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SEGREGATION ENERGIES OF PHOSPHORUS AND SULFUR IN VARIOUS RELAXED STRUCTURES OF GRAIN BOUNDARIES IN Ni BY TIGHT-BINDING APPROXIMATION

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**RESUME**

Les énergies de ségrégation des impuretés de valence s-p aux joints de grains du nickel ont été calculées dans le cadre de l'approximation des liaisons fortes. Les valeurs des intégrales de recouvrement ont été prises à partir des calculs de Harrison et les niveaux relatifs des énergies  $E_s$ ,  $E_p$  et  $E_d$  des orbitales s, p et d ont été déterminées à partir des calculs de structure atomique d'Herman et Skillman. Les impuretés de valence s-p ont été supposées électriquement neutres.

Les énergies de ségrégation ont été évaluées pour les impuretés de phosphore et de soufre aux joints  $\Sigma=5$  (210),  $\Sigma=5$  (310),  $\Sigma=11$  (332) et  $\Sigma=11$  (113) dont la structure a été d'abord relaxée par une méthode de relaxation quasi-dynamique. Nos résultats sont en accord qualitatif avec les données expérimentales.

**ABSTRACT**

Grain boundary segregation of sp-valence impurities in Ni have been investigated using a tight-binding type electronic theory of s, p and d-basis orbitals. Two center integrals both for host and impurity atoms are determined within Harrison's universal scheme. The relative electronic energy levels  $E_s$ ,  $E_p$  and  $E_d$  of s, p and d basis orbital are taken from atomic structure calculations by Herman and Skillman and sp-valence impurities are assumed to be electrically neutral.

Segregation energies are calculated for phosphorus and sulfur at  $\Sigma=5$  (210),  $\Sigma=5$  (310),  $\Sigma=11$  (332),  $\Sigma=11$  (113) grain boundaries, the structure of which was first relaxed by a quasi-dynamical technique. Our results show a qualitative agreement with experimental data of P and S segregation.

**INTRODUCTION**

It is now well established that grain boundary (GB) embrittlement and intergranular corrosion in nickel can be correlated to the intergranular sulfur segregation [1].

The purpose of this paper is to investigate the segregation of sp-valence impurities (sulfur, phosphorus) at various relaxed structures of grain-boundary in nickel. We use the tight-binding (TB) electronic theory within the second moment approximation and calculate the segregation energies  $E_{seg}$  of sp-valence impurities in nickel.

**PRINCIPLES OF CALCULATIONS**

The relaxed GB used to evaluate  $E_{seg}$  was obtained by the following procedure.

The starting geometrical configuration is constructed by putting together two single crystals along the required crystallographic planes. For fixed GB plane and rotation angle, numerous configurations have been then considered by translating one crystal with respect to the other in directions parallel to the GB plane. We used translations belonging to the DSC lattice. Taking into account the periodicity of GB structure, we have sampled as much as 70 different configurations for fixed GB angle and plane.

The relaxation at  $T = 0$  K of the geometrical structures have been achieved by using a quasi-dynamical procedure which consists of a Molecular Dynamics calculation modified to include a damping force [2]. For, periodic conditions have been imposed to the bicrystal in directions parallel to the GB plane and free surfaces in the direction perpendicular to it.

The particles interact via a potential derived from the second moment approximation of the TB scheme for transition metals. The cohesive energy is written as the sum of an attractive part (d band contribution) :

$$E_B = B \sum_i \left[ \sum_{j \text{ NN}} \exp - 2q \left( \frac{r_{ij}}{r_0} - 1 \right) \right]^{1/2}$$

and a Born-Mayer repulsive part :

$$E_R = A \sum_{i \text{ j NN}} \exp - p \left( \frac{r_{ij}}{r_0} - 1 \right)$$

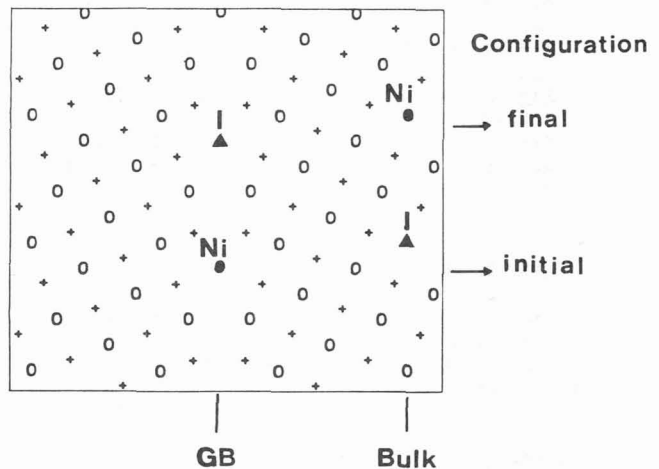
(NN stands for all the first nearest neighbours  $j$  of particles  $i$  ;  $r_{ij}$  is the distance between  $i$  and  $j$  and  $r_0$  the nearest neighbour distance at  $T = 0$  K).

The parameters  $p, q, A$  and  $B$  have been determined by adjusting the cohesive energy, the bulk modulus and the shear constants ( $c'$  and  $c_{44}$ ) on the experimental data and by prescribing the equilibrium condition  $P = 0$  ( $P$  : hydrostatic pressure) [3]. The following values have been used :  $E_c = E_R + E_B = - 4.46$  eV ;  $p = 10.36$  ;  $q = 2.59$ . The energy and the excess volume of the different stable GB, we used in segregation calculations, are given in table I (see also fig. 1 and 2).

TABLE I : (a : fcc parameter ; S : atomic surface in GB plane)

	$\Sigma = 5$		$\Sigma = 11$	
	(210)	(310)	(332)	(113)
$E_{GB}$ (erg $\text{cm}^{-2}$ )	1390	2010	500	2070
$V$ ( $10^{-2}$ a $^{-1}$ )	10	13	4	6
$S$ (a $^{-2}$ )	1.12	1.58	0.83	2.35

Figure 1 :  $\Sigma = (310)$  relaxed GB  
I and Ni : respectively impurity  
and nickel site.



The segregation energy  $E_{seg}$  is defined as the change in the band structure energy when a substitutional solute atom (I) located in the bulk (initial configuration : IC) exchanges position with a host atom (Ni) at GB (final configuration : FC) (Fig. 1):

$$E_{seg} = E_{FC} - E_{IC}$$

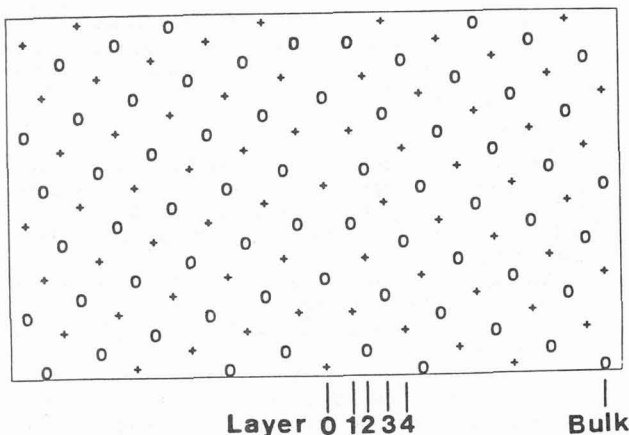
If we express the different contributions to the segregation energy, we can write, the FC energy for instance as :

$$E_{FC} = E_{GB} + E_{bulk} + \sum_{j=NN, Ni} \frac{N_i}{E_j} + \sum_{j=NN, I} \frac{N_i}{E_j}$$

The last two terms give the energies of all neighbours of Ni atom in the bulk and of I atom at GB (a similar expression may be obtained for  $E_{IC}$ ).

No lattice relaxation have been done around solute atom. It has been show indeed that for high angle tilt GB and substitutional impurities, the electronic contributions to the segregation energy are dominant [4].

Figure 2 :  $\Sigma = 5$  (210) relaxed GB



The details of calculational method of band structure energy have been presented elsewhere [5]. We shall recall here only the main points.

We have used the universal TB electronic theory of the s, p and d orbitals [6] to describe the electronic structure of sp-valence impurities (S, P) in nickel. This theory allows us to treat the solute and the solvent on the same footing. The band structure energies of solute or nickel atoms are calculated using the second moment approximation. The major hypothesis we have done are the followings :

- each atom is electrically neutral ;
- the second moment are calculated by using the Slater-Koster table [7] and by taking into account the s, p, d hybridization effects, the relative magnitude of the two center integrals are determined using the theory by Harrison [6] ;
- the atomic levels  $E_s$ ,  $E_p$  and  $E_d$  for the host basis orbitals are ajusted to reproduce the number of bands electrons determined by the first principle LMTO-ASA band structure calculations [11] ;
- the number of electrons for sp-solute atoms are determined using the condition that the impurity is electrically neutral. The relative energies of s, p and d atomic levels of impurities are taken to be the same as those of the isolated free atom [8].

**RESULTS AND DISCUSSION**

The results of our calculations are presented in Table 2 ; layers 0, 1, 2... correspond to different sites at GB (Fig. 2).

Table II :  $E_{seg}$  in eV/atom

GB	$\Sigma = 5$		$\Sigma = 11$		
	(210)	(310)	(332)	(310)	(310)
Solute	S	P	S	S	S
Layer					
0	-0.65	-0.09	-0.56	-0.45	-0.17
1	0.56	0.87	0.27	0.45	0.1
2	-0.23	+0.33	-0.11		-0.01
3	-0.11		-0.04	-0.14	
4	0.12		0.06		+0.04

The calculated values show a strong attractive interaction at the inner most site (layer 0) for all the grain boundaries. Moreover it is worth mentioning that GB segregation have an oscillating behavior : layer 1 presents a repulsive interaction whereas the neighbouring sites (0 and 2) show an attractive interaction. The results for sulfur are in agreement with experimental data. For instance, one of the authors have found 1.015 eV/atom for the intergranular segregation energy of sulfur in polycrystalline nickel using AES and electrochemical testing [1]. Other experimental works support that sulfur tends to segregate at GBs in nickel. On the other hand, GB segregation of phosphorus have never been detected by AES [1] ; this observation is in good agreement with the very weak calculated segregation energy for P in  $\Sigma = 5$  (310) GB (Table II).

Recent experimental work [10] has postulated that the interplanar spacing rather than the  $\Sigma$  value is a good criterion to describe the propensity for GB segregation : the lower the planar density, the larger the segregation is. Our numerical results are not inconsistent with these experimental observations more particularly for  $\Sigma = 11$  grain boundaries (see Table I and II).

### CONCLUSION

We have used the tight binding electronic theory of s, p and d basis orbitals to investigate the segregation behavior of sp-valence impurities at grain boundaries in Ni bicrystals. We have introduced the typical low index tilt GBs  $\Sigma = 5$  (210), (310) and  $\Sigma = 11$  (332), (113). GB structures have been relaxed towards stable configuration by a quasi-dynamical technique.

Though the present theoretical calculations are based on simplifying assumptions, we have found two important results :

a : the segregation energy depends strongly on the type as well as on the atomic site of GB ;

b : much stronger attractive binding energy is obtained for S impurity than for P. It is worth noting that this behavior is due to the filling of sp band of impurity atoms and thus could not be understood by using the usual pair potentials.

Moreover we have shown that our results are semi-quantitatively consistent with the experimental observations on S segregation in Ni polycrystals.

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