Effect of rare earth elements on the structures and mechanical properties of magnesium alloys

LÜ Zhong¹, ZHOU Jian^{1*}, SUN ZhiMei¹ & CHEN RongShi²

¹ Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China;

² State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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By means of first-principles calculations, we have investigated the effects of rare earth elements (REEs) on the structures and mechanical properties of magnesium. The lattice parameters, elastic constants, bulk moduli, shear moduli, Young's moduli and anisotropic parameter of these solid solutions have been calculated and analyzed. The nearest-neighbor distance between Mg and the REEs is also analyzed to explore the correlation with the bulk moduli. The results show that the 4f-electrons and atomic radii play an important role in the strengthening process. The anomalies of the lattice parameters and mechanical properties at Eu and Yb are due to the half-filled and full-filled 4f-electron orbital states. Finally, the increase of directional bonding character near the alloying elements may account for the anisotropy and brittleness of these magnesium alloys.

magnesium alloys, solid solution hardening, first-principles, chemical bonding

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There has been a rapid growth of interest in the development of magnesium alloy in the past decade since it is an important lightweight structural material as a replacement for aluminum and steels in automotive applications [1–4]. However, inherent limitations of strength and formability are obstacles to widespread application of magnesium in transportation industries. The strength of pure magnesium is lower than that of most aluminum alloys [5]. Hence, how to improve the strength of magnesium alloy is of great importance and interest.

Solid solution strengthening is considered one of the most effective ways to improve the mechanical properties of the alloy and the mechanism contains elastic and electrical origin [1,6]. The elastic origin has been quantitatively established based on the impurity-dislocation interaction theory [7]. The atomic size factor makes great contribution in solid solution strengthening [8]. It is interesting that though the atomic size factor of Gd and Y is smaller than that of Al and Zn, they improve the mechanical properties more effectively than Al

and Zn, according to Akhtar et al. [9] and Gao et al. [10]. Analogous phenomenon exists in Mg-Dy and Mg-Y alloys [11]. Gao et al. [10] give an explanation of the anomalous hardening of Mg-Y and Mg-Gd alloy from the view of the increase of chemical bonding strength. However, the systematic research of the Mg-Rare-Earth (Mg-RE) alloy has not been taken yet and the mechanism of the solid solution strengthening of Mg-RE alloy has not been elucidated. Therefore, it is necessary to systematically investigate the effect of the REEs on the structure and mechanical properties of magnesium. To shed light on the above problem, in this paper we have performed a systematic investigation of the lattice parameter, elastic constants and mechanical properties of the Mg-RE alloys by first principle calculations. Electron localization function (ELF) is also analyzed to give further interpretation of the mechanical properties from the electronic origin.

1 Calculation methods

Our calculations are performed on the basis of density func-

*Corresponding author (email: jzhou@xmu.edu.cn)

tional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) [12,13]. Projector augmented-wave pseudo-potentials (PAW) are used to describe the ion-electron interaction [14]. The generalized gradient approximation (GGA) [14] of Perdew-Burke-Ernzerhof (PBE) pseudopotentials was used to describe the exchange-correlation interactions. An energy cut-off of 400 eV is adopted. A 3×3×3 super-cell of magnesium is used and the REE atom substitutes one magnesium atom at the center of the super-cell. The optimization of atomic arrangements and the calculation of elastic constants are performed using the Gaussian smearing [15,16]. For both geometry optimization and elastic constants calculations, a 5×5×5 mesh of K-POINTS is used and it has been tested to be sufficient to provide reliable results. Elastic constants were obtained by the stress-strain method [17]. Burr et al. [18] pointed out that most REEs have a very stable 4*f* configuration which is predominately free-ion like. It has been proposed that the pseudopotentials in the VASP database which regards some *f*-electrons as frozen in the core could be used as a general framework for analyzing REE impurities [19,20]. Hence pseudopotentials with valence states 3*s*² for Mg, 5*s*²5*p*⁶5*d*¹6*s*² for La, 5*p*⁶6*s*² for Eu, 5*p*⁶6*s*² for Yb and 5*p*⁶4*f*¹6*s*² for other REEs were used in this study.

2 Results and discussions

2.1 Thermodynamic stability and lattice parameters

To investigate the thermodynamic stability of the Mg-RE alloy, the formation energy E_{form} is calculated by the following equation:

$$E_{\text{form}} = E_{\text{tot}} - 53E_{\text{Mg}} - E_{\text{REE}}, \quad (1)$$

where E_{tot} is the total energy of Mg-RE alloys, E_{Mg} and E_{REE} represent the total energy of the most stable phases of magnesium and REEs in the ground states, respectively. As seen from the negative formation energy in Table 1, the Mg-RE alloys are thermodynamically stable except that La, Eu and Yb have no, half-filled and full-filled 4*f* orbital states, respectively. From the energetic point of view, the addition of *f*-electrons would enhance the stability of the solid solution.

The lattice parameters a , c and the ratio of c/a are demonstrated in Figure 1. The calculated lattice constants of pure magnesium are $a=3.20$ Å and $c=5.15$ Å, which is in good agreement with the experiment data of $a=3.21$ Å and $c=5.21$ Å [21]. The lattice parameter is found to be dependent on the atomic radius of the alloying elements. Since the atomic radii of REE atoms are larger than that of magnesium, hence the REEs increase both a and c of magnesium alloys. The lattice parameter decreases with the increase of the REEs atomic numbers. This trend coincides well with the atomic radius of REEs. It is worth noting that the growth range of c is larger than that of a , thus, the c/a ratio of these solid solutions is larger than that of the pure magnesium.

Table 1 The calculated formation energy, nearest neighbor distances and anisotropy parameter A of the Mg-RE alloys

Alloying element	E_{form} (eV)	d_{N} (Å)	A
Mg	0	3.17	0.195
La	0.107	3.30	0.179
Ce	−0.002	3.29	0.180
Pr	−0.032	3.28	0.181
Nd	−0.054	3.27	0.182
Pm	−0.072	3.26	0.182
Sm	−0.072	3.26	0.183
Eu	2.1	3.30	0.175
Gd	−0.089	3.24	0.184
Tb	−0.079	3.24	0.184
Dy	−0.066	3.23	0.184
Ho	−0.049	3.23	0.184
Er	−0.032	3.23	0.184
Tm	−0.009	3.22	0.184
Yb	0.163	3.27	0.181

Figure 1 The calculated lattice parameter of the Mg-RE alloys.

This phenomenon enhances the anisotropy of magnesium alloys and the effect of solid solution strengthening.

2.2 Mechanical properties

Elastic constants measure the resistance of a crystal to an external stress. For a hexagonal lattice, there are five independent factors: c_{11} , c_{12} , c_{13} , c_{33} and c_{44} . The estimated elastic constants as shown in Figure 2 meet the Born stability criteria as given below very well [17,22]:

$$c_{11} > 0, \quad (2)$$

Figure 2 The calculated elastic constants c_{ij} of the Mg-RE alloys.

$$(c_{11} - c_{22}) > 0, \quad (3)$$

$$c_{44} > 0, \quad (4)$$

$$(c_{11} + c_{12})c_{33} - 2c_{12}^2 > 0. \quad (5)$$

Hence, these Mg-RE alloys are all mechanically stable. The experimental data of the elastic constants of the pure magnesium is 60, 26, 22, 62 and 16 GPa for c_{11} , c_{12} , c_{13} , c_{33} and c_{44} respectively [21]. From the calculated theoretical elastic constants of the pure magnesium in Figure 2, it can be seen that the average differences between calculated and experimental data are less than 5%, which guarantee the accuracy of our calculations. As summarized in Figure 2(a) and (e), the addition of REEs results in an increase of c_{11} and c_{44} from La to Sm, followed by a decrease trend from Gd to Tm with abnormal low value at Eu and Yb, while c_{12} , c_{13} and c_{33} in Figure 2(b)–(d) show an ascend trend from La to Tm with abnormally low value at Eu and Yb.

In order to examine the effect of doping concentration of rare earth elements, we substituted two RE atoms for Mg atoms in the supercell and obtained the $\text{Mg}_{52}\text{RE}_2$ alloys. Thus, the concentration of rare earth elements increased to 1/27. The calculated elastic constants are shown in Figure 3.

Figure 3 The calculated elastic constants c_{ij} of the $\text{Mg}_{52}\text{RE}_2$ alloys.

It is clear that the variation trend of the elastic constants for $\text{Mg}_{52}\text{RE}_2$ alloys is consistent with the results for $\text{Mg}_{53}\text{RE}_1$ alloys, which ensures the reliability and conclusions of our calculations.

From the calculated elastic constants, we can estimate the bulk moduli B , shear moduli G and Young's moduli E by Voigt's methods as below:

$$B = \frac{(c_{11} + c_{12} + c_{13}) + 2(c_{12} + c_{13} + c_{23})}{9}, \quad (6)$$

$$G = \frac{(c_{11} + c_{12} + c_{33}) - (c_{12} + c_{13} + c_{23}) + 3(c_{44} + c_{55} + c_{66})}{15}, \quad (7)$$

$$E = \frac{9GB}{3G + B}. \quad (8)$$

The results of pure magnesium in our calculations are $B=37$ GPa, $G=18$ GPa and $E=48$ GPa, which agree well with the former calculations ($B=35$ GPa, $G=17$ GPa and $E=44$ GPa) [23] and experimental data ($G=17$ GPa and $E=45$ GPa).

The bulk moduli indicate a substance's resistance to a uniform compression. As shown in Figure 4(a), the bulk moduli generally increase with increasing atomic number of the REEs, while there are anomalies at Eu and Yb. The trend is consistent with that of c_{13} . It is notable that the addition of REEs results in a lower bulk moduli than pure

Figure 4 The bulk moduli (B), shear moduli (G), Young's moduli (E) and B/G of the Mg-RE alloys.

magnesium. A significant factor that corresponds directly to the bulk moduli of these solid solutions is the nearest-neighbor distance between Mg and the doping element X. The inverse dependent of bulk moduli on the nearest-neighbor distance of these solid solutions observed here is similar to the results reported by Cohen [24]. We note that, as shown in Figure 4(a) and Table 1, with the increase of the distance between Mg and X, the bulk moduli decrease due to the lattice expansion. Solid solutions, with the addition of Eu and Yb, which have larger nearest-neighbor distance between Mg and X, have lower bulk moduli than that of the others.

In the case of shear moduli, which reflect the stiffness of a material, the results are different. As displayed in Figure 4(b), all of the shear moduli are larger than that of pure magnesium. The value increases from La to Sm and then decreases from Gd to Yb, with the lowest point at Eu. This trend goes well with c_{44} .

The ratio of the bulk moduli and the shear moduli introduced by Pugh [25] provides us with an empirical judge to predict the brittle and ductile behavior of materials. The higher the value is, the more ductile the materials are. Materials which have a B/G ratio larger than the critical value 1.75 are considered to be ductile, and smaller than 1.75 are considered to be brittle. The calculated values for these Mg-RE alloys are illustrated in Figure 4(c). It is remarkable that the addition of the REEs decrease the ductility of magnesium.

It is known that Young's moduli present the responds of a material to a linear strain. The larger it is, the stiffer the material is. Figure 4(d) shows the Young's moduli of the Mg-RE alloy. It is seen that the variation trend of the Young's moduli is similar to that of the shear moduli, which increases at first and then decrease, showing anomalous values at Eu and Yb.

To investigate the effect of the enhancement of the c/a ratio, the anisotropy is analyzed. We quantify it with a parameter A [15]. For hexagonal crystal:

$$A = \frac{4c_{44}}{c_{11} + c_{33} - 2c_{13}}, \quad (9)$$

when A equals to 1, it indicates that the material is isotropic while any value larger or smaller than 1 indicates anisotropy. The magnitude deviation from 1 is a measure of the anisotropic degree possessed by the solid solution. As seen from Table 1 anisotropic, REEs increase the anisotropy of magnesium and the results agree well with the analysis of c/a ratio.

2.3 Chemical bonding

To further understand the mechanical properties of these solid solutions, the contour plots of electron localization function (ELF) [26] on the (110) plane is illustrated in Figure 5, in which Mg_{53}Ce and Mg_{53}Dy are taken as examples for the light and heavy REE, while the pure magnesium is also illustrated for comparison. Clearly, with the addition of REE, the chemical bonding between Mg and Mg has been strongly affected. It is worthy to note that the Mg-Mg bonding above the alloying region is enhanced while the one below the alloying region is weakened, suggesting an angular bonding character in this area [27]. This may account for the above obtained anisotropy in the mechanical properties of the Mg-RE alloys. Furthermore, it has been reported that the increase of directional bonding is the main reason for the decrease of the ductility of the M_3B_4 compounds [27]. Therefore, the directional bonding in the Mg-RE alloys as shown in Figure 5 may give us a reasonable explanation of the brittleness of these magnesium solid solutions.

3 Conclusions

In summary, by first-principles calculations, the structure and mechanical properties of magnesium solid solutions with addition of REEs are obtained. The variation tendency of lattice parameter, volumes, elastic constants and mechanical properties has a good correspondence to the variation trend of f -electrons and REE atom's radius. Moreover, REEs play an important role in solid solution strengthening of magnesium alloys. And with the introduction of REEs, the ductility of magnesium decreased, which may attribute to the directional bonding formed in these solid solutions.

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