SEGREGATION OF Mg TO GENERIC TILT GRAIN BOUNDARIES
IN Al: MONTE CARLO MODELING

I.N. Karkin1,2, L.E. Karkina1, A.R. Kuznetsov1, M.V. Petrik1,2, Yu.N. Gornostyrev1,2*,
P.A. Korzhavyi1,3

1Institute of Metal Physics, Ural Branch of RAS, Yekaterinburg, 620990, Russia
2Institute of Quantum Materials Science, Yekaterinburg, 620075, Russia
3Department of Materials Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
*e-mail: yug@imp.uran.ru

Abstract. The formation of equilibrium segregations at tilt grain boundaries of several different types in Al-Mg alloys has been investigated in the framework of a combined approach, which includes molecular dynamics simulation and thermodynamic Monte Carlo modeling. The concentration profile of Mg distribution in GB vicinity was calculated in dependence on the alloy concentration and temperature. We found that width of segregation on generic GB determined by feature of their structure and is match bigger in comparison with special low-energy GB. It is shown that segregation formation is control not only energy gain due to moving solute on GB but also interaction between solute atoms; as results, maximal enrichment of GB is not exceed 25 at.%. Possible origins of the formation of extended segregation on GB in materials subjected by severe plastic deformation have been discussed.

1. Introduction
Segregations of impurities and/or alloying elements at grain boundaries (GBs) have significant effects on many physical properties of polycrystalline materials [1]. The segregation formation in ultrafine grained materials has been the subject of special interest during recent years [2]. In this case, the high density of GBs and their enrichment in the alloying elements can essentially modify the phase content of the alloy [3] and retard the development of recrystallization, thereby increasing stability of the nano-grained structure [4-9] that results in extra hardening. Despite notable efforts by many researchers, the mechanism of solute–GB interaction and segregation formation is still a matter of debate [1, 10-12]).

The investigation of GB chemistry is a challenging task for both experiment and theoretical modeling because the segregation involves different length scales and critically depends on the GB type. Recent progress in the studies of segregation is connected with the use of 3D atom probe tomography [13-15] which is one of the promising techniques for the quantification of solute element distributions in the vicinity of interfaces with a spatial resolution of a few Ångström. Employing this method, unusually broad segregation regions were found near GBs in ultrafine grained alloys produced by severe plastic deformation. Thus, the half-width of segregation layers in ultrafine-grained Al-Mg-Si alloys was about 3–5 nm [16-19]. The formation of such broad segregations is difficult to interpret within the traditional concepts of solute–GB interactions [1]. It may be attributed to structural peculiarities of the GBs formed as a result of severe plastic deformation, but the nature of these peculiarities is not exactly known.
A thermodynamic description of equilibrium GB segregations may be obtained using the Langmuir–McLean type of segregation isotherm \[1, 20\] that relates changes in the solute concentration at the GB with changes in the Gibbs free energy. Within this approach, it is commonly assumed that the segregation is driven by lowering the energy of the system when a solute atom is moved from the bulk to the boundary of a grain \[1, 21\], \( \Delta E_s = E_{\text{sol}}^{\text{GB}} - E_{\text{sol}}^{\text{bulk}} \), where \( E_{\text{sol}}^{\text{bulk}} \) is the solution energy of the solute atom in the bulk (at the GB). Further, all non-configurational entropy contributions (i.e. due to vibrational or other degrees of freedom) are often considered as negligible. The change in the configurational entropy of the solid solution will then be the only factor to limit the GB enrichment by the segregating element. Although this approach does not take into account interactions among the segregated atoms, it correctly captures the qualitative trends of segregation formation via the only parameter, namely, the segregation energy \( \Delta E_s \).

The \( \Delta E_s \) value characterizes the effective interaction of an impurity atom with the GB. The nature of this interaction is often quite complex: it depends on the GB type and includes a deformation as well as an electronic contribution which are difficult to separate from each other \[10, 12\]. Density functional theory (DFT) methods are widely used to study the effects of alloying elements on the electronic structure and energy of GBs \[10-12, 22-26\]. For example, the segregation energy of Mg to different positions near the tilt GB \( \Sigma 11(113) \) in Al has been computed in \[26\] using DFT methods. It has been found that an Mg atom, which preferentially occupies the “loose” site at the GB, weakens the metallic bonds among the neighboring Al atoms.

First principles calculations provide the most reliable information about segregation energies, but are computationally heavy, so that they can only be applied to some symmetric special-type (ST) GBs. Classical molecular dynamics (MD) simulations do not have such limitation and enable large-scale atomistic modeling of polycrystals with general-type (GT) GBs. However, the majority of previous MD studies of impurity segregation have been done for tilt and twist ST GBs \[27-31\]. In addition, the MD approach is limited by reliability of the interatomic interaction potentials, and requires the use of sophisticated models of the interatomic interactions to correctly describe the charge transfer effects between solute and matrix atoms at a GB. As shown in Ref. \[12\], Al–Mg is an example of the alloy system where the solute–GB interaction energy is mainly determined by the size effect. In such a case, classical MD simulations are expected to adequately describe the interactions of solutes with different types of GBs.

Enrichment by Mg of the tilt and twist ST GBs in Al was studied in Ref. \[30\] using a combined approach involving MD and Monte Carlo (MC) modeling. In agreement with the results of Ref. \[12\], it was found that the local strain in GB region and the size mismatch between Mg and Al atoms are the two main reasons for the segregation formation in Al–Mg alloys. For the Al–10 at.% Mg alloy the concentration of Mg on tilt and twist GBs was found to be 40% and 30%, respectively, at temperature \( T=673 \text{K} \). So strong GB enrichment is far beyond the solubility limit and indicates that the interatomic potential used in Ref. \[30\] is not quite reliable. Also, the width of GB segregation region in Ref. \[30\] did not exceed 1 nm. Thus, the consideration of a ST GB only is not sufficient for understanding the origins of unusually broad GB segregations that were observed to form in alloys after severe plastic deformation \[16-19\].

Here we study the formation of segregations at tilt GBs of three different types in Al–Mg alloys using a combined approach involving classical MD simulations and statistical MC modeling. The equilibrium statistical distributions obtained in this work for Mg at GBs of different type are in good agreement with experimental observations. We show that the solute-enriched region around a general-type GB is considerably wider than in the case of a symmetric special-type GB, which is determined by the structural features of these grain boundaries.
2. Modeling method

Reliability of the results obtained by the MD and MC methods critically depends on the choice of interatomic interaction potential. Several interatomic potentials have been developed in the framework of embedded atom method (EAM) for the Al–Mg system to describe the alloys with high \([32]\) or low \([30, 33]\) concentration of Mg. The interatomic potential proposed in Ref. \([33]\) allows one to reproduce well the Al-rich part of the phase diagram and yields the formation energies of possible metastable phases \(\text{Al}_3\text{Mg}(\text{L1}_2)\), \(\text{Al}_3\text{Mg}(\text{DO}_3)\), \(\text{AlMg}(\text{B2})\), \(\text{AlMg}_3(\text{L1}_2)\), and \(\text{AlMg}_3(\text{DO}_3)\), as well as that of the stable \(\beta\)-phase \(\text{Al}_3\text{Mg}_2\), in agreement with \textit{ab initio} calculations.

Within the model adopted in Ref. \([33]\), the total energy of an alloy may be written as

\[
U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi_{ij}(r_{ij}) + \sum_{i=1}^{N} \Phi_i(\rho_i),
\]

where \(ti(tj)\) is the type of atom number \(i(j)\), \(N\) is the total number of atoms, \(r_{ij}\) is the distance between atoms \(i\) and \(j\), \(\phi_{ij}(r)\) is pair contribution to the interaction energy and \(\Phi_i(\rho_i)\) is the so-called embedding function which depends on local electron density

\[
\rho_i = \sum_j \psi_{ij}(r_{ij}).
\]

In this paper we employ this interatomic potential with one additional simplification for electron density. Namely, we assume that

\[
\psi_{ij} = \psi_{ij'},
\]

i.e. the electron density induced on site \(i\) by the neighboring atoms does not depend on type of atom \(t_i\). As it shown in Ref. \([33]\), this is a rather good approximation for dilute solid solutions.

The process of alloy decomposition is controlled by interactions between the solute atoms. To check reliability of the interatomic potential used, we calculated an effective interaction energy \(V(r)\) of Mg atoms in the Al matrix as the difference between the energies of a crystallite with two Mg atoms at a given distance \(r\) and the same crystallite with the two Mg atoms situated far from each other. The dependence \(V(r)\) obtained using MD simulations is presented in Fig. 1 in comparison with the results of \textit{ab initio} calculations by PAW-VASP method \([34, 35]\). A 108-atom supercell (3x3x3 cells) with periodic boundary conditions was used in the calculations. As in Ref. \([12]\), the exchange-correlation energy was treated in the generalized gradient approximation (GGA). For farther details see Ref. \([12]\).

![Fig. 1. Effective interaction energy between two Mg atoms as a function of distance for the first 8 nearest-neighbor shells of in fcc Al. Curves 1 and 3 present the results of MD calculations with the interatomic potentials used in this paper (see text) and with those used in Ref. \([30]\), respectively. Curve 2 shows the results of \textit{ab initio} PAW-VASP calculations.](image-url)

Figure 1 shows that the interaction energies obtained from MD simulations with the EAM potential \((1)-(3)\) used in this work (curve 1) and \(V(r)\) obtained from PAW-VASP calculations (curve 2) are qualitatively similar and correspond to a repulsion between two Mg atoms in the...
Al matrix. At the same time, the interaction energy obtained from MD calculation with the interatomic potential from Ref. [30] (curve 3) is rather different and shows an unreasonably strong attraction between two Mg atoms separated by the 3rd–5th coordination shell distance. This may be a reason for the unusually high concentrations of Mg (30-40 at%) obtained in Ref. [30] near GBs in Al.

The presence of a local minimum on curves 1 and 2 at 2nd nearest neighbor distance between two Mg atoms indicates that formation of Al\textsubscript{3}Mg phase with the L\textsubscript{12} structure is energetically preferable. This phase is actually observed as an intermediate state during the transformation of Guinier-Preston zones into the stable phase Al\textsubscript{3}Mg\textsubscript{2} [36]. The difference between the interaction energies calculated by MD and first-principle methods for 1st nearest-neighbor shell is presumably due to the reconstruction of electronic structure which is not quite well represented by the EAM potentials used. Thus, one should expect that MD simulations with interatomic potential (1)-(3) will correctly describe the qualitative features of Al–Mg alloy, but somewhat overestimate the energy gain due to the Al\textsubscript{3}Mg phase formation.

Fig. 2. (a) Projection on the (001) plane of the polycrystallite containing ST asymmetric tilt GBs Σ5[001]{710}/(110) (Σ5), low-angle (LA) GBs and high angle general-type (GT) GBs after annealing at \( T_{\text{an}} = 500 \) K. Crystallographic axes are given in the bottom left corner. (b) The central part of a Σ5 GB is enlarged to show the atomic structure consisting of units B and C. Filled and open circles show the atoms in the consecutive (001) atomic planes.

To model a variety of tilt GBs, we use the same (poly) crystallite as in our previous paper [12]. A projection of the crystallite onto the (001) plane is shown in Fig. 2a. As the first step to create the model, a Σ5[001]{710}/(110) ST asymmetric tilt GB was created in the center of the simulation box according to the scheme of coincidence site lattice (CSL) [37]. An additional energy minimization was carried out for this GB by a small relative shift of the two conjugated grains along the GB plane. The resulting crystal geometry of the Σ5 GB is shown in Fig. 2b, where the main structural units describing this GB [37, 38] are marked as C and B. The size of the crystallite in the direction perpendicular to the Σ5 GB plane was chosen in such a way that periodic boundary conditions lead to the appearance of the second (fictitious) Σ5 GB of the opposite orientation. The two grains, divided by the Σ5 GB, were placed inside the third grain bounded by the planes \{ 3 5 0 \}, which form angles close to 120° with the Σ5 GB. Thereby, two triple junctions were formed in the crystallite, which connected GBs of three types: asymmetric tilt ST GB Σ5, general type (GT) GB with a misorientation angle of 45°, and a low-angle (LA) GB with a misorientation angle of 8.13° (Fig. 2a). Such a structure allows for MD simulations with periodic boundary conditions along all the three crystallographic directions. The supercell dimensions were 20 nm in the [100] and [010] directions of the third grain and 10 nm in the [001] direction (which coincided with the tilt axis for all the GBs); the supercell contained about 250,000 atoms.
During the supercell construction, the parts of the matrix were rigidly rotated and moved relative to each other along the [010]. To reach the equilibrium structure of the GBs, the crystallite was treated by annealing, including a long exposure at temperature $T_{\text{an}} = 500$ K (0.5 of the melting point $T_{m}$), and then gradually cooled down to $T = 0$ K with a 100 K step. The total duration of the treatment ranged from 75 to 225 ps.

The GB segregation formation was investigated by using the constructed crystallite together with a combined approach which included successive steps of MD and MC [39] modeling. To create the initial configuration, Mg atoms were randomly distributed over the sites of the crystallite in Fig. 2 in accordance with their mean concentration. The segregation formation was simulated at two temperatures (450 K and 700 K) and for two concentrations of Mg (1 at.% and 3 at.%). At each MC step a random choice of atom type 1 (Al) and type 2 (Mg) and their subsequent exchange at the given temperature was performed in accordance with the Metropolis algorithm [39]. The element distribution corresponding to the thermodynamic equilibrium (at a fixed GB structure) was reached after $10^6$ MC steps. After the equilibrium state had been achieved, additional MD simulations at the same temperature ($2\times10^4$ steps) followed by an MC run ($10^6$ steps) were performed. To analyze the GB structure and distribution of interatomic distances, removal of thermal fluctuation was done by an additional quenching and low-temperature MD relaxation ($10^4$ steps).

3. Results and discussion

**Solute atom distribution in the polycrystallite.** Figure 3 shows the distribution of Mg atoms in the polycrystallite for two Al–Mg alloys, obtained after two MD+MC cycles; further repetition of MD+MC runs does not change the results.

![Fig. 3. Distribution of Mg atoms in the polycrystallite of Al–Mg alloys with 1 at.% Mg (b) and 3 at.% Mg (c,d) after MD+MC simulations at temperature of annealing $T = 450$ K (b,c) and 700 K (d). Initial random distribution of 3 at.% Mg is shown in frame (a).](image)
The solute atoms enrich the GB region wherein the resulting concentration profile is dependent on the temperature and concentration of Mg. The solute atoms accumulate only at the GB center (Fig. 3b) if the concentration of Mg is 1 at.%, while at 3 at.% Mg the segregated solute atoms form a broad boundary layer (Fig. 3c, d). The most heterogeneous distribution of solutes is obtained at LA GB; in this case the Mg atoms are concentrated in local regions of tension near the cores of the grain boundary dislocations (the corresponding strain fields clearly seen in Fig. 2a). At the same time, more homogeneous distributions of Mg atoms are observed for the Σ5 and GT GBs whose structure is a dense arrangement of building blocks similar to the units depicted in Fig. 2b.

Local increase of Mg concentration near the triple junctions results in the formation of nuclei of an ordered phase (indicated by arrows in Fig. 3c). The results of MD+MC modeling for alloys of higher Mg concentration (5 at.% and 7 at.%) show that a layer of the Al3Mg phase is formed along the GT GBs. In this paper we focus on the process of segregation formation and restrict ourselves to alloys with low concentrations of Mg where the formation of Al3Mg particles is unlikely.

The increase in temperature from 450 K to 700 K prevents the precipitation of Al3Mg phase and slightly smears the solute element distribution (cf. Fig. 3c and Fig. 3d). To quantify the GB enrichment by alloying element we calculate the Mg distribution profile in the direction perpendicular to the GB plane, by averaging Mg concentration over lattice planes parallel to the GB plane. The results are presented in Fig. 4 which shows that the maximum enrichment (about 20 at.% Mg) is attained in the center of a GT GB at T = 450 K and the width of the segregation layer is about 2 nm.

Fig. 4. Concentration profiles of Mg distribution averaged along Σ5 GB (a), GT GB (b) and LA GB (c). The different curves correspond to alloys with 1 at.% Mg at 450 K (1), 3 at.% Mg at 450 K (2) and 3 at.% Mg at 700 K (3).

A decrease of the alloy concentration leads to lowering of the maximum value and narrowing of the concentration profile. In particular, the width of GB enrichment increases from about 1 to 2 nm when the Mg concentration is increased from 1 to 3 at.%. The increase in temperature from 450 K to 700 K practically does not change neither the maximum value of concentration nor the width of concentration profile in cases of Σ5 and GT GBs (cf. curves 2 and 3 in Fig. 4a,b). At the same time, at LA GB where the concentration of Mg is much smaller, the increase of temperature results in a remarkable decrease of the maximum value of concentration. Note, that the segregation formation in the considered nano-grained polycrystallite is accompanied by a significant decrease of the Mg concentration inside the grains (especially at the lower temperature), which should change the conditions of phase equilibrium in the alloy.

To characterize relative spatial arrangement of different type of atoms we calculate the radial distribution function (Fig. 5). The Figure shows that lattice distortions in the GB vicinity lead to broadening of the first peak (R1) corresponding to the first nearest-neighbor distance.

From comparison of curves 1 and 2 in Fig. 5 we conclude that Mg atoms are located
mainly at the second nearest-neighbor distance (peak $R_2$) relative to each other. This means that segregation formation is determined not only by the solute–GB interactions, but also by the interactions of the segregated solute atoms with each other leading to a strong short-range order. As seen from Fig. 1, a significant energy cost is associated with the placement of two Mg atoms at the first nearest-neighbor distance, while the formation of second nearest-neighbor Mg–Mg pairs is preferable. Thus, the effective Mg–Mg interaction restricts the maximum concentration to values not exceeding 25 at.%. The maximum increase in the Mg concentration is achieved in the GB center (Fig. 4) and the width of enriched region is determined by the features of GB structure.

Fig. 5. Radial distribution function (RDF) for all types of atoms (curve 1) and for Mg–Mg pairs (curve 2) near $\Sigma 5$ GB for Al–3 at.% Mg alloy after MD+MC simulations at $T = 450$ K.

Mg segregation at high-energy GBs in Al. The results presented in the previous section show that segregation formation on generic GBs is determined by the structural state of GB, by the solute–GB interactions, as well as by the interaction between the solute atoms. To clarify the role of the different factors in the segregation formation we calculated the interaction energy between two Mg atoms at different positions nearby GB; the role of solute–GB interaction energy has been considered previously in Ref. [12]. The Mg–Mg interaction energy near a GB was determined as

$$
\Delta E_{\text{int}}(x) = E(\text{Mg}_1^{\text{GB}};\text{Mg}_2^{\text{GB}}) - E(\text{Mg}_1^{\text{int}};\text{Mg}_2^{\text{int}}),
$$

where $E(\text{Mg}_1^{\text{GB}};\text{Mg}_2^{\text{GB}})$ is the (relaxed) energy of a crystallite containing two Mg atoms in positions 1 and 2 near a GB, $E(\text{Mg}_1^{\text{int}};\text{Mg}_2^{\text{int}})$ is the energy of the same crystalline with the two Mg atoms inside a grain (far from any GB) in similar positions 1 and 2, $x$ is the distance from the GB center to position 1. For the former configuration, position 2 of the second Mg atom is subsequently changed to scan over the lattice positions belonging to the given coordination shell relative to position 1.

The results of calculations of segregation energy $\Delta E_{\text{sg}}$ [12] and Mg–Mg interaction energy $\Delta E_{\text{int}}$ are presented in Fig. 6 in dependence on the distance from the high-angle GBs for particular directions X indicated in Fig. 2a.

One can conclude from Fig. 6a,b that moving a Mg atom from the bulk to the GB region (about 1 nm width) results in an energy gain and is the driving force for segregation. Surprisingly, the Mg–Mg interaction energy for 2nd nearest-neighbor shell shows a giant variation depending on the choice of position 2. Thus, the value of $\Delta E_{\text{int}}$ becomes strong and negative in a broad region near a GB (about 2 and 3 nm in cases of asymmetric $\Sigma 5$ and GT GBs, respectively). By analyzing the atomic displacement field, we have found that a stronger attraction for a Mg–Mg pair is realized when the distance between the Mg atoms becomes larger than the 2nd nearest-neighbor distance in the bulk Al. It means that lattice distortions in the vicinity of a GB have strong effect on the interaction between solutes, as well on the
thermodynamic stability of the alloy. In particular, the strong attraction between Mg atoms at 2nd nearest-neighbor distance will facilitate broad segregations and stabilize the Al₃Mg phase (or the corresponding short-range order) in the GB region.

Thus, segregation formation is a complex phenomenon and there are several factors which control the solute concentration profile at a GB. The first factor is the solute–GB interaction energy $\Delta E_{sg}$. In the considered case the value $\Delta E_{sg}$ is negative and attains the maximum absolute values on the most distorted sites (the central sites of ST GBs, vertices of the structural units in GT GBs, or the grain boundary dislocation cores of LA GBs). Therefore, features of the GB structure play an important role in the segregation formation. The second factor is the solute–solute interaction which can change essentially (even by sign) in the vicinity of a GB. In the case of Al–Mg alloys the attraction between the solutes at 2nd nearest-neighbor distance becomes stronger near a GB, which increases the GB segregation capacity and broadens the segregation layer. At the same time, the Mg–Mg interaction at the first nearest neighbor distance is strongly repulsive and, together with the configurational entropy term, is a factor that limits the GB enrichment by the solute. The entropy contribution results in a smearing of the segregation profile when the temperature is above some critical value $T_{cb}$ which corresponds to the decomposition temperature of the solid solution in the GB vicinity. In the opposite case, when $T < T_{cb}$, the solute concentration at GB is weakly dependent on temperature (see Fig. 4 a,b).

4. Conclusions
Using a combined atomistic modeling approach involving molecular dynamics and Monte Carlo simulations, we obtained the equilibrium statistical distributions for the solute atoms at three different types of tilt grain boundaries and analyzed the factors controlling the grain
boundary segregation formation in Al–Mg alloys. As shown in Ref. [12], the atomic size effect plays an important role in the Mg–GB interactions. Therefore, Mg, as a large solute atom in the Al lattice, tends to enrich regions with a lower atomic density such as grain boundaries.

We find that the value of grain boundary enrichment by the solute element is determined not solely by the energy gain upon moving a solute atom from the bulk to the grain boundary, but also by the interactions of the segregated solutes with each other. In the case of Al–Mg alloy system exhibiting a positive enthalpy of mixing, these interactions limit the maximum solute concentration that is attainable at grain boundaries to 25 at.%, in agreement with experimental observations. At the same time, the Mg–Mg attraction at the second nearest-neighbor distance in Al is found to become stronger near grain boundaries, which increases the grain boundary segregation capacity and broadens the segregation layer. Due to these interactions between the Mg atoms, the segregation profile becomes weakly dependent on temperature below the critical value \( T_{cb} \) corresponding to the decomposition temperature in the GB vicinity.

The width of the solute segregation region is found to be determined by the degree of lattice distortion in the near-boundary region and can reach 3 nm in the considered case of a general-type grain boundary. One can expect that, for grain boundaries formed as a result of severe plastic deformation and possessing an increased density of lattice defects, the width of solute-enriched region may be even larger.

Acknowledgements
The authors acknowledge financial support from the Russian Science Foundation (grant 14-12-00673). The results of the work have been obtained using the computational resources of MCC National Research Center “Kurchatov Institute” (http://computing.kiae.ru) and using Uran supercomputer of IMM Ural Branch of the Russian Academy of Sciences. The authors acknowledge prof. J. Rifkin (University of Connecticut) for providing the code for the MC+MD simulations. Fruitful discussions with Prof. R.Z. Valiev are acknowledged.

References