Geometries, Stability and Growth Strategies of Small Al_nCu (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_nCu (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_nCu are slightly higher than that of Al_N clusters. Local peaks of the HOMO-LUMO gaps are found at n=1, 4, 6, and 9. The reaction energies of Al_nCu (n=1-2) are higher which means that Al_nCu 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 A1-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_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_nCu (n=1-9) clusters. For the sake of comparison, the Al_{2-10} clusters are also computed.

Computational Details

To acquire the initial structures of the Al_nCu (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 $DMol^3$ 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 1×10^{-5} Hartree/Bohr and 5×10^{-3} Å, respectively. Corresponding to a total energy convergence of 1×10^{-5} Hartree, the charge density in the self-consistent iterations converged to within 1×10^{-6} e/Å^3. Mülliken population analysis was adopted to acquire the atomic charge of the clusters [17].

The average binding energy $E_b(n)$

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

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

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

$$\Delta E = (E_m + E_{n-m} - E_n)/(n+1) \quad (2)$$

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_2Cu clusters in Ref.[8] is unstable and that of Al_6Cu and Al_7Cu clusters in Ref.[8] are not the lowest energy structures. From Fig.1 it can be seen that the small Al_nCu 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_nCu 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 3*d* 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_nMg [16] and Al_nN [24] clusters.

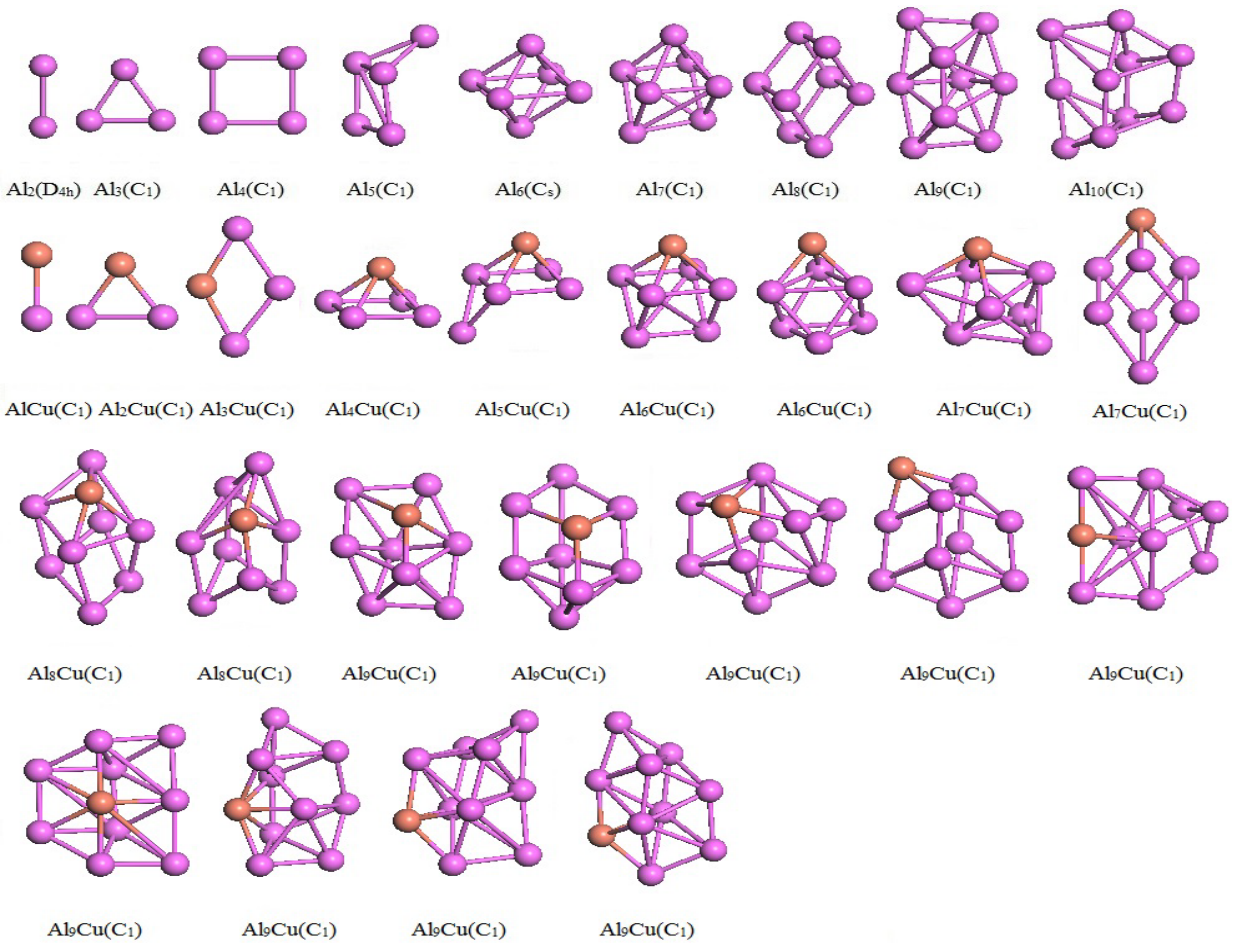

Fig. 1. The lowest-energy structures of Al_N (N=2-10), the lowest-energy structures and low-lying isomers of $Al_{n-1}Cu$ (n=1-9) clusters.

Stability

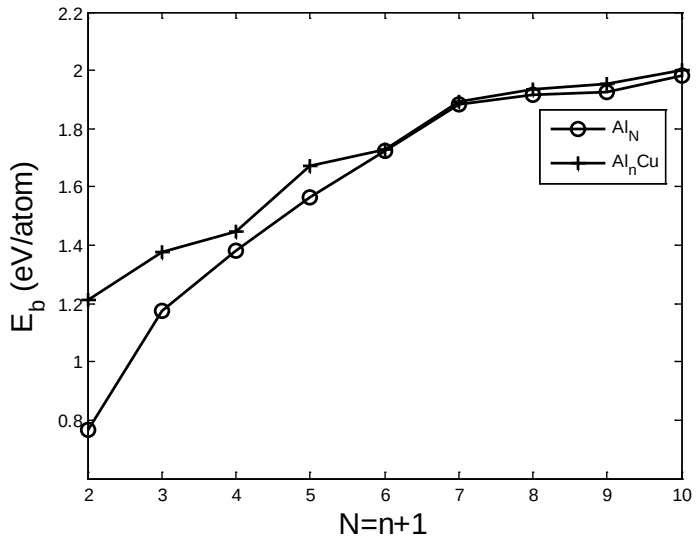

Fig.2. Size dependence of the binding energies per atom (eV/atom) for the Al_N (N=2-10) and Al_nCu (n=1-9) clusters.

The binding energies per atom of Al_N (N=2-10) and Al_nCu (n=1-9) clusters are displayed in Fig. 2. From Fig. 2 it can be seen that the average binding energies of Al_N and Al_nCu clusters monotonic-increasing as the cluster size evolves, which indicates that the stability of Al_N and Al_nCu

clusters were enhanced as the size of the clusters increases. The average binding energies of the Al_nCu clusters are slightly higher than that of correspondent pure Al_N clusters. It indicates that the doping Cu atom leads to increase the stability of Al_N clusters.

Electronic Properties

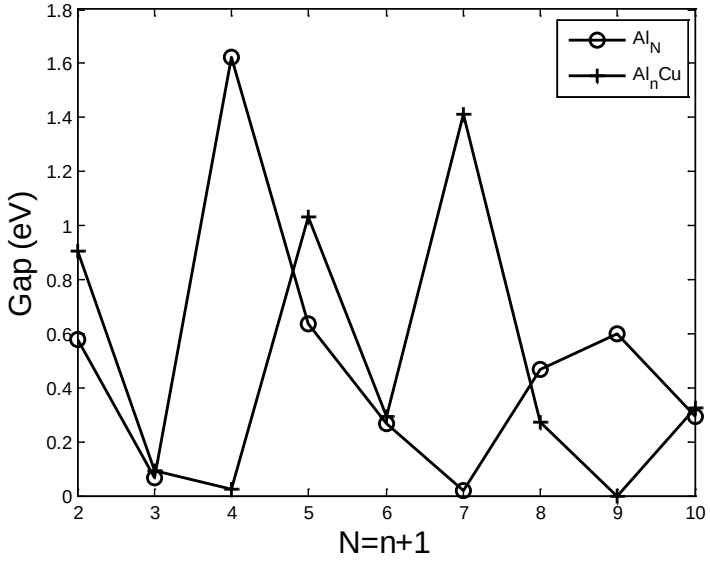

Fig.3. Size dependence of the HOMO-LUMO gaps for the Al_N (N=2-10) and Al_nCu (n=1-9) clusters.

Even all these physical properties of the alloys are correlated with the electronic structures [25]. The size dependence of the HOMO-LUMO gaps for Al_N (N=2-10) and Al_nCu (n=1-9) clusters are plotted in Fig. 3. From Fig. 3 it can be seen that Al_nCu clusters have a different HOMO-LUMO gap curve from pure Al_N clusters. For Al_N clusters, local peaks are found at n=2, 4, and 9. For Al_nCu 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 Al_nCu (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 Al_nCu 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 Al_N clusters are almost obtained by Al_{N-1} clusters which adsorbed a Al atom at lower temperature. However, Al_3Cu preferentially react with Al_2-Al_5 clusters. Al_5Cu preferentially react with Al_4 clusters. Al_2Cu, Al_3Cu, and Al_4Cu clusters are preferentially acquired by Al_2-Al_4 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 Al_nCu (n=1-2) are higher which means that Al_nCu clusters are easier to react with Al clusters. The reaction energy ΔE of $Cu+Al \rightarrow AlCu$ is the largest than the other ΔE of $Al_mCu+Al_{n-m} \rightarrow Al_nCu$. It means that the Cu atom prior reacts with Al atom.

Table 1 The reaction energy ΔE [eV/atom] for $Al_mCu+Al_{n-m}\rightarrow Al_nCu$.

	m=0	m=1	m=2	m=3	m=4	m=5	m=6	m=7	m=8
n=1	0.7147								
n=2	0.6430								
n=3	0.4896	0.6146							
n=4	0.4465	0.5524							
n=5	0.4132	0.5471	0.5521						
n=6	0.3995	0.5495	0.5929						
n=7	0.2587	0.4295	0.4983	0.5326					
n=8	0.2179	0.2891	0.3854	0.4433					
n=9	0.2446	0.2978	0.3118	0.3956	0.4203				
n=1	1.2209								
n=2	0.8851	0.5476							
n=3	0.5822	0.4540	0.4006						
n=4	0.5795	0.4829	0.5401	0.5055					
n=5	0.4370	0.4022	0.4548	0.5093	0.3263				
n=6	0.4257	0.4311	0.5154	0.5663	0.4808	0.4053			
n=7	0.2935	0.3378	0.4424	0.5211	0.4500	0.4465	0.2705		
n=8	0.2597	0.2183	0.3465	0.4439	0.4112	0.4113	0.3104	0.2288	
n=9	0.2757	0.2276	0.2703	0.3897	0.3849	0.4124	0.3245	0.3011	0.2381

Conclusions

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

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