Synthetic Metals 162 (2012) 119–125

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Theoretical study of the effect of nickel and tin doping in copper clusters

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ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form
10 November 2011
Accepted 17 November 2011
Available online 14 December 2011

Keywords:
DFT
Cluster
Copper alloys
Active site
Corrosion

ABSTRACT

The equilibrium geometries, electronic properties, bonding behavior, stability and active sites of copper clusters doped with Ni or Sn atom have been studied using density functional theory. The results indicate that the impurity atoms change the equilibrium geometries, lower the total energies, and modify the HOMO–LUMO gaps and active sites of copper clusters. Meanwhile impurities prefer to be the surface or outer layer of the cluster, may form an oxide film from the active sites on the surface of materials, preventing oxygen and aggressive ions diffusion and protecting the copper alloy against corrosion.

1. Introduction

Extensively studies have shown that bimetallic systems present better physical and chemical properties than pure metals, such as selectivity, structure, stability, electronic property and activity [1–4]. They have been used in many different industrial processes, such as catalyst [1], electrocatalytic [5,6], semiconductor [7], corrosion [8,9] and so forth. In particular, the bimetallic systems of many metals (Ni, Zn, Sn or others) doping "host metals" like Cu have been reported using as corrosion-resistant materials [8–10].

Sohn and Kang [9] considered that while tin doped alone was a good corrosion inhibitor, even better inhibition resulted when nickel was also present in tin-alloyed brass. Becearia and Poggi [11] figured that forming dense SnO_2 film was essential in corrosion-resistant tin-alloyed brass. Milošev and Metikoš-Huković [12] performed an electrochemical study in combination with microscopic investigation and photopotential measurements for Cu–*x*Ni alloys (x = 10–40 wt%) in slightly alkaline solution (pH = 9.2). For lower chloride concentrations an increase in nickel content worsens the resistance to passive film breakdown, whereas for higher chloride concentrations an increase in the nickel content is beneficial. From all these experimental results, we can conclude that doping elements affect the "host metals", and improve the overall performance including corrosion-resistant properties.

Small clusters exhibit rich properties being partly controllable, unique physical and chemical properties, which can be related to the large surface-to-volume ratio as well as to finite-size or quantum-confinement effects [13–15]. They are known as precursors of bulk material. In the past few years, several density functional theory (DFT) calculations have been performed to predict the geometric and electronic structures of copper and its bimetallic clusters. Massobrio et al. [16] investigated the equilibrium geometries and electronic properties of neutral Cu_n (n = 2, 3, 4, 6, 8, 10) clusters via first principles calculations, they found ground states and local minimum structures similar to those of Na_n. Jug et al. [17] studied the structure and stability of small copper clusters with up to ten atoms using the all-electron type, and the results showed that the trends corresponded very well with available experimental data. In the report of Derosa et al. [18], geometric and electronic properties of Cu–Ni clusters' planar configurations containing up to five atoms were examined, they figured that geometry had great influence on the reactivity, but significantly different atomic structure of copper and nickel atoms are strong factors on the nucleation, stability, and adsorption properties. Plass et al. [19] investigated the molecules X_2, CuX, Cu_2X and CuX_2 (X = Si, Ge or Sn) by first-principles calculations using energy-adjusted pseudopotentials, giving the corresponding harmonic frequencies ω, bond lengths R, and dissociation energies D for the ground state of these molecules. The overall majority of these papers have only reported very small $Cu_{n-1}Ni$ clusters ($n \leq 6$). Nevertheless, to our knowledge, there are few studies in Cu–Sn clusters aimed at predicting their properties.

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doi:10.1016/j.synthmet.2011.11.021

With the backgrounds provided above, the present study was directed towards explore equilibrium geometries of $Cu_{n-1}Sn$ (n = 2–9) clusters and larger $Cu_{n-1}Ni$ (n = 2–9) clusters, and then to investigate the variations of the equilibrium geometries, electronic properties, stability and active sites of copper clusters doped Ni or Sn atom. More importantly, we attempted to confirm that an oxide film of foreign elements formed on the surface of copper alloy first, protecting the substrate against corrosion.

2. Methods

All calculations have been carried out using DFT provided by the $DMol_3$ package [20–22] in the Materials Studio. The isomers of smaller clusters are numerous and their so-called ground-state structures have been calculated at the generalized gradient approximation (GGA) corrected-exchange potential of the BLYP (the Lee–Yang–Parr correlation functional) [23,24] level of theory. All-electron symmetry-unrestricted treatment, double numerical basis set augmented with d-polarization and p-polarization functions (DNP) [25] were chosen. The most accurate results should be obtained by the DNP basis set, which is comparable to 6-31G** sets [21–26] and the numerical basis set is much more accurate than a Gaussian basis set of the same size [27]. The convergence thresholds for self-consistent field (SCF) and geometry optimizations were 1.0×10^{-5} Hartree for the energy change and 2.0×10^{-3} Hartree/Å for the forces, 5.0×10^{-3} Å for the displacement. Mix the charge density between the current and previous iterations with a value of 0.2. Self-consistent field (SCF) calculations were done at a convergence criterion of 1.0×10^{-6} Hartree on the total energy. The direct inversion in an iterative subspace (DIIS) approach was used to speed up the SCF convergence.

The accuracy of the current computational scheme had been tested by the calculation on the Cu_2, Ni_2 and CuNi dimer, we calculated their bond lengths, dissociation energies, frequencies, and the results are summarized in Table 1. All these results are in well agreement with the previous theoretical and experimental values, therefore, our methods are reasonably suitable for describing the properties of Cu_n, $Cu_{n-1}Ni$ and $Cu_{n-1}Sn$ clusters.

As the number of possible configurations increases very rapidly with the cluster size, it is difficult to explore all possible configurations. In our work, we firstly calculated the geometrical structures of pure Cu_n (n = 2–9) clusters based on the previous calculation [1,18,28,46,47] and other reasonable geometries as appropriate, so that these pure clusters might be regarded as the reference of the initial geometries of $Cu_{n-1}Ni$ and $Cu_{n-1}Sn$ bimetallic clusters. Then the lowing isomers of bimetallic clusters would be easily constructed as follows:

(1) Re-optimizing the results of previous calculations by others [1,18,48].
(2) Replacing one Cu atom in the isomer of optimized Cu_n cluster.
(3) Adding one Ni or Sn atom into the isomer of optimized Cu_n cluster.
(4) Constructing other configurations by hand abiding by a certain symmetry and Jahn–Teller theory.

3. Results and discussion

With the aid of the computational scheme described in Section 2, a series of calculation results for the lowest-energy structures of $Cu_{n-1}Ni$ and $Cu_{n-1}Sn$ (n = 2–9) clusters were obtained, such as the binding energy per atom $E_b(n)$, the fragmentation energy $\Delta E(n)$, the second-order difference of total energy $\Delta_2 E(n)$, the HOMO–LUMO gap and the Fukui function. The information given by these parameters have been used successfully in analyzing and characterization of different kinds of molecular structures and chemical reactions. These results can be obtained as the following formulas (setting $Cu_{n-1}Ni$ as the representative of the bimetallic systems here),

$$E_b(Cu_n) = \frac{nE(Cu) - E(Cu_n)}{n} \quad (1)$$

$$E_b(Cu_{n-1}Ni) = \frac{(n-1)E(Cu) + E(Ni) - E(Cu_{n-1}Ni)}{n} \quad (2)$$

$$\Delta E(Cu_n) = E(Cu) + E(Cu_{n-1}) - E(Cu_n) \quad (3)$$

$$\Delta E(Cu_{n-1}Ni) = E(Cu) + E(Cu_{n-2}Ni) - E(Cu_{n-1}Ni) \quad (4)$$

$$\Delta_2 E(Cu_n) = E(Cu_{n-1}Ni) + E(Cu_{n+1}Ni) - 2E(Cu_nNi) \quad (5)$$

$$\Delta_2 E(Cu_{n-1}Ni) = E(Cu_{n-2}Ni) + E(Cu_nNi) - 2E(Cu_{n-1}Ni) \quad (6)$$

where E(Cu), E(Ni), $E(Cu_{n-2}Ni)$, $E(Cu_{n-1}Ni)$ and $E(Cu_nNi)$ represent the total energies of the most stable Cu, Ni, $Cu_{n-2}Ni$, $Cu_{n-1}Ni$ and Cu_nNi clusters, respectively. The quantities of corresponding to pure Cu_n clusters are also given for comparison.

Table 1
Comparison of bond lengths (in Å), dissociation energies (in eV), frequencies (cm^{-1}) Calculated (BLYP) with others' work and experimental data of the ground state of Cu_2, Ni_2 and CuNi clusters.

Parameters	Cu_2			Ni_2			CuNi		
	Ours	Others	Exp	Ours	Others	Exp	Ours	Others	Exp
Bond length (Å)	2.257	2.257 [1,28] 2.21 [17] 2.255 [18]	2.22 [29] 2.219 [13] 2.2195 [14] 2.2197 [15]	2.148	2.112 [30] 2.273 [18] 2.13 [1] 2.01 [31]	2.20 [2] 2.155 [32] 2.1545 [3,33]	2.263	2.259 [1] 2.281 [18]	2.233 [4] 2.235 [16]
Do/E_b (ev)	2.033	1.91 [18] 2.069 [34] 2.08 [35]	2.04 [36] 2.01 [14]	2.044	2.10 [37] 2.042 [34] 1.95 [18]	2.068 [38] 2.042 [33] 2.03 [29]	1.804	2.05 [34] 1.79 [18]	2.10 [39]
Freq (cm^{-1})	254.3	263.2 [28] 256 [18]	264.401 [40] 265.0 [41] 266.4 [42]	299.4	280 [18]	280 ± 20 [43] 250.4 380.9 [37]		250 [18]	273 [44,45]