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Formation of single-component metallic glasses on amorphous substrates

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A great deal of progress has been made in synthesizing bulk amorphous metallic glasses since the original successes in 1960 of amorphous Si and Ge using cooling rates of 10^6 K/sec. Indeed with multicomponent metals containing a variety of metals having dramatically different character and radii, it is possible to obtain amorphous sheets of cm size *(1-3)*. In this paper we take up the challenge of forming *single-component* metallic glasses (SCMGs), which is intriguing but extremely demanding given the low glass-forming ability of pure metals. High cooling rates can be achieved by injecting small droplets onto a rotating, highly conductive cylinder *(4,5)* or thermal spray coating. The highest cooling rates are achieved in such processes as thermal spray coating of nanodroplets since the nanodroplets spread during impact on a substrate with rapid cooling sustained by the large temperature gradients between the thinned nanodroplets and the bulk substrate. The substrate may or may not serve as the heterogeneous nucleation sites for crystallization. Here SCMGs form if the glass transition outruns crystal nucleation. Thus we explored the formation of SCMGs on amorphous substrates via thermal spray coating of nanodroplets, using realistic simulations with molecular dynamics (MD). Here we report a comparative MD study on thermal spray of elemental nanodroplets on crystalline and amorphous substrates, and show that SCMGs can form on amorphous substrates under cooling rates of $>10^{13}$ K/sec.

Our MD simulations considered two simple representative systems, pure Cu which is difficult to stabilize in an amorphous structure and the $Cu_{46}Zr_{54}$ binary known to be one of the best metallic glass formers. These MD studies used an embedded-atom potential *(6)* derived to

fit quantum mechanics calculations. We start with a Cu nanodroplet with 39081 atoms (10 nm in diameter) at 1300 K where it is liquid, and then assign it a velocity of 0.1 km/s along the substrate normal toward the target. We consider two targets at 300 K: (a) bulk single crystal Cu or (b) amorphous $Cu_{46}Zr_{54}$ glass substrate. Details of MD simulations can be found in Supplementary Information.

The snapshots in Fig. 1 show the structure analysis of the Cu nanodroplets after impact on crystalline or amorphous substrates. On the crystalline substrate, we find that a Cu nanocrystal grows epitaxially with growth twins and stacking faults (Figs. 1A and 1B). In sharp contrast, we find that collision with the $Cu_{46}Zr_{54}$ glass substrate leads to an amorphous Cu nanoparticle (Figs. 1C and 1D). This amorphous nanoparticle is similar in short-to-medium-range order atomic packing to the $Cu_{46}Zr_{54}$ glass and to Cu liquid (Fig. 1E). Our calculated diffusion coefficients of the liquid nanodroplet (3.6×10^{-5} cm^2/s) and the stabilized amorphous nanoparticle (8.0×10^{-7} cm^2/s) show that the amorphous nanoparticle is a solid-like SCMG. We find similar results for impact velocities of 0.01 to 0.5 km/s and for nanodroplet sizes of 10 nm to 30 nm Clearly the nature of the substrate has a dramatic effect on the competition between crystallization and glass formation. Our interpretation is that the glass substrates do not have the heterogeneous nucleation sites characteristic of the single crystal substrates. Thus the high energy-barrier for homogeneous crystal nucleation leads to kinetics too slow to compete with glass transition, and thus to SCMG formation. We consider that the high temperature gradient at the substrate surface initiates growth of the SCMG.

We expect that the synthesis of SCMGs via thermal spray of nanodroplets on amorphous substrates be viable for other elemental metals. It has been suggested that free-standing submicron droplets of high purity metals may become amorphous solid-like phases in vacuum via thermal radiation cooling *(7)*. However, formation of SCMG via thermal spray coating of nanodroplets brings on exciting opportunities for broad applications that fully exploit the uniqueness of metallic glasses.

References and Notes

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Figure 1

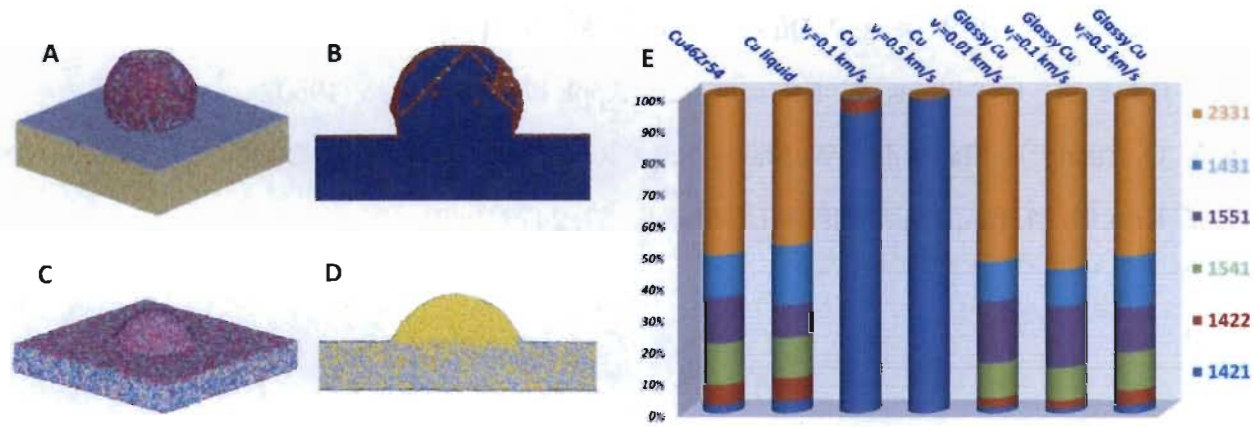

Fig. 1. Snapshots of Cu nanodroplet (10 nm in diameter) impacting on a Cu single crystal substrate (**A,B**) and on a $Cu_{46}Zr_{54}$ glass substrate (**C,D**) at 0.1 km/s. (**E**) analyzes the structure of crystalline, liquid and glassy Cu and $Cu_{46}Zr_{54}$ glass using the Honeycutt-Andersen (HA) metric. Here 1421 is characteristic of fcc (face-centered cubic) crystal while equal amounts of 1421 and 1422 are characteristic of hcp (hexagonal close pack). On the other hand 2331 and 1551 indicate icosahedral packing characteristic of liquid metals. (**B**) and (**D**) are cross-sectional views; here B shows some growth twins and fcc stacking faults are). The HA indices for $Cu_{46}Zr_{54}$ glass, Cu glasses and Cu liquids are similar (e.g., 2331), but drastically different from those for crystalline Cu (e.g., 1421).

Supplementary Information

Formation of single-component metallic glasses on amorphous substrates

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MD simulation details

Our MD simulations used the embedded-atom-method potential for the Cu-Zr system [1] and the LAMMPS MD package (large-scale atomic/molecular massively parallel simulator) [2]. We constructed a liquid Cu droplet with a radius of 5 nm (39,081 atoms) and equilibrated at 1300 K using constant-volume-temperature ensemble with non-periodic boundary conditions. We also prepared two different substrates at 300 K and 1 atm:

a) $Cu_{46}Zr_{54}$ glass.

b) Cu (100) single crystal.

Here we started a configuration with randomly positioned Cu and Zr atoms, which was melted at 2000 K and then cooled continuously to 300 K within 1 ns to form a glass, and then annealed at 1000 K for 4 ns and cooled to 300 K with free surfaces along the *x*-axis under the constant-pressure-temperature (NPT) ensemble. The $Cu_{46}Zr_{54}$ glass substrate contains 320,000 atoms (4.85 nm×34.21 nm×35.91 nm along the *x*-, *y*- and *z*-axes, respectively). The Cu (100) single crystal substrate contains 432,000 atoms (10.96 nm×21.93 nm×21.93 nm), and was equilibrated at ambient conditions with free surfaces along the *x*-axis using NPT ensemble. The Cu nanodroplet was assigned an initial impact velocity along the *x*-axis (the substrate normal), and impacted the substrate. The impact velocity varies from 0.01 km/s to 0.5 km/s. We used the microcanonical ensemble for impact simulations. The time step in MD simulation was 1fs and the total simulation time was up to 2.5 ns. Radial distribution function (RDF) and Honeycutt-Anderson analyses [3] were performed on crystalline, liquid and glassy Cu and $Cu_{46}Zr_{54}$ glass for structural comparison. Mean square displacement (MSD) of the Cu nanodroplet was also calculated after the system reaches equilibrium. The diffusion coefficient was derived from the MSD using the Einstein relation. We also examined larger nanodroplets (15 nm in radius) and substrates, and different orientations for Cu substrate, and the results are similar. The cooling rates were estimated to be about 10^{13} K/s (using a temperature gradient of ~1000 K and a time scale of 100 ps).

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