# Atomic-scale modeling of cluster-assembled $Ni_xAl_{1-x}$ thin films

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Thermodynamic and structural properties of Ni-Al cluster assembled materials are investigated at the atomic scale. Model predictions are available for elemental systems but the field of bimetallic nanostructured systems remains close to unexplored. The aim of the present work is to model at the atomic scale the structural and segregation properties in the Ni<sub>x</sub>Al<sub>1-x</sub> bimetallic cluster assembled materials that are synthesized in two different ways. In the first, isolated clusters are compacted at high pressure. We consider the  $L1_2$  and B2phases of the initial free clusters. Compaction of clusters at thermodynamic equilibrium is modeled by classical molecular dynamics combining isobaric and isothermal schemes. After compaction, interface segregation is computed by Metropolis Monte Carlo importance sampling in the semigrand canonical ensemble. After this model treatment, clusters are found to keep their identity, and their structural and segregation states do not differ much from those in the initial free clusters. The cluster cores keep the stable bulk phases while segregation may take place at the interfaces. The second method is low-energy cluster beam deposition. Cluster impact is found to influence chemical and structural order in the films formed. This is shown and discussed on the example of  $L1_2$  cluster deposition. Molecular dynamics is used therefore, which accounts for electronphonon coupling in the equations of motion. The slowing down of a single cluster is examined in detail. It is found that the expitaxial accommodation of the cluster with the substrate and chemical order in the cluster depend on the mechanical properties of the substrate material. Competition between chemical order and epitaxy is observed. The harder the material, the higher the epitaxy and the lower the chemical order. The cluster impact induces significant chemical disorder but the clusters forming the cluster assembled film keep their initial identities. Similarly to the sample obtained by compaction, this one displays partial structural and chemical order at its interfaces. The film density is particularly low and the open volumes form a fully interconnected network of pores.

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### I. INTRODUCTION

Properties of metallic nanostructured materials (NM's), formed by structural elements of a few nanometer size, is quite broad and may strongly deviate from those of single crystal or amorphous solids with the same composition. These properties range over magnetism, optics, electronic transport, thermodynamics, and mechanics. The range of known nanostructures in metallic systems is quite broad as well. Whatever zero-dimensional-like quantum dots, onedimensional-like cluster arrays, two-dimensional-like multilayers, or three -dimensional-like nanocrystalline solids, they are stimulating a high level of interest, both applied and fundamental. Mechanical deformation properties of NM's depend on the nanostructure and may be quite peculiar. Superplasticity, for instance, has been evidenced in metals and alloys at low temperatures.<sup>1</sup> In the bulk coarse-grained polycrystalline materials the plastic deformations results to a large extent from dislocation activity and grain boundary

junctions instability. However, in NM's, when the grain size is typically less than 500 nm, due to large intergranular volume as compared to polycrystals, the role of interfaces may be of primary importance. Superplasticity should be expected when the rate of dislocation emission from interfaces equals the rate of absorption by interfaces. If we consider NM, with grain sizes smaller than about 10 nm, no significant dislocation activity is expected and the role of interfaces and interface junctions in mechanical properties may become dominant. Several mechanisms (such as GB sliding, grain rotation, interfacial viscosity, etc.) have been discussed.<sup>2</sup> As multicomponent NM's are concerned, additional phenomena (such as inhomogeneous distributions of components due to segregation) may be responsible for specific properties of the interfaces. Because of the lack of periodicity, the accurate experimental characterization of NM's is unfortunately an arduous task. For instance, high resolution transmission electron microscopy (HRTEM) requires very thin films and the influence of surfaces on observed properties may be significant. In addition some damage is possible during sample preparation. Positron lifetime spectroscopy (PLS) has a poor resolution in case of groups of more then a few point defects. Surface tunneling microscopy and atomic force microscopy only provide information about surfaces. Studying deformation mechanisms at the nanoscale experimentally is particularly difficult and, to our knowledge, no experimental technique is yet available for characterizing thermodynamic interface phases in nanograins. Therefore, atomic scale modeling represents a useful method for predictions beyond the limit of presently available experimental capabilities. The effort achieved in this direction is quite substantial.<sup>3–11</sup> In addition, atomic scale modeling has often been combined to experiment in order to characterize nanostructures quite efficiently.<sup>12–22</sup>

One class of nanostructured solids is obtained by assembling clusters. Many properties of cluster assembled materials are still not well known. Although such materials can be synthesized in different ways for more than two decades, their systematic fundamental study is quite recent. The present work focuses on their study.

As far as atomic scale modeling of metals is concerned, simple cohesion models<sup>23–25</sup> nowadays allow studying systems formed by several millions of atoms over times of the order of the nanosecond. As a consequence, atomic scale approaches can be used to model several real systems at the one to one scale. In such a way, nanograin interface configurations can be modeled,<sup>7,26</sup> cross checked with experimental measures,<sup>21</sup> and correlated with measurable mechanical properties.<sup>27,28</sup>

Simulated NM's may be constructed in different ways mimicking different experimental preparation methods. Two basic groups of NM preparation techniques may be mentioned: one-step and two-step methods. One-step methods (as electrodeposition or severe plastic deformation) result in dense compact materials. The atomic scale structure of such materials is modeled, for instance, by Voronoi constructions, starting from seeds randomly distributed and oriented in space (see, for instance Ref. 26). Nanostructured solids can also be synthesized in two steps as by inert gas condensation followed by compaction or nanocluster synthesis followed by low energy cluster beam deposition (LECBD)]. Produced in such ways, they contain voids and may have significantly lower densities than polycrystalline or single crystal solids. The atomic scale modeling of such materials can also be achieved (for, instance, the synthesis of NM films by LECBD is modeled in (Refs. 17 and 18). The formation of cluster assembled layers by cluster slowing down at various energies was first predicted by molecular dynamics simulations in Ref. 5. However, the sensitivity of the obtained NM models on the synthesis methods still needs thorough investigation, and an important question is thus the relation between the synthesis method, the nanostructure and the properties of the materials obtained. The purpose of the present paper is to make one step in this direction. The question addressed is to predict the relation between the properties of free clusters and the nanostructured material after processing. We focus on bimetallic systems. Two methods are considered for synthesising a nanostructured material, namely, assembling clusters by cluster compaction (CC) and by LECBD on a metallic single crystal surface. With the former, it will be possible to discuss the relation between the surface segregation state in a free cluster and the interface segregation in a nanostructured film. With the latter, it will be possible to discuss the influence of the cluster deposition on long- and short-range order.

Clusters used for compaction and for low-energy cluster beam deposition are of ideal size to be studied at the atomic scale, as well as solid films formed by such clusters. Indeed, they do not contain more than a few hundred to a few thousand atoms each. As a result, less than one hundred thousand atoms are sufficient to model a thin film and its surface realistically.<sup>5</sup> In a previous work,<sup>17</sup> the deposition of gold clusters on Au(111) was modeled by molecular dynamics (MD), using similar cluster size distributions and incident kinetic energies as in real LECBD experiments.<sup>18</sup> The problem with MD is that the method does not allow modeling the long term evolution of a system and, for instance, cluster diffusion on a surface and segregation at a surface or an interface cannot be predicted. However, it was observed experimentally that gold clusters deposited on a gold (111) surface are not diffusing.<sup>18</sup> Hence, the film growth takes place as deposition proceeds by stacking of clusters only. Therefore, the modeled film agreed very well with STM observations on real samples, and the modeling was even useful to evaluate the influence of experimental conditions on the film nanostructure. Segregation is a too slow process to be accounted for by MD and an alternative is necessary. Metropolis Monte Carlo importance sampling (MMC) was found to be well suited therefore, in combination with MD. It is currently applied to several systems.<sup>29,30</sup> Combining MC and MD is motivated by the previous success in modeling cluster beam deposition  $^{17,31,32}$  and by questions raised in a first study with intermetallic Cu-Au clusters.<sup>19</sup> Bulk Cu<sub>3</sub>Au displays the same  $L1_2$  structure as Ni<sub>3</sub>Al at room temperature and undergoes an order-disorder first order phase transition at T = 663 K. This is confirmed by atomic scale modeling.<sup>33</sup> HR-TEM demonstrates that nanoclusters are disordered at room temperature, while atomic scale modeling predicts a smooth order-disorder phase transition.<sup>19</sup> On the one hand, specific work is in progress to understand this apparent discrepancy, and on the other hand, the study of deposited Ni<sub>3</sub>Al clusters started, for which system, no order-disorder transition is expected below the melting temperature. The line which will be followed in the present paper is first to briefly remind the reader of the thermodynamic properties of free  $Ni_{1-r}Al_r$ clusters containing no more than a couple of thousand atoms. These properties will then be compared to those of a CC material synthesised with these clusters in a second step and special emphasis will be put on the nanostructure and the segregation state. In a third step, the effect of cluster impact on the nanostructure and on disordering in the LECBD regime will be considered on the example of Ni<sub>3</sub>Al.

The present paper is organized as follows. Section II briefly describes the cohesion model and the simulation methods used. Section III describes the simulation techniques for preparing initial clusters, to model cluster compaction, the single cluster slowing down and the low energy cluster beam deposition. Section IV is devoted to the characterization of samples prepared by cluster compaction. Section V describes the simulation results of single cluster deposition. Section VI is devoted to characterization of films synthesised by LECBD. The main results are summarized in Sec. VII.

### II. ATOMIC SCALE INTERACTION MODEL AND SIMULATION METHODS

#### A. The interatomic potential

The basic parameter in any classical atomic scale model is the interatomic potential describing the interaction between atoms. Many-body potentials based on two different models are currently used for modeling metals. One is the so-called embedded atom model (EAM) Refs. (24,34, and 35) based on the local density-functional theory. The second is based on the second moment approximation of the electronic density distribution<sup>23,25</sup> as derived from the tight-binding (TB) theory for transition metals. Both models may be expressed by similar mathematical expressions, namely, a combination of many-body noncumulative contributions and a sum of pairwise contributions. According to these models, the cohesive energy projected onto one atom can be written as

$$E_i = F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \varphi(r_{ij}), \qquad (1)$$

where  $F(\rho_i)$  is a function of the electronic density  $\rho_i$  at site *i* and  $\varphi(r_{ij})$  is the repulsive energy between atoms *i* and *j* separated by the distance  $r_{ij}$ . The electronic density at the site *i* is expressed as a functional of pairwise contributions. It may be written as

$$\rho_i = f\left(\sum_{j \neq i}^N \Phi(r_{ij})\right). \tag{2}$$

In the second moment TB approximation, this functional is a square root. The total cohesive energy of the system is

$$E_T = \sum_{i=1}^{N} E_i \,. \tag{3}$$

In the present work, for modeling Ni-Al systems, we select the expression based on the second moment TB approximation suggested in Refs. 36 and 37. In this expression  $\varphi(r_{ii})$  and  $\Phi(r_{ii})$  are approximated by a set of cubic splines which parameters are used to fit the potential to the cohesive energy, the equilibrium condition and the elastic constants. A cutoff distance equal to 1.225a0, where a0 is the lattice parameter, limits the range of the local interactions. This is the same potential as was used in the study isolated Ni-Al clusters presented in Ref. 30. This method was successfully applied to describe the properties of ordered Ni-Al (Ref. 38) and Cu-Au (Ref. 33) alloys. In order to select the best suitable parameters for the potential to study Ni-Al alloys, several calculations of basic properties of pure Ni and Al fcc metals as well as of the Ni<sub>3</sub>Al alloy were achieved. The parameters suggested in Ref. 38 allow an excellent prediction of the elastic constants of  $Ni_3Al$  as well as of the cohesive energy and of the equilibrium lattice parameter of  $Ni_3Al$ . These were used in the present work.

### B. The atomic scale models

The MMC method is widely used for studying the thermodynamic equilibrium properties of liquids and solids. In the present work the MMC method is used for modeling clusters at equilibrium before deposition and segregation after cluster assembling by compaction. The general MMC method is described in detail elsewhere.<sup>39</sup> Here we employ the so-called semi-grand-canonical ensemble ( $\Delta \mu \text{NPT}$ ).<sup>40</sup> In this approach the total number of the particles [N=N(AI)]+N(Ni)], the temperature (T), pressure (P), and the chemical potential difference  $[\Delta \mu = \mu(Al) - \mu(Ni)]$  are fixed while the number of atoms of each kind [N(AI), N(Ni)] may be changed. The Metropolis importance sampling scheme includes three types of trial. (i) Random displacement of each atom of the model box from its current position. (ii) Random selection of the chemical identity of an atom, accounting for the fixed chemical potential difference  $\Delta \mu$  between the two species. (iii) Random site exchange between two chemically different atoms.

One set of these three trials applied to all atoms in the system is called a macrostep. In order to account for volume fluctuations at constant pressure, after several macrosteps, the box size in one of three randomly selected orthogonal directions is changed at random as well. More detail about this algorithm is given in Ref. 30.

Similar algorithms proved to be efficient in the study of segregation at surfaces<sup>40</sup> and interfaces.<sup>33,41-44</sup> As will be shown below, it is efficient as well in the study of segregation at interfaces in nanostructured materials.

As far as molecular dynamics is concerned, in its simplest form, it merely consists in numerically solving a system of coupled Newton equations of motion in the microcanonical (NVE) statistical ensemble for the particles contained in the simulated box.<sup>39</sup> In systems such as nanostructured materials, which are characterized by deep inhomogeneities, it is possible to account for the dynamics of the macroscopic deformation of the simulation box, at constant external pressure and temperature. This is achieved in the canonical ensemble according to the constrained MD scheme introduced by Rahman and Parinello (RP-MD).<sup>45,46</sup> The dynamics of the exchange of energy with the external reservoir at constant temperature is monitored according to method of Nosé.<sup>47</sup> The number of degrees of freedom is then extended from 6N to 6N+10, where N is the number of particles. The particle Cartesian coordinates as well as these additional degrees of freedom evolve according to equations of motion derived from an appropriate Lagrangian.<sup>45</sup> In the present study we only allow orthogonal macroscopic changes of the model box in order to warrant consistency with the MMC simulation model. When a cluster slows down on a surface, it is necessary to account for the dynamic exchange of energy between the ionic and the electronic systems, which is responsible for a large part of the energy dissipation after the cluster impact. In the present work, the approach suggested in Ref. 48 is used, which accounts for the electron-phonon coupling on the basis of the Sommerfeld theory of metals. In this approach, a velocity dependent force  $\mathbf{F}_i = -\mu \mathbf{v}_i$  describes the electron-phonon energy exchange through small electron-atom transfers. Taking this force into account, the equation of motion of atom *i* can be written as

$$\frac{d^2 \mathbf{r}_i}{dt^2} = \frac{1}{m_i} \nabla_{\! r_i} E_T - \mu \mathbf{v}_i, \qquad (4)$$

where  $\mu = \alpha (T_i - T_e)/T_i$ ,  $\alpha$  is the inverse of the characteristic coupling time, and  $T_i$  and  $T_e$  are the temperatures of the atoms and electrons, respectively. It can be shown<sup>17</sup> that the inverse of the electron-phonon coupling time can be estimated as

$$\alpha = \frac{\Theta_D T_e \mathcal{L} n e^2 k_B Z}{2m_e \kappa \epsilon_E},\tag{5}$$

where  $\Theta_D$  is the Debye temperature,  $k_B$  is the Boltzmann constant,  $\mathcal{L}$  is the Lorentz number, *n* is the electronic density, Z is the valence,  $\kappa$  is the thermal conductivity,  $\epsilon_F$  is the Fermi energy, and e and  $m_e$  the electron charge and mass, respectively. According to Eq. (5) and using the experimental values of the Lorentz number and thermal conductivity, the electron-phonon coupling time  $\tau = 1/\alpha$  at room temperature can be estimated as 1.0 ps for pure Ni and 1.7 ps for pure Al, respectively. The coupling time in a bimetallic system depends on the local environment. In principle, it thus cannot be derived directly from Eq. (5). However, since its value in pure Ni and pure Al are close to each other at room temperature, in what follows, it is approximated locally as the weighted average (with respect to atomic concentrations) of the elemental values. Equation (4) is integrated numerically using the scheme proposed in Ref. 49. The force evaluation makes use of the third Newtons law and Verlet neighbor lists combined with a linked cells algorithm (see, for instance Refs. 39 and 50).

#### **III. PREPARATION OF MODEL NANOSAMPLES**

#### A. Isolated clusters

The sequence to set up the initial slowing down conditions is as follows. Initial clusters are prepared as described in Ref. 30. Each cluster is obtained by cutting a sphere with a given radius in a perfect geometrical Ni<sub>3</sub>Al crystal. Then, in order to account for possible segregation, the chemical potential difference is fixed at  $\Delta \mu = 0$  eV, which corresponds to the stable  $L1_2$  phase in the bulk Ni<sub>3</sub>Al material. MMC sampling is used to predict the equilibrium atomic configuration of the cluster at room temperature. Next, the atomic velocities in the center of mass system of the cluster are determined by MD. To this purpose, atoms are first slightly and randomly displaced from their static equilibrium positions. Velocities are then gradually rescaled until the system finds a thermal equilibrium state at 300 K. By this method, the thermal excitation is distributed among vibrational modes only and the angular momentum of the cluster is kept equal to zero, making the definition of the tempera-



FIG. 1. Calculated equilibrium concentration of Al  $x_{Al}$  as a function of the chemical potential difference between nickel and aluminum at zero pressure. The results are shown for an isolated cluster that contains 959 atoms at room temperature. The function is represented for the whole cluster and for its core only.

ture equivalent in a cluster and in a bulk material. The rotational temperature of slowing down clusters in a LECBD experiment is not known and is not expected to have a substantial influence on deposition. The structural and thermodynamic properties of free  $Ni_{1-r}Al_r$  clusters were already studied in Ref. 30 and they are thus only briefly summarized in this section. In the present work, we focus on the clusters containing no more than several thousands atoms in order to prevent dislocation activity in the process of cluster compaction. Figure 1 represents the Al concentration as a function of the chemical potential difference predicted by MMC at 300 K, for a free cluster of 959 atoms. The dependence found is not quite sensitive on the temperature in this range. Results are displayed for the whole cluster and for its core only. At nonzero temperature, the cluster cores may adopt the  $L1_2$ and B2 stable structures, depending upon the stoechiometry driven by the chemical potential difference. For each equilibrium phase, a disordered mantle in which Al segregation arises may surround the core. A solid solution may thus take place in the mantle, which always coexists with a stable phase in the core. The relative thickness of the disordered mantle is not much cluster size dependent as far as the cluster contains more than about 1000 atoms. In contrast with the bulk material, no  $L1_0$  metastable phase is found to take place in nanoclusters where the offset from stoechiometry is systematically taken over by surface segregation, leaving the core in the stable B2 phase.

### B. Synthesis of model nanostructured samples by cluster compaction

A limited number of different clusters is considered for modeling cluster assembled materials within a realistic cluster size distribution. Whatever the experimental techniques, this distribution is close to follow a log-normal law. Therefore, model NM's are synthesized with clusters which sizes are distributed according to a log-normal law as well. The mean number of atoms per cluster is 7000 and the mean cluster diameter is 5.2 nm. The free clusters prepared at 300 K as described above are stacked at random in an imaginary orthogonal box, leaving some separation between their surfaces of no more than about one lattice unit. Periodic boundary conditions are applied to this simulation box. Once filled with clusters, it contains about  $10^5$  atoms. The system is then ready for compaction by means of a Rahman Parinello MD simulation. An external pressure of 2 GPa is reached at 300 K by three steps. In the first, no pressure is applied and the system freely evolves during 50 ps, which is sufficient to reach interfacial accommodation. A pressure of 1 GPa is then applied for another 40 ps and finally, a pressure of 2 GPa is applied during 40 ps again. At each intermediate step, 10 to 20 ps evolution was sufficient to reach thermal equilibrium. The time to bring the system to 2 GPa and thermal equilibrium by this method is about 14 to 15 orders of magnitude shorter than in a real compaction experiment. In particular, processes resulting from thermal diffusion are not accounted for. This is the reason why a MMC simulation follows the MD compaction, using the same scheme as for free clusters, though applying suitable periodic boundary conditions. This simulation is done at room temperature, letting the system relax to zero pressure. Four assembled nanosamples were modeled this way. Two B2 samples were prepared by assembling isolated clusters designed, fixing the chemical potential difference at  $\Delta \mu = 1.6 \text{ eV}$  and  $\Delta \mu = 1.0 \text{ eV}$ , respectively, that is, with and without segregation in the mantles (see Fig. 1) now forming interfaces. Two  $L1_2$  samples were prepared, starting from isolated clusters with  $\Delta \mu = 0.6 \text{ eV}$  and  $\Delta \mu$ =0.0 eV respectively, also with and without segregation in the cluster mantles. The atomic density of the NM samples prepared this way, relative to the bulk material is typically 88% at 2 GP and room temperature, independently of the segregation state. No trend for grain coalescence was observed during the compaction procedure and disordered area were essentially found at the interfaces. The question now arises of how to characterize the possible modifications of the segregation state which might result from the assembling. The MMC was applied therefore to the whole assembled samples similarly and with the same values of the chemical potential differences as were used for preparing isolated cluster. The external pressure was set to zero and the temperature was still 300 K. This way, the thermodynamic conditions were the same as for preparing the free clusters. Only limited further relaxation of the boxes was observed and, as was found for planar interfaces in the work quoted above, overall nanostructured interface configurations were unchanged with the MMC algorithm employed. The atomic density after relaxation at zero pressure is 87.5% and this value does not depend on the segregation state. Typical slabs in the NM boxes obtained are displayed in Fig. 2, showing that clusters may be deformed and are separated by both pores and grain boundaries. They keep their identity and their structure.

### C. Simulation of single cluster deposition

Three substrates were modeled as fcc Ni and Al and  $L1_2Ni_3Al$ . In the geometry used, the free surfaces have a (111) orientation. Periodic boundary conditions were applied



FIG. 2. Slabs of a few atomic layers thick in assembled samples at the end of the MMC simulation. Dark spheres represent aluminum and light ones represent nickel atoms. (a)  $\Delta \mu = 1.6$  eV and the structure is *B*2; (b)  $\Delta \mu = 0.6$  eV and the structure is *L*1<sub>2</sub>.

to the two orthogonal directions  $[\overline{1}10]$  and  $[11\overline{2}]$  parallel to the free surfaces. Substrates were brought to thermal equilibrium, independently of the cluster, using the electron-phonon coupling model in Eq. (7). Initially, the cluster was positioned at a distance from the substrate, which is just sufficient for the cluster atoms closest to the surface to interact with surface atoms. For the investigation of single cluster slowing down, the case study of a cluster consisting of 369 atoms (81 of Al and of 288 Ni) was used. Before starting the dynamics of the cluster-surface interaction, the cluster was rotated at random around its center-of-mass and directional correlations between the cluster and the surface initial orientations were avoided. The impact (translation) energies of the clusters were selected as 0.5, 1, and 1.5 eV per atom. This way, the energy range typical of low energy cluster beam deposition<sup>51</sup> is covered. The evolution of the system was followed during 150 ps. This period is much longer than the impact itself and the electron-phonon characteristic coupling time (a few picoseconds). When an energetic cluster is impacting on a solid surface, an elastic shock is known to be generated, which needs to be damped in a finite simulation box in order to avoid possible artifacts. Since slowing down energies are low in the LECBD regime (a fraction of an eV per atom), the problem is not crucial. In the present simulations, an additional coupling force expressed by Eq. (4) was applied to the bottom of the substrate, with a very short coupling constant. This force was switched off shortly after the shock can reach the bottom of the simulation box. The box size was checked to be large enough to prevent any significant size effect on the dynamics of deposition.

In order to characterize the evolution of the system during deposition and atomic configurations after deposition, one makes use of a long-range order parameter denoted  $S(\mathbf{k})$ , a short-range order parameter denoted  $\eta(AI)$ , a density function denoted  $\rho(r)$ , and a pair correlation function denoted g(r). Order parameters are useful to investigate the evolution of the structure, as well as the impact induced damage in the cluster and the level of epitaxy between the cluster and the substrate. Epitaxy is characterized by means of the long-range order (LRO) parameter. In the present work, a structure factor is defined as

$$S(\mathbf{k}) = \frac{1}{N} \sum_{i=1}^{N} e^{ikr}, \qquad (6)$$

where N is the number of atoms in the system (cluster or substrate), **k** is a wave vector defined by **k** = $(4\pi/a)(n_x, n_y, n_z)$ , where *a* is the lattice parameter in the system.  $(n_x, n_y, n_z)$  are the Miller indices of substrate crystallographic directions. The value of  $|S(\mathbf{k})|^2$  measured in the cluster depends on two contributions: thermal vibrations and epitaxy. In order to distinguish the former from the latter,  $|S(\mathbf{k})|^2$  is normalized to the structure factor in the initial free cluster taken at the same temperature and with the same orientation as the substrate. This way, the epitaxial contribution is singled out. Indeed, with such a definition  $|S(\mathbf{k})|^2$  measured in the cluster and, independently, in the substrate, are equal if the cluster is fully epitaxial. It is equal to zero if the cluster is totally disordered or its orientation is uncorrelated with the substrate orientation. To study short-range order (SRO) in the Ni<sub>3</sub>Al clusters we use the following parameter:

$$\eta(\mathrm{Al}) = \frac{N^{\mathrm{Ni}}(\mathrm{Al})}{N^{\mathrm{tot}}(\mathrm{Al})},\tag{7}$$

where  $N^{\text{Ni}}(\text{AI})$  is the average number of nickel first neighbors of the Al atoms.  $N^{\text{tot}}(\text{AI})$  is the average number of first neighbors of the Al atoms, irrespective to their chemical nature. This definition of  $\eta(\text{AI})$  is independent of the coordinance and it is thus free of spurious surface effects. When  $\eta(\text{AI})$  is calculated for the cluster, only the cluster atoms are considered as neighbors in the estimate of  $\eta(\text{AI})$ . Since clusters may be highly strained, first neighbor distances cannot be assumed constant. For this reason, we consider as first neighbors of a given atom all those that are closer than the arithmetic mean distance between first and second neighbors in the bulk of an infinite perfect crystal. In a perfect  $L1_2$  Ni<sub>3</sub>Al cluster,  $\eta(\text{AI})=1$  while it is equal to the Ni concentration in case of full chemical disorder [ $\eta(\text{AI})=0.75$ ].

#### D. Synthesis of model nanostructured films by LECBD

The simulation of nanostructured film growth by cluster beam deposition was done by the same classical MD scheme as for modeling the deposition of a single cluster. The initial conditions were selected in such a way as to model a realistic experiment. In this respect, boxes of elemental Al and Ni



FIG. 3. Time evolution of the SRO parameter  $\eta$ (Al) for the whole film and for selected clusters during deposition on a Ni surface with 1.25 eV/at. energy.

consisting of 24192 atoms were used as model substrates. Their size was about  $22 \times 22 \times 12$  lattice units. The orientation and boundary conditions were the same as in the case of single cluster deposition. The Ni<sub>3</sub>Al clusters of five different sizes were used in simulations. The clusters contain 201 (144 of Ni and 57 of Al), 321 (239 and 82), 555 (408 and 147), 959 (708 and 251), and 2315 (1728 and 587) atoms, respectively. The deposition temperature was 300 K. The incident cluster sizes were sampled at random according to a lognormal distribution function, which is typical of experimental conditions. The deposition of 50 clusters on each film was modeled. The cluster stacking was calculated in the cases of 0.25 and 1.25 eV per atom incident energy. All deposited clusters had normal incidence. The impact points and initial clusters orientations were selected uniformly and at random. The time interval between impacts of consecutive clusters was 100 ps. During the cluster accumulation process, the LRO and SRO parameters were followed independently for each cluster, as well as for the whole film. Values of the LRO parameter  $|S(\mathbf{k})|^2$  were found to be small for all clusters. Only in the case of the Ni substrate, a minor amount of deposited clusters displayed partial epitaxy. In the case of gold clusters on a gold surface, it was found in Ref. 17 that the slowing down may stimulate the epitaxy of the previously deposited clusters. No such phenomenon was found to take place with Ni<sub>3</sub>Al clusters. Large variations of the SRO were found from one deposited cluster to another. In order to illustrate this, the time dependence of the SRO measured in selected clusters are presented in Fig. 3. In this example, the clusters slowed down one by one on an Al substrate with 0.25 eV/at. incident energy. Most of the impacts result in a significant decrease of  $\eta(AI)$ . Later impact may result in a further decrease of  $\eta(Al)$  in previously deposited clusters, thus introducing chemical disorder in the growing film. The evolution of the SRO parameter calculated for the whole deposited film is shown in the same figure. It tends to decrease monotonically as the slowing down proceeds and to level off at a value close to  $\eta(AI) = 0.96$ , which represents about 15% disorder. Fluctuations from one cluster to another around the mean values are quite significant. The simulations were repeated with Al and Ni as substrates with 0.25 and



FIG. 4. View of the  $Ni_3Al$  film obtained by deposition of 50 clusters at 0.25 eV/at. on the Al substrate.

1.25 eV/at. incident energies. Only minor differences in  $\eta$ (Al) values were found, showing the very small influence of the substrate nature and of the impact energy (within the investigated energy range) on the level of disorder. An overall view of the film formed by 50 clusters is presented in Fig. 4. The slowing down conditions were the same as those for which the evolution of the SRO is shown in Fig. 3. The film structure is particularly complex. It is characterized by a stacking of clusters that look keeping their identity (see below for a detailed analysis). Huge open volumes remain and the surface roughness is particularly high. The average density is 60% of that of a Ni<sub>3</sub>Al single crystal.

### IV. CHARACTERIZATION OF THE CLUSTER ASSEMBLED SAMPLES

Three main characteristics of the model material obtained by compaction may be emphasized. The first is the occurrence of holes. Several of these holes are interconnected and their size is typically of several nanometers, which scales with the sizes of the initial clusters. The second is the abovementioned low density. The density is not quite sensitive to the cluster structure and the predicted value is in reasonable agreement with the experimental value of 89% quoted in Ref. 21 for a  $L1_2$  nanostructured sample synthesized by means of inert gas condensation followed by pressing at 2 GPa. It should be noticed that, in this pressure range and because of the occurrence of holes, the density is a fast growing function of pressure. Much higher pressures, above 15 GPa, lead to a limiting value of the density but smaller than for an ordinary polycrystal because some spherical holes still remain, that are quite stable. A shear deformation might be necessary for their collapse. The third characteristic is segregation at the interfaces and at the internal surfaces. In order to gather some quantitative information, segregation is studied by coordinance analysis. This allows distinguishing the interfacial atoms from other ones by checking the number of first neighbors to each atom. The first neighbor coordinance in the  $L1_2$  and fcc structures is 12 and, for a large majority of the atoms, it is different from 12 at the interfaces. In contrast, the first and second neighbors in the B2 and bcc lattices are rather close. Because of thermal vibrations and lattice distortion, they are therefore difficult to distinguish. In order to avoid possible confusion, we perform the coordinance analysis, taking into account both the first and second neighbors in the case of B2. For this structure, the estimated coordinance is therefore 14. As in the  $L1_2$  case, interfaces are identified as the areas where atoms have coordinance different from 14. In principle, this coordinance criterion is not sufficient to detect special grain boundaries with relative orientations corresponding to a well-defined common site lattice. Such boundaries turn out to be infrequent in the present assembled samples. On the basis of this coordinance criterion, the fraction of atoms in interfaces is evaluated as 45.3% in the case of the B2 sample and as 32.0% in the case of the  $L1_2$ sample. Segregation does not change these fractions significantly. The improperly coordinated atoms thus represent a substantial fraction of the material in all cases, upon which special attention is paid below. Segregation may be analyzed quantitatively by a measure of the relative excess aluminum. This one is defined as

$$\zeta(AI) = \frac{x_{AI} - x_{pft}}{x_{pft}},$$
(8)

where  $x_{Al}$  is the current aluminum relative concentration and  $x_{\text{pft}}$  the aluminum concentration in the perfect single crystal at a given  $\Delta \mu$ . The excess Al in core and interfacial areas for the samples considered are compared in Table I. One can see that the excess aluminum in the NM is systematically located in interfacial areas, while inside the grains the composition corresponds to that of the perfect structure  $(L1_2 \text{ or } B2)$ , just as in the case of isolated clusters. The excess Al in the NM is close to that in free clusters both in the cluster cores and at the interfaces. As found for isolated clusters, it is also not dependent on the cluster size in the range presently considered. This shows that the surface stress in free clusters is taken over by the internal stress after assembling. Segregation of excess Al at interfaces is not the only chemical process driven by the small size of the clusters. Indeed, a close look to Table I indicates some 10% Al depletion in the case of B2 clusters after assembling. To analyze this depletion further, rather than using a coordinance criterion, we check the stoehiomenty in the small spherical volume (two lattice units radius) near the center of mass of each grain. In this sphere, a perfect B2 composition is found ( $\zeta = 0$ ). This

Sample	$\Delta \mu$ (eV)	Whole sample	Core	Mantle (interface)
Free B2 cluster (averaged over all cluster sizes)	1.0	0.032	0.0	0.122
	1.6	0.116	-0.002	0.42
Cluster compacted B2	1.0	-0.008	-0.106	0.112
	1.6	0.10	-0.068	0.304
Free <i>L</i> 1 <sub>2</sub> cluster (averaged over all cluster sizes)	0.0	0.0	0.0	0.0
	0.6	0.16	-0.02	0.35
Cluster compacted L1 <sub>2</sub>	0.0	-0.036	0.0	-0.12
	0.6	0.204	0.12	0.36

TABLE I. Excess Al $\zeta$  in the B2 and in the L1<sub>2</sub> samples.

depletion thus takes place in the intermediate areas between the cores and the interfaces. This demonstrates an oscillation is the excess Al which, in the average, is zero in the cluster cores, negative in the intermediate area and positive at the interface. Since no such fluctuations are observed in free clusters, they can be attributed to spatial inhomogeneities of the internal stress induced by the compaction. Similarly to free clusters, segregation has consequences on structural order that can be evidenced by the pair correlation functions for the B2 and the  $L1_2$  samples given in Figs. 5 and 6, respectively. In these figures, the pair correlation functions are constructed distinctly for the grain cores and the interfacial areas defined on the basis of the coordinance criterion given above. The B2 structure clearly comes out in Fig. 5(a)for the NM synthesized from B2 free clusters with surface segregation ( $\Delta \mu = 1.6 \text{ eV}$ ). The effect of Al depletion coming out of Table I is cross-checked by Fig. 5, where Al peaks are all of lower magnitude than the Ni peaks. One additional consequence of Al depletion may be the structure which occurs in the first neighbor peak. Indeed, the depletion has the consequence that a significant number of Ni atoms are now first neighbors (which is not the case in perfect B2 ordering). The Ni sublattice undergoes some distortion therefore, hence the structure in the closest distance peak. The resulting distortion in the Al sublattice turns out to be less pronounced. As the interfacial area is concerned, no pronounced structure



FIG. 5. Ni and Al pair correlation functions for the cluster assembled sample at  $\Delta \mu = 1.6 \text{ eV}$  (structure *B*2) (a) estimated in the core regions only and (b) estimated in the interfaces only.

shows up in the pair correlation function between Ni atoms, demonstrating that there is no Ni ordering on a periodic lattice. The function, however, displays a first neighbor Ni peak in the bcc structure. Interfaces are thus not structureless, which better comes out the aluminum pair correlation function. This one displays clear B2 ordering superimposed to background. The closest distance Al peak contains some first neighbor bcc contribution, which cannot be resolved from the first B2 Al contribution. Interfaces between B2 cores are thus partially disordered, but B2 ordering remains and some bcc structure shows up, which is characteristic of a solid solution. The situation is better clear for the NM material formed by  $L1_2$  clusters with Al segregated in their surface  $(\Delta \mu = 1.6 \text{ eV})$ . Figure 6(a) shows the results for the  $L1_2$ grain cores areas. These areas remain almost perfect  $L1_2$ after pressing and the pair correlation functions do not differ substantially from those in the bulk materials [Fig. 6(a)]. At the interfaces [Fig. 6(b)], Ni remains to a large extent organized on its L12 sublattices, although a substantial background indicates disorder. On the contrary, the Al pair correlation function is almost structureless and only displays a minor fcc first neighbor peak. Interfaces thus appear as formed by a solid solution where Al is distributed at random on a fcc lattice.



FIG. 6. Ni and Al pair correlation functions for the cluster assembled sample at  $\Delta \mu = 0.6 \text{ eV}$  (structure  $L1_2$ ) (a) estimated in the core regions only and (b) estimated in the interfaces only.

## V. CHARACTERIZATION OF SINGLE CLUSTERS DEPOSITED ON A SUBSTRATE

In this section, we focus on the effect of the substrate on the cluster slowing down in the LECBD regime. The values of the LRO and SRO parameters in final configurations differ from one impact to the other. In order to understand the overall trends and to evaluate the statistical variations in the results, selected simulations were repeated ten times with statistically independent initial conditions at given impact energy. Mean values of the order parameter were calculated. Statistical independence of the initial conditions was warranted by the random selection of initial cluster orientations and positions in front of the substrate surface. The visual inspection of final atomic configurations revealed significant differences between deposition on an Al surface on the one hand and on Ni and Ni<sub>3</sub>Al surfaces on the other. Typical snapshots obtained after 150 ps evolution are shown in Fig. 7. In the three cases considered, all initial conditions are identical except the nature of the substrate. In the cases displayed, the incident kinetic energy is 1.5 eV/at. The interaction between the Ni<sub>3</sub>Al cluster and the Al surface is characterized by a pronounced cluster penetration. About half of the cluster atoms are embedded in the Al substrate [Fig. 7(a)]. A sizable penetration is also found when the incident energy is as low as 0.5 eV/at. No significant epitaxy is observed. In contrast, in the case of cluster slowing down on Ni and Ni<sub>3</sub>Al substrates, the penetration was not significant. At 1.5 eV/at. incident energy, only a few atoms penetrated the first surface atomic plane. For these two substrates both epitaxial [Fig. 7(b)] and nonepitaxial [Fig. 7(c)] configurations were found at the end of 150 ps simulations. The average values of the LRO and SRO parameters and their standard errors for the deposition on different substrates at 300 K are presented in Fig. 8. The data presented in Fig. 8 confirm the features in Fig. 7. The crystallographic orientation of the cluster deposited on Al is uncorrelated with the orientation of the substrate and this contrasts with the cases of Ni and Ni<sub>3</sub>Al substrates. The epitaxy on Ni and Ni<sub>3</sub>Al appears to be enhanced by the impact energy. It is also found to be enhanced by the temperature. The simulation of the impact was repeated at higher temperatures and, at 900 K, the average LRO parameter value after 150 ps evolution is above 0.8, that is, more than twice as much as at room temperature. The combined effect of temperature and impact energy on epitaxy is discussed in further detail in Refs. 52 and 53. Short range (chemical) order is found to be the highest with clusters deposited on the Al substrate, consistently with the snapshots in Fig. 7. On all substrates, and contrary to long-range order, chemical order is found to be a decreasing function of the impact energy. The difference in the penetration, epitaxy, and chemical order for deposition on an Al substrate and on Ni and Ni<sub>3</sub>Al substrates can be explained on the basis of the mechanical properties of the materials. The magnitude of the bulk and shear elastic constants of Al are more than twice lower than those of Ni and Ni<sub>3</sub>Al. Hence, as can be expected, cluster penetration is correlated with the softness of the material, as already suggested about cluster penetration in a higher energy range than LECBD.<sup>4</sup> The lack of epitaxy



FIG. 7. Snapshots of typical final atomic configurations after deposition of a Ni<sub>3</sub>Al cluster on an Al surface (a) and a Ni surface (b),(c). The surface orientation is  $\{111\}$ . The impact energy is 1.5 eV/at. In the clusters, dark spheres represent Al atoms, light spheres represent Ni atoms.

between the cluster and the Al substrate and the minor chemical disorder in the cluster can also be explained by the Al softness, as the largest deformation will be taken over by the softest material. The mechanical properties of the materials are thus evidenced to play an important role in cluster penetration and also in cluster epitaxy and chemical order. As already noticed above and discussed in Ref. 53, a correlation is found between long-range and short-range order, which was clearly evidenced by the time dependence of  $|S(\mathbf{k})|^2$  and  $\eta(Al)$  on the example of one given cluster. This example is shown in Fig. 9. In this case, the Ni<sub>3</sub>Al cluster is incident on a Ni surface with 1.5 eV/at. at 300 K. The structure factor in the cluster slowly increases with time from zero during the first 60 ps evolution, showing a slow accommo-



FIG. 8. Mean values of the long-range (a) and the short-range (b) order parameters estimated after deposition on different substrates at 0.5 eV/at. and 1.5 eV/at. impact energies.

dation with the substrate. During the impact, the short-range order parameter decreases from  $\eta = 1$  to  $\eta = 0.85$  within a few picoseconds. It then partially restores to  $\eta \approx 0.94$ . Despite the large fluctuations of  $\eta$  with time, a slow decrease of  $\eta$  may be seen, simultaneous to the 60 ps slow increase of  $|S(\mathbf{k})|^2$ . At t = 65 ps, a thermally activated global rearrangement of the cluster takes place. This one is characterized by a simultaneous sudden raise of  $|S(\mathbf{k})|^2$  characteristic of thermally activated epitaxial ordering and a sudden decrease of  $\eta$  characteristic of chemical ordering. This case illustrates a competition between long- and short-range ordering. Such a competition was found in most cases investigated and, generally, LRO is an increasing function of temperature and impact energy while SRO displays the opposite trend.

### VI. CHARACTERIZATION OF THE FILM SYNTHESIZED BY LECBD

#### A. The interface with the substrate

One issue specific to LECBD is the formation of an interface between the single crystal substrate and the nanostructured layer. This interface is now characterized. The clustersubstrate interface properties emphasized in Sec. V naturally generalize to the interface between the obtained nanostructured film and the substrate. Some penetration is possible in the Al substrate, giving rise to mixing with no more than three atomic layers when the cluster incident energy range is 0.25-1.25 eV/at. In this energy range, the penetration is not quite energy dependent. Partial interfacial epitaxy is found



FIG. 9. Time dependencies of the structure factor, as measured with three different substrate k vectors (a) and the short-range order parameter (b). The results are shown for the case of the deposition of a Ni<sub>3</sub>Al cluster with 1.5 eV/at. impact energy on a Ni(111) surface.

on harder materials while no significant mixing then takes place. Impact induced mixing is better quantitatively appreciated in Fig. 10 where depth density profiles are displayed. At all depths, the cluster atoms densities are found close to stoechiometric. As a result, in the Al substrate, the Ni concentration is always less then 30 at./%. Some aluminum originating from the substrate is found in the cluster layer as well. As a consequence of both processes, an interface about 10 Å thick is formed with stoechiometry  $Ni_{0.75-x}Al_{0.25+x}$ , where x decreases monotonically from 0.75 in the substrate to 0.0 in the cluster layer. It cannot be excluded that this composition change induces structural changes since, in the bulk phase, x = 0.25 corresponds to the thermodynamically stable B2 phase. The tetragonal  $L1_0$  metastable phase cannot be excluded either. The coexistence between the three phases at the nanoscale is most likely energetically unfavorable and this may be the reason why they are not observed here.



FIG. 10. Concentration profiles of the different elements in the interfacial region. The impact energy is 1.25 eV/at. and the substrate is aluminum.



FIG. 11. Density distribution measured in two films along the (111) direction of the Ni substrate. The reference (zero distance) corresponds to the substrate (111) surface position.

### B. The nanostructured film morphology

Density and cavities. The spatial density distributions of the modeled nanostructured films are highly nonuniform. The main reasons therefore are the cluster size distribution, the random selection of the impact points and the occurrence of cavities. The density distribution measured in the nanosturctured film along a direction perpendicular to the surface of a Ni substrate is presented in Fig. 11. The density is evaluated as relative to single crystalline Ni<sub>3</sub>Al at 300 K. The porous film morphology makes the density significantly lower than in the compacted film obtained with 2 GPa compaction pressure. The Fig. 11 confirms that it is not significantly dependent on the impact energy. The shape of the distribution at the interface is perfectly sharp, as no mixing takes place between the substrate and the nanostructured film. On the other hand, the shape of the distribution at the surface is smoother, as a consequence of roughness. This roughness does not appear significantly dependent on the impact energy either, and it is thus mainly determined by the cluster size distribution. Similar results are found with the other substrates used. The density found in the bulk part of the films is not quite sensitive to the nature of the substrate, nor to the impact energy, in the range investigated. The mean film density of 60% of bulk Ni<sub>3</sub>Al, is evaluated with a standard error of 15%. It is thus at the limit of significantly higher than that of the stacking of equal size hard spheres  $(\pi/6)$ , showing that the impact energy is not sufficient to induce large cluster deformations. This is confirmed by an analysis of cavity distributions in the nanostructured film. The spatial extent of cavities may be estimated as follows. First, the bulk area of the nanostructured film has to be distinguished from the surface area. Figure 11 indicates that the film density starts to be influenced by the surface at a distance close to 27 Ni lattice distances, that is, 95 Å. Cavities will only be analyzed at distances from the interface closer than this. This area is mapped by a cubic network and the cubic cells thereby defined were checked to be empty or not. Those that are empty belong to a cavity. The size of the cubes was chosen as small as the size of elementary cell of Ni<sub>3</sub>Al unit cell, which turns out to be sufficient to prevent the



FIG. 12. Slab in the film. Atoms with coordinance Z=12 are represented by open circles. Those with  $Z \neq 12$  are represented as dark spheres.

occurrence of empty cubes in cluster cores and interfaces. Counting the empty cubes allows us to estimate the fraction of the film volume occupied by cavities. It is found that they occupy an area somewhat smaller than the complement of the atomic occupancy deduced from the analysis of densities. One thus cannot exclude the occurrence of zones outside the cavities with densities lower than in the bulk. The mapping method used also allows us to evidence that all cavities are interconnected, forming a continuous network from the substrate interface to the nanostructured film surface. Only a few cavities are isolated.

Grains and boundaries. The Ni<sub>3</sub>Al clusters are generally not losing their identity as a consequence of the slowing down and no cluster coalescence is found. As a result, as in the model compacted material, the building blocks of the nanostructured film are the clusters themselves that only very partially accommodate to each other. They form interfaces that may have specific properties, at least at short range. The distinction between grain cores and their interfaces is made on the basis of a coordinance criterion. In a single  $L1_2$  crystal, the first neighbor coordinance is Z=12. The first neighbor coordinances at (110), (100), and (111) surfaces are Z =6, 8, or 9, respectively. Because of their defective state, interfaces between nanograins are characterized by a coordinance different from 12 and higher than at a surface. It is thus tempting to try differentiating between these areas in a nanostructured material on the basis of a first neighbor coordinance analysis, as in Sec. IV. One example of a thin slab in a film is given in Fig. 12 where the difference between atoms



FIG. 13. Coordinance distribution for the films grown on the Al substrate.

with coordinance Z=12 and  $Z\neq 12$  is shown. Interfaces and grain cores are generally well distinguished. The coordinance distribution for all atoms in the film is shown in Fig. 13. This distribution is characteristic of all cases investigated. It is broad and close to unimodal. Nonzero frequencies are found for  $4 \le Z \le 14$ . Figure 12 demonstrates that the large majority of core atoms have Z=12. A more detailed examination of the sample indicates that the broadest coordinance distribution is found at the surface of cavities ( $4 \le Z \le 11$ ) while it is narrower in the interfaces ( $9 \le Z \le 14$ ). The two latter contributions thus overlap in Fig. 13. The minimum at Z=8, which is at the limit of statistical significance, may result from this overlap.

# C. Order

*Chemical order.* Since the overall short range order is not much sensitive to the initial conditions, the mean value of the SRO parameter, which may be a measurable quantity, does not bare much information about the film. A more detailed analysis is necessary. In what follows, the SRO parameter was estimated for each cluster contained in the film and the distinction is made between the grain cores and the interfacial areas. The distribution of  $\eta(AI)$  values of the nanograin cores and interfacial areas is presented in Fig. 14 for the film grown on the Ni substrate with 0.25 eV/at. deposition energy.



FIG. 14. Distribution of the SRO parameter values,  $\eta$ (Al), as obtained in the grain cores and in the interfacial areas. The film is grown on a Ni substrate with 0.25 eV/at. impact energy. Only atoms of the same cluster are considered as first possible neighbors.

The distribution presented in Fig. 14 is built with Eq. (7) by taking into account the first neighbors of Al atoms belonging to the same cluster. The distributions are found quite broad, showing statistical distribution of chemical disorder in both the grain cores and in the interfaces. The overall degree of order is high, especially in the grain cores where  $\eta(Al)$  is close to one. It is also worth noticing that full disorder [ $\eta(Al) = 0.75$ ] is never reached, even at the interfaces. A similar analysis was performed with the Al substrate and impact energies of 0.25 and 1.25 eV/at. Similar distributions were found. This confirms that the SRO properties of nanocluster layers grown by LECBD are not significantly dependent on the nature of the substrate.

Structural order. In order to investigate structural order in grains and interfacial areas, the analysis of the pair correlation function g(r) is useful, keeping the distinction made above between areas with 12-coordinated atoms and others. In order to further characterize structural order in the investigated porous films, it is necessary to distinguish grain boundaries from cavity surfaces. As shown above, this is not possible on the basis of coordinance distributions. Nevertheless, a reasonable discrimination between interfaces and cavity surfaces may be made in the following way. The idea is to look at correlations between first neighbor coordinances. The atoms with low coordinance ( $Z \leq 8$ ) belong to cavity surfaces. For atoms with  $9 \le Z \le 11$ , if at least one of the first neighbors has small coordinance ( $Z \leq 8$ ), it is considered as a cavity surface atom too. Otherwise, it is considered to be located at an interface. Atoms with coordinance higher than 12 are considered to be located at interfaces. Pair correlation functions for atoms in grain cores and at grain boundaries (excluding cavity surfaces) are constructed for the film grown on a Ni substrate with 0.25 eV/at. impact energy. The results are shown in Fig. 15. The pair correlation function calculated for a perfect single Ni<sub>3</sub>Al crystal at 300 K is shown as a reference. The comparison of pair correlation functions obtained for the single crystal [Fig. 15(a)] with the pair correlation function measured in the grain cores [Fig. 15(b)] demonstrates the very good crystallinity. Peak intensity ratios agree quantitatively well, up to the fourth neighbor distance. The pair correlation function obtained for the interfacial atoms is presented in Fig. 15(c). It can be seen that the second and third neighbor peaks are still noticeable, confirming that some crystal order remains in the interfaces.

### VII. SUMMARY

The effect of assembling on structural and segregation properties of bimetallic nanoclusters was described in a first step. Isolated equilibrium Ni-Al clusters were studied in Ref. 30. Clusters containing more than 200 atoms were found to crystallize and to be partitioned into two areas; a core in one of a stable phase known in bulk materials and a mantle where, depending on the offset of stoechiometry, Al may segregate. The mantle then has the fcc or bcc structure of a solid solution which coexists with a stable phase in the core that may either be  $L1_2$  or B2. In the present work, NM samples are modeled with these clusters by combining isobaric-isothermal molecular dynamics with Metropolis



FIG. 15. Pair correlation function measured in a perfect  $Ni_3Al$  single crystal at 300 K (a), in the grains cores (b), and in the grain boundaries (c) at the same temperature. The cluster deposition energy is 0.25 eV/at.

Monte Carlo in the semigrand canonical ensemble. A realistic cluster distribution was employed but the cluster sizes were, however, selected to be small enough to avoid structural effects related to the motion of dislocations. The clusters were found to keep their identity and the nanostructure may then be characterized as formed by cluster cores, cluster interfaces, and holes. Except some possible local fluctuations in stoechiometry induced by inhomogeneous internal stress, the segregation state of the clusters is similar when they are assembled or isolated, and the cluster cores keep the stable bulk phase. In a second step, a study is presented of the consequences of slowing down in the LECBD regime on long- and short-range order. The case study of Ni<sub>3</sub>Al clusters and different substrates (Al, Ni, and Ni<sub>3</sub>Al) was selected therefore.

The slowing down of one bimetallic cluster on a metallic surface is considered first, and particular attention is paid to the cluster-substrate interaction. With the incident energies considered (0.5, 1, and 1.5 eV/at.), and consistently with earlier work using different systems,<sup>4</sup> clusters penetrate in Al, but not in Ni and Ni<sub>3</sub>Al. They undergo weaker short-range disordering with the former substrate than with the two latter. The impact on Ni and Ni<sub>3</sub>Al clearly enhances epitaxial

accommodation of the cluster, and a competition is found between short-and long-range ordering, that is, between epitaxy and chemical order. The formation of nanostructured films by low-energy cluster beam deposition is considered next. A previous study<sup>18</sup> demonstrated in the case of gold that modeling cluster film formation by classical MD is realistic provided cluster surface diffusion is not involved in the film growth. This may also be the case for Ni<sub>3</sub>Al on the substrates considered, especially on Al substrates where pinning takes place. A visual inspection of the model films immediately reveals several main characteristics. Similarly to the cluster compacted material, a complex stacking of nanograins separated by grain boundaries and nanocavities forms the film. The grains are, however, less deformed and the film ressembles to a stacking of hard spheres. The volume occupied by cavities is larger and the average density is consequently lower. All cavities are interconnected. No significant correlation between grain orientations and the substrate orientation is found. Only minor epitaxy is found at the interface with Ni and Ni<sub>3</sub>Al substrates. The analysis of shortrange order reveals various levels of disordering. No deposited cluster displays full disorder. The overall chemical disorder is insensitive to the substrate and to the slowing down energy. The interface formed between the nanostructured film and the Ni and Ni<sub>3</sub>Al surfaces is perfectly sharp. Mixing with an Al substrate occurs over no more than 1 nm. One common characteristics of the cluster compacted and the LECBD nanostrucutres is that the initially free clusters keep their identity after processing and their cores keep crystalline. They display pronounced chemical and structural order and no pressure or impact induced coalescence is observed. The pair correlation functions indicate significant crystallinity in the grain boundaries.

Other model predictions can be made, that are of obvious interest and allow direct comparison with experiment. These are planned for future work. One series concern mechanical testing. The mechanical properties of such inhomogeneous materials are unknown and are worthwhile to investigate in order to establish a link between macroscopic and nanoscopic scales. The energetics of the model nanostructures studied is not yet addressed either. From the high inhomogeneity of their configurations, such systems may reasonably be anticipated to display high enthalpy areas that may be responsible for specific thermodynamic behaviors. These again represent a class of problems about which experimental and modeling approaches may help to bring substantial understanding.

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