Stress distribution and mechanical properties of free and assembled Ni₃Al nanoclusters

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Classical molecular dynamics with a semiempirical N-body potential is used to study the distribution of local stress in bimetallic Ni₃Al nanoparticles and in cluster-assembled materials. The materials considered are synthesized with these particles by low-energy deposition at 0.5 eV per atom and by compaction with an external pressure of 2 GPa, thus featuring different nanostructures. Both are nanoporous, the lowest density being obtained by deposition. Their mechanical response to an uniaxial external load is then studied and deformation mechanisms are identified and are found to be similar in both nanostructures. In the core of isolated clusters, the partial pressures on the nickel and aluminium subsystems are found to differ by several GPa and, as a balance to surface tension, the hydrostatic core pressure is positive and depends on the cluster size. The surface stress is tensile and, because of structural disorder, the partial pressures distributions on Ni and Al at the surface are scattered. When nanostructured systems are formed, strong and highly inhomogeneous shear stress appears, the cluster cores may become tensile, and the interfacial areas remain mainly tensile as well. The partial pressure difference between Ni and Al is somewhat reduced. It is shown that the effect of temperature is to reduce this difference still further and to homogenize the spatial stress distribution. When subjected to a uniaxial stress, both materials display an elastic and a plastic regime. The elastic limit is the lowest for the most porous material and decreases with increasing temperature. Plastic deformation is dominated by both grain boundary sliding and by the enlargement of the open volumes, without evidence for the nucleation of cracks. These open volumes are found to facilitate dislocation activity which is evidenced in grains with sizes as small as two nanometers. This dislocation activity is found to result in the production of stacking faults as well as to the recovery of defects induced by the deposition or by the compaction.

I. INTRODUCTION
Nanostructured materials cover a huge range of different systems described in the literature. The nanometer scale represents the lower limit at which macroscopic laws still apply. In addition to these laws, others show up, specific to the nanostructure. They are well known to deviate from those of crystals and polycrystals with the same chemical composition, as a consequence of the reduced size of the grains forming them. Size however is not sufficient to explain their specific properties. Nanostructured materials indeed are formed by grain cores where the crystalline structure of bulk materials is often preserved, separated by interfaces occupying a volume of the same order as the grain cores and, depending on the synthesis method, open volumes. Much attention is currently paid to the interfaces in nanostructured materials, as reviewed in Ref. 2. Among others, mechanical properties of nanostructured materials combine those of the grain cores with those of the interfaces. A well-known example is the deviation from the Hall-Petch relation between hardness and grain size, another is the occurrence of superplasticity. Because of the high surface-to-volume ratio at the nanoscale, surfaces play an important role in the thermodynamic stability of the materials as well. For instance, segregation enhanced by the small grain size may lead to core-shell structures in nanostructured alloys where each stoichiometric core is surrounded by a segregated shell, eventually leading to compositions that cannot be obtained in coarse-grained materials. Hence, materials properties depending on nanograin interfaces may be expected to differ from micro-grain materials where segregation is weaker and the surface-to-volume ratio three orders of magnitude smaller. An interesting class of nanostructured materials is formed by assembled nanoparticles. Nanoparticles display specific structural, electronic, magnetic, and optical properties, and one challenging question is to determine the extent to which these properties can be transferred to the macroscopic scale by assembling the particles. There are various methods for synthesizing nanoparticles. In some, like inert gas condensation, particles nucleate and grow in conditions close to thermodynamic equilibrium. Alloy nanoparticles may be formed this way, with close to stoichiometric composition. In others, like laser vaporization, particles are formed outside equilibrium and exotic compositions may be obtained that are not predicted by macroscopic phase diagrams. In this work, we focus on the former and we use Ni₃Al as a case study. Ni₃Al is a material with well-known high-quality mechanical properties, but the literature about nanostructured Ni₃Al is sparse. Elemental metallic nanostructured materials have already been the subject of several experimental, modeling, and theoretical studies involving grain sizes down to about 5 nm. These materials...
were designed in such a way that open volumes are minimized. Though small, these open volumes were found to play an important role in the nucleation of dislocations, whose activity is limited by the grain size and vanishes at the smallest size considered. Ni$_3$Al is a $L\,1_2$-ordered alloy made of atoms with fairly different sizes. At the atomic scale, the material, although ordered, is therefore pronouncedly inhomogeneous and this may be important in nucleation problems. Since nucleation usually takes place at defects or interfaces, such inhomogeneities may only be speculated as being important as far as they display similarities with those at defects and interfaces. However, because of their size, nanograins cores may be expected largely free of defects. If this is the case, like in elemental metals, mechanical properties and the nucleation of deformation will mainly depend on the interfacial structure. Considering nanoparticles as the building blocks of cluster-assembled materials, in what follows, their static mechanical properties will be studied in a first step. Namely, stress invariants will be estimated at the atomic scale. In a second step, the modification of these properties resulting from assembling will be identified. Two usual methods for assembling nanoparticles will be considered. One is the compaction by mean of a hydrostatic pressure and another is low-energy cluster beam deposition (LECBD). Compacted samples may have a higher density and particles synthesized in a laser vaporization source are usually somewhat smaller than those grown by inert gas condensation. Hence, the two methods lead to different nanostructures. The mechanical response of both materials to a uniaxial load will then be examined and the role of temperature will be emphasized. This response, as well as the deformation mechanisms, will be correlated to the nanostructure.

II. SIMULATION MODEL

Ni$_3$Al is here modeled at the atomic scale. Many-body interatomic potentials are currently used for modeling cohesion in metals. The potential adopted here is based on the second-moment approximation of the electronic density distribution as derived from the tight-binding theory for transition metals. We select the approximated potential expression proposed by Ackland and Vitek. Using a set of cubic splines with parameters fitted on the basis of cohesive energy, the equilibrium condition, and the elastic constants. We use the improved set of parameters suggested in Ref. 37. The range of the local interaction is limited by a cutoff distance taken in Refs. 35 and 36, as 1.225$a_0$, where $a_0$ is the lattice parameter. This is the same potential as used in the study isolated Ni-Al clusters presented in Ref. 5. The method proved successful in describing the equilibrium properties of ordered Ni-Al (Ref. 37) and Cu-Au (Ref. 38) alloy phases. Numerical detail is available in Refs. 36 and 37. With this model potential, Ni$_3$Al nanoparticles, particle deposition on a substrate, and particles compaction were modeled, using different atomic-scale methods. Stoichiometric equilibrium nanoparticles were modeled at 300 K by a Metropolis Monte Carlo (MMC) method in the semi-grandcanonical ensemble. In this approach the total number of particles ($N=N_{\text{Al}}+N_{\text{Ni}}$), temperature ($T$), pressure ($P$) and chemical potential difference ($\Delta \mu = \mu_{\text{Al}} - \mu_{\text{Ni}}$) are fixed. The partial number of each kind of the atom ($N_{\text{Al}}, N_{\text{Ni}}$) may be changed, and the chemical potential difference determines the equilibrium composition. The method includes four types of trials according to the Metropolis scheme: namely, random displacement of each atom of the cluster from its current position, random selection of the chemical identity of an atom selected at random, site exchange of this atom with another of different chemical nature selected at random, and random change of the lattice parameter in one of randomly selected among three orthogonal directions. More detail is given in Ref. 5. This way, spatial equilibrium configurations were obtained for particles containing from 200 to 12 000 atoms as well as for cluster assemblies. The chemical potential difference between Ni and Al was fixed in such a way that no segregation occurs at the surface of the free clusters. Velocities are then assigned by a microcanonical molecular dynamics equilibration. Cluster compaction, cluster deposition and the formation of cluster layers by deposition are modeled by molecular dynamics (MD). The MD scheme adopted for modeling deposition allows for two free substrate surfaces and periodic boundary conditions in two orthogonal directions parallel to the surfaces. A parallel monokinetic beam of clusters is modeled by selecting their impact points on one of the surface at random and assigning them a well-defined momentum perpendicular to this surface. Slowing down energies typical to realistic neutral cluster beam deposition experiments are of the order of a fraction of an eV. Within this range, in the case of Ni$_3$Al clusters, the nanostructure of deposited films at room temperature is not quite energy sensitive. The MD model accounts for exchange of energy between the ionic and electronic systems by means of velocity-dependent forces to model electron-phonon coupling. The characteristic electron-phonon coupling time is of the order of a few picoseconds, which is also the characteristic time for the deposition of one cluster. In order to form a cluster layer they are deposited one by one at time intervals of 100 ps. This allows for thermally activated cluster rearrangements after the impact, before the next cluster slows down. For modeling the synthesis of the compaction of clusters into a nanostructured material, the dynamics of the macroscopic deformation of the whole simulation box, at constant external pressure and temperature, is accounted for. This is achieved in the canonical ensemble according to the constrained MD scheme introduced by Rahman and Parinello. The number of degrees of freedom is then extended from $3N$ for the physical system to $3N+10$, where $N$ is the number of particles. One of the additional degrees of freedom governs the dynamics of the exchange of energy with the external reservoir at constant temperature according to method of Nosé, and the nine further ones are the components of three vectors spanning the MD box. The particles Cartesian coordinates as well as these additional degrees of freedom evolve according to equations of motion derived from an appropriate Lagrangian. The free clusters, brought to thermal equilibrium at 300 K, 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. The detail of the procedure is described in Ref. 6. An external pressure of 2 GPa is reached by successive steps at 300 K. Since the time necessary to bring the system to 2 GPa and thermal equilibrium by the present MD technique is about 14–15 orders of magnitude shorter than a real compaction experiment, 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. This way, the thermodynamic conditions are the same as for preparing the free clusters. Only limited further relaxation of the boxes is observed. The equilibrium atomic density after relaxation at zero pressure is 87.5% and no sizable segregation results from compaction. One of the essential ingredients of the Rahman-Parinello Lagrangian is the stress tensor defined as

$$\sigma^{\alpha\beta} = \frac{1}{\Omega} \sum_{i=1}^{N} \left( m_i v_i^{\alpha} v_i^{\beta} + \sum_{j \neq i} F_{ij}^{\alpha} F_{ij}^{\beta} \right),$$

where \( N \) is the number of atoms in the system, \( \Omega \) is the current box volume, \( v_i \) is the atomic velocity, \( F_{ij} \) is the force component of particle \( j \) on particle \( i \), \( r_{ij} \) is the vector distance between particles \( i \) and \( j \), and \( \alpha \) and \( \beta \) refer to the vector components. This tensor is a dynamical parameter of the Lagrangian of which appropriate components may be frozen in order to model an external constrain. This is the method used below in order to study the mechanical response of model samples to a uniaxial load. Two stress invariants are derived from the stress tensor: namely, the pressure

$$P = -\frac{1}{3} \text{tr}(\langle \sigma \rangle) = -\frac{1}{3} \langle \text{tr}(\sigma) \rangle$$

and the von Mises shear invariant

$$J = \frac{1}{2} \left[ \text{tr}(\langle \sigma \rangle^2) - 3P^2 \right].$$

A local shear invariant may be defined as well by

$$J_i = \frac{1}{2} \left[ \text{tr}(\langle \sigma_i \rangle^2) - 3P_i^2 \right],$$

where the suffix \( i \) refers to the site of atom \( i \) and \( \sigma_i \) to the stress tensor on atom \( i \). It should be noted that such a local shear invariant is made of nonadditive contributions and, contrary to the case of pressures [Eq. (2)], it cannot be used to reconstruct the overall shear invariant \( J \) by summing up the atomic contributions \( J_i \). In the case of a perfect crystal, however, because of translational invariance, Eq. (3) applies to individual unit cells. In the \( L1_2 \) \( Ni_3 Al \) structure, \( Al \) atoms only have \( Ni \) first neighbors and their local environment is fully symmetrical. For this, reason, \( J_i \) at \( Al \) sites is zero. In contrast, \( Ni \) atoms have eight \( Ni \) and four \( Al \) first neighbors and are sheared, with the consequence of a nonzero \( J_i \) value. In what follows, the distinction will be made between the macroscopic shear invariant [Eq. (3)], the nanoscopic shear invariant [Eq. (2) applied to one unit cell], and the atomic shear invariant \( J_i \) [Eq. (4)]. Although not necessary, for convenience, the same distinction will be made between macroscopic, nanoscopic, and atomic pressures. In several instances, it will also be appropriate to carry on the discussion in terms of partial pressures: namely, the pressures on the \( Ni \) and \( Al \) subsystems.

### III. EQUILIBRIUM PROPERTIES

Bimetallic clusters and cluster assemblies differ from pure metallic ones in several respects. In Ref. 5, segregation in \( Ni-Al \) clusters was studied in clusters with different sizes and shapes. Cluster surface effects are also discussed in Ref. 44. Segregation in nonmiscible clusters is discussed in Ref. 8. Here, we focus on stress properties. We first recall previous work\(^{45} \) about stress distributions in a perfect infinite \( L1_2 \) \( Ni_3 Al \) crystals which is used as a reference. The case of isolated nanoparticles is examined next, and the section ends with a discussion of cluster-assembled materials synthesized by cluster deposition and by compaction. The stress distribution in the ordered alloy is not homogeneous at the atomic scale and differs from one sublattice to the other. One equilibrium condition is a balance between tensile and compressive stresses at the atomic scale in order to warrant a macroscopic zero pressure. At 0 K, with the present model potential, the partial pressure measured on \( Ni \) atoms is \(-3 \) GPa while that measured on \( Al \) is 9 GPa, and according to the stoichiometry of \( Ni_3 Al \), the net nanoscopic pressure is, as expected, exactly zero. The macroscopic shear also has to be zero. However, as noticed in the previous section, it cannot result from a balance between contributions at the atomic scale. For symmetry reasons, in the \( L1_2 \) structure, the shear at \( Al \) locations is exactly zero while, because of the breakdown of symmetry, a nonzero magnitude of the shear invariant on each \( Ni \) atom is measured: namely, 3 GPa\(^2 \). The nanoscopic shear is found to be zero, as expected. At nonzero temperature, the overall equilibrium pressure, of course, remains zero. However, the difference between the balancing partial pressures on the two subsystems decreases with increasing temperature. This decrease is slow and the difference between overpressurized and underpressurized subsystems remains of the order of the 0 K value well above 1000 K: namely, several GPa. Small particles are known to undergo self-compression due to surface stress. This was measured experimentally\(^{46-48} \) and estimated theoretically\(^{49,50} \) for elemental clusters. The question now arises to know to which extent the situation is different in isolated \( L1_2 \) clusters. Pressures were measured at 0 K in isolated clusters of all sizes considered, and we here describe the cases of clusters containing 2315 and 8247 atoms, which are typical. The radial distributions of atomic pressures at 0 K in both clusters are shown in Fig. 1 where the distinction is made between the \( Al \) and \( Ni \) subsystems. Like in the infinite single crystal, a difference of several GPa is seen in the cluster cores between overpressurized \( Al \) and underpressurized \( Ni \). The magnitude of these partial pressures slowly decreases with cluster size. Namely, they do not decrease by more than 10% when the cluster size is reduced from 8247 to 2315 atoms. Atomic pressures in the vicinity of the surface are significantly modified, as a consequence of the different environment, and sig-
significantly scattered, as a consequence of disorder in the surface shell. The two subsystems cannot be differentiated anymore on the basis of partial pressures. Indeed, both tend to some negative value, consistently with the case of contracted planar surfaces of a semi-infinite metal that are under tensile stress at equilibrium. The radial distribution of the shear invariant is also measured at the atomic scale. The distinction between the two subsystem is made and the results are shown in Fig. 2. As expected, a similar dependence as for pressures is observed. In the cores, the shear is zero on Al atoms and close to 1 GPa² on Ni. It is slightly higher in the largest cluster, but still a factor of 3 smaller than in bulk Ni₃Al. Hence, the effect of the cluster surface is to reduce the atomic shear stress on Ni. In the surface shell, much scattering is observed, subsequent to the structural disorder. The nanoscopic pressure in the cluster cores is found to be positive and, in contrast with partial pressures, it is found to increase with decreasing cluster size. A value of 2.2 GPa is found in the 2315 atoms cluster and of 1.5 GPa in the larger one considered at 0 K. These pressure values are of the same order as those estimated for 1–5-nm elemental clusters of different elemental metals.⁵⁰ The ratio between these pressures equals the inverse of the ratio between the cluster radii, consistently with the Kelvin equation for a classical droplet model. Stress tensors on a unit cell in the core and in the vicinity of the surface shell are also compared. The nanoscopic shear invariant in the cores is zero, indicating that the pressure is purely hydrostatic. Close to the surface but still in the ordered area, a negative pressure is measured of a fraction of a GPa, showing that it changes sign with respect to the core values already in the ordered area. The nanoscopic von Mises invariant in the same vicinity is nonzero (a magnitude of the order of 2 GPa² was measured) as a consequence of surface contraction. Clusters are thus sheared in the vicinity of their surface, still consistently with the results obtained for elemental clusters.⁵⁰ The temperature dependence of partial pressures in the grain cores is represented in Fig. 3 and compared with the infinite single-crystal results. The finite cluster size is clearly seen to reduce the differences between the partial pressures, and this difference is further decreased with increasing temperature. The deposition of a cluster on a surface to which it sticks is known to profoundly modify its morphology, even when deposition takes place at low energy.⁶⁵¹–⁵³ In addition, a lattice mismatch between the substrate and the deposited cluster induces a shear in the cluster.⁵⁴ The cluster-surface interaction thus modifies the spatial distribution of stress during deposition. Accumulating clusters on a surface is then also expected to induce further stress, and a similar phenomenon may be expected for nano-
structured materials obtained by cluster compaction. Disordering and stoichiometry deviations at the interfaces in cluster compacted Ni$_3$Al are discussed in detail in Ref. 6. Stress distributions in the two model cluster-assembled materials are now estimated. Figure 4 shows a qualitative pressure map in a slab of the compacted assembly after equilibration at 300 K and subsequent quenching to 0 K. Features in the deposited sample are similar. Typical views of thin Ni$_3$Al cluster films were already published elsewhere, having a similar morphology as observed for elemental cluster films. The clusters keep their identity and form a film with high porosity. Cluster interfaces and internal surfaces are disordered, formed dominantly by miscoordinated atoms. Hence, as structural properties are concerned, the clusters are strongly modified in neither the deposited nor compacted model samples. As partial pressures are concerned, the distributions in the grain cores are qualitatively similar to those in free clusters as well, Al being overpressurized and Ni underpressurized. The interfaces are dominantly delineated by tensile areas. Intergranular areas display no significant difference between atomic pressures on Ni and Al atoms. In order to allow for a quantitative comparison with the case of free clusters, one of the 2315-atom clusters is analyzed in the deposited layer and one of the 8247-atom clusters in the compacted layer. The radial pressure distributions obtained after quenching at 0 K are shown in Fig. 5 and compared with the free-cluster results. Distributions are substantially broader in the assembled samples, regardless of the cluster size and the assembling procedure, the dispersion being the most spectacular at the cluster interfaces. The effect of assembling is to shift the mean partial core pressures to lower values in these clusters. The average stress tensor is also estimated for a unit cell in the cluster center and close to the surface shell in the same clusters, after deposition and compaction, respectively. Similar results are found in both. The
nanoscopic shear invariant in the cluster core is no longer zero, and a magnitude of the order of 50 GPa\(^2\) is found in one of the 2315-atom clusters. In contrast with the case of free clusters, the mean pressure in the selected cluster cores is now negative, with a magnitude of a fraction of a GPa. From compressive, the stress in the clusters core thus became tensile after deposition. In the vicinity of the surface shell but still in order areas, a mean nanoscopic pressure around \(-3\) GPa and a mean nanoscopic shear of about 6 GPa\(^2\) are found. In view of the study of the deformation properties presented in the next section, a slab is cut in the deposited layer, parallel to the substrate surface, and periodic boundary conditions are applied in the direction perpendicular to this slab. This way, an infinite nanostructured material is modeled. The procedure was already used for studying interfacial atomic diffusion properties\(^{55}\) and was found to be satisfactory, despite the artificial planar interface generated by the boundary conditions. In addition, pressure and shear distributions perpendicular to the slab indicate no significant modification of the stress at the artificial interface created by the boundary condition applied. This sample is used with the compacted one in order to characterize the effect of temperature on the stress distributions. As qualitatively indicated in the discussion of Fig. 5, the stress distribution is highly inhomogeneous in both samples and the partial pressures in the grain cores are shown in Fig. 6 as functions of temperature, together with the standard deviation of their distributions. At 0 K, the standard deviation has the same magnitude as the mean core partial pressures and those in the interfacial areas, not shown in the figure, are down to one order of magnitude lower than in the cores. When the temperature is increased, the difference between the overpressurized and underpressurized systems in cluster cores decreases and the standard deviation significantly decreases too, showing that the effect of temperature is to homogenize and to lower the stress.

IV. DEFORMATION PROPERTIES UNDER UNIAXIAL STRESS

A. Deformation regimes

As shown in Ref. 45, in a perfect single crystal, the elastic strain increases linearly with the applied uniaxial stress over a large range of deformations and, in this regime, the slope of the strain-stress function depends on the direction in which the load is applied. For instance, the Young modulus at 0 K is estimated of 276 GPa in (111) directions and 100.4 GPa in (100) directions. The experimental value for polycrystals lies in between.\(^{57}\) The Poisson ratio associated with (111) stress is 0.2 while it reaches 0.4 for (100) stress, which is also the experimental value. The response to a uniaxial stress was also evaluated from 0 to 1000 K, and the linearity is found to be unaffected by the temperature. The Poisson ratio is found to be temperature independent. On the contrary and similarly to the case of homogeneous systems, the estimated Young modulus is a decreasing function of temperature. The overall mechanical response of the assembled model samples under similar loads is quite different. Figure 7 shows the time dependence of strain under the effect of a uniaxial load of 1.5 GPa applied to the compacted sample at 0, 300, and 600 K. Similar dependences were found in nanostructured Ni,\(^{20}\) and the results are qualitatively the same for the deposited Ni\(_3\)Al sample. At 0 K, the time dependence of strain is typically that expected in the case of
an elastic deformation. Deformation takes place within a delay of the order of 1 ps and then remains constant. The deduced Young modulus is 65.6 GPa, which is pronouncedly smaller than the single-crystal values estimated in any direction. Because of the limited number of grains in the cluster-assembled sample, the Poisson coefficient could not be measured accurately and is estimated between 0.24 and 0.28. At room temperature, a similar, though larger, fast deformation takes place within the first ps, evolving further but slower on longer time scales. The short-term deformation is elastic with a lower Young modulus than at 0 K. Within the next 100 ps of simulation, the strain does not stop increasing. The same difference between two regimes takes place at higher temperature, the short-term deformation being still larger and the longer term still faster. The longer-term regime is the signature of plastic deformation. This can be demonstrated by releasing the load and quenching the unloaded system at 0 K. When the deformation is elastic, once the stress is released, the strain vanishes. This is found at 0 K. At 300 K, as a consequence of quenching after 100 ps deformation, the strain decreases as well but tends to a nonzero value, showing that the deformation is plastic. Similar evidence for plastic deformation was found in Ref. 20 in pure nanostructured Ni. Strain rates are represented as functions of stress in Fig. 8 for the compacted and deposited samples at 0 K, showing a clear distinction between an elastic and a plastic regime. Similar results are found at nonzero temperatures, with a lower elastic limit, however, and an elastic limit which is temperature dependent. In the elastic regime, Young’s moduli are systematically lower than estimated for single crystals, but they are also decreasing with increasing temperature. The measured variation spans from 65.6 GPa at 0 K to 42 GPa at 600 K. Figure 8 indicates that the strain rate might raise asymptotically at a limiting stress at which it becomes infinite.

B. Deformation mechanisms

The plastic deformation observed mainly takes place in intergranular areas. In the present assembled sample, it can be evidenced by repeating the model experiment described above and plotting the strain versus time in specific limited areas of the samples. The result is shown in Fig. 9 in the case of the deposited sample. Strain is followed subsequent to an applied load of 2 GPa at 600 K for two areas in grain cores and two intergranular areas selected. The overall strain-stress function is shown as well. Once the load is released, the strain in the grain core gets close to zero, showing that the deformation is dominantly elastic. In one of the intergranular areas, the evolution of the deformation follows the overall evolution, while the magnitude of the second is a factor of 5 larger, showing that the plastic deformation is far from homogeneous. The same behavior is found in the compacted sample. When clusters are small (values less than 5 nm are reported), intergranular plastic deformation is usually explained in terms of grain boundary sliding\textsuperscript{19,20,23} rather than by dislocation activity.\textsuperscript{25–27,29,31–33} In the present case, however, deformation also takes place via an increase of the open volumes. This is illustrated in Fig. 10, showing the sample density as a function of time for three different applied stresses. When the stress is low and the deformation is elastic, a density lowering is found, limited, however, to no more
than 0.1%. When the deformation is plastic, the density continuously decreases with time, consistently with an increase of the open volumes between grain cores. Visual inspection of snapshots during the deformation indicates that this increase is rather homogeneous. No evidence was found for a crack nucleating at one single open volume. Although the deformation of grain cores is dominantly elastic, plastic deformation mechanisms could be identified, more frequently in the deposited than in the compacted sample, associated with the emission and absorption of dislocations. Figure 11 shows a sequence of snapshots taken during the uniaxial load of the deposited film. A detail is shown of one 2-nm-size grain surrounded by three other ones with different orientations and an open volume. Two grains only are represented. Miscoordinated atoms are differentiated from the others and, in the first snapshot, they map the interfaces between grains and the inner surfaces. As time proceeds, a dislocation nucleates at the triple junction, which, as the whole interfacial area in the sample, is disordered. A front of miscoordinated atoms propagates toward the open volume in a (112) direction, and a stacking fault is formed within the small grain, characterized by a \(\frac{1}{6} (112)\) translation. To our knowledge, this is the first time that dislocation activity is predicted in such a small grain. A detailed examination of the event shows that the occurrence of the open volume helps this dislocation to nucleate and to propagate as its motion is accompanied by an overall elastic displacement of the surrounding grains. This displacement, which is only possible because there is room enough, lowers the threshold stress needed for the dislocation motion. This is an unlikely mechanism when large open volumes are unavailable, and it was indeed hardly detected in the compacted sample, which is denser. Hence, the conditions for emitting a dislocation not only appear as depending on stacking faults or generalized stacking faults energies but also on the nanostructure itself. Despite the lack of open volumes, dislocation activity was also detected in the compacted sample, and we give an example where it contributes to the recovery of defective grains. Similar sequences of snapshots as shown in Fig. 11 are displayed in Fig. 12. Here, a preexisting edge dislocation is set into motion and propagates toward a triple junction close to which it stops, leaving the grain perfect. This was observed in a grain of 5 nm size. Finally, it was noticed in the simulation of a uniaxial stress followed by relaxation that the net interfacial area was reduced. The extension of this area was quantified as the fraction of miscoordinated atoms. When applying a load of 2 GPa at 600 K to the deposited sample, the fraction of miscoordinated atoms increased from 37% to 39%, consistently with the enlargement of open volumes. After relaxation, this fraction dropped to 32%. This means that the crystalline structure partially recovered as a consequence of the applied load. A close examination of the nanostructure during traction demonstrated the disappearance of boundaries between grains with small disorientation, hence showing evidence for stress-induced coalescence.
V. SUMMARY

We first compared the properties of the local stress in two free Ni$_3$Al clusters of different sizes at room temperature and found them to be similar. In the core, like in elemental clusters, the mean pressure is hydrostatic, positive, and scales with the inverse of the cluster radius. The cluster cores are ordered and the partial pressures on the Ni and Al subsystems differ by several GPa. Al is under compressive and Ni under tensile stresses. The difference, however, is reduced as compared to bulk Ni$_3$Al and still reduces further as the temperature is increased. We then addressed the question to know whether the cluster properties are preserved after assembling and two different assembling procedures were considered. From a structural point of view, both nanostructures are similar, mainly differing by their densities and by cluster sizes. The clusters keep their identities and their cores remain ordered. As stress is concerned, the interfacial interactions are strong enough to change their state completely. While ever pressurized when isolated, the cluster cores may be under tensile stress and highly sheared when assembled, while the (nanoscopic) shear in free cluster cores is zero. The stress distribution from one cluster to another is highly inhomogeneous. Despite this, in the case of uniaxial deformation, an elastic regime could be evidenced in both nanostructures, making it possible to estimate a Young modulus and, to some extent, a Poisson ratio. It is found that the elastic limit is temperature dependent in a temperature range which can easily be reached experimentally. It is also found, in relation with the highly inhomogeneous initial stress distribution, that the magnitude of the plastic deformation due to the same applied uniaxial load largely varies from one location to another in the samples. This plastic deformation involves grain gliding, but also the enlargement of the pores in the nanostructure, with no nucleation of cracks. Both mechanisms take place at interfaces, which are disordered. Hence, no evidence was found that atomic and nanoscopic stress related to the $L1_2$ structural ordering plays a role in the plastic deformations observed. Some dislocation activity was detected in grains as small as 2 nm, made possible by the occurrence of open volumes in the close vicinity allowing for overall cluster motion during the propagation of the dislocations. This dislocation activity may either result in defect production (stacking faults) or in the recovery of preexisting defects.

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