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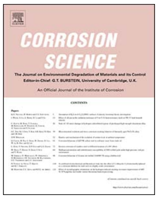

Nanoscale reactivity of Zn_xMg_{20-x} investigated by structural and electronic indicators

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ABSTRACT

First-principles calculations are reported for a small Zn—Mg nanoalloy, to get insight into fundamental physico-chemical properties that can be at the roots of the improved efficiency of Zn—Mg coatings against corrosion. We identify and rationalize composition-dependent features which modulate the noticeable charge transfer from Zn to Mg atoms. Local reactivity indicators demonstrate that Mg sites are, on average, the most reactive ones. Global reactivity indicators show that oxidation of the doped surface is a faster and more exothermic process as compared to a pure zinc surface.

1. Introduction

Magnesium and zinc are metallic elements of great importance to industry and bio-medical applications. Their alloying properties have been investigated for decades. For alloys with a high zinc content, the focus is on their protective coating properties. For example, the application of steel-based construction materials is largely dependent on the use of protective metallic coatings containing zinc [1]. These coatings provide barrier and galvanic protection to the steel substrates employed in automotive, building, and other industries, improving durability and aesthetic properties of final products. To extend the lifetime of steel-based constructions and save costs, big efforts have been devoted to optimize the chemical composition of the coating by alloying zinc with other metals such as aluminum, magnesium, iron, or nickel. Hosking et al. [2] tested coatings consisting of a $MgZn_2$ layer, about 2-μm thick, deposited on another Zn layer of 6 μm in a standard automotive laboratory corrosion test, comprising several cycles of humidity, drying and intermittent spraying with a 1 wt.% NaCl solution at pH 4.2. The time for appearance of significant amounts of red rust was 3 times longer for the Zn—Mg alloy as compared to pure Zn. The improved coating properties of Zn—Mg alloys would apparently stem from the superior capability of Mg atoms on the surface to form a protective oxide layer, which is more insulating and stable than the ZnO layer that would be formed on pure zinc [3]. The effect of magnesium was most beneficial at 4–8 wt.% magnesium in the alloy. Weight loss of such alloy coatings was up to 10 times lower than that of pure zinc. More recently, a combined infrared spectroscopy, X-ray diffraction, ion chromatography, and X-ray photoelectron spectroscopy study [4] has clarified the role played by the Mg-based protective layer in explaining the improved corrosion protection properties of $MgZn_2$. Such layer modifies the relative proportion of hydroxide and carbonate species in the corroded products as compared to a pure zinc coating, increasing the electrical resistivity and work function of the sample. This observation explains the reduction of charge transfer across the interface. The detailed distribution of corrosion products across the interface has been analyzed as a function of depth in a later paper by the same authors [5]. Additionally, the Mg-based corrosion film is thicker as compared to a pure Zn sample, which further contributes to lower the gradient potential across the metal-oxide interface, thus passivating the sample in a chloride environment and limiting the efficiency of oxygen reduction. Finally, the microstructure of the coating is also often a key ingredient for a long useful time of the protective film, because penetration and fast diffusion of water molecules, oxygen or other ion species is easier through local defects in the protecting layer, which causes degradation of the coating and finally corrosion of the metal. In this respect, charge transfer at the grain boundaries is more limited in Zn—Mg alloys because of a higher proportion of OH and CO_3 groups as compared to a pure zinc surface. Indeed, those groups attract electrons and reduce the amount of charge transfer through local defects. Hausbrand *et al.* have reported experiments demonstrating that use of Zn—Mg alloys leads to a decrease in the delamination rate of the coating/paint interface that forms upon applying an external layer of painting to the alloy [6], which is interesting in an applied technological context.

At the opposite limit of the phase diagram, pure magnesium and/or Mg-rich alloys possess many advantageous physicochemical and biolo-

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gical characteristics, such as a good biocompatibility and similarity of its mechanical properties to those of the human bone tissue, which renders those materials as promising candidates for bio-medical and implant applications. Unfortunately, a major limitation with employing Mg-based materials in bio-medical applications is their fast degradation/corrosion rate as compared to the time span of the healing process [7–9]. Several attempts have been made to reduce the degradation rate of Mg-based materials through doping with specific elements that are also biocompatible, such as Ca, Zn, Al, Y and Fe. In Mg-rich alloys, only small amounts of Zn have been considered, Zn being mixed with other elements such as yttrium to strengthen the material by changing its stacking arrangement [10].

All the applications of Zn−Mg coatings explored up to date refer to macroscopic systems. However, it is well known that the physical and chemical properties of a material can be drastically modified at the nanoscale, and this is why nanoparticle research is in fact such a fascinating branch of science. The properties of a Zn−Mg nanoalloy will show a strong and non-monotonous dependence on both cluster size and composition, as well as on the number of electrons, and one could envisage taking advantage of all those degrees of freedom to fine tune a desired property such as the resistance against corrosion. The often unexpected and difficult to rationalize behavior of nanoparticles poses a great challenge for science, but at the same time is a breeding ground for surprising discoveries and innovative technological applications. In previous work [11,12], we have reported on the structural and electronic properties of pure zinc clusters with up to 80 atoms, and have identified a specific property which might be a key factor in explaining why zinc-based materials offer a good protection against corrosion. Specifically, the distance separating the outermost atomic shell from the remaining interior or core atoms is anomalously long as compared to typical interatomic distances, and the empty space thus generated in the subsurface region is strongly depleted of electrons. We explicitly checked that under an oxidizing atmosphere, the very stable and distant shell provides then a natural barrier that protects the metal core from environmental agents [12]. Alloying with magnesium might further improve these protection properties, which motivates the study of Zn−Mg nanoalloys. Additionally, small nanoalloy clusters may provide useful and simple models for the complex processes that occur in extended surfaces, and may be also useful in contributing to understand the several factors that stabilize Laves phases as the number of atoms increases, a problem of ongoing interest [13]. A final motivation comes from the observation that anti-corrosive coatings can also be obtained by directly spraying the alloy surface with nanoparticles, which might have advantageous properties as compared to Mg−Zn bulk phases. For example, Shen and Zuo [14] have shown how adding ZnO and Mg particles to an epoxy coating results in a better protection and prolonged lifetime of the coating.

As an initial step towards gaining a better understanding of the action of Zn−Mg binary systems against corrosion, we have selected a small cluster of 20 atoms. Zn and Mg are isoelectronic and contribute two valence electrons each, so with 40 valence electrons, all the Zn_xMg_{20-x} nanoalloys have a closed electronic shell structure in agreement with the predictions of a spherical jellium model. Because of a large HOMO-LUMO gap, these nanoalloys are expected to be little reactive. But although low reactivity is expected throughout the whole composition range, we will demonstrate that for specific compositions this reactivity could be minimal. Prior to explicitly considering any sort of chemical attack by a corroding agent, we will examine here the structural and electronic properties of the bare nanoalloys, as well as the charge transfers and several reactivity indices. In Section 2, we briefly describe the theoretical approach. Section 3 reports the structures of the putative global minima as well as their energetic stability. Section 4 shows the results about charge transfer based on the Bader partial charge of each atomic site and also the analysis of the metallic bonding pattern based on the electron localization function (ELF). Section 5 provides a discussion on the expected reactivity of selected nanoalloys based on several global and local indicators of conceptual density functional theory, such as the Fukui function. Finally, the main results are summarized in the concluding section.

2. Computational methods

Putative global minimum (GM) geometries of Zn_xMg_{20-x} are obtained following a similar computational strategy as the one used in our previous work on pure Zn_N clusters [11]. It contains three main steps. To start with, an initial pool of trial structures is generated through unbiased basin hopping (BH) optimizations [15] based on a Gupta potential [16]. Briefly stated, the BH method employs a Monte Carlo (MC) technique to locate the global minimum on a transformed staircase-like potential energy landscape, mapped from the true potential energy surface by a local optimization operator. The transformed surface has the same local minima as the true surface, but the energy barriers between minima are significantly reduced on the transformed surface, which makes the MC sampling much more efficient. At least five independent BH runs are performed for each value of the composition $x = 0$–20, all of them starting from a randomly generated structure. We employ two different types of atomic moves to generate new structures along the MC sampling: random large-amplitude displacements of all the atoms in the nanoalloy, which serve to sample structural isomers with different atomic skeletons; and swap moves in which the chemical identity of two randomly selected Zn and Mg atoms is exchanged. This second type of move is essential for an efficient sampling of the different homotops associated with each structural isomer.

In a second step, we select around 100 competitive structures for each value of x, and re-optimize them at the Kohn–Sham density functional theory (KS-DFT) level. After this step, we can compare the *ab initio* and Gupta predictions, focusing on the energetic ordering of the different local minima. From such a detailed comparison, we could confirm that the Gupta potential reproduces quite well the relative stabilities of the different structural isomers. However, the relative stabilities of homotops of the same atomic skeleton do not compare well with the *ab initio* results, so Gupta predictions about the chemical ordering are not so reliable. This means that the pool of trial structures that has been chosen for re-optimization at the DFT level may leave out some relevant homotops. We ascribe this problem to a significant degree of charge transfer from Mg to Zn atoms (see Section 4), an effect that is not contemplated in (and so can not be captured by) the Gupta model potential. To solve this problem, in a last step we have performed a more complete sampling of homotops directly at the DFT level. We have followed a composition comparison approach: [17] for each composition x, we consider the five more stable minima as seeds to generate new homotops for compositions $x \pm 1$, by transmuting a Zn-atom into a Mg-atom or viceversa. When one of the homotops thus generated becomes the new putative GM for a certain composition, it is considered as a new seed for the next iteration of a composition comparison cycle, which is continued up to a point where no better homotops can be generated through this procedure. After this final step, more than 200 local minima have been fully optimized at the DFT level for most values of x.

The first-principles calculations themselves have been performed employing two different codes: SIESTA [18] and VASP [24,25], with exchange-correlation effects treated within the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) [19] in both cases. SIESTA employs norm conserving pseudopotentials to describe the effect of core electrons [20,21], and a basis of localized atomic orbitals to expand the wave function of the cluster. The basis set we have used is of DZP (double zeta plus polarization) quality. The individual clusters were placed in a cubic supercell of 30 Å × 30 Å × 30 Å, a size large enough as to make the interaction between the cluster and its replicas in neighboring cells negligible, allowing to consider only the Γ point ($k = 0$) when integrating over the