

## COMPUTER MODELING OF ATOMIC CLUSTERS FORMATION IN GRAIN BOUNDARIES

**A. Itckovich<sup>1</sup>, M. Mendeleev<sup>2</sup>, A. Rodin<sup>1</sup> and B. Bokstein<sup>1</sup>**

<sup>1</sup>The National University of Science and Technology MISiS, Moscow, Russia

<sup>2</sup>Ames Laboratory, Ames, IA, USA

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**Abstract.** The mobility of atomic pairs in Cu grain boundary was investigated by molecular dynamic simulations. The energy of interaction between the atoms inside the pairs (dipole energy) was introduced as well as the segregation energy. The complexes formation leads to decrease of mean-square atomic displacements. The diffusion coefficients decrease with increasing the dipole interaction energy and segregation energy. The dipole energy influences more strongly, than segregation energy.

Atomic interaction in grain boundaries (GB) leads to the complexes formation. Up to now two types of the complexes were analyzed for binary systems with restricted solubility:  $A_m B_n$  for systems with intermediate phases and  $B_2$  – without them [1]. The equilibrium between grain and GB is usually defined as the change of atoms between grain and GB

$$A_b + B = A + B_b, \quad (1)$$

with the equilibrium constant

$$b = \frac{X_A X_B^b}{X_B^b X_A}, \quad (2)$$

and leads to the well-known Langmuir-McLean adsorption isotherm [2]. The simplified treatment [3] was based on the model of associated solutions [4]. It was assumed that atomic complexes in GB's are close (by composition and chemical bonds) to the nearest phase in grain [5-7]. For the complex AB type a quasichemical reaction of formation is of the form

$$A_b + B_b = ([AB])_b, \quad (3)$$

with the equilibrium constant

$$K = \frac{X_{AB}^b}{X_A^b X_B^b}. \quad (4)$$

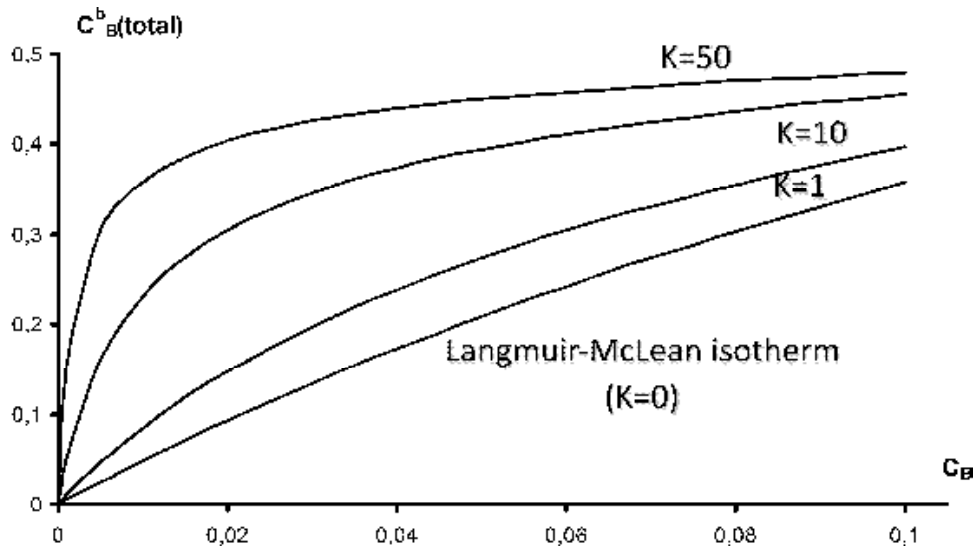
The simplest estimation supposes

$$K \approx \exp\left(-\frac{\Delta H^0}{RT}\right), \quad (5)$$

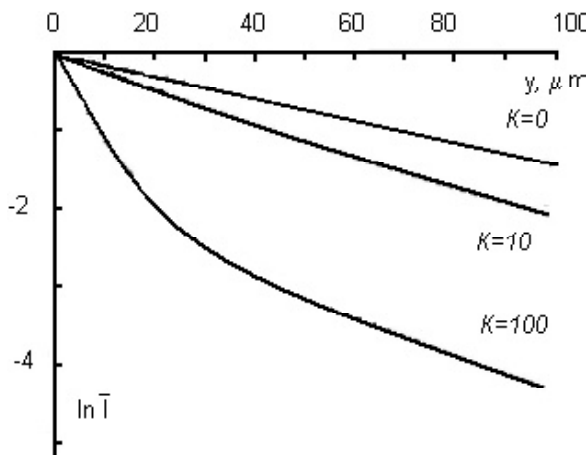
where  $\Delta H^0$  is the formation enthalpy of the appropriate phase in grain. It was shown, that effect leads to the increase of segregation and decrease of diffusion flux and diffusivity. Fig. 1 shows GB segregation isotherm when the complexes formation is the predominating process in the GB, comparing with the absence of the complexes formation. Fig. 2 shows the dependence of the mean diffuser concentration on the depth of penetration for different  $K$ .

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Corresponding author: A. Itckovich, e-mail: alexey84.box@gmail.com



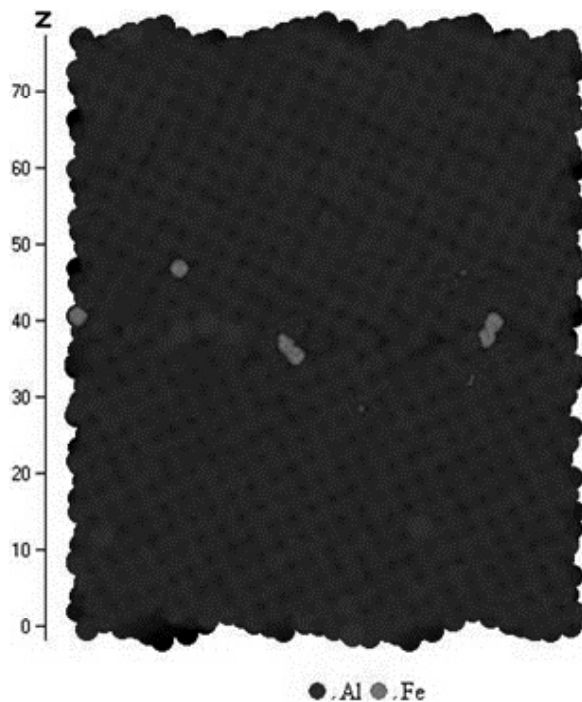
**Fig. 1.** Segregation isotherms for  $b=5$ ,  $C_B^b(\text{total})$ - is the total (due to segregation and complex formation) concentration of component in GB.



**Fig. 2.** Dependence of the mean concentration of diffuser  $I/I_0$ , where  $I_0$  is the mean concentration on the surface,  $y=0$  on the depth of penetration for  $b=5$  and different  $K$ .

There are no direct experimental data on the complexes in GB, only indirect results, obtained by molecular dynamics modeling [8]. The authors used model of GB containing 18000 Al atoms. The part of them was replaced by Fe atoms. With the use of the half-empiric potential Al-Fe it was shown that in the Al-based alloy with 2.5 at.% Fe, in symmetric GB (100) the complexes of  $\text{Fe}_2$ -type are formed (Fig. 3) and the coordination number Fe-Fe is close to 1, that is much more than in random distribution. It was also shown that the complexes formation leads to decrease of the mean-square atomic displacements and therefore of diffusion coefficient.

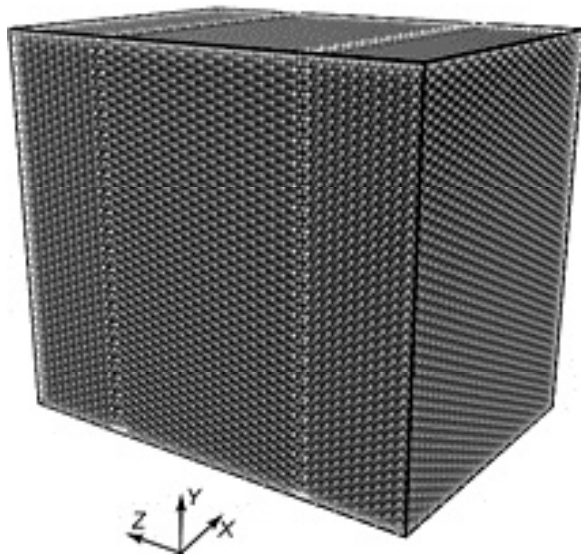
At the present study we investigated the mobility of the atomic pairs in copper. We started from a semi-empirical potential designed for Cu [9,10]. The potentials of such type are employed in molecular



**Fig. 3.** Fe complexes at Al-Fe system in the symmetric GB (100), in Al with 2.5% Fe.

dynamics (MD) simulations to investigate how different kinds of atomic interaction energy affect a diffusion mobility.

The calculated model contained 269640 Cu atoms and two symmetrical GB's sigma 5 (001) (012). (Fig. 4). After minimization at 0K structure of the grain boundary was set corresponding to the minimum energy. Structure (001) plane and the (100) plane are shown in Fig. 5. 70 pairs of identical accidental atoms  $\text{Cu}_2$  with the same properties, as other Cu atoms, were placed near the GB, at



**Fig. 4.** General view of the simulation model.

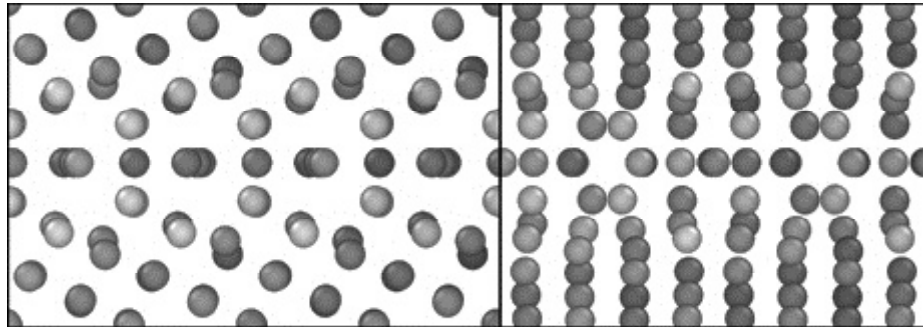
distance 2.6 nm from each other, sufficient to exclude interaction between pairs.

The energy of interaction (dipole energy,  $\Delta E_{\text{dipole}}$ ) between the atoms was introduced, as well as the energy of segregation at GB ( $\Delta E_{\text{seg}}$ ). The mean

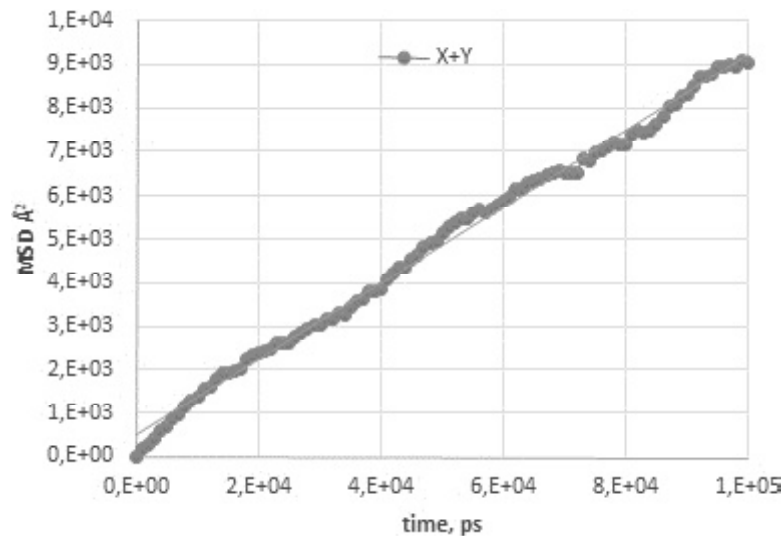
square displacement of atoms within 100 ns at 1000 and 1200K was measured (Fig. 6). The data on displacement were recalculated to diffusion coefficients by the formula (6), Table 1.

$$D = \sum \frac{dx^2 + dy^2}{4t}. \quad (6)$$

It is seen that diffusion coefficients decrease with increasing the dipole interaction energy and segregation energy. Comparing results for #1-3 with the segregation energy close to zero, one can see that the increase of the module of dipole energy from -0.06 to -0.5 eV/atom leads to decrease of diffusion coefficient from  $3.9 \cdot 10^{-7}$  to  $4.0 \cdot 10^{-8}$  cm<sup>2</sup>/s (order of magnitude) at 1000K and from  $2.2 \cdot 10^{-6}$  to  $1.0 \cdot 10^{-7}$  cm<sup>2</sup>/s (twenty times) at 1200K. On the other hand at the close values of dipole energy (specimens #1 and #4) the segregation energy which changes from 0.008 to 0.48 eV/atom decreases D also, but only from  $3.9 \cdot 10^{-7}$  to  $2.0 \cdot 10^{-7}$  at 1000 K (i.e. at 3 times) and from  $2.2 \cdot 10^{-7}$  to  $9.5 \cdot 10^{-7}$  cm<sup>2</sup>/s (2 times) at 1200K. Hence, both energies decrease



**Fig. 5.** Structure of grain boundary in the planes a) (001) b) (100).



**Fig. 6.** Typical dependence of the mean square displacement of atomic pairs vs time, at 1200K, for potential version #1.

**Table 1.** Data of dipole energy, energy of segregation and diffusion coefficients at 1000 and 1200K.

Version	$\Delta E_{\text{dipole}}$ eV/atom	$\Delta E_{\text{seg}}$ eV/atom	$D$ cm <sup>2</sup> /s	
			1000K	1200K
#1	-0.059	0.008	$3.94 \cdot 10^{-7}$	$2.19 \cdot 10^{-6}$
#2	-0.199	0.006	$2.08 \cdot 10^{-7}$	$1.46 \cdot 10^{-6}$
#3	-0.497	0.014	$4.01 \cdot 10^{-8}$	$1.03 \cdot 10^{-7}$
#4	-0.063	0.478	$2.06 \cdot 10^{-7}$	$9.47 \cdot 10^{-7}$
#5	-0.285	0.463	$5.94 \cdot 10^{-8}$	$4.87 \cdot 10^{-7}$

diffusion coefficient, but dipole energy influences more strongly.

## CONCLUSIONS

- The complexes formation lead to decrease of mean-square atomic displacements.
- The diffusion coefficients decrease with increasing the dipole interaction energy and segregation energy.
- The dipole energy influences more strongly, than segregation energy.

## ACKNOWLEDGMENTS

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