H_K & H_{SK} \\
A & 1 & 2 & 0.1 & -1.6 & -0.6 & -2.5 & -4.2 \\
B & 1 & 2 & 0.5 & 1.85 & -0.4 & -2.1 & -0.75 \\
C & 1 & 2 & 1.5 & 1.85 & -0.5 & -1.1 & -0.75 \\
D & 1 & 2 & 2.6 & 2.3 & -0.3 & -0.6 & 0 \\
A_1 & 1 & 2 & 0.5 & 2.1 & -0.5 & -1.4 & -2.1 \\
A_2 & 1 & 2 & 0.1 & -1.6 & -0.6 & -2.5 & -4.2 \\
A_3 & 1 & 2 & 0.1 & -1.6 & -0.6 & -2.5 & -4.2 \\
A_4 & 1 & 2 & 1.9 & 0 & -1.5 & -0.7 & -2.6 & -4.1 \\
\end{array}
\]

*Figure 6.* Examined grain boundary sites and corresponding mixing enthalpies (in eV).

In the second part of our calculation, we have performed the grain boundary simulation with segregant atoms placed simultaneously in sites A,B,C and D. If the oxygen-oxygen interaction is neglected, the segregation enthalpies are very close (differences less than 10%) to those calculated previously. However, for such high oxygen concentration, the solute-solute interaction may be very important.
Finally, in order to determine the influence of supplementary atom presence and \( \Delta \) pattern width on the segregation enthalpies, we have performed some simulations of G-2 structure (see figure 2). The enthalpies of segregation found in this case are presented on the figure 6.

II.3 Influence of Solvent-Solvent Potentials

Unfortunately no data exists on the oxygen-oxygen interaction in molybdenum. If this interaction is attractive, the absolute values of the segregation energies of the sites and the differences between the segregation sites in the grain boundary core (A and B) and exterior (C and D) increase in proportion to the depth of the solvent-solvent potential. If the solvent-solvent interaction is repulsive, the absolute value of the segregation energies and the differences between the segregation sites in the grain boundary core and the sites in the exterior part of grain boundary decrease in proportion to the solvent-solvent potential depth. These effects are only pronounced for high oxygen concentrations, when a large number of solvent-solvent interaction occurs.

II.4 Grain Boundary Structure

Some expansion around the site caused by segregated atom was observed, but no drastic change of grain boundary structure has been seen. Rigid translation parallel and perpendicular to the grain boundary caused by segregation do not exceed 0.2 Å. In the case of rigid translation perpendicular to the grain boundary plane, both the attraction and repulsion can be observed, depending upon both segregation site and solute-solvent and solute-solute potentials.

CONCLUSION

If one compares the present results to the grain boundary segregation measurement [5], one can conclude that the simulation has allowed a determination of segregation sites for the oxygen atoms in agreement with experiment. The comparison of the results obtained with different potentials suggests that this result can be generalized for other interstitial atoms. However, without more information on solute-solvent interactions, it is impossible to predict the grain boundary segregation energy with precision. It would be useful to compare calculated structures with high resolution observations of grain boundaries containing segregated atoms. The simulation of high resolution grain boundary images performed on the basis of the presented structures show that such an observation is possible.

REFERENCES