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The electronic origin of strengthening and ductilizing magnesium by solid solutes

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Abstract—Electron work function (EWF) is a simple and fundamental parameter which largely reflects or characterizes the behavior of electrons in metals. This parameter can be used to guide the selection of solutes for effective modification of mechanical properties of Mg, an important metal for lightweight materials. From our prediction, adding solutes with EWFs lower than that of Mg can improve both strength and ductility of Mg, while adding elements with higher EWFs results in higher strength but lowered ductility. This study reveals the electronic origin of such influences of solutes on the strength and ductility of Mg and suggests an EWF-based principle or law for selecting appropriate solutes to achieve the optimal combination of strength and ductility for advanced Mg alloys.

Keywords: Magnesium alloys; First-principles calculation; Dislocations

1. Introduction

Because of their low density and high strength-to-weight ratio, Mg-based alloys are actively pursued for weight-critical applications, particularly for automotive and aerospace sectors [1,2]. Mg has a hcp structure whose (0001) basal plane is close-packed with close-packed directions along $\langle 11\bar{2}0\rangle$. Besides the basal slip plane, the prismatic planes $(10\bar{1}0)$ are second active planes on which dislocations can also slip (see Fig. 1) but this requires a higher stress up to 96 times as large as that required to operate the basal slip system [3,4]. The basal and prismatic planes possess less than five independent slip systems in total, which does not satisfy the von-Mises criterion [5]. Thus, pure Mg has poor room-temperature ductility and produces anisotropic deformation under external stress.

The mechanisms for strengthening and ductilizing of Mg alloys are rather complicated, and determined by several factors simultaneously, such as the electronegativity, radius, misfit and chemical bonding between alloying elements and Mg atoms [2,4,6–15]. Introducing second phases may strengthen Mg but in general this is achieved at the expense of ductility. Alloying with solutes within their solubility is an effective approach for elevated strength with less negative effect on ductility, since they affect the energy barrier to dislocation movement but usually not the number of slip systems. As a matter of fact, solute atoms may even bring beneficial effects on slip systems, twinning and defect activities, as demonstrated in this article. Nowadays, more and more material developers are looking for universal laws or principles that can fundamentally guide to achieve both strengthened and ductilized Mg alloys based on limited parameters. Electron work function [16] has been demonstrated to be such a parameter, which can be used to guide the selection of effective alloying elements.

EWF is the energy required to move an electron at the Fermi level from inside a solid to its surface without kinetic energy, which can be measured using the Kelvin probe or ultraviolet photoelectron spectroscopy. Although EWF represents the behavior of electrons at the surface, it fundamentally characterizes atomic interactions or the interactions between electrons and nuclei in the bulk. It has been shown that Young's moduli, yield strength and hardness of metals are intrinsically correlated to or dependent on EWF [17]. It has also been demonstrated that EWF is a fundamental parameter that characterizes the electron behavior not only for pure metals [17] but also for alloys [18].

In order to strengthen and ductilize Mg alloys by adding solutes, selected solutes should have the ability to increase the slip stress of the basal (0001) plane, while simultaneously lower the stress for cross-slip from the basal (0001) plane to the secondary prismatic $(10\bar{1}0)$ planes. Effective solutes may also have the ability to decrease the energy of I_1 stacking fault in Mg. Recent studies show that the I_1 stacking fault may act as heterogeneous nucleation sources for pyramidal $\langle c + a\rangle$ dislocations [12]; activating these dislocations would provide more than five independent slip systems, thus benefiting the ductility of Mg.

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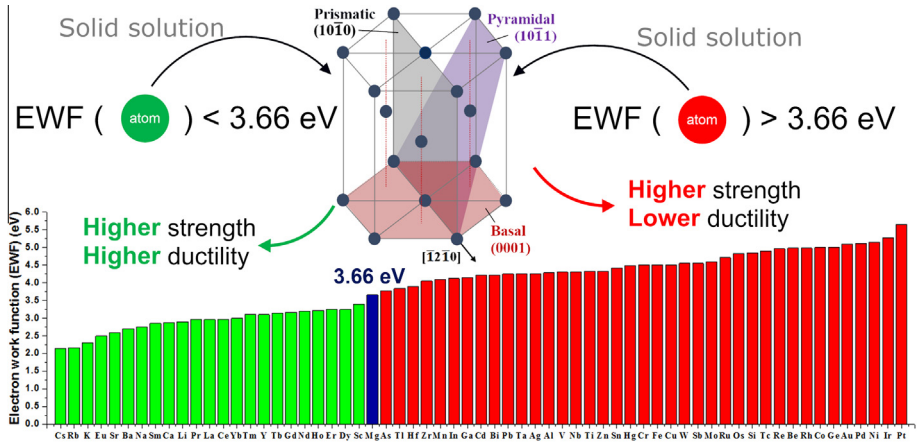

Fig. 1. A schematic illustration of effects of elements as solute on the strength and ductility of Mg with respect to their electron work function (EWF).

The objective of this work is to propose a new strategy for alloying solute selection based on the electron behavior to obtain strengthened and ductilized Mg alloys. Results of the research have shown that low-EWF solutes are able to increase both the strength and ductility of Mg, while high-EWF solutes only strengthen Mg at the expense of its ductility, as schematically illustrated in Fig. 1. In this study, 63 solutes were investigated and their EWFs listed in Appendix A.

2. Methodology

All energy calculations were performed using the density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) [19–21] with projector-augmented wave (PAW) potential [22]. The generalized gradient approximation (GGA) with the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE) [23] was employed. A cutoff energy of 350 eV and dense k-points sampling (such as $7 \times 7 \times 5$ for $Mg_{95}X$ and $15 \times 15 \times 3$ for $Mg_{47}X$) with a Methfessel–Paxton smearing of 0.2 eV are used to guarantee high numerical accuracy for both energy and stress optimization. The global break condition for the electronic self-consistency was chosen as 10^{-5} eV per supercell for all calculations. In addition, we found that increasing the number of bands was necessary for calculating energies and charge density distribution of supercells with embedded rare-earth element. Due to the ferromagnetic nature of some solutes, such as Mn, Fe, Co and Ni, all related calculations were performed within the spin-polarized approximation. For f solutes, we employed potentials where the valence f-electrons were treated as core electrons (appended with _3 in VASP potentials). Some radioactive elements are not included in this study. The calculations of geometries for misfits and dislocations were coupled with lattice Green function flexible boundary condition methods [6].

The differential electron density of hexagonal $Mg_{95}X$ supercell is defined by:

$$\Delta\rho = \rho_{SC} - \rho_{SP} \quad (1)$$

where ρ_{SC} represents the valence charge density from self-consistent DFT calculations, whereas ρ_{SP} is the superposition charge density of all involved atoms, obtained by non-selfconsistent calculations. $\Delta\rho$ is thus associated with the charge transfer upon the bonding formation between atoms. Plots were drawn using VESTA [24]. This definition has been successfully applied to the study on charge density distribution of the S-phase in Al–Cu–Mg alloys [25].

3. Results and discussion

3.1. Size and chemical misfits of solid solutes

In order to understand the effect of solute on the mechanical behavior of Mg, size and chemical misfits of solid solutes need to be analyzed. The atomic radius of solid solute is crucial to the stress caused by the difference in atomic size between the solute and Mg. Fig. 2 illustrates atomic radii of 63 solutes versus EWF, which shows a secondary polynomial relationship. The decrease in atomic radius with EWF is understandable, since higher EWF corresponds to stronger atomic bonding and thus smaller spacing between adjacent atoms. The size misfit can be determined using a Mg supercell with one Mg atom substituted by a solute. The size misfit is defined as the logarithmic derivative of the Burgers vector $b = \frac{a}{3}[2\bar{1}10]$ with the concentration of solute within its solubility limit. Five Mg

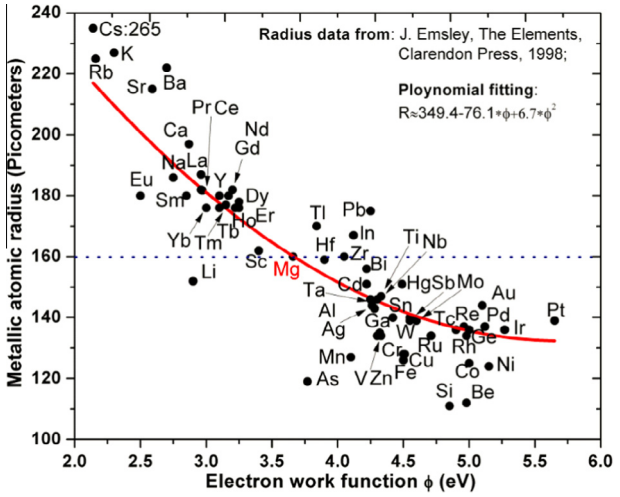

Fig. 2. The atomic radius of solid solutes versus EWF, which shows a secondary polynomial relationship.