Effect of grain boundary segregation of rare earth element on deformation behavior of Mg alloys

S. Li; H. Y. Song

J. Appl. Phys. 136, 064301 (2024)
https://doi.org/10.1063/5.0219468
Effect of grain boundary segregation of rare earth element on deformation behavior of Mg alloys

Cite as: J. Appl. Phys. 136, 064301 (2024); doi: 10.1063/5.0219468
Submitted: 17 May 2024 · Accepted: 25 July 2024 · Published Online: 9 August 2024

S. Li1,2 and H. Y. Song1,a)

AFFILIATIONS
1 College of New Energy, Xi’an Shiyou University, Xi’an 710065, China
2 College of Material Science and Engineering, Xi’an Shiyou University, Xi’an 710065, China

a) Author to whom correspondence should be addressed: hysong@xsyu.edu.cn

ABSTRACT
Alloying with rare earth (RE) elements is an effective way to improve the mechanical properties of the Mg alloys. However, the strengthening mechanism of RE element Y on the Mg alloys still needs to be further revealed. The effect of grain boundary (GB) segregation of RE element Y on the mechanical properties and the GB stability of the Mg alloys are investigated by the molecular dynamics simulation method. The results show that the GB segregation of Y atoms can significantly increase the yield strength and GB stability of the Mg alloys. The higher the content of Y atoms at the GB, the stronger the stability of the GB and the higher the strength of the alloys. The results also show that the GBs thicken significantly with increasing Y content at the GBs, which is attributed to the diffusion of Y atoms, leading to the solid-state amorphization of the Mg alloys. The results indicate that with the increase of Y content at the GBs, the Mg alloys undergo a transition from the plastic deformation dominated by the co-sliding of GBs and dislocations to the slip of dislocations only. This work provides a theoretical basis for the design and preparation of high-performance Mg alloys.

© 2024 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/5.0219468

I. INTRODUCTION

As the lightest structural metal on earth, Mg and its alloy are expected to become an excellent candidate material for lightweight structures in automotive, aerospace, and other industries.1–3 Mg alloys are considered as “green materials” due to their special rigidity, high specific strength characteristics, and low mass density, which have great potential for development and application in the 21st century.4–6 However, Mg alloys have limited slip systems due to their typical hexagonal close-packed (HCP) structure, which hinders their practical industrial applications. The basal slip is the only slip system that is preferentially activated at room temperature in the Mg alloys, while other slip systems are not easily activated, so they cannot meet the requirements of uniform deformation, resulting in poor plasticity.7,8 Therefore, finding effective measures to enhance the mechanical properties of the Mg alloys has become an urgent problem to be solved.

In recent years, nanocrystalline metals have been actively studied due to their exceptional mechanical properties compared to coarse-grained metals.9,10 As stated in the Hall–Petch relationship, which is widely used to elucidate the relationship between the strength and grain size of polycrystalline material, grain refinement to the nanoscale generally significantly enhances the mechanical properties of metallic materials.11 Numerous experimental and simulation studies have also indicated that nanocrystalline metals are materials with both high ductility and high strength.12–15 In nanocrystalline metals, grain boundaries (GBs) act as nucleation and pinning sites for dislocations, which have a strong impact on the mechanical properties of the materials.16,17 However, grains may spontaneously grow or deform severely during the deformation process of the materials due to the higher energy at the GBs than within grains, leading to coarsening of the material’s grains and a decrease in its mechanical properties.18–20 The segregation of solutes at the GBs usually reduces their energy, thereby limiting their migration, stabilizing the microstructure of the material, and maintaining its excellent performance.21,22 Chen et al. found that adding an appropriate amount of Co atoms at the GBs can improve the tensile strength of the nano-polycrystalline Ni through solid solution strengthening.23 Hu et al. discovered that Mo segregation can enhance the stability and strength of the GBs in nanomaterials, thereby enhancing their comprehensive properties.24 That is to say,
the stability and strength of the GBs play an important role in designing high-performance metal materials, especially when the grain size of the material is refined to the nanoscale.

Many studies have found that alloying with rare earth (RE) elements is an effective way to improve the mechanical properties of Mg alloys. Generally, RE alloying can prevent the (a) base slip of the Mg alloys and activate their potential prismatic and pyramidal slips to obtain five independent slip systems, thus improving the plasticity of the Mg alloys. Ding et al. found that the slip system of pyramidal (c + a) dislocations in the Mg alloys is activated and plasticity is enhanced at room temperature by alloying with the RE element Y. Yu et al. analyzed the deformation mechanisms of extruded Mg–5Y–0.08Ca (wt. %) alloys and found that the presence of Y atoms led to large changes in the critical resolved shear stress for slip and tensile twinning, which changed the dominant deformation mechanisms of the Mg alloys. In addition, Hadorn and Agnew demonstrated that Y preferentially segregates to interfaces during continuous dynamic recrystallization in the Mg alloys, in agreement with transmission electron microscopy by Nie et al. Although a great deal of research has been done on the effect of RE element Y on the mechanical properties of the Mg alloys and some achievements have been made, the internal mechanism of Y segregation affecting the mechanical behavior of the Mg alloys is still unclear. Here, the effect of GB segregation of RE element Y on the mechanical properties and the GB stability of the Mg alloys are studied using the molecular dynamics (MD) simulation method. The results indicate that the GB segregation of Y atoms enhances the stability of GB and improves the mechanical properties of the Mg alloys. This study provides a theoretical basis for the preparation and design of high-performance Mg alloys.

The rest of this paper is organized in the following way. The simulation model and method are detailed in Sec. II. The results and discussion are provided in Sec. III. Finally, some concluding remarks can be drawn in Sec. IV.

II. SIMULATION MODEL AND METHOD

The effect of RE element Y on the deformation behavior and the GB stability of the nano-polycrystalline Mg alloys under tensile loading are investigated using the MD simulation method. The simulation model of the Mg alloys is shown in Fig. 1(a), and each sample is composed of eight hexagonal grains with a columnar structure. Here, Mg atoms at the GBs are randomly replaced by Y atoms, ultimately forming Mg alloys where Y atoms segregate at the GBs. Figure 1(b) shows the partially enlarged view of the GBs. Figure 1(a) is the simulation model of the Mg–Y alloys. (b) The enlarged view of the GBs.

FIG. 1. (a) The simulation model of the Mg–Y alloys. (b) The enlarged view of the GBs.
III. RESULTS AND DISCUSSION

A. The mechanical behavior of the Mg alloys

The GB plays an important role in the deformation behavior of polycrystalline materials. Here, the effect of Y element segregation at the GBs on the mechanical behavior of the Mg alloys is investigated. Five models with the Y content of 0%, 5%, 10%, 15%, and 20% are established for comparative purposes. The stress–strain curve is one of the ways to reflect the mechanical properties of the materials, which provides the overall mechanical response of the materials to a certain extent. Figure 2 shows the stress–strain curves of the models with different Y contents at the GB. It can be observed from Fig. 2 that in all cases, stress increases linearly first with the increase of strain in the elastic range, regardless of the Y content. In the elastic stage, the stress–strain curves basically coincide, as shown in Fig. 2, indicating that the introduction of the Y element at the GBs has little effect on the elastic deformation of the Mg alloys. As the strain continues to increase, the stress–strain curves of the alloys shift to the right, but they are still in the nonlinear elastic stage. Taking the model with the Y content of 5% as an example, when the strain reaches 2.94%, corresponding to point A in Fig. 2, there is a significant fluctuation in stress, indicating that dislocations nucleate and slip at the GB, and the alloys enter the plastic stage. This point is defined as the yield point and the stress at this point is defined as the yield stress. In the initial stage of plasticity, the stress of the alloys increases continuously with the increase of strain, but the rate of increase gradually slows down. After the yield point, with the further increase of strain, the stress-strain curve of the alloys reaches a peak value, which is called the peak stress, and then stress decreases with the increase of strain, corresponding to the slip of a large number of dislocations, accompanied by the event of dislocation crossing the GBs.43

It can be seen from Fig. 2 that the content of Y element at the GBs has a significant impact on the mechanical properties of the alloys. Figure 3 gives the curves of yield strain, yield stress, and peak stress of the alloys as a function of the Y content at the GBs. It can be seen from Fig. 3(a) that both the yield strain and yield stress of the Mg alloys exhibit an increasing trend with the increase of Y content at the GBs. The yield point indicates the nucleation and slip of the first dislocations. The results show that the addition of the Y element at the GBs can dramatically affect the nucleation and slip of dislocation from the GBs, leading to considerable increases in the mechanical properties of the Mg alloys. In other words, the segregation of the Y element at the GBs delays the generation of the first dislocation, which is consistent with the research results of Borovikov et al.44 This may be because the introduction of Y solute atoms changes the structure of the GB and enhances its...
stability. This effect first becomes more pronounced with the content of Y atoms increases, and there is an optimized content to achieve the most stable GB structure, which will be explained in detail later. It can be seen from Fig. 3(b) that when the Y content increases from 0% to 5%, the peak stress of the alloys does not change much, while an obvious increasing trend of the peak stress occurs as the Y content continues to increase. This may indicate that a high content of Y solutes has a strengthening effect on the GBs of the Mg alloys, and the strength of the GBs increases with increasing Y solute content. The segregation of Y atoms at the GB increases the strength of the alloys. The enhancement of GB strength by segregation atoms has also been found in the Al–Zr system alloys in first-principles calculations.

In addition, as shown in Fig. 2, in the later stage of plastic deformation of the alloys, the stress–strain curve almost becomes stable, and the average flow stress of this stage reflects the material’s ability to resist deformation. Figure 4 shows the curve of the average flow stress of the Mg alloys with respect to the Y content at the GB during the strain range of 0.12–0.15. It can be seen from Fig. 4 that when the Y content is 15%, the alloy has the strongest resistance to deformation during the plastic stage, and there is a turning point in the average flow stress. When the Y content of the alloys is greater than 15%, the average flow stress of the alloys slightly decreases with the increase of Y content. The results indicate that the excessive introduction of Y atoms will increase the activity of the atoms at the GBs and disrupt the interface structure of the GBs. In addition, it is worth noting that the trend of the average flow stress of the alloys as a function of Y content shown in Fig. 4 is not contradictory to the change trends of yield stress and peak stress shown in Fig. 3. They reflect the mechanical properties of the alloys at different deformation stages.

The results also indicate that there are two types of stress–strain behavior depending on the Y content at the GBs, as shown in Fig. 2. When the Y contents at the GBs are 0%, 10%, and 20%, there is a sharp decrease in stress for all three models. However, when the Y contents are 5% and 15%, the tensile stress decreases relatively smoothly beyond the peak point. To explain this mechanical behavior of the alloys, Fig. 5 takes the atomic snapshots of the Mg alloys with the Y content of 10% at different strains for example. When the stress of the model reaches the yield point (corresponding to the strain of 0.035), two partial dislocations almost simultaneously nucleate at the GBs and slide in the grains, leaving traces of stacking faults (SFs) represented by green, which are due to the concentration of stress at the GBs, as shown in Fig. 5(a). Subsequently, as the strain continued to increase and dislocations continued to nucleate and slip, leaving a significant number of SFs in the grains, as shown in Fig. 5(b). During this period, the stress-strain curve exhibited a phenomenon of first increasingly deviating from the initial linear increasing state and then fluctuating, as shown in Fig. 2. When the stress exceeds the peak stress, a rapid decrease occurs, mainly due to the nucleation and growth of twins in the grain as shown by the black dashed rectangle in Fig. 5(c), resulting in a rapid release of stress. A similar phenomenon is also observed in the models with the Y contents of 0% and 20%, where the nucleation of twins released a large amount of stress. It is well known that the nucleation of twins requires large stresses and their growth is extremely fast, which leads to a rapid release of stress. In contrast, for the models without twin nucleation, the tensile stress decreases relatively smoothly beyond the peak point. It is worth noting that not all models exhibit twins during plastic deformation, which may be due to the variations in Y element content at the GB in different models, resulting in different degrees of the GB deformation (as will be elaborated on later). This diversity causes the models with different Y contents to form different GB structures.
B. The grain boundary stability of the MG alloys

It is well known that the GB plays two complementary roles during the deformation of polycrystalline materials. On the one hand, the GB usually acts as a barrier to hinder the movement of dislocation, thereby enhancing the strength of materials. On the other hand, it may be the nucleation site of dislocation, coordinating the deformation of polycrystalline material and improving their plasticity. The two roles of the GB in the deformation process of the materials largely depend on their stability and strength. To specifically explore the effect of Y element content on the strength and stability of the GB, the atomic potential energy of the alloys is calculated as shown in Fig. 6. For the convenience of observation, the atoms inside the grains are removed, and only the atoms on the GBs are retained in the figure. It can be seen from Fig. 6 that as the Y content at the GB increases, the potential energy of the GB gradually decreases. As is well known, the lower the potential energy of the GB, the higher the strength and the stability of the GB. Therefore, it can be concluded from Fig. 6 that the stability of the GB increases due to the presence of the Y element, and the higher the Y content, the more stable the GB, which is consistent with the research results of Peng et al. In other words, the strength of the GB increases with the increase of Y content at the GB. Of course, the excessive introduction of Y atoms at the GBs will increase the activity of GB atoms, destroy the stability of the GBs, and accelerate the appearance of material yielding. In addition, it is found that the potential energy of the GB is higher than that of the crystal grains in the absence of element Y. However, when the Y content at the GB exceeds 10%, the potential energy of the crystal grain is higher than that of the GB. It is well known that the properties of grain and GB will have a great impact on the deformation behavior of the material, whose strength is low is prone to plastic deformation. This means that as the Y content at the GBs increases, the plastic deformation modes of the alloys may change.

To elucidate the influence of the Y element on the structure of the GB, the number of atoms at the GBs, which are all recognized as non-structured atoms by the CNA method in OVITO soft, is used to characterize the thickness of the GB. Figure 7 shows the number of atoms at the GBs for the models with different Y initial contents. It can be seen from Fig. 7 that as the Y initial content at the GBs increases from 0% to 20%, the number of atoms at the GBs of the alloys increases from approximately 20 000 to 27 000.
The corresponding Y contents of the alloys after relaxation for the four models investigated (5%, 10%, 15%, and 20%) are 4.5%, 8.3%, 11.5%, and 14.5%, respectively. That is to say, the GB is significantly thickened with the increase of Y content at the GB after relaxation. This indicates that the solid-state amorphization phenomenon of the alloys has occurred at the GBs. Previous studies have reported that the presence of element Y leads to a significant increase in the amorphous phase thickness of the crystalline/amorphous dual-phase Mg alloys after relaxation. This is due to the presence of the amorphous–crystalline interface (ACI), which causes the diffusion of element Y from the amorphous phase to the ACI and promotes the solid-state amorphization of the Mg alloys. The ACI is also a specific type of the GB. Here, the diffusion of the Y element leading to the thickening of the GB and the amorphization of the Mg alloys is observed. However, the degree of solid-state amorphization of the alloys in this study is small, mainly because the amorphization of the Mg alloys depends on the original thickness of the amorphous phase, which actually refers to the original thickness of the GB in this paper. Here, the GB thickness is about only 1–1.5 nm, and the diffusion of Y atoms caused an increase in the amorphous phase thickness, which would also lead to a decrease in the concentration of Y in the amorphous phase, thereby suppressing the solid-state amorphization of the Mg alloys. In other words, the low degree of solid-state amorphization of the Mg alloys is here attributed to the lower number of atoms in Y. A similar phenomenon is found in the MD simulations of the Ni–Zr system; the interdiffusion between Ni and Zr results in a slight amorphization of the Ni–Zr interface zone.

To further reveal the influence of the Y element on the stability of the GB, Fig. 8 gives the atomic snapshots of the Mg alloys with the Y contents of 0% and 20% at different strains. For all the models in Fig. 8, dislocation multiplies with the increase of strain and leaves the traces of SFs constantly during the deformation of the alloys. Here, the green surface perpendicular to the paper represents SFs. By comparing the atomic snapshots of the models with different Y contents at the same strain, it can be observed from Fig. 8(a) that many SFs have formed in the model without Y atoms when the strain is 5%. However, for the model with the Y content of 20%, only a few SFs are formed at a strain of 5%, which is consistent with the results in Fig. 3. This further illustrates that the addition of the Y element at the GBs inhibits the generation of dislocations, leading to considerable increases in the mechanical properties of the alloys. Research has shown that with the increase of the Y content at the GBs, the Mg alloys undergo a transition from the plastic deformation dominated by the co-sliding of GB and dislocation to the slip of dislocation only. Of course, during the plastic deformation of the alloys, a very small amount of twin nucleation and growth will occur for some models. It can be also observed from Fig. 8 that with the increase of strain, the models with different Y contents also show different states during deformation. For the model without the Y element at the GBs, as shown in Figs. 8(a)–8(c), the deformation of the GB is very serious, and the shape and size of the GB change significantly with the increase of strain. The original regular hexagonal form of the GB almost disappeared during the loading of the alloys. The GBs are almost destroyed at a strain of 15% [see Fig. 8(c)], which means a very serious deformation occurred. It is well known that GB is able to accommodate plastic deformation by itself via GB sliding and migration. This indicates that the plastic deformation of the Mg alloy is dominated by co-sliding of GB and dislocation. However, for the model with the Y content of 20%, the GBs almost maintain the original intact hexagonal shape when the strain is 15% or even 20%, and only dislocation slip is observed during deformation, while the GB sliding and migration are not obvious. This indicates that the plastic deformation is dominated by dislocation slip only. It is well known that the stability of the GB is mainly governed by the sliding of atoms in the GBs. Gola et al. also showed that the systems with GB segregation own a stronger force to hinder GB sliding.
deformation. This indicates that the segregation of the Y element in the GBs improves the stability of the GBs by suppressing the sliding and deformation of atoms at the GBs.13

IV. CONCLUSION

The effects of GB segregation of RE element Y on the mechanical properties and the GB stability of the Mg alloys are investigated by the MD simulation method. The effect of content of RE element Y at the GBs on the deformation behavior of the alloys is systematically analyzed. The results show that the GB segregation of Y atoms significantly increases the yield strength and the GB strength of the Mg alloys, and the higher the content of the Y element at the GBs, the higher the strength of the alloys, which can be explained by the introduction of Y atom changes to the structure of the GB and enhancing of its stability. The introduction of the Y element at the GBs has little effect on the elastic deformation of the Mg alloys. Of course, the excessive introduction of Y atoms at the GB will increase the activity of GB atoms and disrupt the interface structure of the GB. The results also show that the presence of the Y element at the GB reduces the potential energy of the GB and improves the stability of the GB. The higher the content of Y atoms, the more stable the GB is. The results also show that the GBs thicken significantly with increasing Y content at the GBs, which is attributed to the diffusion of Y atoms, leading to the solid-state amorphization of the alloys. However, the degree of solid-state amorphization of the alloys in this study is small, mainly because the amorphization behavior of the Mg alloys depends on the original thickness of the amorphous phase, which actually refers to the original thickness of the GBs in this paper, because it is very small, thus affecting the degree of amorphization of the Mg alloys. The results indicate that with the increase of Y content at the GBs, the Mg alloys undergo a transition from the plastic deformation dominated by the co-sliding of GBs and dislocations to the slip of dislocations only. This work can provide new insights into understanding the GB segregation of RE element Y on the mechanical properties of the Mg alloys and provide preliminary guidance and theoretical basis for the design and preparation of high-performance Mg alloys.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of Shaanxi Province (No. 2021J2-53) and Program for Graduate Innovation Fund of Xi’an Shiyou University (No. YCS23213136).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

S. Li: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). H. Y. Song: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Project administration (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

REFERENCES