Geometries, Stability and Growth Strategies of Small Al\textsubscript{n}Cu (n=1-9) Clusters

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Abstract. To improve the anti-crack performance of Al-Cu alloys, the geometries, relative stability as well as growth strategies of Al\textsubscript{n}Cu (n=1-9) clusters were investigated with spin polarized density functional theory: BLYP. The results reveal that the Cu atom tends to convergence aluminum clusters to close-packed structures. The average binding energies of Al\textsubscript{n}Cu are slightly higher than that of Al\textsubscript{N} clusters. Local peaks of the HOMO-LUMO gaps are found at n=1, 4, 6, and 9. The reaction energies of Al\textsubscript{n}Cu (n=1-2) are higher which means that Al\textsubscript{n}Cu clusters are easier to react with Al clusters. Cu atom prior reacts with Al atom.

Introduction

Al-Cu alloys are widely applied to various fields due to the characteristics such as high strength and high toughness [1]. However, hot crack, loose, segregation of Al-Cu alloys limits their applications [2]. Nowadays, micro-structures are generally considered to affect the fatigue crack propagation behavior of age-hardened alloys [3]. It is an inevitable choice to control chemical composition variations and micro-structures [4]. Wagner et al. [2] explored the effect of Cu on the microstructure and mechanical properties of Al alloys. Li et al. [5] investigated the influence of Cu contents on the precipitated phases and the resultant properties of Al alloys. The cluster-based model has been successfully used to describe the complex alloy phases on the basis of the obtained principal clusters, and the atomic configurations of the stable characteristic principal clusters in the complex alloys and their crystalline derivatives remain similar to each other [6,7].

The Cu atom is selected as the ‘impurity’ to probe into its influences on the structural, electronic and magnetic properties of host small Al\textsubscript{N} (N=2-10) clusters. It is necessary to find whether some novel properties could be unfolded after doping Cu atom on small Al clusters. To our knowledge, there has been a theoretical study of Al-doped Cu clusters [8] while has not been a theoretical study for Cu-doped Al clusters so far. In this present work, the structural, electronic and growth strategies are investigated within the DFT framework for small Al\textsubscript{n}Cu (n=1-9) clusters. For the sake of comparison, the Al\textsubscript{2-10} clusters are also computed.

Computational Details

To acquire the initial structures of the Al\textsubscript{n}Cu (n=1-9) clusters, we replaced an Al atom on each possible site of various Al clusters studied previously [9,10]. Geometry optimization must be performed to all the hypothetical initial structures. Our calculations were done by the spin polarized density functional theory (DFT) implemented in the DMol\textsuperscript{3} package [11,12] within the generalized gradient approximation (GGA) using BLYP functional [13,14]. All-electron density functional method which is an adequately accurate and efficient procedure for clusters was adopted [15]. The double numerical polarization (DNP) basis set [11] was chosen. To avoid trapping in the local minima of the potential energy surface, all the geometries with unconstrained symmetry and various
possible spin multiplicities were considered [16]. Harmonic vibrational frequency analysis was performed to verify that the obtained geometries and the stable structures with no imaginary frequencies [16]. In the geometry optimization processes, the energy gradient and atomic displacement converged to within $1 \times 10^{-5}$ Hartree/Bohr and $5 \times 10^{-3}$ Å, respectively. Corresponding to a total energy convergence of $1 \times 10^{-5}$ Hartree, the charge density in the self-consistent iterations converged to within $1 \times 10^{-6}$ e/Å³. Mülliken population analysis was adopted to acquire the atomic charge of the clusters [17].

The average binding energy $E_b(n)$

$$E_b(n) = [nE(Al) + E(Cu) - E(Al_n Cu)]/(n + 1)$$

where $n$ is the number of Al atoms. $E(Al)$ and $E(Cu)$ are the single atom energies of the Al and Cu atoms. $E(Al_n Cu)$ is the total energy of the lowest-energy structure for the $Al_n Cu$ cluster.

To understand the growth mechanism, in this study only $Al_n Cu + Al_{n-m} \rightarrow Al_n Cu$ is considered to the lowest-energy structures of $Al_n Cu$ ($n=1-9$). The reaction energy $\Delta E$

$$\Delta E = (E_m + E_{n-m} - E_n)/(n + 1)$$

To evaluate the accuracy of our selected scheme on describing the $Al_n-1 Cu$ clusters, we first carried out the test calculations on $Al_2$ and $Cu_2$ dimers. As for $Al_2$ dimer, the geometry predicted for bond length is 2.723 Å in comparison with the experimental value of 2.701 Å from high-resolution spectroscopy measurement [18] and the calculated value of 2.766 Å from $ab$ initio calculation [19] and 2.771 Å from CCSD(T)/aug-cc-pVDZ [20]. As for the dissociation energy [21], our predicted value of 1.429 eV is well reproduced in comparison with experiment (1.34 eV) [22] and $ab$ initio result (1.40 eV) [19] and CCSD(T)/aug-cc-pVDZ result (1.33 eV) [20]. As for $Cu_2$ dimer, the geometry predicted for bond length and the dissociation energy are $R_e=2.277$ Å, and $D_e=1.96$ eV. Our results are in excellent agreement with experimental ($R_e=2.22$ Å, and $D_e=1.96$ eV [21]) and previous theoretical values ($R_e=2.256$ Å, and $D_e=1.92$ eV [23]) predicted with B3PW91 functional. Therefore, the BLYP scheme is reliable and accurate enough for describing the systems involving Al and Cu atoms.

**Results and Discussion**

**Structures**

The lowest-energy structures of $Al_N$ ($N=2-10$), the lowest-energy structures and low-lying isomers of $Al_{n-1} Cu$ ($n=1-9$) clusters are depicted in Fig.1. Compare this calculated results with the calculated results from the Ref.[8], the structures of $Al_2 Cu$ clusters in Ref.[8] is unstable and that of $Al_6 Cu$ and $Al_7 Cu$ clusters in Ref.[8] are not the lowest energy structures. From Fig.1 it can be seen that the small $Al_{n} Cu$ clusters usually inherit the configurations of the host $Al_N$ clusters [16]. The differences arise as the cluster size $n$ increased. The Cu atom leads to distort $Al_N$ clusters to close-packed structures. The doped Cu atom leads to the decrease of the bond lengths for $Al_6 Cu$ compared with corresponding bond lengths of $Al_N$ clusters. The influence of the impurity Cu atoms on the structures of the host Al clusters derives from the 3d orbital hybridization of the Cu atom with the orbits of Al [8]. Due to the atomic radius of Cu(1.57Å) is smaller than that of Al(1.82Å). The Cu atom prefers to stay on the surface of $Al_N$ clusters. The same phenomenon is observed in $Al_{n}Mg$ [16] and $Al_{n}N$ [24] clusters.
Fig. 1. The lowest-energy structures of AlN (N=2-10), the lowest-energy structures and low-lying isomers of Al_{n-1}Cu (n=1-9) clusters.

Stability

Fig. 2. Size dependence of the binding energies per atom (eV/atom) for the AlN (N=2-10) and Al_{n}Cu (n=1-9) clusters.

The binding energies per atom of AlN (N=2-10) and Al_{n}Cu (n=1-9) clusters are displayed in Fig. 2. From Fig. 2 it can be seen that the average binding energies of AlN and Al_{n}Cu clusters monotonic-increasing as the cluster size evolves, which indicates that the stability of AlN and Al_{n}Cu...
clusters were enhanced as the size of the clusters increases. The average binding energies of the AlₙCu clusters are slightly higher than that of correspondent pure Alₙ clusters. It indicates that the doping Cu atom leads to increase the stability of Alₙ clusters.

**Electronic Properties**

![Graph showing size dependence of the HOMO-LUMO gaps for AlN (N=2-10) and AlₙCu (n=1-9) clusters.](image)

Even all these physical properties of the alloys are correlated with the electronic structures [25]. The size dependence of the HOMO-LUMO gaps for Alₙ (N=2-10) and AlₙCu (n=1-9) clusters are plotted in Fig. 3. From Fig. 3 it can be seen that AlₙCu clusters have a different HOMO-LUMO gap curve from pure Alₙ clusters. For Alₙ clusters, local peaks are found at n=2, 4, and 9. For AlₙCu clusters, local peaks are found at n=1, 4, 6, and 9. It indicates that the chemical reactivity of the above clusters is better than their neighbors. In general, the clusters with odd number of atoms tend to have relatively larger gaps than their adjacent clusters with even number atoms [16]. A large HOMO-LUMO gap generally corresponds to a closed-shell electronic configuration with high stability [24]. The results indicate that the Al-Cu couplings in the AlₙCu (n = 1-9) clusters play an important role in determining the HOMO and LUMO states which have evident 3d orbital character [26].

**Growth Strategies**

To understand the growth strategies of the AlₙCu clusters at lower temperature, we observed the 82 optimized combinations of reactions in Table 1. From Table 1 it can be seen that the small Alₙ clusters are almost obtained by Alₙ₋₁ clusters which adsorbed a Al atom at lower temperature. However, Al₃Cu preferentially react with Al₂-Al₅ clusters. Al₅Cu preferentially react with Al₄ clusters. Al₃Cu, Al₅Cu, and Al₇Cu clusters are preferentially acquired by Al₃-Al₅ clusters react with a Cu atom. It explained that the origin of Al-Cu inter-metallics. So Cu doping can adjust the Al cluster ratio and the growth strategies. The largest ΔE for the same cluster size n in Table 1 were selected as the reaction energy. It can be seen that for Cu doping, the reaction energies of AlₙCu (n=1-2) are higher which means that AlₙCu clusters are easier to react with Al clusters. The reaction energy ΔE of Cu+Al→AlCu is the largest than the other ΔE of Alₙ₋ₙ₋₃Cu+Alₙ₋₉→AlₙCu. It means that the Cu atom prior reacts with Al atom.
Table 1 The reaction energy $\Delta E$ [eV/atom] for $\text{Al}_m\text{Cu} + \text{Al}_{n,m} \rightarrow \text{Al}_n\text{Cu}$.

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Conclusions

In summary, we have performed computations on the geometries, stability and growth strategies of the $\text{Al}_n\text{Cu}$ ($n=1-9$) clusters using all-electron DFT-BLYP calculations. The results reveal that the Cu atom tends to convergence $\text{Al}_N$ ($N=1-10$) clusters to close-packed structures. The average binding energies of $\text{Al}_n\text{Cu}$ are slightly higher than that of $\text{Al}_N$ clusters. Local peaks of the HOMO-LUMO gaps are found at $n=1, 4, 6, 9$. It indicates that the chemical reactivity of the above clusters is better than their neighbors. The reaction energies of $\text{Al}_n\text{Cu}$ ($n=1-2$) are higher which means that $\text{Al}_n\text{Cu}$ clusters are easier to react with Al clusters. Cu atom prior reacts with Al atom.

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References


