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Density functional study of copper segregation in aluminum

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ABSTRACT

The structural and electronic properties of Cu segregation in aluminum are studied in the framework of the density functional theory, within the projector augmented plane-wave method and both its local density approximation (LDA) and generalized gradient approximation (GGA). We first studied Al–Cu interactions in bulk phase at low copper concentration (≤3.12%: at). We conclude to a tendency to the formation of a solid solution at $T=0$ K. We moreover investigated surface alloy properties for varying compositions of a Cu doped Al layer in the (111) Al surface then buried in an (111) Al slab. Calculated segregation energies show unstable systems when Cu atoms are in the surface position (position 1). In the absence of ordering effects for Cu atoms in a layer ($x_{Cu}=1/9$ and $x_{Cu}=1/3$), the system is more stable when the doped layer is buried one layer under the surface (position 2), whereas for $x_{Cu}=1/2$ to $x_{Cu}=1$ (full monolayer), the doped layer is more accommodated when buried in the sub-sub-surface (position 3). First stage formation of GP1- and GP2-zones was finally modeled by doping (100) Al layers with Cu clusters in a (111) Al slab, in the surface then buried one and two layers under the surface. These multilayer clusters are more stable when buried one layer beneath the surface. Systems modeling GP1-zones are more stable than systems modeling GP2-zones. However the segregation of a full copper (100) monolayer in an (100) Al matrix shows a copper segregation deep in the bulk with a segregation barrier. Our results fit clearly into a picture of energetics and geometrical properties dominated by preferential tendency to Cu clustering close to the (111) Al surface.

1. Introduction

Aluminum has the capacity to form a very stable oxide. Thus, it leads to high temperature resistant coatings with good resistance to oxidation and corrosion in aggressive environments. It is often alloyed to modify some of its intrinsic properties and various treatments such as precipitation hardening are needed to improve its mechanical properties. The properties of these alloys are not due simply to their chemical composition but are particularly influenced by the involved phases and the alloy microstructure. Copper–aluminum alloys that have good mechanical properties are the most used alloys in the aeronautical field. In microelectronics, Cu/Al joints are widely used in high-direct-current systems to transmit the electric current, and could be used as alternative to Au/Al joint in high-power interconnections and fine-pitch bonding applications due to the very good mechanical, electrical and thermal properties of Cu [1,2]. The oxidation of such alloys can have crucial consequences on the phase properties. We thus want to investigate the first stages of oxidation of copper–aluminum alloys. We need first to study the clean material and understand the Cu–Al interactions. We present here the results of our computations on copper segregation in aluminum. The copper bulk segregation and copper surface segregation are both studied.

During the last two decades several studies on aluminum and its alloys were carried out using first principle calculations. Various bulk phases (perfect phases or in presence of bulk defects) as well as clean Al surfaces were fully investigated. Hoshino et al. [3] showed that the stability of an aluminum based binary alloy Al–M, with a transition metal M, is related to the middle range interactions between the transition atoms, by a strong sp-d hybridization (Al–M). The energy of interaction between two impurities depends strongly on the distance separating them. Using the full potentials Green functions KKR [4,5] for a better description of the crystal defects, they showed that the energy of the copper–copper interaction tends towards 0 eV for $d_{Cu-Cu}>5.5$ Å.

According to the Al/Cu equilibrium phase diagram, at Cu massic concentration lower than 4%, one is in the presence of a solid solution α while the first defined compound is $Al_2Cu-\theta$. Even for low copper concentration, there is a demixion at $T<350$ K and one should thus be in the presence of a two-phase microstructure ($\alpha+\theta$). The formation of the θ phase is also observed at equilibrium when the Cu concentration in the Al matrix is increased. The Cu first precipitates within the bulk into Guinier–Preston-zones [6,7] (GP-zones) and that later transformed to metastable θ' and stable θ phases. Subsequent GP-zones stages are distinguished as GP1- and GP2-zones as they change their structure during annealing. Experimental determination of the atomic structure of the GP-zones is rather difficult owing to

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their small size of few nanometers. The GP-zones were first observed with early X-ray experiments suggesting GP1-zones composed of a single (100) Cu layer and a GP2-zone composed of an ordered platelet of two Cu layers separated by three Al(100) layers in the Al matrix [8,9]. Recent results using high-angle annular detector dark-field (HAADF) techniques and diffuse scattering led to unambiguous results confirming single layer platelet zones of copper atoms at irregular distances from each other as the main constitution of GP1-zones and showed the possibility for the existence of multilayer Cu zones [10,11]. Two-layer copper zones are occasionally seen in Al–Cu alloys [12].

Several theoretical studies are also available for some Cu/Al microstructures such as GP-zones in intermetallic compound [13,14]. Using first principles, Wang et al. [15] studied the formation of Guinier–Preston zones in Al–Cu alloys by investigating the atomic structures and formation enthalpies of layered Al–Cu superlattices. They highlighted a supercell total energy decrease with Cu content rise, equivalent to a reduction of spacing of the copper lattice in the superlattice. They considered that the formation and evolution of GP-zones in Al–Cu alloys can be considered as a process of increasing accumulation of copper atoms by means of local coagulation of Cu platelets. Zhou et al. [1] have calculated the structural, elastic and electronic properties of Al–Cu intermetallics from first principle calculations. They obtained polycrystalline elastic properties from elastic constants. They correlated the calculated anisotropy of elastic properties to the electronic nature of Al–Cu intermetallics, as a high charge density is observed in the core region of the Cu atoms, while the density is lower in the interstitial area. Their observations showed a strong directional bonding between the nearest-neighbor Cu atoms and a weak directional bonding between Cu and Al atoms. Vaithyanathan et al. [16] conducted a multiscale modeling study on the growth of Al_2Cu–θ' phase. Wolverton et al. [17–21] produced many first principle studies on the determination of the structural properties and energetics of some Al–Cu phases. Results obtained from a density functional theory (DFT) [22,23] study of Al_2Cu–θ were in excellent agreement with experimental results, suggesting a good reliability of the calculation methods. Moreover, this study made it possible to highlight the stability of the metastable phase θ' over the stable phase θ at low temperature (T<200 K). The reason for this unexpected stability compared to experimental observations was attributed to a large difference of vibrational entropy of the two polytypes at low temperature.

Experimental techniques have been developed that allow for detailed investigations of surfaces such as Low Energy Electron Diffraction (LEED) [24] and Scanning-Tunneling Microscopy (STM) [25–28]. A necessary condition for a full theoretical interpretation of the results of such experiments is an accurate description of the surface potential and the surface electronic structure [29]. The recent progress in the material sciences has led to the production of surfaces of high purity, and has allowed the design of various structures with desired properties. The understanding of the physicochemical processes of these systems needs a detailed knowledge of the electronic structure of these materials, and in this context surface states play an important role. The ground-state electronic and structural properties of solid surfaces such as the electronic charge density, surface energy, work function or lattice relaxation can now be determined from first principle calculations, inducing a growing interest in accurate theoretical descriptions of the surface properties of solids.

In this paper, Section 2 is a brief description of our computational method. In Section 3 we discuss bulk and clean surface properties. In the first sub-section, we present the results of Al–Cu interactions in bulk phase at different Cu atomic concentrations (0.926%, 1.56% and 3.125%). The calculated negative mixing enthalpies at 0 K, indicate that the alloy will form a solid solution in the absence of any competing ordered phase. The second sub-section is devoted to the clean (111) and (100) Al surfaces. The calculated surface energies are in good agreement with experimental data and other theoretical calculations. Copper segregation at infinite dilution in the (111) and (100) surfaces are studied in Section 4, by the mean of the first, substituting the copper following the (111) plane and then, by the study of the first stage formation of Guinier–Preston zones. In the first sub-sub-section, we discuss the segregation at infinite dilution (1/9 atom of copper in a layer), and then we increase the Cu concentration until a full Cu monolayer in the second sub-section. Cu-doped layers at different Cu concentrations have their geometry and energetics dominated by preferential homoatomic interactions. Finally, we show that Cu clusters in the (100) plane representing the GP-1 zones are more stable when buried one layer under the surface, following the Cu segregation behavior in the (111) plane. There is moreover no tendency to surface segregation of GP-zones at the (100)Al surface.

2. Computational details

All calculations were performed in the framework of DFT with the Vienna *ab initio* simulation package [30–32] (VASP) implementing the projector augmented wave (PAW) method [33,34]. PAW pseudopotentials were defined with ($3s^2 3p^1$) valence electrons for Al and ($3d^{10} 4s^1$) for Cu. For Cu, we checked that it is not necessary to inlcude the $3p$ electrons in the valence shell. Both the local density approximation (LDA) [35] and the generalized gradient approximation (GGA) [36] were used to describe the exchange-correlation energy-functional. For LDA functional, we used the formulation proposed by Ceperlay and Alder [35] and parameterized by Perdew and Zunger [37] while for GGA functional, we used the formulation proposed by Perdew, Burke and Ernzerhof, [38] commonly called PBE. Convergence with respect to cutoff E_{cut}, Methfessel-Paxton [39] smearing σ and size of Monkhorst-Pack [40] mesh of k-points were carefully checked for each model, in order to have the same energy precision in all calculations (less than 1 meV), leading to the following values: $E_{cut}=450$ eV, smearing $\sigma=0.2$ eV. These values, if not otherwise stated, were used in all calculations. The grid of k-points was set to ($15\times15\times15$) for bulk calculations of pure Cu and Al. For other calculations, the used grids of k-points are reported in the corresponding sections. All calculations were done allowing for spin polarization. Atomic positions were relaxed with the conjugate gradient algorithm [41] until forces on moving atoms where less than 0.05 eV/Å.

3. Bulk and surface properties

3.1. Bulk cohesive properties

Bulk fcc Al and Cu were simulated using a primitive trigonal unit cell. Their equilibrium volumes and bulk modulus B_0 were calculated by fitting the total energy of 12 regularly spaced volumes around the

Table 1
Calculated bulk properties for Al and Cu using GGA (LDA) XC functionals in the PAW scheme compared to experimental results and other recent DFT calculations (US = ultrasoft Vanderbilt pseudopotential, PW91 = Perdew Wang 91 XC functional).

Material	Cal. type	a_0 (Å)		B_0 (GPa)		E_c (eV/at.)		Ref.
Al	Experiment	4.05/4.04		76.93/77.30		−3.39/−3.39		[42]/[43]
		LDA	GGA	LDA	GGA	LDA	GGA	
	PAW	3.98	4.04	113.38	67.72	−4.01	−3.43	This work
	US/PW91		4.04		72.05		−3.50	[44]
	All electron		4.04		75.00		−4.07	[45]
	All electron	3.97		80.00		−4.09		[46]
Cu	Experiment	3.61		137.00		−3.49		[42]
		LDA	GGA	LDA	GGA	LDA	GGA	
	PAW	3.52	3.64	185.20	142.00	−4.51	−3.46	This work
	Pseudopotential		3.67		134.00		−3.38	[47]
	Pseudopotential	3.53	3.97	190.00	140.00	−4.75	−3.76	[48]
	All electron	3.52	3.63	192.00	142.00	−4.57	−3.51	[49]