Structural modification of a multiply twinned nanoparticle by ion irradiation: A molecular dynamics study

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We study the possibility of modifying the structure of a multiply twinned nanoparticle by ion irradiation. Molecular dynamics simulations are carried out for the prototypic case of a metastable icosahedral Pt particle bombarded with He and Xe ions in the energy range of 0.1–10 keV. A single xenon impact can be used to melt the particle. It can also induce partial melting, which causes a collapse of the twin boundary structure in the solid part and transformation to single crystalline morphology. Under He irradiation, we observe a saturation of the vacancy concentration, but no untwinning. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2825045]

I. INTRODUCTION

Metallic nanoparticles have gained much attention because of their catalytic, magnetic, and optical properties, which are determined in a delicate way by the particle size, structure, and shape. The catalytic activity of platinum particles, for instance, depends sensitively on the shape[1] and it is therefore desirable to devise methods which allow to adjust the particle shape in a controlled manner. Depending on the synthesis conditions, however, as-prepared particles do not necessarily exhibit the desired structure and shape, since kinetic processes can lead to the occurrence of metastable nonequilibrium structures during synthesis. One example is the formation of multiply twinned structures in particles prepared by inert gas condensation.[2]

In the case of fcc metals, nanoparticles below a certain critical size can thermodynamically exhibit transitions from single crystalline Wulff shapes to multiply twinned structures. Such a transition is driven by the reduction of the number and size of (100) facets at the expense of the formation of internal twin boundaries and elastic strain.[2] While one certain structural motif represents the minimum free energy configuration of a particle at given conditions, kinetic effects can be exploited to produce, or produce undesirably, other metastable structures.[2]

Ion beams are a versatile tool for many kinds of material modification[3] and the irradiation of embedded nanoparticles has been widely studied. Much less, however, is known on the interaction of ion beams with free or supported nanoparticles.[4,5]

In the present study, we present molecular dynamics simulations, which were carried out in order to investigate possibilities for the structural modification of multiply twinned particles by ion irradiation. We have chosen a multiply twinned icosahedral Pt particle of 4 nm (3871 atoms) in size, which has a strong thermodynamic driving force for untwinning. From an application point of view Pt can be considered as a prototypical material in catalysis,[1] but also as a model system for other metallic nanoparticles, e.g., FePt.[5]

In our study we compare the effect of both light (He) and heavy (Xe) ion irradiation on the particle structure. Because of the high twinning energy in Pt, the icosahedron represents a metastable state, which is deeply kinetically trapped, since the untwinning process would in principle require to nucleate a series of partial dislocations at the surface.

Irradiation is most often done on supported particles. In the present study, however, we focus on ions impacting on free particles, a choice which is made for two reasons. First, a substrate would certainly affect the sputtering yields by stopping most atoms ejected towards it, depending on the nature of the substrate, while it is desirable to first understand the "pure" response of the particles to irradiation. Second, bombarding free particles mimics an experimental setup of in-flight irradiation of condensed particles.

II. METHODS

In the following we briefly outline the technical details of our simulations. Interatomic interactions were described by an analytic bond-order potential[6] that reproduces the high twin boundary energy of platinum, $\gamma_{TB}=166(mJ/m^2)$. At short distances this was smoothly joined to the universal repulsive Ziegler-Biersack-Littmark potential[7] that was also used for the ion-platinum interactions. Inelastic energy losses due to electronic stopping were included in the equations of motion of all atoms with kinetic energy higher than 5 eV.[7] For technical reasons, the stopping was also applied somewhat outside the nanoparticle but this amounted on average to less than ~1% of the total stopping for the incoming ion.

In the case of platinum, the truncated octahedron is always the minimum free energy state, followed by the decahedron and the icosahedron. With the bond-order potential, the energy difference between the icosahedron and the truncated octahedron is 21 meV/at.

For simulating the effect of helium and xenon ions on the nanoparticle, the particle was placed in vacuum after relaxing it to 0 K. The particle was then rotated randomly and

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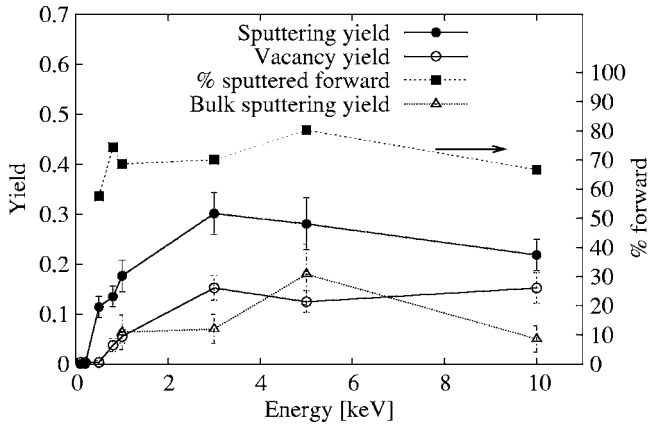

FIG. 1. Sputtering and vacancy yields of a 3871 atom Pt cluster under helium bombardment.

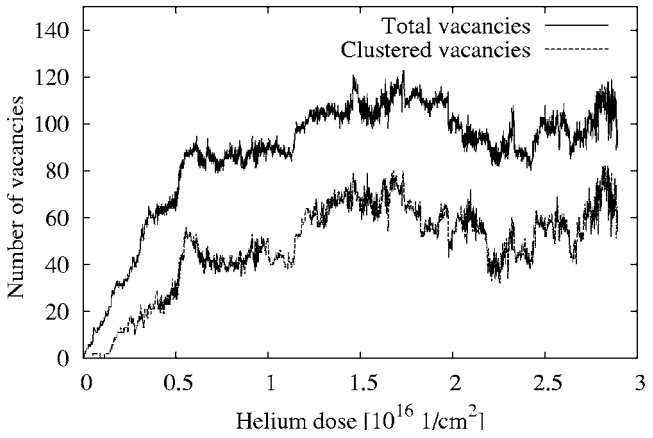

FIG. 2. Evolution of the number of vacancies in a 3871 atom Pt particle as a function of helium dose.

bombarded with an impact parameter chosen randomly inside a radius, which is given by a cylinder wrapped around the cluster. This procedure caused some ions to miss the target, an effect which has been corrected for in the data presented here. After the impact, the sputtering yield from the particle was determined using a clustering algorithm. For helium bombardment, the vacancy production was obtained by analyzing the free volume inside the particle, in the form of spheres of ~2.2 Å radius. In those cases, where the particle was partly molten after Xe impact, structural analysis was also done by the common next neighbor analysis.[8] For both impacting ions, the sputtering yield from a bulk (111) surface was determined for comparison.

III. RESULTS AND DISCUSSION

A. Helium irradiation

We begin by addressing the irradiation of the nanoparticle by light ions, namely, with 100 eV–10 keV helium. Because of its small mass a He beam only generates Frenkel pairs in the irradiated material. All interstitials that escape from the recombination volume can easily reach the surface. Therefore it is of primary interest to compare the energy dependence of the sputtering and vacancy production rate with the case of a bulk material. The results are shown in Fig. 1. The calculated yields increase with increasing energy until they reach a constant value at about 3 keV energy. At this point the collision cross section decreases, making efficient energy transfer less likely, although the maximum deposited energy increases. For all energies, forward sputtering (defined by the incident ion direction) is slightly favored, as can be expected. Comparison with the calculation for a (111) bulk surface shows that the sputtering yield of the nanoparticle is significantly higher. This can mainly be attributed to the large amount of atoms sputtered in the forward direction.

If we assume that a structural modification of the particle could be induced by the agglomeration of athermal vacancies as suggested in Ref. 5, we can conclude from the calculated sputtering yields and vacancy production rates that He irradiation is not practical unless significant mass loss of the particle is tolerated. It should be noted, however, that it is not obvious how athermal vacancies could induce an untwinning mechanism.

In Ref. 5, the mechanism was suggested to be atomic diffusivity, increased by the high irradiation-induced vacancy concentration. However, the vacancies' role in the process can be estimated by calculating the number of jumps a single vacancy makes before the creation of the next vacancy, $N_{\text{jumps}}=\Gamma_0 e^{-E^m/k_BT}/\Gamma_{\text{vac}}$, that is, the rate of vacancy jumps divided by the production rate of vacancies, Γ_{vac}. Above, Γ_0 is a prefactor, which is taken to be[9,10] 4×10^{13} s^{-1}. (We use values for Pt but the same conclusion can be drawn for FePt also.) The vacancy migration energy is $E^m=1.45$ eV (Refs. 9 and 10) and the vacancy production rate is given by the ion flux times the vacancy yield per ion, which from Fig. 1 is around 0.15. Assuming that a dose of 3×10^{17} cm^{-2} is deposited over 10 h at room temperature, we get $N_{\text{jumps}}\sim10^{-10}$. Thus, vacancies are stationary during deposition and atomic diffusivity can be expected to be low. This is in accordance with the observed absence of $L1_0$ ordering in particles irradiated by He.[5]

On the other hand, since the vacancies do not move during irradiation, extensive accumulation of damage can be expected. This could then cause a structural transformation by destabilizing the icosahedral morphology, still not leading to $L1_0$ ordering. The morphology of the 4 nm particle, however, turns out to be quite stable against the creation of vacancies. To study the effect of continued helium irradiation, we bombarded the particle with 3 keV He ions every 7.5 ps. After each impact, the particle was allowed to float freely for 5 ps after which it was quenched back to 0 K in 2.5 ps. This was repeated until ~31% of the atoms in the particle had been sputtered away corresponding in magnitude to the experimental damage in Ref. 5. With the particle size being 3871 atoms, this required a dose of $\sim3\times10^{16}$ cm^{-2}. During the simulation, the number of vacancies in the particle rose quickly and saturated, as shown in Fig. 2. It is clear that subsequent impacts have lead to a recombination of immobile athermal vacancies with newly generated interstitials. After saturation, about half of the vacancies are found in vacancy clusters.

Surprisingly, the particle's icosahedral structure survived the continued irradiation despite the high energy of the twin boundaries, even after postirradiation annealing of 5 ns at ~1700 K. The simulations indicate that the mechanism of

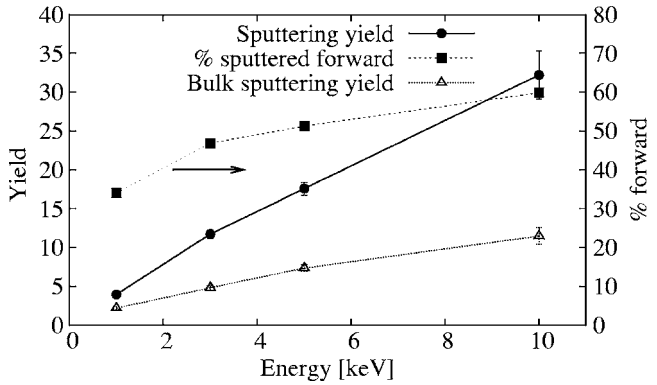

FIG. 3. Sputtering yield of a 3871 atom Pt cluster and bulk Pt under xenon bombardment.

untwinning observed in Ref. 5 is not simply accumulation of damage in the cluster, nor is it likely to be mediated by vacancy migration. One possibility is that a substrate, effectively stopping most forward-sputtered atoms, would allow for a reorganization of the particle, perhaps through interstitial loop formation. This question, however, is outside the scope of this study and will be addressed in the future.

B. Xenon irradiation

We now turn to discuss the possibility of structural modification by ion irradiation with heavier ions, namely, xenon, and investigate impacts on the same Pt particle in the energy range of 1–10 keV. The resulting sputtering yields are shown in Fig. 3. Now, the sputtering yield per ion is much higher and rises linearly with energy, as expected from collision cascade theory.[11] Also, back and forward sputterings compete, with higher energy naturally favoring the forward direction.

As xenon is a heavy element, only a single ion impact results in changes in the cluster structure. In particular, a single impact can bring the cluster close to its melting point. For supported particles, this provides a way to melt without thermal annealing, avoiding agglomeration and sintering. The final morphology is then a question of the kinetics of resolidification. On the other hand, if a cluster melts only partially, as can be expected to happen in some range of deposited energies,[12] the remaining solid part could undergo a structural transition into a lower energy configuration. Such structural changes are seen, for example, for palladium and nickel clusters that, partly molten, go from a decahedral to an icosahedral structure (Pd) or vica versa (Ni) close to the melting point.[13,14]

After 5 keV Xe bombardment, for example, some of the clusters are indeed found in a coexisting solid-liquid state. Some of these partly molten clusters were simulated for an additional period of 10 ns in vacuum to see whether structural changes appeared. A few possible outcomes were detected. In one case the cluster melted completely after about 5 ns. In many cases, there was a single transition where the fcc atom content of the cluster went up while the number of hcp atoms decreased only slightly or not at all. This indicated a transition from a partly molten icosahedron to a decahedron, such as the one reported in Ref. 14.

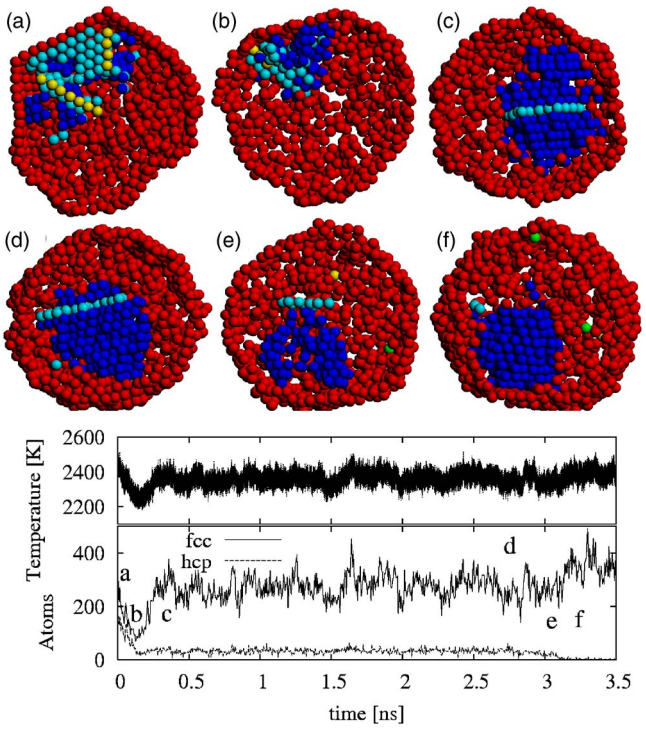

FIG. 4. (Color online) Transition from icosahedral to single crystalline morphology in a partly molten cluster. The upper part shows snapshots of the transition. The atoms (color online), from darkest to lightest, are fcc (blue), surface (red), hcp (light blue), and fivefold symmetry axis (yellow). Liquid atoms are not shown. The lower part shows the number of fcc and hcp atoms and the temperature. Initially (a), the cluster is a partly molten icosahedron but at some point the liquid part absorbs the solid almost completely (b). The solid then recrystallises with only one twin boundary between two fcc parts (c). The boundary exists for several nanoseconds (d) but migrates in the crystalline part of the cluster. At some point it reaches the liquid boundary (e) and vanishes, leaving a single crystalline solid part (f).

More interestingly, a partly molten particle was also observed to make a transition from icosahedral to single crystalline morphology. Such a transition is detailed in Fig. 4. The transition involves an oscillation in the size of the melt, leaving behind a singly twinned particle. This is followed by migration of the twin boundary to the solid-melt interface, resulting in a single crystalline, partly molten particle. After slow cooling, a rough truncated octahedron was then obtained. A similar oscillation in the size of the melt was observed to cause transitions from single crystalline and decahedral palladium clusters to icosahedral ones in Ref. 13. Also, deposited metal nanoparticles have been shown to untwin by thermally activated dislocation motion,[15] similar to what is observed here.

IV. CONCLUSIONS

We have discussed the different possibilities for structural modification of platinum nanoparticles using irradiation with light and heavy ions. For light (He) ions, we show that the simple accumulation of damage is not sufficient to turn a multiply twinned particle single crystalline, nor is it likely that the experimentally observed[5] untwinning would be vacancy mediated. With heavy (Xe) ions, supported particles could be melted without thermal annealing, avoiding agglomeration and sintering. We also demonstrate that ion irra-

diation of free nanoparticles can be used as a means to reach the partially molten configurations described by Hendy[12] and Schebarchov and Hendy.[13,14] Furthermore, in such partially molten clusters, an untwinning process is reported in which the solid part of a partly molten cluster turns single crystalline by a combination of oscillations of the melt and twin boundary migration.

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