Mechanical Instability of Oxidized Metal Clusters

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A mechanism to explain the complete oxidation of small metal clusters is proposed, based on the occurrence of a mechanical instability driven by the expansion of the progressively oxidized cluster surface and the subsequent stress relaxation. Molecular dynamics simulations of spherical Pd clusters show that an expanded surface layer is capable of straining the inner core of the cluster up to the point of inducing cavitation. These findings allow the interpretation of recent experimental results in which oxidized Pd clusters exhibit a hollow spherical shape. [S0031-9007(96)01155-6]

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The properties of metal clusters have been investigated in a number of different experimental conditions, significantly increasing our knowledge of the evolution of the solid state from the aggregation of isolated atoms [1]. Oxygen reactivity of metal clusters has recently attracted interest [2–5] because of the possible use of noble-metal clusters in heterogeneous catalysis, sensor technology, and other applications. The direct oxidation of 4–10 nm diameter Cu clusters appears to involve a fast process of Cu to $CuO_{0.67}$ and a slow process of $CuO_{0.67}$ to CuO [2], while in indirect co-implantation experiments a Cu_2O shell is found to cover the Cu core [5]. In the same temperature range (300–600 K) the oxidation of Cu thin films mainly results in Cu_2O [6]. From the structural point of view, a number of interesting experiments have been carried out on Pd clusters of 5–10 nm diameter by two different groups. Datye *et al.* [3] characterized metal Pd particles subjected to oxidation-reduction treatments, while Catalano *et al.* [4] studied the PdO particles obtained after in-air oxidation of Pd clusters at $T \sim 700$ K. In both cases the final clusters exhibit a hollow spherical shape. While the results based only on high resolution electron microscopy imaging could not unambiguously attribute the image contrast to an empty cavity inside the cluster, the electron holography technique [3] clearly confirms the presence of a central void zone in the expanded particles after oxidation.

In this Letter we propose a dynamic interpretation of the process of the complete oxidation of metallic clusters and, more generally, address the issue of mechanical stability of finite-size systems under strain [7,8]. It turns out that the lattice expansion induced at the cluster surface by the oxidation process brings the cluster core to a severely strained condition which is capable of inducing a mechanical instability. Molecular dynamics simulations of strained Pd clusters at $T = 700$ K clearly show that, when the cluster is isotropically expanded above some critical strain value, the inner cluster core becomes structurally unstable and develops cavitation, accompanied by the formation of point and extended defects. Under such conditions oxygen diffusion into the cluster core can be largely enhanced [9] leading to the complete oxidation of the cluster.

In the experimental data on Pd clusters recently published by Catalano *et al.* [4] complete oxidation of the metallic Pd into perfectly crystalline, stoichiometric PdO was reported. They estimated an initial compact particle diameter of 4.5 ± 0.5 nm and a final particle outer diameter of 5.5 ± 0.5 nm, enclosing an inner empty zone of about 1.5 nm diameter. Considering that the volume per Pd atom in the tetragonal unit cell of PdO is 1.69 times larger than in the fcc elemental unit cell, the above dimensions are consistent with the picture of a spherical shell of PdO containing the same number of atoms of the initial Pd metallic cluster.

The typical process of oxidation of bulk metal surfaces is rate limited by the diffusion of oxygen atoms into the bulk once the surface layers of the metal are saturated during the early stages of chemisorption [10]. The oxidized surface layers expand upon the metal-oxide transition, while the underlying bulk layers relax into an equilibrium configuration, somewhat strained with respect to the unperturbed crystal, as elsewhere demonstrated by the increase without shift in ion-scattering yields [11]. Under such conditions further penetration of oxygen atoms into the bulk is difficult, as the O diffusion coefficient is relatively small and the underlying metal does not easily accommodate further deformation. While in bulk oxidation only a minor fraction of the atoms at the metal-oxide interface are affected by the misfit strain, if oxidation takes place at the surface of a nanometer-size cluster the hydrostatic strain induced by the metal-to-oxide lattice expansion covers a length scale affecting the whole system.

Two ideal, limiting relaxation kinetics can be considered in cluster surface oxidation: (A) the structural metal-oxide transformation at the surface region is slow enough to allow a progressive, homogeneous strain accommodation in the rest of the cluster; (B) the structural transformation occurs on a time scale short with respect to relaxation dynamics, resulting in a strain initially localized at the cluster surface. In both cases the cluster is subjected to an unusual state of isotropic stress deriving from the expansion of the surface layers upon oxidation.

These conditions have been casted into an atomistic model of Pd clusters of size comparable to the experimental samples of Refs. [3,4], whose structural properties have been studied by means of molecular dynamics (MD) computer simulations under the hypothesis of either homogeneous (A) of localized (B) strain. A system of 8851 Pd atoms was arranged in a truncated-octahedron initial fcc geometry, resulting in a quasispherical cluster with diameter of about 6.3 nm. The interatomic potential adopted in this study is derived by a second-moment approximation of the tight-binding scheme for d-band transition metals [12] and includes the basic features of metallic bonding at a phenomenological level. Previous studies [13,14] have shown that the truncated-octahedron fcc geometry is the minimum energy configuration in this size range. We define a "surface region," comprising the atoms within a shell of thickness 0.615 nm from the surface (i.e., one potential cutoff length) and a "core region," comprising all the remaining atoms in the cluster. The slow-kinetics mechanism (A) was reproduced by imposing a homogeneous, isotropic strain to the whole cluster. To reproduce the fast-kinetics mechanism (B), in turn, the deformation was initially localized by imposing a homogeneous, isotropic strain only to the surface region. In both cases, thermal equilibration MD runs at $T = 700$ K were performed only for the atoms in the core region, holding the surface region fixed. Thermal equilibration runs lasted about 10^5 time steps (1 time step $\sim 10^{-15}$ sec).

A first series of simulations was performed for the mechanism (A) at increasing strain values ε. The potential energy per atom $U(\varepsilon)$ and the internal pressure $P(\varepsilon)$ (the trace of the atomic-level stress tensor [15]), averaged over the core region, are shown with full symbols in Figs. 1(a) and 1(b), respectively. Lattice stability is expressed by nonvanishing second-order variations of the elastic potential [16], such that the discontinuity in the curves at about $\varepsilon = 0.04$ points to a mechanical instability of the system. Above this critical value stress relaxation results in the formation of a large void inside the cluster core, as verified by direct inspection of atomic configurations. This qualitative behavior is characteristic of lattice decohesion [7], the appearance of quasispherical cavitation being the result of the hydrostatic stress relaxation [8].

In order to verify the mechanical instability origin of this effect, we studied the behavior of the elastic moduli of a perfect, infinite Pd crystal at different levels of hydrostatic pressure. Once the finite-temperature cubic elastic moduli C_{11}, C_{12}, and C_{44} are determined by means of the fluctuation formula of Ray and Rahman [17], the finite-strain stability criteria for a homogeneously imposed isotropic expansion derived in Ref. [7] can be expressed as (i) $(C_{11} + 2C_{12}) + P > 0$, (ii) $(C_{11} - C_{12}) - P > 0$, and (iii) $C_{44} - P > 0$, where $P < 0$ is the pressure value for a state of hydrostatic tension corresponding to the imposed isotropic strain. Violation of any of the above inequalities is related to the occurrence of a mechanical instability due to bulk decohesion, "tetragonal" shear (or "Born instability"), and "rombohedral" shear, respectively. Figures 2(a) and 2(b) report the left-hand side of the three stability criteria at increasing values of strain and at two different temperatures. As expected, based on the fact that the strain eigenvector corresponding to hydrostatic expansion has the same symmetry of the undeformed lattice, the first instability to occur is always the bulk decohesion, (i) above. The critical strain level which at $T = 0$ K in absence of thermal fluctuations has the value $\varepsilon_c = 0.080$, decreases with increasing temperature. We found, by linear extrapolation, $\varepsilon_c = 0.048$ at $T = 300$ K and $\varepsilon_c = 0.040$ at $T = 700$ K. Since the strain value marking the discontinuity at $T = 700$ K in Figs. 1(a) and 1(b) is roughly consistent with the ε_c bulk value, we infer the bulk lattice instability to hold also for the homogeneously strained cluster. The above elastic moduli analysis demonstrates that, in the considered temperature

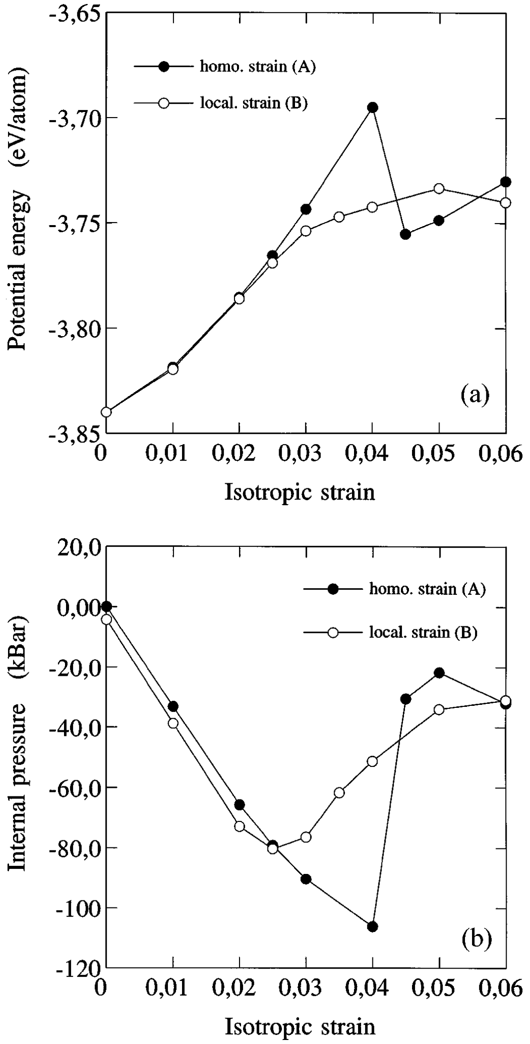

FIG. 1. Potential energy (a) and internal pressure (b) for the atoms in the cluster core region as a function of the isotropic strain: (A) homogeneously applied to the whole cluster (full symbols), or (B) initially localized to the atoms in the surface region (open symbols).

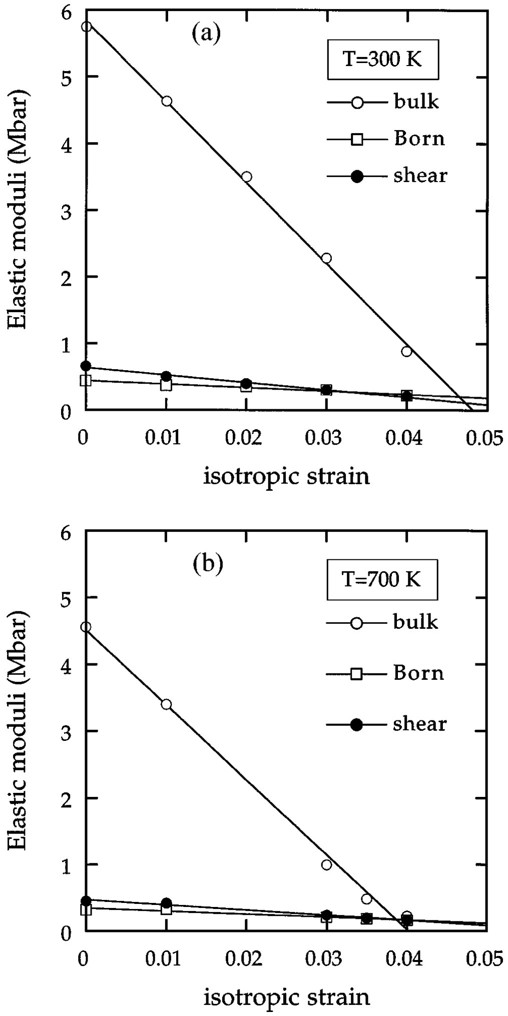

FIG. 2. Elastic stability criteria as a function of the homogeneous isotropic strain ε in a bulk Pd crystal at different temperatures: (a) $T = 300$ K; (b) $T = 700$ K. The elastic moduli referred to in the caption as *bulk, Born,* and *shear* are the left-hand sides of criteria labelled (i), (ii), and (iii) in the text, respectively.

range, the critical strain for mechanical instability through bulk decohesion is sufficiently low to be attained during the cluster expansion.

A second series of simulations was performed for the mechanism (B) at increasing strain values ε. Open symbols in Figs. 1(a) and 1(b) show the behavior of $U(\varepsilon)$ and $P(\varepsilon)$ in this case. For $\varepsilon < 0.25$ the negative pressure of the inner core decreases and the internal energy monotonically increases because the imposed strain introduces a positive elastic energy contribution. Beyond $\varepsilon = 0.025$ the internal pressure starts decaying to a small, finite value, while the energy curve experiences a smooth inflexion. In this case the stress relaxation mechanism cannot be associated to the onset of a mechanical instability because of the absence of any discontinuity. However, a direct inspection of the atomic structures obtained by MD runs at $\varepsilon \geq 0.025$ shows a cavitation phenomenon qualitatively similar to that occurring in mechanism (A) beyond ε_c. The equilibrium structure in (B) establishes through propagation of a pressure wave, tending to concentrate the free volume towards the cluster center. The presence of a centripetal pressure wave has been clearly detected by evaluating, as a function of time, the radial pressure distribution in the core region [18]. For $\varepsilon < 0.025$ the core region keeps its solidlike behavior and no stable point or extended defects are found, while the centripetal pressure wave is dispersed into homogeneous deformation. Above that strain value, in turn, the nucleation of a void becomes possible. Figure 3 shows two subsequent equilibrium states of the central section of the cluster projected on a {100} fcc symmetry plane: at a strain $\varepsilon = 0.025$, when a small central void is nucleated together with several lattice defects [Fig. 3(a)], and at a strain $\varepsilon = 0.04$, when cavitation has taken over the whole cluster core [Fig. 3(b)]. While the results obtained by the application of a homogeneous strain in mechanism (A) are independent on the system size, the above de-

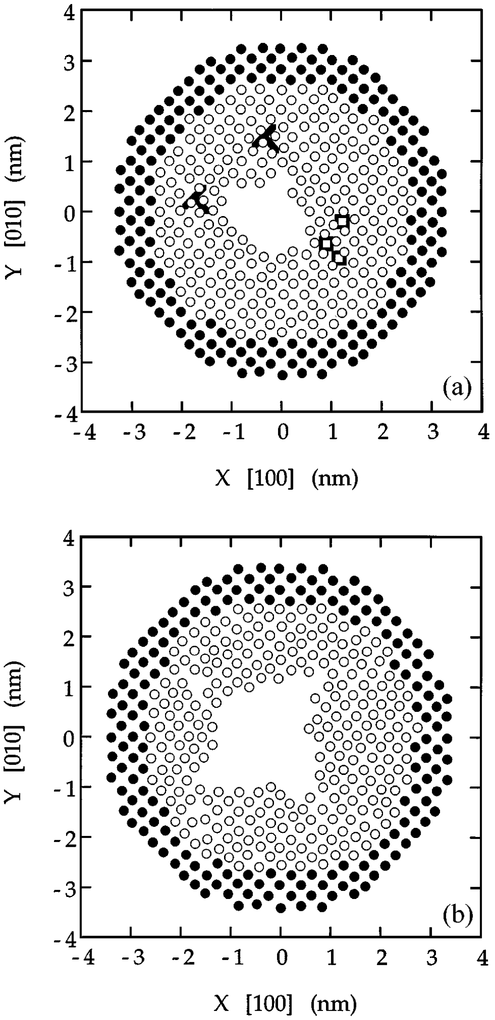

FIG. 3. Snapshots of thermally equilibrated MD states of the central section of the cluster, projected on a {100} fcc symmetry plane, at different values of the strain imposed to the surface region (represented by the black atoms): (a) $\varepsilon = 0.025$, (b) $\varepsilon = 0.04$. The position of some lattice defects such as vacancies (□) and dislocations (**T**) is marked in (a).

scribed kinetics for mechanism (B) is peculiar to finite-size clusters. Based on the fact that below $\varepsilon_L = 0.025$ the strain is always homogeneously redistributed for both mechanisms (A) and (B), we infer that above this (possibly size-dependent) limiting strain value ε_L the enthalpy of a single, large void inside the cluster becomes smaller than that of a homogeneously strained cluster. The fact that a homogeneously strained cluster (A) above ε_L is not able to nucleate a single void suggests that there is a large kinetic barrier for the volume fluctuation necessary to spontaneously form a large central cavity. For the locally strained cluster (B) the centripetal pressure wave is responsible for overcoming the kinetic barrier. Despite their apparently different physical origin, the resulting final structures are very similar for both mechanisms, with a similar size of the central void zone and a like density of point and extended defects.

In view of the present results, a scheme for the kinetic process leading to the oxidation of small Pd clusters can be proposed. The process starts at surface specific adsorption sites. As far as surface coverage proceeds and the correct oxide stoichiometry is attained, the oxidized surface region expands up to the PdO cell volume. MD simulations reproducing two ideal, limiting kinetics for stress relaxation have shown that, above a critical strain value, the cluster develops cavitation. This phenomenon has the accompanying effect of producing a high concentration of point and extended defects which decreases the migration barrier for oxygen diffusion. In fact, it has been recognized that transport in growing oxide films on metals can be greatly enhanced by the presence of fast diffusion paths at the metal-oxide interface, such as grain boundaries, dislocations, and point defects [10]. Such enhanced oxygen diffusion allows the oxidation of the whole cluster structure, resulting in an empty spherical shell of crystalline oxide. The occurrence of bulk decohesion and the resulting complete cluster oxidation depend on the interplay between a large atomic volume increase upon formation of the oxide phase and the thermal softening of elastic moduli to lower the critical strain value. However, the further requirement of a complete surface oxygen coverage is needed to insure isotropic expansion as modeled in our MD simulations. In fact, recent experimental data obtained on Cu clusters with highly nonspherical shape did not show any similar effect, despite the presence of a large volume deformation related to a partial surface oxidation [5].

The homogeneous value ε_c of the critical strain represents the upper limit for the mechanical stability of the system, above which the symmetry of the imposed deformation forces the system to develop cavitation. However, our results indicate that there exists a lower stability limit ε_L above which cavitation and decohesion can develop through a particular void nucleation path—identified with a centripetal pressure wave—which is kinetically suppressed in the homogeneously strained system. This lower limit should be determined by the free-energy competition between the tendency of the free volume to aggregate into a large spherical void and the tendency to redistribute the deformation homogeneously among the system. In this sense, the two values ε_L and ε_c acquire a meaning and a physical origin similar to the thermodynamic melting temperature and the "mechanical melting" temperature at zero pressure [19].

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