Atomistic origin of the anisotropic grain boundary segregation in a Mg-Mn-Nd alloy

Risheng Pei1*, Zhuocheng Xie1*, Sandra Korte-Kerzel1, Julien Guénolé2, 3, Talal Al-Samman1

1 Institut für Metallkunde und Materialphysik, RWTH Aachen University, D-52056 Aachen, Germany
2 Université de Lorraine, CNRS, Arts et Métiers ParisTech, LEM3, 57070 Metz, France
3 Labex Damas, Université de Lorraine, 57070 Metz, France

Abstract

Sharp texture after thermal processing is one of the biggest barriers restricting the wide usage of magnesium alloys. Rare earth elements (e.g., neodymium and gadolinium) can essentially weaken and modify the texture of magnesium alloys. However, the underlying mechanisms for texture modification by rare earth elements remain debated. Here, we use 3D atom probe tomography to systematically characterize the solute distribution, especially Nd atoms, on six different general grain boundaries in a Mg-Mn-Nd alloy. The peak Nd segregation concentration varies from boundary to boundary changing from 2.0 at.% to 5.0 at.%. In addition, the segregated clustering on the grain boundaries is also anisotropic, characterized as some islands features with different Nd concentrations. Atomistic simulations suggest that the local atomic arrangement is responsible for the anisotropic grain boundary segregation. These findings indicate the texture modification by Nd in magnesium alloys could be related to the anisotropic segregation on grain boundaries, which triggers preferential grain growth of non-basal grains.

Introduction

To meet the requirement of energy saving and environmental protection, lightweight materials attract more and more attention in the automotive and aerospace industry recently. Magnesium and its alloys are regarded as one of the most promising structural materials due to their low density and high specific strength and stiffness 1, 2, 3. However, their widespread applications are restricted by some bottlenecks, such as relatively low
absolute strength and formability\textsuperscript{4, 5}, sharp basal-type texture after thermomechanical processing\textsuperscript{6} and mechanical asymmetry\textsuperscript{7, 8, 9}. Micro-alloying and optimization of processing parameters are two of the most effective approaches to meet these challenges.

Rare earth (RE) elements, such as Gd\textsuperscript{10, 11}, Ce\textsuperscript{12, 13, 14} and Nd\textsuperscript{11, 15}, have been proved to substantially modify the texture of Mg alloys. The effects in this regard are related to the element type, individual content as well as the combination of non-RE elements\textsuperscript{16}. However, the mechanism of texture modification by RE addition remains not fully understood. Nucleation of grains with a widespread of orientation spectrum\textsuperscript{10, 17} or preferential growth of non-basal grains by RE addition\textsuperscript{18, 19} are two dominant hypotheses. In the latter case, the additional driving force (e.g., local grain size advantage and anisotropic segregation of solute atoms on boundaries) grants the boundaries shared by non-basal grains higher mobility and results in their preferential growth by eclipsing the neighboring grains. Recently, solute segregation behaviors on symmetrical tilt grain boundaries (GBs) and twin boundaries (TBs) were investigated using high-resolution transmission microscopy with aberration. Periodical segregation patterns of Gd and Nd atoms are clearly evidenced by bright Z-contrast\textsuperscript{20, 21, 22, 23, 24}. The atomic arrangement of general boundaries lacks periodical patterns and is much more complicated than the symmetric GBs. Solute clusters of a few nanometers size were observed segregate at large-angle general GBs in a Mg-Gd alloy\textsuperscript{25}. However, the chemistry characterization in transmission microscopy is hard to avoid the influence of neighboring matrix. The segregation behavior in terms of the RE concentration on the GBs has not been systematically investigated experimentally.

Atomistic simulations are a powerful complement to experimental techniques for revealing the grain boundary natures and atomic arrangement. The spectrum of GB segregation energy in face-centered cubic (FCC) polycrystals was identified using molecular dynamics (MD) and molecular statics (MS) simulations\textsuperscript{26, 27}. For hexagonal close packing (HCP) metals, atomistic simulations were carried out to investigate the interface segregation of solute atoms in TBs and specific GBs (such as coincident site lattice boundaries and symmetric tilt GBs) in Mg\textsuperscript{28, 29}. The per-site segregation energies of 23 solute elements at tensile and compression TBs in Mg were systematically studied by density functional theory (DFT) calculations\textsuperscript{28}. The interaction of RE elements with Mg Σ7 GB was quantified using the DFT method\textsuperscript{29}, where a model based on the linear elasticity theory for the solute-GB binding energy was developed which accurately captures the segregation behavior of RE solutes at Mg Σ7 GB\textsuperscript{29} as well as general tilt GBs in FCC Al alloys\textsuperscript{30}. The segregation of Al solute to Mg <0001> symmetric tilt GBs were successfully studied using MS simulations\textsuperscript{31}. The per-site segregation energy was correlated to the descriptors of the local atomic environment, such as site volume and atomic stresses. Nonetheless, until now, the segregation behaviors of RE solute at Mg general GBs are not fully understood. In this work, the segregation behaviors of Nd atoms in a Mg-1.0 wt.%Mn-1.0 wt.% Nd alloy (hereafter, MN11) in six different GBs are characterized by 3D atom probe tomography (APT). Both the anisotropic segregation among boundaries and on the boundary planes are systematically investigated. In order to find out the underlying mechanisms of anisotropic segregation of Nd atom, atomistic simulations were performed to investigate the correlation between per-site segregation energy and the local site environment.
Results

Experimental evidence of grain boundary segregation anisotropy

Nd solute with an atomic radius of 206 pm can introduce a large atomic misfit in Mg (173 pm) matrix. Therefore, for the sake of lowering energy, Nd atoms tend to segregate at GBs which are rich in defects (e.g., dislocations and vacancies). The atomic distributions (Mg, Mn and Nd) of a reconstructed tip from 3D APT are illustrated in Fig. 1 (a). This tip was milled by the transmission Kikuchi diffraction (TKD) assisted technique and the corresponding TKD maps are shown in Fig. 6 (c). Misorientation analysis shows this tip contains a GB with a characteristic of 11.3° [10-10]. As can be seen, Nd segregated evidently on the GB, while the tendency of Mn segregation was limited. The concentration profile inside a cylinder with a diameter of 15 nm outlined in Fig. 1(a) (region of interest, ROI 1) is extracted and plotted in Fig. 1(b). The peak Nd concentration was characterized as $3.04\pm0.19$ at.%, which is about 20 times higher than the counterpart in the matrix ($0.15\pm0.07$ at.%). By contrast, the peak Mn concentration was only $0.29\pm0.10$ at.%. These results indicate a higher tendency of GB segregation of Nd atoms in the alloy. To elucidate the segregation along the boundary, another ROI (ROI 2) was chosen as marked in Fig. 1 (a). The atomic distribution inside of ROI 2 and the 2D Nd concentration along the X-axis are presented in Fig. 1 (c). As stated above, a high concentration of Nd atoms was observed. More importantly, the concentration of Nd solutes in the 2D plot is also quite inhomogeneous, characterized as some red spots with a concentration of 3.50 at.% and some green spots with a concentration of 1.5% at.%. Taking such in-plane anisotropic effect into consideration, the global concentration of this boundary was calculated by the average value on the 2D plot along the black dash line as marked in Fig. 1 (c). The average Nd concentration on the boundary was characterized as $2.46\pm0.33$ at.%.
Fig. 1 Reconstructed 3D APT tip of the MN11 alloy with a long segment of a detected GB milled by guidance of TKD shown in Fig. 6: (a) elemental distributions of Mg, Mn and Nd; (b) concentration profile across the GB, extracted from a cylindrical ROI 1 (diameter of 15 nm) outlined in (a); (c) atom distribution (Mg, Mn and Nd) and 2D Nd concentration along X-axis shown in the atom extracted from a cubic ROI 2 outlined in (a).

To find out the segregation behaviors among boundaries, another four tips were milled for comparison. Fig. 2 presents the TKD and reconstructed APT tip with two segments of boundaries. Orientation analysis (cf. Fig. 2 (a)) reveals those two boundaries shared a misorientation of 59.3° [-3121] and 86.5 [12-31], respectively. According to the element distribution (Fig. 2 (b)), a large amount of Nd atoms segregated on those two boundaries with limited Mn atoms. On the top of the tip, one Mn precipitate was characterized, where Nd atoms also showed an evidently segregated trend on the interface between Mn and Mg matrix. Similarly, two cylinders (ROIs 1 and 2) were inserted perpendicular to the GBs and the corresponding concentration profiles are shown in Fig. 2 (c) and (d). It is evident that those two boundaries exhibited different peak concentrations of Nd atoms. The peak Nd concentration on the first boundary was 2.93±0.22 at.%, while the second one was much higher, reaching 3.73±0.21 at.%. For a better comparison, a ROI 3 around the GBs is magnified and presented in Fig. 2 (e). Fig. 2 (e-1) and (e-2) show the distribution of Nd atoms and the iso-surface with 1.0 at.% of Nd. These two maps predominantly reveal the segregation of Nd atoms on the two boundaries. The 2D Nd concentration is illustrated Fig. 2 (e-3). Different segregation tendency of Nd atoms on the two boundaries could be clearly observed, although these two boundaries are connected by a triple junction. Similar to the boundary shown in Fig. 1, the distributions of Nd atoms on the two boundaries are also not homogeneous. Interestingly, the Nd concentration of the bottom
boundary in the area adjacent to the triple junction seems to be much higher than the other parts. This indicates the segregation behaviors of Nd atoms are closely related to not only the macroscopic features of GBs but also the local arrangement of atoms in the boundary network.

Fig. 2 Reconstructed 3D APT tip of the MN11 alloy. (a) TKD-EBSD of the tip before evaporation, illustrating a target GB triple junction containing three GBs; (b) elemental distributions of Mg, Mn and Nd; (c) and (d) concentration profiles across the GBs, extracted from cylindrical ROI 1 and ROI 2 (diameter of 30 nm) outlined in (b); (e) Nd atom distribution, 1.0 at. % Nd isosurface and 2D Nd concentration in the cubic ROI 3 in (b).
As shown in the 2D concentration plot in Fig. 1(c) and Fig. 2(e-3), in-plane GB segregation is not homogeneous. The in-plane GB 2D plots of Nd concentration on the 11.3° [10-10], 59.3° [-3121] and 86.5° [12-31] boundaries are presented in Fig. 3 (a-c). On all of these three boundaries, there are some red spots with concentrations reaching 2.9 at.% and blue spots with concentrations around 0.5 at.%. This could be related to the local arrangement of the atoms in the plane and will be discussed further in the simulation part.

To get rid of the effect of in-plane anisotropic segregation, the segregation concentrations of six measured GBs are calculated by the average concentration along the middle line on the 2D plot as described in the previous part (viz. Fig. 1 (d)). The peak concentrations are compared in Fig. 3 (d). The investigated boundaries exhibited an evidently anisotropic peak segregation concentration ranging from 1.91 ±0.29 at.% on the 35.8° [01-10] boundary to 4.79±0.30 at.% on the 61.1° [01-10] boundary.

Fig. 3 Anisotropic segregation of grain boundaries: (a) ~ (c) 2D concentration plot of Nd atoms on 11.3° [10-10], 59.3° [-3121] and 86.5° [12-31] boundaries; (d) variation of Nd peak concentrations along GBs with different misorientation angles and axis.
Atomistic evidence of anisotropic grain boundary segregation

To further understand the atomistic origin of the anisotropic GB segregation, we performed atomistic simulations on general GBs with experimentally informed crystallographic orientations of two grains and the GB plane. The substitutional Nd segregation at individual Mg GB sites is investigated and solute-solute interactions are not considered in the simulations. More details of the simulation methods and atomistic configurations are introduced in the Methods part.

Two representative GBs with small (11.3°) and large (59.3°) misfit angles are investigated in detail to illustrate the anisotropic segregation among GBs as well as in-plane anisotropic GB segregation. Fig. 4 shows the statistics of per-site segregation energy which is binned according to the distance from the GB center. The 11.3° low-angle GB (LAGB) shows distinct segregation behavior compared to the 59.3° high-angle GB (HAGB). Both 11.3° LAGB and 59.3° HAGB exhibit roughly symmetric distribution of segregation energy at both sides of the GBs. For most GB sites with distance of 8 Å off the GB center, the segregation energy is close to zero. The maximum value of the per-site segregation energies of each bin is higher for the 11.3° LAGB than the 59.3° HAGB. For the 11.3° LAGB, the distributions of mean, median and third quartile segregation energies are sharper approaching the GB center and the deviation between mean and median in each bin is more significant than the 59.3° HAGB. In contrast, the mean, median and third quartile segregation energies within 2.5 Å off the GB center of the 59.3° HAGB stay at similar levels (see Fig. 4(b)). Similar results were obtained in the 86.5° HAGB as shown in Fig. S 1.

Fig. 4 Atomistic simulations of substitutional Nd segregation to Mg (a) 11.3° and (b) 59.3° GBs. Boxplots of segregation energy as a function of distance from the GB center. The data are divided into bins with sizes of 1 Å. The upper and lower whisker ends are maximum and minimum values,
respectively. The upper and lower bounds of the boxes are third and first quartiles, respectively. The horizontal lines in the boxes indicate median values. The blue dots represent the mean values.

The scatter plot of the segregation energy density reflects the in-plane distribution of per-site segregation energies within a GB, see Fig. 5(a, b). The 11.3° LAGB shows more extreme patterns of distribution of segregation energy density than the 59.3° and 86.5° HAGBs (see Fig. 5(a, b) and Fig. S1(b)). In the 11.3° LAGB, the regions with high segregation energy density correlate well with the lines and junctions of misfit dislocation networks (see Fig. S2(a)). Additionally, all simulated GBs in this study show the anisotropic distribution of segregation energy within the GBs. The correlation between anisotropic segregation and local atomic environment within a GB is discussed in the Discussion part.

Fig. 5 Scatter plots of (a, b) segregation energy density of the GBs and (c-d) mean squared displacement (MSD) of the GBs with a substitutional Nd atom with respect to the pure Mg
counterparts. The data are divided into 2 Å × 2 Å bins. Only GB sites within the distance of 10 Å from the GB center are calculated.

Discussion

Local site environment and anisotropic segregation

The experimental observations of inhomogeneous distribution of Nd solutes in general GBs (see Fig. 1(c), Fig. 2 (e) and Fig. 3 (a~c)), especially the strong Nd concentration near the triple junction (see Fig. 2 (e)), imply the segregation behavior is more related to the local GB features rather than the macroscopic GB characters such as misorientation and GB plane normal. The concentrations of GB sites with high segregation energy in our simulations (see Fig. 5(a,b) and Fig. S 1* (b)) agree well with the Nd-solute concentrations at GBs in our experiments (see Fig. 3 (a~c)) and previous experimental observations of solute clusters at Mg HAGBs. The atomic origin of such anisotropic GB segregation is illustrated by correlating the segregation energy to the local structural features of a GB site in atomistic simulations. As shown in Fig. 5 and Fig. S 1(b,c), the distribution of the spots with high MSD values correlates well with the spots with high segregation energy density. The MSD value represents the displacements of a solute atom at the GB site and its neighboring atoms, which indicates the magnitude of local structural rearrangement by introducing the substitutional solute. The high MSD value means the local site environment has excess free volume to adapt to the substitutional solute, especially when the solute atom has a much larger atomic radius than the host element, which makes the site favorable for substitutional segregation. The excess free volume is directly related to the GB energy and GB segregation, and it was often treated as a macroscopic feature of GB in previous study. In this work, the strong association between the distributions of per-site segregation energy and MSD of the GBs demonstrates the impact of the local excess free volume on per-site segregation energy. The microscopic structural features of a GB such as atomic ledge, dislocation junction and GB curvature which affect the local site environment could thus have effects on the local segregation behavior and bring the anisotropic segregation feature within the GB.

Such local structural rearrangement also indicates the widely used linear elasticity model in the atomistic modelling of high symmetric GBs based on the site atomic volume may not be applicable in the study of general GBs. As shown in Fig. S 3, the per-site segregation energy shows a deviation from the predicted segregation energy using the linear elasticity model, especially for the sites with high segregation energies. In addition, there is almost no correlation of hot spots between the scatter plots of the simulated and predicted segregation energy density of the general GBs (see Fig. S 2). To better predict the per-site segregation energy in general GBs, a model requires at least to take into account the excess free volume surrounding the GB site, namely a space including the first and second nearest neighbors of the GB site, in addition to bulk modulus and bonding strength and environment as proposed in previous models.

Link between anisotropic segregation and texture modification
The anisotropic segregation of Nd atoms in the alloy among boundaries sheds a light on the understanding of texture modification in the Mg-Nd-Mn alloy, even though the coverage of the GBs reported in this work is limited. Texture evolution during recrystallization nuclei growth or grain growth depends on the mobility of boundaries. In a micro-alloyed Mg alloy, there are two-aspect effects of these segregated solutes on the GB mobilities. On the one hand, as shown in our atomistic simulations, the segregation energy of Nd atoms is anisotropic on the GBs. Segregation of Nd atom on the GBs could significantly reduce the total energy of the systems (anisotropy among boundaries) and the solute atoms are preferential to stay at the specific positions (in-plane anisotropy). Therefore, any movement of GBs will bring the solutes to a higher energy state, causing a drag force (namely solute drag 39). Solute drag pulls the boundary back to its original position, lowering the GB mobility 40. The magnitude of the solute drag is reported to be related to the segregation concentration 39 and the GB complexity 40. On the other hand, according to the simulated GB energy of <c>−axis symmetrical tilt boundaries in the pure Mg and Mg-Y alloys 41, the addition of Y could significantly homogenize the energy of these boundaries. The selection of special boundaries (such as Σ13 and 60° 〈0001〉) during grain growth will, therefore, be less dominant. This theory is consistent with the results reported by Zeng et al. 19. The authors propose that the preferential segregation of Ca and Zn atoms on the high energy boundaries shared by basal grains in a Mg-Zn-Ca alloy could restrict their high mobility and trigger homogeneous growth to keep the weak texture after recrystallization nucleation. On these primes, we believe the anisotropic segregation of Nd atoms contributes to lowering the mobility gap of different types of GBs and even granting the boundaries shared by non-basal grains higher mobility, resulting in texture weakening and modification.

Methods
Experiments
The studied material was a MN11 alloy containing 1.05 wt.% Mn, 1.14 wt.% Nd and Mg (balance). For the chemical analysis of the alloy composition, inductively coupled plasma-optical emission spectrometry (ICP-OES) was used. After casting and homogenization heat treatment, the specimen was extruded at 300 °C. The detailed parameters of sample production could be found in our previous work15. Before APT tips milling, the orientation information on the sample surface was characterized by the electron backscatter diffraction (EBSD) performed in a FEI Helios 600i dual-beam electron microscope with an operation voltage of 20 kV, as shown in Fig. 6 (a). The specimen for EBSD was prepared by conventional mechanical grinding and polishing as well as electro-polished in Struers AC-2 reagent at 20 V for 90 s. During the milling, the target grain boundaries were selected based on the EBSD map. The selected boundaries were marked by a Pt deposition (cf. Fig. 6 (b)). After being lifted out, during each thinning step with inner diameter changing from 750 to 300 nm, TKD-EBSD was performed on the tip at 30 kV with a current of 5.5 nA to trace the depth and position of grain boundary (viz. Fig. 6 (c))). In the end, the depth from the top of the tip to the boundary was controlled to be around 200 nm in order to catch the boundary by evaporation. The tips were prepared
by focused ion beam milling at 30 kV voltage and 2 kV voltage for cleaning. A Local Electrode Atom Probe 4000X HR from Cameca was used to evaporate the tips under laser-pulsing mode with an ultraviolet laser (wavelength: 355 nm, pulse energy: 30 pJ and pulse frequency: 125 kHz). The temperature during the measurement was set to 30 K. After evaporation, the tips were then reconstructed by the commercial IVAS 3.8.0 software package from Cameca.

![Image](image_url)

**Fig. 6** Examples of TKD guided APT tips milling: (a) EBSD Confidence index map on the sample before APT tips milling; (b) second electron image of the selected grain boundaries marked in (a); (c) TKD maps at different milling steps, illustrating the misorientation information of grain boundary and the depth of the boundary from top of the tip.

**Atomistic simulations**

The atomistic simulations were performed using the open-source MD software package LAMMPS. The interatomic interactions were modeled by the modified embedded atom method (MEAM) potential for Mg-Nd by Kim et al. The per-site segregation energies of Nd solutes at Mg $\Sigma 7 21.8^\circ \{12\overline{3}0\}\{0001\}$ GB, $56.2^\circ \{10\overline{1}1\}\{10\overline{1}2\}$ twin boundary (TB) and $86.2^\circ \{10\overline{1}2\}\{10\overline{1}1\}$ TB sites agree well with previous DFT calculations, as shown in Fig. S 4.
The atomistic configurations of general GBs were constructed using Atomsk \cite{44} based on the experimentally-informed crystallographic orientations of two grains and the GB plane (normal to the z-axis) obtained from TKD mapping and reconstructed APT tips. Two crystals were merged along the z-axis and a cylindrical configuration with the axis aligned to the z-axis and the GB sitting in the middle of the sample was lifted out. The diameter of the cylinder is 22.4 nm which is equal to the dimension of height. One atom from each pair of atoms whose distance of separation within 2 Å (62.5% of first nearest neighbor distance) was considered as an overlapping atom and was deleted. Since there is no periodic repeat distance for general GBs, the in-plane scanning over all possible translations of one crystal relative to the other, which is routinely applied in the study of CSL GBs, is intractable. An alternative way to optimize the general GB structures is to vary the deletion distance of overlapping atoms near the interface \cite{30}. Since we focus on per-site segregation energies and local GB structures instead of global GB properties, only one deletion distance was chosen in this work. A reasonable distribution of local site environments which samples the space of possible environments similar to the minimum energy GB is expected \cite{30}. The schematic of the cylindrical setup is shown in Fig. 7. The top and bottom layers of the cylinder with a thickness of 1.2 nm (2 times interatomic potential cutoff) were fixed in the z-direction. The outermost layers of the cylindrical surface with a thickness of 1.2 nm were fixed in x and y directions. Periodic boundary conditions were applied in the z-direction and a vacuum layer with a thickness of 4.8 nm was imposed between the periodic images.

The atomistic configurations were relaxed using the conjugate gradient (with box relaxation in the z-direction) and the FIRE \cite{45,46} algorithms with the force tolerance of $10^{-8}$ eV/Å. A substitution region (80 Å $\times$ 80 Å $\times$ 20 Å) where the Nd substitutions take place located in the center of the cylindrical setup across the GB (see Fig. 7) to reduce the effect of the boundary conditions. The local site environments within the selected substitution region represent the possible environments of the GB as indicated from the hydrostatic stress maps as shown in Fig. S 5. By swapping one Mg atom by one Nd atom near the GBs in the substitution region, the per-site segregation energies were calculated:

$$E_{\text{seg}} = (E_{\text{GB}} + E_{\text{bulk}}^X) - (E_{\text{GB}}^X + E_{\text{bulk}}),$$

where $E_{\text{bulk}}$ is the energy of a Mg bulk, $E_{\text{bulk}}^X$ is the energy of the Mg bulk with a Nd solute, $E_{\text{GB}}$ is the energy of a Mg system with a GB, $E_{\text{GB}}^X$ is the energy of the Mg system with a Nd solute at the GB. After each swapping, an energy minimization using the FIRE algorithm was performed.

The per-site mean squared displacement (MSD) was calculated to characterize the structural rearrangement after each Nd substitution. The mean squared displacement was calculated:

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \left| x^{(i)}(\text{GB}) - x^{(i)}(\text{GB}(X)) \right|^2,$$

where $x^{(i)}(\text{GB})$ is the coordinate of $i$th atom in a Mg system with a GB, $x^{(i)}(\text{GB}(X))$ is the coordinate of $i$th atom in the Mg system with a Nd solute at the GB. The substitution region
was divided into $2 \, \text{Å} \times 2 \, \text{Å} \times 20 \, \text{Å}$ bins. For each bin, mean values of $E_{\text{seg}}$ and MSD were obtained. The segregation energy density of each bin was calculated by dividing the mean $E_{\text{seg}}$ by the volume of the bin (80 Å$^3$).

The Open Visualization Tool (OVITO) $^{47}$ was used to visualize the atomistic configurations, analyze misfit dislocation networks and calculate the atomic displacement.

![Schematic of the cylindrical setup of atomistic simulations. (b) Atomistic configuration of Mg 11.3° GB. (a) Only atoms close to the grain boundary with hydrostatic stress $|\sigma_H| > 0.2$ GPa are shown here. The half-transparent isosurface is constructed using the filtered atoms ($|\sigma_H| > 0.2$ GPa) with color-coding transferred from the atomic hydrostatic stress. The surface mesh of the simulation](image)

Fig. 7 (a) Schematic of the cylindrical setup of atomistic simulations. (b) Atomistic configuration of Mg 11.3° GB. (a) Only atoms close to the grain boundary with hydrostatic stress $|\sigma_H| > 0.2$ GPa are shown here. The half-transparent isosurface is constructed using the filtered atoms ($|\sigma_H| > 0.2$ GPa) with color-coding transferred from the atomic hydrostatic stress. The surface mesh of the simulation.
sample is half-transparent. (c) Zoomed-in view of the atoms in the substitution region (80 Å × 80 Å × 20 Å) in the center of the simulation sample colored by the segregation energies of corresponding GB sites. Other filtered atoms (|σ_H| > 0.2 GPa) and the isosurface are half-transparent.

Data availability
The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request.

Acknowledgements
We thank Dr. -Ing. Sangbong Yi and Dr. Sang Kyu Woo for the alloy casting and extrusion. The authors are grateful for the financial support from the German Research Foundation (DFG) (Grant Nr. AL1343/8-1). The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) through the projects A02, A05 and C02 of the SFB1394 Structural and Chemical Atomic Complexity – From Defect Phase Diagrams to Material Properties, project ID 409476157. This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 852096 FunBlocks). Simulations were performed with computing resources granted by RWTH Aachen University under project (rwth0591) and by the EXPLOR center of the Université de Lorraine and by the GENCI-TGCC (Grant 2020-A0080911390). We want to thank Dr. Liam Huber and Dr. Dimitri Chauraud (MPIE Düsseldorf) for fruitful discussions.

Author contributions
R. Pei and T. Al-Samman designed the experiments, analyzed the data and interpreted the experimental results. Z. Xie and J. Guénolé designed and performed the MD simulations. S. Korte-Kerzel participated the project and provided guidance. All authors discussed the results and contributed to writing.
Supplementary Information

Fig. S 1 Atomistic simulations of substitutional Nd segregation to Mg 86.5° GB. (a) Boxplots of segregation energy as a function of distance from the center of the grain boundary. Scatter plots of (b) segregation energy density of the GB and (c) mean squared displacement of the GB with a substitutional Nd atom with respect to the pure Mg GB counterpart.
Fig. S 2 Scatter plots of (a-c) segregation energy density of the grain boundaries and (d-f) predicted segregation energy density from the linear elastic model of the grain boundaries. The misfit dislocation networks at 11.3° GB are colored half-transparent in (a). The data are divided into 2 Å × 2 Å bins. Only grain boundary sites within the distance of 10 Å from the center of the grain boundary are calculated.
The predicted segregation energy was calculated using the linear elastic model\textsuperscript{29}:

$$E_{\text{seg}}^{\text{Elast}} = P_X \Delta V^i,$$

$$P_X = B \frac{V_X^{\text{bulk}} - V_{\text{bulk}}}{V_{\text{bulk}}/N},$$

where $\Delta V^i$ is the difference between Voronoi volume of the $i$th GB site and the bulk ($V_{\text{bulk}}/N$), $B$ is the host bulk modulus, $V_X^{\text{bulk}}$ is the volume of the bulk with the solute.

Fig. S 3 Correlation between segregation energies and the predicted segregation energies from the linear elastic model of the (a) 11.3°, (b) 59.3° and (c) 86.5° grain boundaries.
Fig. S 4 GB sites in (a) \( \Sigma 7 \ 21.8^\circ \ \{1230\}\{0001\} \) GB, (b) \( 56.2^\circ \ \{10\overline{1}1\}\{10\overline{1}2\} \) TB and (c) \( 86.2^\circ \ \{10\overline{1}2\}\{10\overline{1}1\} \) TB. Atoms in different atomic layers along the view direction are colored differently and have different radii. (c) Per-site segregation energies calculated using the MEAM potential\(^{43}\) and from previous DFT calculations\(^{28,29}\).

Fig. S 5 Scatter plots of atomic hydrostatic stress at the (a) \( 11.4^\circ \) \( \{11\overline{4} 7 \overline{4} \overline{0} \overline{1} \overline{0} \} \) \( 11.3^\circ \), (b) \( 59.3^\circ \) \( \{7 0\overline{7} 10\}\{3 1 2 1\} \) \( 59.3^\circ \) and (c) \( 86.5^\circ \) \( \{2 0 2 1\}\{1 2 3 1\} \) \( 86.5^\circ \) GBs. The data are divided into 2 Å × 2 Å bins. Only GB sites within the distance of 10 Å from the center of the GB are calculated. The substitution regions are marked by black boxes.
References

1. Barnett MR, Nave MD, Bettles CJ. Deformation microstructures and textures of some cold rolled Mg alloys. Mater Sci Eng, A 386, 205-211 (2004).
2. Polmear IJ. Magnesium alloys and applications. Mater Sci Technol 10, 1-16 (1994).
3. Pérez-Prado MT, Ruano OA. Texture evolution during annealing of magnesium AZ31 alloy. Scripta Mater 46, 149-155 (2002).
4. Barnett MR. A taylor model based description of the proof stress of magnesium AZ31 during hot working. Metall Mater Trans A 34, 1799-1806 (2003).
5. Agnew SR. Deformation mechanisms of magnesium alloys. In: Advances in Wrought Magnesium Alloys (eds Bettles C, Barnett M). Woodhead Publishing (2012).
6. Gehrmann R, Frommert MM, Gottstein G. Texture effects on plastic deformation of magnesium. Mater Sci Eng, A 395, 338-349 (2005).
7. Chino Y, Kado M, Mabuchi M. Compressive deformation behavior at room temperature-773 K in Mg-0.2 mass%(0.035at.%)/Ce alloy. Acta Mater 56, 387-394 (2008).
8. Chino Y, Kado M, Mabuchi M. Enhancement of tensile ductility and stretch formability of magnesium by addition of 0.2 wt%(0.035 at%)Ce. Mater Sci Eng, A 494, 343-349 (2008).
9. Yoo MH. Slip, twinning, and fracture in hexagonal closed-packed metals. Metall Trans A 12, 409-418 (1981).
10. Basu I, Al-Samman T. Triggering rare earth texture modification in magnesium alloys by addition of zircon and zirconium. Acta Mater 67, 116-133 (2014).
11. Al-Samman T, Li X. Sheet texture modification in magnesium-based alloys by selective rare earth alloying. Mater Sci Eng, A 528, 3809-3822 (2011).
12. Hantzsche K, Bohlen J, Wendt J, Kainer KU, Yi SB, Letzig D. Effect of rare earth additions on microstructure and texture development of magnesium alloy sheets. Scripta Mater 63, 725-730 (2010).
13. Li X, Al-Samman T, Mu S, Gottstein G. Texture and microstructure development during hot deformation of ME20 magnesium alloy: Experiments and simulations. Mater Sci Eng, A 528, 7915-7925 (2011).
14. Mackenzie LWF, Pekguleryuz MO. The recrystallization and texture of magnesium-zinc-cerium alloys. Scripta Mater 59, 665-668 (2008).
15. Woo SK, Pei R, Al-Samman T, Letzig D, Yi S. Plastic instability and texture modification in extruded Mg-Mn-Nd alloy. J Magnes Alloy, (2021).
16. Bohlen J, Nuernberg MR, Senn JW, Letzig D, Agnew SR. The texture and anisotropy of magnesium-zinc-rare earth alloy sheets. Acta Mater 55, 2101-2112 (2007).
17. Basu I, Al-Samman T, Gottstein G. Shear band-related recrystallization and grain growth in two rolled magnesium-rare earth alloys. Mater Sci Eng, A 579, 50-56 (2013).
18. Basu I, Pradeep KG, Mießen C, Barrales-Mora LA, Al-Samman T. The role of atomic scale segregation in designing highly ductile magnesium alloys. Acta Mater 116, 77-94 (2016).
19. Zeng ZR, et al. Texture evolution during static recrystallization of cold-rolled magnesium alloys. Acta Mater 105, 479-494 (2016).
20. Xie H, et al. Nonsymmetrical Segregation of Solute in Periodic Misfit Dislocations Separated Tilt Grain Boundaries. Nano Lett, (2021).
21. Xie H, et al. Twin Boundary Superstructures Assembled by Periodic Segregation of Solute Atoms. Nano Lett, (2021).
22. Bugnet M, Kula A, Niewczas M, Botton GA. Segregation and clustering of solutes at grain boundaries in Mg-rare earth solid solutions. Acta Mater 79, 66-73 (2014).
23. Nie JF, Zhu YM, Liu JZ, Fang XY. Periodic Segregation of Solute Atoms in Fully Coherent Twin Boundaries. Science 340, 957-960 (2013).
24. Zhu YM, Bian MZ, Nie JF. Tilt boundaries and associated solute segregation in a Mg–Gd alloy. Acta Mater 127, 505-518 (2017).
25. Bugnet M, Kula A, Niewczas M, Botton GA. Segregation and clustering of solutes at grain boundaries in Mg–rare earth solid solutions. Acta Mater 79, 66-73 (2014).
26. Wagih M, Schuh CA. Spectrum of grain boundary segregation energies in a polycrystal. Acta Mater 181, 228-237 (2019).
27. Wagih M, Schuh CA. Grain boundary segregation beyond the dilute limit: Separating the two contributions of site specularity and solute interactions. Acta Mater 199, 63-72 (2020).
28. Pei Z, Li R, Nie J-F, Morris JR. First-principles study of the solute segregation in twin boundaries in Mg and possible descriptors for mechanical properties. *Mater Des* **165**, 107574 (2019).
29. Huber L, Rottler J, Militzer M. Atomistic simulations of the interaction of alloying elements with grain boundaries in Mg. *Acta Mater* **80**, 194-204 (2014).
30. Huber L, Grabowski B, Militzer M, Neugebauer J, Rottler J. Ab initio modelling of solute segregation energies to a general grain boundary. *Acta Mater* **132**, 138-148 (2017).
31. Messina J, *et al.* Machine learning to predict aluminum segregation to magnesium grain boundaries. *Scripta Mater* **204**, 114150 (2021).
32. Seeger A, Schottky G. Die energie und der elektrische widerstand von grosswinkelkorngrenzen in metallen. *Acta Metall* **7**, 495-503 (1959).
33. Huang Z, Chen F, Shen Q, Zhang L, Rupert TJ. Combined effects of nonmetallic impurities and planned metallic dopants on grain boundary energy and strength. *Acta Mater* **166**, 113-125 (2019).
34. Mehrer H. *Diffusion in Solids*. Springer, Berlin, Heidelberg (2007).
35. Steyskal E-M, Oberdorfer B, Sprengel W, Zehetbauer M, Pippan R, Würschum R. Direct Experimental Determination of Grain Boundary Excess Volume in Metals. *Phys Rev Lett* **108**, 055504 (2012).
36. Bean JJ, McKenna KP. Origin of differences in the excess volume of copper and nickel grain boundaries. *Acta Mater* **110**, 246-257 (2016).
37. Sun H, Singh CV. Temperature dependence of grain boundary excess free volume. *Scripta Mater* **178**, 71-76 (2020).
38. Mahjoub R, Stanford N. The electronic origins of the “rare earth” texture effect in magnesium alloys. *Sci Rep* **11**, 14159 (2021).
39. Devra VK, Maity J. Solute drag effect on austenite grain growth in hypoeutectoid steel. *Philos Mag Lett* **100**, 245-259 (2020).
40. Mahjoub R, Ferry M, Stanford N. Grain boundary kinetics in magnesium alloys from first principles. *Comput Mater Sci* **111042** (2021).
41. Barrett CD, Imandoust A, El Kadiri H. The effect of rare earth element segregation on grain boundary energy and mobility in magnesium and ensuing texture weakening. *Scripta Mater* **146**, 46-50 (2018).
42. Thompson AP, *et al.* LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput Phys Commun* **271**, 108171 (2022).
43. Kim K-H, Lee B-J. Modified embedded-atom method interatomic potentials for Mg-Nd and Mg-Pb binary systems. *Calphad* **57**, 55-61 (2017).
44. Hirel P. Atomsk: A tool for manipulating and converting atomic data files. *Comput Phys Commun* **197**, 212-219 (2015).
45. Bitzek E, Koskinen P, Gähler F, Moseler M, Gumbsch P. Structural Relaxation Made Simple. *Phys Rev Lett* **97**, 170201 (2006).
46. Guénolé J, *et al.* Assessment and optimization of the fast inertial relaxation engine (fire) for energy minimization in atomistic simulations and its implementation in lammps. *Comput Mater Sci* **175**, 109584 (2020).
47. Stukowski A. Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool. *Modell Simul Mater Sci Eng* **18**, 015012 (2009).