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Crystallization of Nanodroplet Prefers Closest-packed Planes Regardless to Substrate Orientations

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Supporting Information

ABSTRACT: We report molecular dynamics simulations of thermal spray coating of Cu nanodroplets on Cu substrates with different orientations, and show that the droplets crystallize by adding the closest-packed {111} planes regardless of the substrate orientations. Such preferential growth along the closest-packed planes may be common in a broad range of crystallization and melting processes.

Crystallization is the natural or artificial process of forming solid crystals from a melt as well as a solution or gas [1]. Not surprisingly, there is an immense interest across disciplines in a fundamental understanding of crystallization in order to predict, control and optimize crystal growth for many applications, such as coating, catalysts and novel materials. It is well known that a crystal grown on a seed substrate assumes the substrate orientation. In conventional wisdom, the growth is achieved by consecutively adding solid layers parallel to the substrate. Volmer [2] suggested a crystal growth theory in terms of layer-by-layer adsorption. However, the exact growth processes remain elusive given the experimental challenges in directly observing the fast dynamics at the atomic level. On the other hand, molecular dynamics (MD) with accurate interatomic potentials allows us to simulate certain realistic processes, and thus to gain insights into the crystal growth mechanisms. In this communication, we report MD simulations of thermal spray coating of Cu nanodroplets on Cu substrates with different orientations, and show that a crystal grows by adding the closest-packed {111} planes regardless of the substrate orientations, while the as-grown crystal is still oriented along the substrate orientation. During crystallization, moving solid-liquid interfaces are not necessarily parallel to the substrate surface, and may be at an angle determined by the substrate and {111} and form facets, in contrast to the conventional wisdom.

Thermal spray is a melt-spray process in which particles of virtually any materials are melted and accelerated to high velocities and the liquid droplets (e.g., nanodroplets) impinge on a substrate and rapidly solidify to form a thin splat [3,4]. Thermal spray has been used in fabrication of various kinds of nanostructures, and thermal spray of nanodroplets can be realistically simulated with MD (at similar time and size scales) [5,6]. Here we choose a simple system for MD simulations, face-centered cubic (fcc) Cu described by an accurate embedded-atom-method potential [7], to investigate crystallization dynamics. A liquid nanodroplet (1320 K) is assigned an impact velocity (v_{imp}), and impacts a cold single crystal substrate. We explore four representative substrate orientations: (111), (001), (011) and (112) (Fig. 1); v_{imp} ranges from 1 m/s to 5 km/s; two nanodroplet sizes (5 nm and 15 nm in diameter), and two substrate temperatures (300 K and 660 K) are examined. Details of MD simulations can be found in Supporting Information.

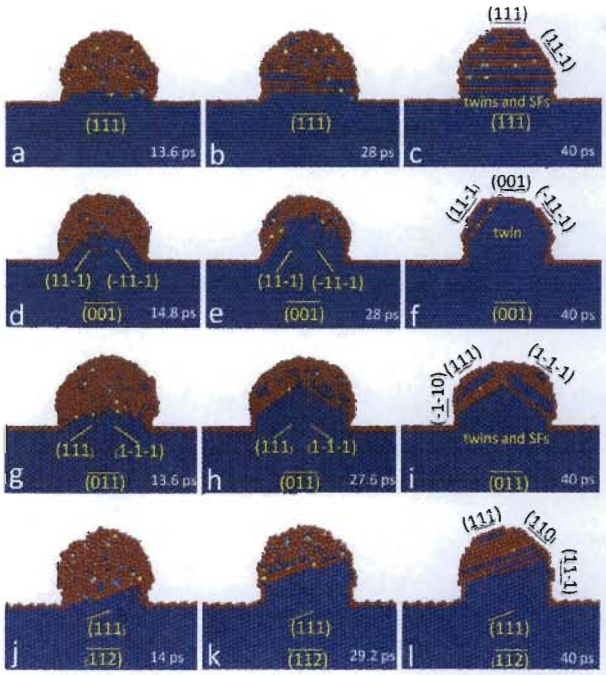

Figure 1. Snapshots of Cu nanodroplet crystallization on different Cu substrates. (a-c) (111) substrate; (d-f): (001) substrate; (g-i) (011) substrate; and (j-l): (112) substrate. The blue atoms are the atoms in the normal fcc packing, while the red atoms, those in the local hexagonal close packing (as in stacking faults) or other defects. Nanodroplet diameter: 5 nm; impact velocity: 100 m/s; substrate temperature: 300 K.

Upon impact, the solid substrate serves as the heterogeneous nucleation site ("seed") for crystallization, and the crystal growth is driven by the temperature gradient between the droplet and the substrate ("heat sink"). The snapshots in Fig. 1 illustrate the crystallization dynamics for four different substrate orientations and v_{imp}=100 m/s. For the (111) substrate (Figs. 1a-1c), the solid-liquid interface is parallel to the substrate plane and moves up with increasing time, i.e., the crystal grows layer by layer from the substrate by adding consecutively single-atom layers parallel to the substrate, as predicted by the crystallization theories [1,2]. We refer to the moving solid-liquid interface plane as the growth

plane, and it is (111) for the (111) substrate. At the final stage, some growth twins and stacking faults (SFs) are preserved.

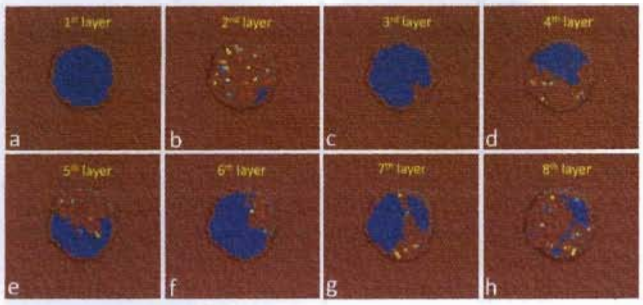

Figure 2. The layer-by-layer structure of the crystallizing nanodroplet on the (111) substrate. The blue atoms are the atoms in the normal fcc packing, while the red atoms, those in the local hexagonal close packing (as in SFs) or other defects. Nanodroplet diameter: 5 nm; impact velocity: 100 m/s; substrate temperature: 300 K; snapshot at 40 ps.

For the other three substrate orientations, the growth plane is also {111} but at a certain angle with the substrate. For the (001) substrate (Figs. 1d-1f), nucleation occurs in the middle part of the droplet from the substrate and the growth planes (two intersecting {111} planes or "facets") spread toward the edges and the top. (The growth planes are distorted by their interactions and the nanoparticle free surface at later stages.) Some SFs remain at complete crystallization. The crystallization process is largely similar for the (011) substrate (Figs. 1g to 1i), and the final structure contains twins and SFs along two {111} planes. In contrast, there is only one {111} growth plane in the case of the (112) substrate, owing to the particular crystallographic relation between (112) and (111) (Figs. 1j-1l). For the (112) substrate, one {111} growth plane is at about 19.5° with (112) and another {111} is normal to (112). Growth along the former {111} is favored since it is closer to the substrate, and begins with the right side (Fig. 1j). After complete crystallization, all the resultant nanocrystals show facets (Figs. 1c, 1f, 1i and 1l), including high-symmetry and low formation energy {111} and {100} facets according to Wulff construction [8]. Such features were also observed in experiments [9].

We also examine in detail the layer-by-layer growth process using the (111) substrate as an example (Fig. 2). We denote the crystallized single-atom layers as the 1st, 2nd, ..., and 8th layer, starting from the top substrate layer. The growth SFs almost form in every layer by adsorption, with random shape and location. The SFs within the next layer do not necessarily follow the locations of the SFs in the preceding layer. However, some of those SFs disappear via local relaxation, while the other ones grow across the nanocrystal and become stable growth SFs or twins. Defect formation may accompany crystal growth.

At high impact velocities (>500 m/s), damage to the substrates is induced. Fig. 3 shows two snapshots for the impact of a 5 nm droplet on the (111) substrate at v_{imp}=5 km/s. Upon impact, a crater is formed with an elevated rim and melt inside, and stacking faults and other defects in the substrate (Fig. 3a). The melt crystallizes subsequently; however, the crater morphology and the defects formed in the substrates appear to have negligible effect on crystallization: the growth plane is still {111} plane, and facets and defects in the final structure are also similar to the low velocity impact cases (Fig. 3b). Simulations with larger nanodroplets (15 nm) and higher substrate temperature (660 K) yield similar results. Despite the differences in exact dynamics, our simulations with different impact velocities, droplet sizes, substrate temperatures and substrate orientations all reveal that the growth plane is closest-packed {111}. Previous MD simulations of an fcc system found that the solid-liquid interfacial energy is lowest for {111} [10]; {111} also represents low energy planes. Thus, the {111} growth is energetically favorable. Consistent with our result, a previous study on melt crystallization in grooves showed that the nucleation rate is highest for the wedge angle of 70.5°, the dihedral angle between two {111} planes [11]. The {111} facets observed during melting of Si (100) are also in accord with the preferential growth along {111} during crystallization in our simulations [12]. However, the as-grown crystal as a whole is still oriented crystallographically along the substrate normal as observed in experiments; regardless of the substrate orientations, the added {111} layers are commensurate with the substrate orientation to lower free energy, and deviation from this orientation would be energetically unfavorable since it would lead to the formation of such defects as a grain boundary.

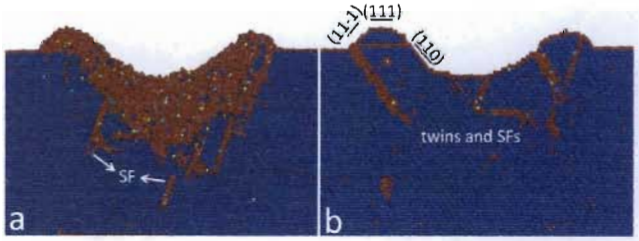

Figure 3. Snapshots of high speed impact and crystallization of nanodroplets on the (111) substrate: an impact crater and plastic deformation in the substrate (a) and subsequent full crystallization (b). Nanodroplet diameter: 5 nm; impact velocity: 5 km/s; substrate temperature: 300 K.

Our MD simulations of a model fcc system demonstrate that crystal growth from melt assumes closest-packed {111}, not necessarily the substrate plane; however, the as-grown crystal is still oriented along the substrate normal. We expect that this growth mechanism be typical of general crystallization and melting processes, and can be exploited for engineering nanomaterials or bulk materials with desired microstructure.

ACKNOWLEDGMENT

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SUPPORTING INFORMATION

Details of the MD simulations of nanodroplet crystallization on different substrates and movies showing the whole crystallization process.

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