Eur. Phys. J. D **9**, 543–546 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Embedded atom model calculations of the structures of small Ni clusters and of a full Ni monolayer on the (001) surface of Al

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Received: 2 September 1998 / Received in final form: 18 November 1998

Abstract. Using the Voter and Chen embedded-atom model potential for the Ni–Al system, we performed quenched molecular dynamics simulations to obtain the structures and binding energies of small clusters and of a full monolayer of Ni atoms on the Al(001) surface. Our results show that both clusters and the monolayer undergo surface alloying, i.e., there is a tendency for the Ni atoms to be embedded in the substrate, displacing Al atoms from their initial positions. However, whereas the surface alloying of the clusters occurs rapidly, that of the monolayer requires an appreciable prior equilibration period at a temperature allowing atomic mobility; quenching without this equilibration period can freeze the system in a metastable state in which the Ni adlayer remains on an Al surface that is hardly altered. An analogous metastable state may have been achieved in experiments by other authors with ultrathin Ni films.

PACS. 36.40.c Atomic and molecular clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

1 Introduction

In recent years, the study of phenomena involving the interaction of clusters with surfaces has attracted considerable theoretical and experimental attention [1]. In particular, interest has focused on the geometrical structures assumed by the clusters on single-crystal surfaces, which reflect fundamental aspects of adatom–adatom and adatom–substrate interactions and afford insights into the initial stages of crystal growth modes. Certain unusual effects have been observed, such as the surface alloying of metals which are mutually insoluble in the bulk phase [2].

Because of the difficulty of using *ab initio* quantum mechanical methods for studying the properties of supported metal clusters, much of the theoretical work done so far in this area has been based on semiempirical methods, such as the embedded-atom model (EAM) [3–7]. In particular, the Foiles, Baskes, and Daw (FBD) version of the EAM [8], which uses only bulk solid properties in the parameterization of the embedding function and pair interaction (the two contributions to the EAM expression for the energy), has been widely used. Schwoebel *et al.* [3] have used the FBD EAM to analyze the structures of small Pt clusters on the Pt(001) surface, Wright *et al.* have used it [4] to investigate the structures and energies of Ni, Pd, and Pt clusters on Pt(001), and Roy *et al.* have used it [6] to interpret the structural features of Pd and Pt clusters on Ag(110). Theoretical predictions obtained with the FBD EAM are generally in good agreement with experimental results (for instance, the calculations of Schwoebel *et al.* for Pt clusters on Pt(001) agreed with field electron microscopy findings in predicting that clusters oscillate between chain and island-type configurations as the number of adatoms is increased from three to six [3]); this reflects the reliability of the FBD EAM for describing, at least qualitatively, phenomena not included in the construction of the potentials.

In a recent EAM-based computer simulation study of Ni clusters on Ni surfaces, we have shown that the kind of empirical data used in the parameterization of the EAM potential has a strong influence on computed binding energies and other cluster properties [9]. For instance, the melting temperature of the particularly stable seven-atom Ni cluster on the Ni(111) surface, as computed using the FBD EAM, is about 20% smaller than the value obtained using the Voter and Chen (VC) EAM version [10]. The VC EAM version differs from the FBD approach in two main ways: (a) the core–core pair interaction has a medium-range attractive contribution (rather than being entirely repulsive); (b) properties of the diatomic molecule as well as bulk properties are used for parameterizing the embedding function and pair interaction. In spite of the good general agreement between theory and experiment in the above-mentioned FBD EAM-based studies of supported metal clusters, the inclusion of the properties of the diatomic molecule among the data to which the VC EAM potential is fitted makes the VC approach more accurate than the FBD version for studying the properties of small clusters of metal atoms, as has been shown by comparison of FBD and VC EAM-based results on the structures and binding energies of free clusters of fcc transition metals with those derived from *ab initio* calculations [11].

This paper describes a VC EAM computer simulation study of the structures of Ni formations on the Al(001) surface. The choice of this system was not arbitrary; the considerable amount of experimental data on Ni–Al alloys allowed Voter and Chen [10] to construct a potential that is capable of describing pure Ni (fcc), pure Al (fcc), diatomic Ni_2, diatomic Al_2, Ni_3Al ($L1_2$), and NiAl ($B2$), and it is reasonable to hope that this potential may also give a satisfactory description of the properties of Ni clusters on Al surfaces. In fact, the VC EAM Ni–Al potential, which we have recently used to determine the ground-state atomic configurations of free Ni–Al clusters [12], has been employed by Shutthanandan *et al.* [13] in Monte Carlo simulations to interpret their experiments on the reaction of thin Ni films with Al(110) surfaces, which show that for low Ni coverage (up to the equivalent of 8.1 monolayers) there occurs a surface alloying process in which the Ni atoms intermix with and displace Al substrate atoms. In this paper we analyze the structures of both small Ni clusters and a full Ni monolayer on Al(001), and compare our results for the latter with those obtained by Shutthanandan *et al.* [13] for the rougher Al(110) surface.

The organization of this paper is as follows. In Sect. 2, we describe the simulation procedure used to compute the structures and binding energies of small Ni_n clusters (up to $n = 10$) and of a full Ni monolayer on Al(001), and we discuss the results obtained. In Sect. 3, we summarize our main conclusions. The VC EAM potential for the Ni–Al system used in this work has been described in detail in [10], and will not be explained here.

2 Computational procedure, results, and discussion

The Al(001) surface was modeled by the top (001) layer of a 15-layer slab of atoms, with the bottom 4 layers fixed, and periodic boundary conditions along the [100] and [010] directions. The slab comprised 6750 atoms, and its free surface 15 × 15 square unit cells (in additional calculations using a 7680-atom slab with a (16 × 16)-cell surface, computed cluster binding energies were within 0.2 meV of the 6750-atom results). The atoms in the slab were initially arranged as in bulk Al, but before addition of Ni adatoms the top 11 layers were relaxed to the minimum energy configuration by the use of a conjugated gradient procedure [14]. This preadsorption relaxation reduced the top interlayer distance by 2.78%, a figure much smaller than the 10.36% obtained by Chen *et al.* [15], likewise using the VC EAM potential for Al, for the Al(110) surface. The binding energy E_b of an n-adatom cluster (i.e., the energy required to dissociate it into isolated adatoms) was computed as

$$E_\mathrm{b}(n) = (E_\mathrm{cs} - E_\mathrm{s}) - n(E_\mathrm{as} - E_\mathrm{s}) \qquad (1)$$

where E_cs is the total energy of the slab plus the adatom cluster, E_s is the energy of the slab alone, and E_as is the total energy of the slab with one adatom.

As in our work on Ni clusters on the Ni(001) surface [9], the lowest-energy structures of Ni_n clusters on Al(001) were computed by the choice of various initial configurations for each value of n and, for each configuration, the calculation of the minimum energy of the cluster+substrate system using a quenched molecular dynamics minimization technique [16]. Specifically, four kinds of initial configuration were chosen: linear chains oriented along the [110] direction (l), and angular (a), island (i), and three-dimensional (t) arrangements (the latter only for $n > 4$). In these calculations, the atoms of one- and two-dimensional structures, and the bottom-layer atoms of three-dimensional ones, were initially placed a distance $a/2$ above the fourfold sites of the relaxed Al(001) surface, where $a = 4.05$ Å is the bulk lattice constant of Al [17].

In the upper panel of Fig. 1, we show the predicted lowest-energy structures of Ni clusters on Al(001), and in the lower panel the corresponding starting geometries before optimization of the cluster+substrate system. In general, there is a tendency for some or all of the Ni atoms of the cluster to become embedded in the substrate, displacing Al surface atoms from their initial positions, instead of remaining on top of the slab at fourfold adsorption sites (the energies of adsorbed and substitutional Ni structures could be compared, within the framework of the VC EAM, using the ideas of Neugebauer and Scheffler [2], but this possibility has not be explored here).

The surface alloying tendency noted above, which parallels the behavior of the Ni/Al(110) system that was observed and discussed by Shutthanandan *et al.* [13], is consistent with the fact that Al has a lower surface energy than Ni [18] and with the strong compound-forming tendency of bulk Ni–Al alloy [19]. However, when the Al(001) surface was covered with a full monolayer of Ni atoms (computed binding energy −154.396 eV), our quenched molecular dynamics calculations showed no significant embedding of Ni. Although this prediction appears to be in keeping with Shutthanandan *et al.* [20] experimental results on the growth of ultrathin Ni films on the Al(001) surface, it contrasts strongly with the surface alloying observed when the Al(110) surface is covered by the equivalent of up to 8.1 Ni monolayers [13,21]. In principle, this difference could be attributed to Al(110) being a more open surface than Al(001) and to its having a higher surface energy [22], two factors which both favor mixing between the Ni and Al atoms. However, to check whether the Ni adlayer on the Al(001) surface was in a metastable state, i.e., whether the quenched molecular dynamics simulation had got trapped in a local minimum of the energy, we performed a standard constant energy molecular dynamics simulation, assigning a room temperature ($T = 300$ K) Maxwell distribution to the atomic velocities of the Al(001) substrate+Ni adlayer system, and then allowing the system to equilibrate over 70 ps. At this point, the Ni layer was practically embedded in the Al substrate. Subsequent quenching showed that at $T = 0$ K, the energy of the embedded state was lower than that of the

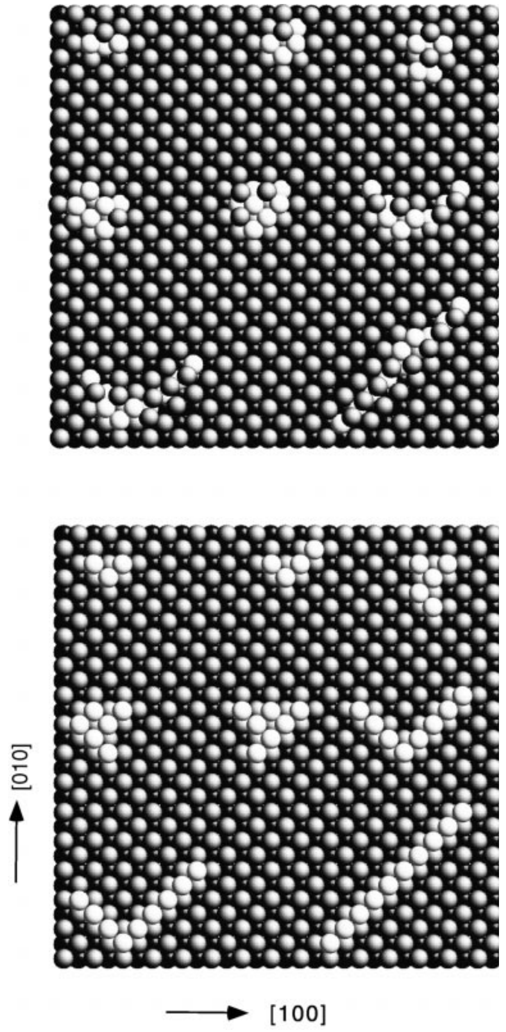

Fig. 1. Predicted minimum energy configurations of Ni_n clusters on Al(001) (upper panel) and the corresponding starting geometries before relaxing the cluster+substrate system (lower panel).

state identified previously, which accordingly is indeed a metastable state.

Figure 2a shows the calculated binding energies of Ni_n clusters on the Al(001) surface for the four types of initial configuration considered (for a, i, and t arrangements, data are only shown for the minimum energy structure found for each n). It is worth noting that the computed cluster binding energies are quite different from those obtained if the initially relaxed Al(001) substrate is allowed to relax no further after deposition of the Ni clusters (for brevity, the results of these calculations are not shown here). This contrasts with the behavior of the Ni_n/Ni(001) system, for which substrate relaxation makes a negligible contribution to cluster binding energies [9]. This difference between Ni_n/Al(001) and Ni_n/Ni(001) is attributable to the relaxation energies (defined as the differences between the total energies E_{cs} calculated for the relaxed and frozen substrates) being much higher for Ni_n/Al(001) (Fig. 2b) than for Ni_n/Ni(001) [9].

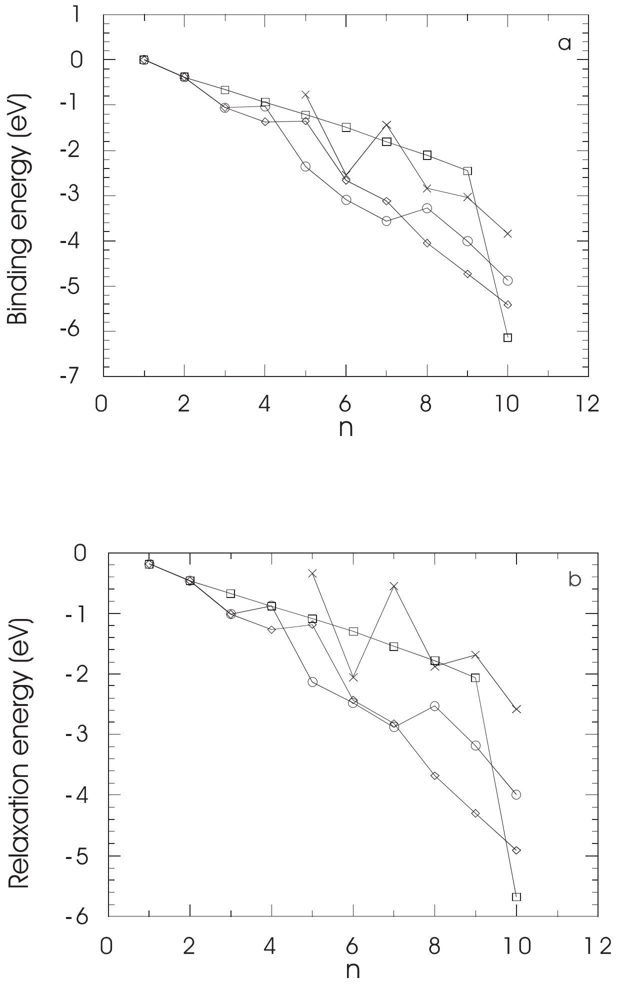

Fig. 2. Panel (a): computed binding energies of the initial linear (squares), three-dimensional (crosses), island (dots), and angular (diamonds) clusters. Panel (b): computed relaxation energies for the same configurations as in panel (a).

3 Summary and conclusions

In this work we used the VC EAM Ni–Al potential, in conjunction with quenched molecular dynamics simulations, to compute the structures and binding energies of small clusters and of a full monolayer of Ni atoms on the Al(001) surface. Our results show that both clusters and the monolayer undergo surface alloying, i.e., there is a tendency for the Ni atoms to be embedded in the substrate, displacing Al atoms from their initial positions. However, whereas the surface alloying of the clusters occurs rapidly, that of the monolayer requires an appreciable prior equilibration period at a temperature allowing atomic mobility; quenching without this equilibration period can freeze the system in a metastable state in which the Ni adlayer remains on an Al surface that is hardly altered. An analogous metastable state may have been achieved in the experiments of Shutthanandan *et al.* with ultrathin Ni films on the Al(001) surface [20].

In contrast with the behavior of Ni_n/Ni(001) [9], substrate relaxation significantly affects the binding energies and structures of Ni_n clusters on the Al(001) surface.

This work was supported by the DGICYT, Spain (Project No. PB95-0720-C02-02) and the Xunta de Galicia (Project No. XUGA20606B96). We are grateful to an anonymous referee of the first version of this paper for helpful suggestions.

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