

# **First-principles studies on structure stability, segregation and work function of Mg doped different metal elements**

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## **Abstract**

The first-principles methods based on the density functional theory were employed to study the structural stability, segregation and work function of Mg doped with fourteen metal elements existing in human body. The calculated results show that there is a simple correlation between solid solution and segregation. Doping Sn, Y, Li, Gd, Nd, Sc and Zn atoms have a negative formation energy as well as a positive segregation energy. This suggests that these elements which are not easier to be dissolved in Mg matrix tend to segregate on the Mg (0001) surface. An opposite trend was observed for Ba, Fe, Mn, W, Sr, Ca and Mo. On the other hand, the electronic work function of Mg (0001) surface was increased significantly for doping Mo, W, Fe, and Mn, and was reduced markedly for Ba, Ca and Sr. For Li, Sn, Sc, Gd, and Y, their doping on Mg surface generate a relatively small change in work function. In addition, the relationships of corrosion behavior to segregation and work function were discussed. This study may provide an avenue for seeking a more appropriate alloying element of Mg alloys with improved corrosion resistance in biomedical applications.

**Keywords:** Magnesium alloy; Biomaterial; Electronic work function; Segregation; Corrosion resistance

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## 1 Introduction

Magnesium (Mg) and its alloys have become the first choice for new-generation biodegradable materials because of the good biocompatibility and degradability as well as appropriate mechanical properties [1–4]. However, the high electronegative potential and poor protection of the surface oxide films formed on Mg would result in too quick corrosion rate in physiological environment, which restricts the application of Mg alloys as degradable biomaterials [5–8]. Many experimental studies have been carried out to improve the corrosion resistance by means of alloying and understand the influence mechanisms of various alloying elements. C   ek et al. [9] found that the addition of Pb could decrease significantly the corrosion current and increase the corrosion resistance in Mg–Al–Si alloy. Liu et al. [10,11] reported that the secondary phases containing rare earth elements exhibit an active potential, which could reduce the micro-galvanic corrosion caused by the coupling with the anodic Mg-base phase. Kang et al. [12] and Du et al. [13] reported that Zn could effectively elevate the corrosion potential, and thus improve the corrosion resistance of Mg alloys. It was demonstrated that the corrosion rate of Mg–6Zn alloy in vitro is slower than that of high-purity Mg in simulated body fluid (SBF) [14]. On the contrary, Fe is insoluble in the Mg matrix and tends to precipitate in the form of elemental Fe. Zhang et al. [15] reported that the galvanic coupling between the Fe particles scattered in the matrix and Mg substrate would accelerate the corrosion of Mg alloys. However, researches of the effect of alloying elements on corrosion properties are still insufficiently thorough, and their influence mechanisms are not completely clear.

Computational studies of the different Mg alloys may provide more help for the experimental design of biomedical Mg alloys with better corrosion properties. Recently, surface energy and work function calculated with the density functional method were proved as effective physical parameters to correlate the surface corrosion phenomena. Surface energy is the amount of energy needed to create one square meter of new surface. Generally, the lower surface energy of a crystal plane, the better its corrosion resistance. Song et al. [16] reported that the anisotropic corrosion-resistant behavior could be simply interpreted by the concept of surface energy, although it is unclear how the surface energy is related to corrosion properties. The electronic work function is the minimum energy required to withdraw an electron completely from a metal surface. There are some significant relationships of work function with electrode potential and exchange current density of the anodic dissolution [17,18]. Wang et al. [19] studied the surface corrosion behavior of Al alloys by calculating the electronic work function, and elucidated the cause of galvanic corrosion from the electronic level. The electrochemical activity of materials and the tendency of corrosion were discussed. Ma et al. [20] analyzed the anode dissolution behavior of the adding of several alloying elements into Mg alloys and found that surface energy density and work function play significant roles in corrosion.

From the biocompatibility point of view, Liu et al. [21] screened the metal elements in the periodic table and pointed out that Ca, K, Mg, Fe, Zn, Sr, Sn, Mn, Y, Nd, etc. in ionic form are tolerated and even deemed essential in the human body. It is suggested

that Mg alloys containing these metal elements may not cause any substantial toxic effects in human environment during degradation. Therefore, these elements could be considered to be used as alloying elements in biomedical Mg alloys. In this paper, 14 metal elements mentioned above were selected, and their doping effects on the structural stability, segregation and electron work function of Mg were investigated by the first-principles method. Furthermore, the relationship of corrosion resistance to segregation and electronic work functions of binary Mg alloys were discussed.

## **2 Computational method**

First-principles calculations based on density functional theory (DFT) were performed by the Vienna Ab-initio Simulation Package (VASP) program [22], using the projector-augmented wave (PAW) approach [23]. Electronic exchange-correlation effects were described by the generalized gradient approximation (GGA) [24] with Perdew-Burke-Ernzerh (PBE) functional. The plane-wave set with a cut-off energy of 450 eV was employed to ensure a high accuracy. And the  $k$ -points of the Brillouin zone adopted the Gamma-centered method. The Pulay density mixing method was used in the self-consistent calculation (SCF). The convergence criterion of calculations for ionic relaxations is  $10^{-6}$  eV between two consecutive steps. The relaxation ends while the maximum force between atoms is less than 0.02 eV/Å.

Mg has a hexagonal crystal structure containing two atoms in the unit cell model. The  $3 \times 3 \times 2$  supercell with 36 atoms was used to calculate formation energy. The standard slab geometry was adopted to model the surface system. The Mg (0001) slabs with 9 layers and 8 layers of  $3 \times 3$  surface and a 1.5 nm vacuum layer in the  $z$

direction were used to calculate segregation energy and electronic work function, respectively.

### **3 Results and discussion**

#### **3.1 Structural parameters and stability**

After relaxation, the lattice constants of Mg are  $a = b = 3.180 \text{ \AA}$ ,  $c = 5.218 \text{ \AA}$ , which agree well with experimental and theoretical studies [25,26]. It is well known that there are two types of solid solution, namely substitutional and interstitial solid solutions. Interstitial solid solution is usually generated when the radius ratio of solute atom and solvent atom is less than 0.59. Otherwise, it is easy to form a substitutional solid solution. The atomic radii of Mg and solute R atoms (R = Fe, Mn, Zn, Mo, W, Li, Sn, Sc, Y, Gd, Nd, Ca, Sr, and Ba) are listed in Table 1. Since all the radius ratios of solute and solvent atoms are much greater than 0.59, the substitutional solid solution model was adopted. For the solid solution  $\text{Mg}_{35}\text{R}_1$ , one of the Mg atoms is substituted by the R atom whose location in the model are shown in Fig. 1(a). The calculated lattice parameters of pure Mg and various binary Mg–R alloys are listed in Table 2. As can be seen, the calculated lattice parameters of Mg, Mg–Zn, Mg–Y, Mg–Ca and Mg–Li are well consistent with that reported in previous studies [27,28], indicating the good reliability and high accuracy for our calculated data.

In order to investigate the structural stability of  $\text{Mg}_{35}\text{R}_1$  solid solutions, the formation energies were calculated. The formation energy is defined as the difference between the total energy of the system and the energy of each component to make up the system. It reflects not only the difficulty of forming a solid solution, but also the

alloying ability of the solid solution. The formation energy ( $\Delta E$ ) was calculated using the following equation [29]:

$$\Delta E = \frac{1}{x+y} (E_{tot} - x E_{solid}^A - y E_{solid}^B), \quad (1)$$

where  $E_{tot}$  is the total energy of the supercell,  $E_{solid}^A$  and  $E_{solid}^B$  are the energies of A and

B atoms in solid states, and  $x, y$  are the number of A and B atoms in the supercell, respectively. The formation energies of  $Mg_{35}R_1$  calculated are shown in Fig. 1(b). The  $Mg_{35}R_1$  solid solutions doped with Zn, Y, Gd, Nd, Sn, Li and Sc have a negative  $\Delta E$  with a sequence of  $Sn < Y < Li < Gd < Nd < Sc < Zn$ . This indicates that these alloying elements could preferentially dissolve in Mg matrix, because a negative and low formation energy means a high stability of solid solution [30-33]. In contrast, the dopants of Sr, Mn, Fe, Ba, Mo, and W destabilize  $Mg_{35}R_1$  structure. The formation energies for  $Mg_{35}Ba_1$ ,  $Mg_{35}Fe_1$ ,  $Mg_{35}Sr_1$ ,  $Mg_{35}Mo_1$ ,  $Mg_{35}Mn_1$ ,  $Mg_{35}W_1$  are 0.002253, 0.0290, 0.01014, 0.04150, 0.05383, and 0.06411 eV/atom, respectively. The positive values suggest the poor forming ability and stability of their solid solution structures. In other words, metal elements Ca, Ba, Fe, Sr, Mo, Mn and W have a thermodynamic driving force to escape from Mg, and thus it is more difficult for them to dissolve in the Mg matrix. According to the binary diagrams [33], Zn, Y, Gd, Nd, Sn, Li and Sc have a relatively high solid solubility, while Ba, Sr, Mn, Fe, Mo, W are almost and even completely no solubility in Mg. This evidences that the calculated result is in conformity with the reality.

### 3.2 Segregation energy

The segregation energy ( $E_{\text{seg}}$ ) is defined as the difference between the energy of the system caused by the doping atoms at the surface location and that at the area away from the surface.  $E_{\text{seg}}$  could be written as [34]:

$$E_{\text{seg}} = E_x - E_{\text{ii}}, \quad (2)$$

where  $E_x$  is the total energy where the doping atoms occupying the position of matrix surface,  $E_{\text{ii}}$  represents the system energy where the doping atoms occupy the position within the matrix. In our slab model as shown in Fig. 2(a), the most common Mg (0001) surface was used. In order to study the segregation energy of alloys, two doping R atoms substitute two Mg atoms in the surface layer and in the fifth layer, respectively, as can be seen in Fig. 2(b) and (c). Fig. 3 shows the calculated segregation energy of fourteen slab models doped with different metal atoms. It is seen that seven of them have a negative segregation energy. The negative value of  $E_{\text{seg}}$  demonstrates that the total energy is lower when the R atoms are placed at the Mg (0001) surface compared with that inside the Mg matrix. It is thus inferred from the results that doping elements Ca, Sr, Mn, Fe, Ba, Mo, and W have a tendency to spontaneously segregate to the Mg (0001) surface for reducing their energy and achieving a more stable structure. This result is in agreement with previous experimental phenomena [15,35]. For example, Mo et al. [35] found that only adding 0.5wt% of Mn to Mg–3Gd–2Ca alloy causes the segregation of Mn and leads to the appearance of polygonal  $\alpha$ -Mn. Zhang et al. [15] also reported that Fe atoms are insoluble in the Mg matrix and exist in the form of simple substance. Different from elements mentioned above, Zn, Y, Gd, Nd, Sn, Li, and Sc have a positive segregation



energy and no significant segregation dynamics. When  $E_{\text{seg}}$  is greater than zero, it suggests that doping R atoms are easier to locate in the inner of Mg instead of segregating to the Mg (0001) surface. By comparison, there exists a simple relationship between segregation energy and formation energy. Except for element Ca, other doping elements which tend to segregate on the surface would lead to a positive formation energy of calculated Mg alloys. It seems that Ca has the possibility to dissolve in the matrix and segregate on the surface simultaneously.

The segregation is a common phenomenon, that usually adversely affects corrosion resistance. Impurities segregate on the surface and could form a primary battery with the substrate during corrosion. Mao et al. [36] and Song et al. [37] found that the segregation of Pb, Sn and Mg on the Al surface can increase corrosion pitting positions of aluminum foil. The lattices of the Mg alloys could be severely distorted accompanying with segregation, which is ascribed to the difference in electron distribution and geometric structure of the R atoms. Fig. 4 shows the distance that doping R atoms deviate from the average position of Mg atoms in the same layer in the  $z$  direction after relaxation. Obviously, Ba, Sr, Mn, Fe, Mo, and W atoms that are prone to segregation exhibit a large offset distance in the  $z$  direction. A longer offset distance could cause a larger lattice distortion of Mg, and thus lead to the appearance of defects on the surface. As a result, the starting points of corrosion induced by defects would accelerate the corrosion rate of Mg alloys.

### 3.3 Electronic work function

A solid material with a higher work function corresponds to a greater barrier for electrons to escape from the solid surface. The electronic work function ( $W$ ) can be calculated by [19]:

$$W = -e\phi - E_F, \quad (3)$$

where  $e$  is the charge of an electron,  $\phi$  is the electrostatic potential in the vacuum near the surface, and  $E_F$  is the Fermi level of the material itself. The Mg (0001) slab model was used to calculate  $W$  value, as shown in Fig. 5(a). In order to study the doping effect of alloying elements on the work function, two doping R atoms replace the central Mg atom on both ends of the termination surface of calculation cell, as shown in Fig. 5(b). Fig. 5(c) presents the work function of Mg (0001) surface doped different R atoms. For comparison, the data of pure Mg (0001) surface is also shown in Fig. 5(c). As can be seen, doping Ba, Sr, Y, Ca, Nd, and Gd atoms reduce the electronic work function, indicating that these elements make electrons more easily to escape from the surface. Especially for Ca, Sr and Ba, their doping significantly lowers the electronic work function compared with pure Mg. On the contrary, Zn, Mn, Sn, Fe, Mo, and W atoms result in an increase in work function.

Doping alloying elements can change the work function of a local area. Thus, there exists a potential difference between this area and the adjacent matrix, which would affect the corrosion properties of Mg alloys. According to the data of work function calculated above, the intrinsic potential difference ( $\Delta V$ ) can be calculated as [38]:

$$\Delta V = (W_R - W_{Mg})/e, \quad (4)$$

where  $W_{\text{Mg}}$  and  $W_{\text{R}}$  are the work function of pure Mg and doped Mg with R atom, respectively. Table 3 shows the intrinsic potential difference between doped Mg with R atoms and pure Mg. Both high and low  $\Delta V$  values may cause local potential difference, and thus result in the occurrence of electrochemical corrosion behavior. Since  $\Delta V$  values for Fe, Mo, W and Mn elements are positive, the local surface doping these metal atoms tends to form a cathode in corrosion environment and cause the adjacent anode Mg matrix to be corroded before them. While a negative  $\Delta V$  value for doping Ba, Sr, Y, Ca, Nd, and Gd suggests that the doped surface acts as an anode, and are corroded earlier than the Mg matrix. Considering that the absolute values of  $\Delta V$  for doping Li, Sn, Sc, Gd, and Y is relatively small, the local galvanic corrosion is not easy to occur in the environment.

#### 4 Summary

The structure stability, segregation, and electronic work function of Mg doped by R (R = Fe, Mn, Zn, Mo, W, Li, Sn, Sc, Y, Gd, Nd, Ca, Sr, and Ba) were studied by the first-principles calculations. The main results obtained are listed as follows:

(1) The substitutional doping of Zn, Y, Gd, Nd, Sn, Li and Sc would lower the formation energy, and thus increase the stability of  $\text{Mg}_{35}\text{R}_1$  solid solution. Sr, Mn, Fe, Ba, Mo, and W are difficult to be dissolved in Mg for their high formation energy of  $\text{Mg}_{35}\text{R}_1$  solid solution.

(2) The segregation behavior of alloying elements R in Mg alloys were studied by using the Mg (0001) surface slab model. By coincidence, the metal elements that are difficult to be dissolved in Mg are prone to segregate on the Mg surface. It is thus

suggested that the segregation would cause defects on the surface, and accelerate the corrosion rate of Mg.

(3) The electronic work function of Mg (0001) surface after doping Mo, Mn, and W atoms were significantly elevated. On the contrary, the doing of Ba, Sr, and Ca atoms cause a drop of electronic work function. However, both high and low work function would generate a large intrinsic potential difference between local doped region and matrix. This may lead to the occurrence of electrochemical corrosion.

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### **References**

- [1] Q. Yang, B. Jiang, L. Wang, J. Dai, J. Zhang, F. Pan, Enhanced formability of a magnesium alloy sheet via in-plane pre-strain paths, *J. Alloys Comp.* 814 (2020) 152278.
- [2] V. Jothi, A.Y. Adesina, A.M. Kumar, M.M. Rahman, J.S.N. Ram, Enhancing the biodegradability and surface protective performance of AZ31 Mg alloy using polypyrrole/gelatin composite coatings with anodized Mg surface, *Surf. Coat. Technol.* 381 (2020) 125139.
- [3] M. Heiden, E. Walker, L. Stanciu, Magnesium, Iron and zinc alloys, the trifecta of bioresorbable orthopaedic and vascular implantation – A review, *J. Biotechnol.*

Biomater. 5 (2015) 1-9.

[4] H. Zhang, A. Jerusalem, E. Salvati, C. Papadaki, K. Fong, X. Song, A.M. Korsunsky, Multi-scale mechanisms of twinning-detwinning in magnesium alloy AZ31B simulated by crystal plasticity modeling and validated via in situ synchrotron XRD and in situ SEM-EBSD, *Int. J. Plast.* 119 (2019) 43–56.

[5] A. Atrens, S. Johnston, Z. Shi, M.S. Dargusch, Viewpoint - Understanding Mg corrosion in the body for biodegradable medical implants, *Scr. Mater.* 154 (2018) 92–100.

[6] S. Agarwal, J. Curtin, B. Duffy, S. Jaiswal, Biodegradable magnesium alloys for orthopaedic applications: A review on corrosion, biocompatibility and surface modifications, *Mater. Sci. Eng. C.* 68 (2016) 948–963.

[7] H. Li, Y. Zheng, L. Qin, Progress of biodegradable metals, *Prog. Nat. Sci. Mater. Int.* 24 (2014) 414–422.

[8] D. Zhao, F. Witte, F. Lu, J. Wang, J. Li, L. Qin, Current status on clinical applications of magnesium-based orthopaedic implants: A review from clinical translational perspective, *Biomaterials.* 112 (2017) 287–302.

[9] B. Çiçek, Y. Sun, A study on the mechanical and corrosion properties of lead added magnesium alloys, *Mater. Des.* 37 (2012) 369–372.

[10] N. Liu, J. Wang, L. Wang, Y. Wu, L. Wang, Electrochemical corrosion behavior of Mg–5Al–0.4Mn–xNd in NaCl solution, *Corr. Sci.* 51 (2009) 1328–1333.

[11] W. Liu, F. Cao, L. Chang, Z. Zhang, J. Zhang, Effect of rare earth element Ce and La on corrosion behavior of AM60 magnesium alloy, *Corr. Sci.* 51 (2009) 1334–

1343.

[12] Y. Kang, B. Du, Y. Li, B. Wang, L. Sheng, L. Shao, Y. Zheng, T. Xi, Optimizing mechanical property and cytocompatibility of the biodegradable Mg–Zn–Y–Nd alloy by hot extrusion and heat treatment, *J. Mater. Sci. Technol.* 35 (2019) 6–18.

[13] B. Du, Z. Hu, L. Sheng, D. Xu, Y. Zheng, T. Xi, Influence of Zn content on microstructure and tensile properties of Mg–Zn–Y–Nd alloy, *Acta Metall. Sin.* 31 (2018) 351–361.

[14] S. Zhang, X. Zhang, C. Zhao, J. Li, Y. Song, C. Xie, H. Tao, Y. Zhang, Y. He, Y. Jiang, Y. Bian, Research on an Mg–Zn alloy as a degradable biomaterial, *Acta Biomater.* 6 (2010) 626–640.

[15] C. Zhang, L. Wu, G. Huang, L. Chen, D. Xia, B. Jiang, A. Atrens, F. Pan, Effects of Fe concentration on microstructure and corrosion of Mg–6Al–1Zn–xFe alloys for fracturing balls applications, *J. Mater. Sci. Technol.* 35 (2019) 2086–2098.

[16] G.L. Song, The effect of texture on the corrosion behavior of AZ31 Mg alloy, *JOM.* 64 (2012) 671–679.

[17] M. Stratmann, H. Streckel, On the atmospheric corrosion of metals which are covered with thin electrolyte layers-I. Verification of the experimental technique, *Corr. Sci.* 30 (1990) 681–696.

[18] P. Schmutz, G.S. Frankel, Characterization of AA2024-t3 by scanning Kelvin probe force microscopy, *J. Electrochem. Soc.* 145 (1998) 2285–2295.

[19] J. Wang, S.Q. Wang, Surface energy and work function of fcc and bcc crystals: Density functional study, *Surf. Sci.* 630 (2014) 216–224.

- [20] H. Ma, X.Q. Chen, R. Li, S. Wang, J. Dong, W. Ke, First-principles modeling of anisotropic anodic dissolution of metals and alloys in corrosive environments, *Acta Mater.* 130 (2017) 137–146.
- [21] Y. Liu, Y. Zheng, X.H. Chen, J.A. Yang, H. Pan, D. Chen, L. Wang, J. Zhang, D. Zhu, S. Wu, K.W.K. Yeung, R.C. Zeng, Y. Han, S. Guan, Fundamental theory of biodegradable metals – Definition, criteria, and design, *Adv. Funct. Mater.* 29 (2019) 1–21.
- [22] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B.* 54 (1996) 11169–11816.
- [23] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B.* 50 (1994) 17953–17979.
- [24] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [25] C. Kittel, *Introduction to Solid State Physics*, 8th ed., Wiley, New York, 2005.
- [26] H. Lei, C. Wang, Y. Yao, Y. Wang, M. Hupalo, D. McDougall, M. Tringides, K. Ho, Strain effect on the adsorption, diffusion, and molecular dissociation of hydrogen on Mg (0001) surface, *J. Chem. Phys.* 139 (2013) 224702.
- [27] S. Ganeshan, S.L. Shang, Y. Wang, Z.K. Liu, Effect of alloying elements on the elastic properties of Mg from first-principles calculations, *Acta Mater.* 57 (2009) 3876–3884.
- [28] O.I. Velikokhatnyi, P.N. Kumta, First principles study of the elastic properties of magnesium and iron based bio-resorbable alloys, *Mater. Sci. Eng. B Solid-State*

Mater. Adv. Technol. 230 (2018) 20–23.

[29] F. Wang, S.J. Sun, B. Yu, F. Zhang, P.L. Mao, Z. Liu, First principles investigation of binary intermetallics in Mg–Al–Ca–Sn alloy: Stability, electronic structures, elastic properties and thermodynamic properties, Trans. Nonferrous Met. Soc. China 26 (2016) 203–212.

[30] B.R. Sahu, Electronic structure and bonding of ultralight LiMg, Mater. Sci. Eng. B. 49 (1997) 74–78.

[31] N. I. Medvedeva, Y.N. Gornostyrev, D.L. Novikov, O. N. Mryasov, A. J. Freeman, Ternary site preference energies, size misfits and solid solution hardening in NiAl and FeAl, Acta Mater. 46 (1998) 3433–3442.

[32] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, First-principles simulation: Ideas, illustrations and the CASTEP code, J. Phys. Condens. Matter. 14 (2002) 2717–2744.

[33] T.B. Mossalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, Binary alloy phase diagrams vol. 3, 2nd ed., ASM International, USA, 1990.

[34] M. Zhang, L.G. Hector Jr, Y. Guo, M. Liu, L. Qi, First-principles search for alloying elements that increase corrosion resistance of Mg with second-phase particles of transition metal impurities, J. Phys.-Condes. Matter. 14 (2002) 2717–2744.

[35] N. Mo, I. McCarroll, Q. Tan, A. Ceguerra, J. Cairney, H. Dieringa, Y. Huang, B. Jiang, F. Pan, M. Bermingham, M.X. Zhang, Roles of Nd and Mn in a new creep-resistant magnesium alloy, Mater. Sci. Eng. A. 779 (2020) 139152.

[36] W. Mao, H. Jiang, P. Yang, H. Feng, Y. Yu. Distribution of microelements and



their influence on the corrosion behavior of aluminum foil, J. Mater. Sci. Technol. 21 (2005) 43–46.

[37] J. Song, W. Mao, H. Yang, H. Feng, Effect of trace Sn on pitting behaviors of high voltage anode aluminum foil, J. Mater. Sci. Technol. 24 (2008) 718–722.

[38] Y. Hou, G. Xiong, L. Liu, G. Li, N. Moelans, M. Guo, Effects of  $\text{LaAlO}_3$  and  $\text{La}_2\text{O}_3$  inclusions on the initialization of localized corrosion of pipeline steels in NaCl solution, Scr. Mater. 177 (2020) 151–156.

## Figure Captions

**Fig.1** (a) Calculation model of  $\text{Mg}_{35}\text{R}_1$  solid solution, where larger and smaller balls represent R atoms and Mg atoms, respectively. (b) Formation energy of  $\text{Mg}_{35}\text{R}_1$  solid solution.

**Fig. 2** (a) Clean Mg (0001) surface slab model. (b) and (c) Doped Mg (0001) surface slab models with two doping R atoms substitute two Mg atoms in the surface layer and in the fifth layer, respectively.

**Fig. 3** Segregation energy for Mg (0001) surface doped different R atoms.

**Fig. 4** Displacement in the z-direction of the substituting atoms relative to the relaxed position of the replaced Mg atoms.

**Fig. 5** (a) Clean and (b) doped Mg (0001) surface Slab models. (c) Work functions of clean and doped Mg (0001) surfaces.