Atomic-scale Relaxation Dynamics in the Supercooled Liquid State of a Metallic Glass Nanowire by Electron Correlation Microscopy

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Electron correlation microscopy (ECM) is a new way to measure atomic dynamics with nanometer-scale spatial resolution using time-resolved coherent electron scattering [1]. ECM is the electron equivalent of (x-ray) photon correlation spectroscopy [2]. Coherent electron scattering yields speckle patterns that correspond to a particular arrangement of atoms with certain internal order at the length scale of probe size. In a fluctuating system, the speckle intensity changes with the rearrangement of the atoms, so the lifetime of each speckle can be used to measure the time over which that particular structure persists in the sample. ECM experiments measure the characteristic time for structural rearrangements from the time autocorrelation function of the speckle intensity.

Previous ECM experiments were performed in scanning transmission electron microscopy (STEM) mode on the supercooled $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass [1]. Those data revealed the relaxation time at one position. Here we report ECM measurements in tilted dark field image mode which reveal spatial maps of the dynamics in the supercooled liquid state of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanowire. Tilted dark field imaging maps the intensity of a single speckle in real space, where a fast CCD camera records a time series. With an objective aperture 10 μm in diameter or 2.83 mrad of half angle, the speckle in the image, and thus the spatial resolution, is of ~0.7 nm.

Figure 1(a) shows a typical frame taken from a series of dark field images of a $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanowire recorded at 250 ˚C, 16 ˚C above the glass transition temperature of 234 ˚C. The speckles in the image arise from arrangements of atoms with different degrees of internal order and different orientations. The speckle intensity fluctuates with the rearrangement of atomic structures. Figure 1(b) shows the autocorrelation function $g_2(t)$ of the intensity time series from one pixel inside the nanowire in Figure 1(a). This data mimics the previous STEM ECM measurements. By fitting the $g_2(t)$ to the Kohlrausch–Williams–Watt (KWW) equation, we can extract the relaxation time τ and the stretching exponent β.

Repeating such fitting pixel by pixel creates spatial maps of the relaxation time of the supercooled liquid, such as the example shown in Figure 2. Inside the nanowire, there are clear nanoscale domains with different structural relaxation times. These data represent the first direct visualization of nanometer-scale spatially heterogeneous dynamics in a liquid. This spatial heterogeneity may play a key role in the glass transition. The observed distribution of relaxation times grows wider with decreasing temperature, reaching hundreds of seconds near the glass transition temperature. Near the surface, the relaxation time is much smaller and the distribution of relaxation time is much narrower compared to the bulk. Faster near-surface dynamics may arise from atomic trajectories that sample the higher mobility available to atoms at a free surface [3], and may give rise to preferential crystallization of the nanowires at the surface.

Because ECM experiments require time series thousands of second long to produce reliable results, especially at low temperatures, we must apply drift correction to the time series. The bright spot in Figure 1(a) is a crystallized chunk of nanowire. Since its intensity does not change over the whole image series, it can be used as good reference for drift correction by cross correlation [4].

References:
[1] L. He *et al*, Microsc. Microanal. **21** (2015), 1026–1033.
[2] B. Ruta *et al*, Phys. Rev. Lett. **109** (2012), 165701.
[3] C. R. Cao *et al*, Appl. Phys. Lett. **107** (2015), 141606.

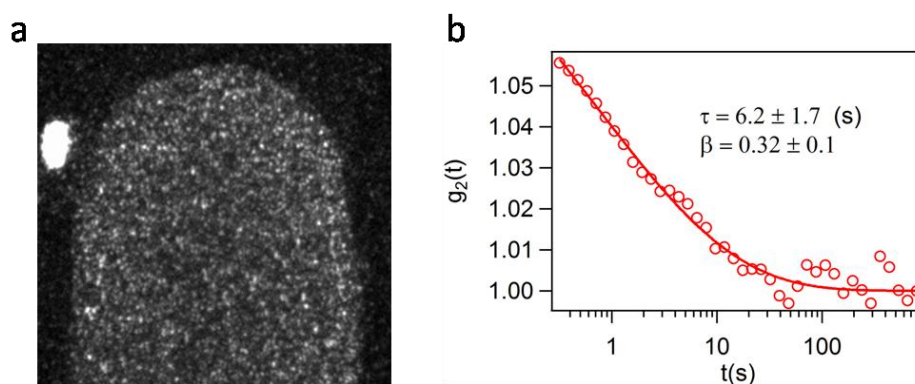**Figure 1.** (a) A typical dark field image of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanowire at 250 °C. (b) The time autocorrelation function $g_2(t)$ (circles) and the fitting curve (solid line) based on KWW equation.
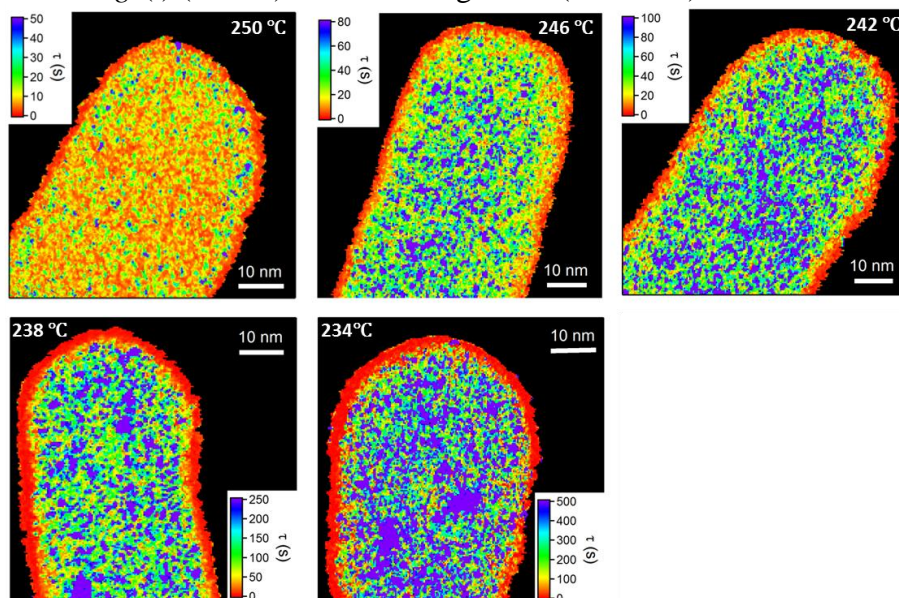

Figure 2. Spatial maps of the structural relaxation time of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ nanowires in the supercooled liquid state at various temperatures. The data show substantial spatial heterogeneity in the dynamics within the wires and direct evidence for fast dynamics in the surface layer of the wires.