

Four Dimensional Scanning Transmission Electron Microscopy during the *in situ* Annealing of a CuZrAl Bulk Metallic Glass

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Four dimensional scanning transmission electron microscopy (4D-STEM) is a powerful, diffraction-based imaging technique used to measure and map strain, polarization, and orientation, across a large field of view, typically in crystalline materials [1-5]. The technique relies on the processing and analysis of hundreds of thousands of rapidly acquired diffraction patterns to extract a rich set of information. 4D-STEM as a technique has been enabled by fast detectors and image processing codes capable of handling large amounts of data. The speed of data acquisition has in turn made *in situ* 4D-STEM possible, allowing for materials to be analyzed as they are dynamically perturbed [4, 6].

Recent developments in 4D-STEM analysis have been made in adapting this technique to amorphous materials [6, 7]. The adaptation of 4D-STEM to amorphous materials has resulted in analysis that goes beyond fluctuation electron microscopy, which is the traditional electron microscopy based technique for amorphous specimens [8,9]. Particularly, the addition of a spatial component to the structural characterization of amorphous materials has allowed for the mapping of structural inhomogeneities that exist in bulk metallic glasses [7, 10]. Here, we extend 4D-STEM to *in situ* annealing of a bulk metallic glass (BMG) to analyze the relationship between amorphous and crystalline phases during the crystalline phase's growth in a Cu₄₆Zr₄₆Al₈ BMG.

Figure 1 shows the one frame from the *in situ* 4D-STEM time series. While the sample was annealed 400 C for over two hours on a Protochips heating holder, this virtual bright field image shows the crystallite's size, from a region that originally had no crystallinity. From the same dataset, the virtual selected area diffraction patterns show the various crystalline orientations present in the crystallite, and their relationship to each other. These diffraction patterns can further be analyzed to show both amorphous and crystalline strain, simultaneously. Figure 2 shows subsequent *ex situ* energy dispersive x-ray spectroscopy (EDS) to provide chemical information of these phases. This research shows how 4D-STEM can be used to simultaneously study crystalline and amorphous phases *in situ*, to understand more fully the dynamic processes that govern phase nucleation and growth in amorphous materials [11].

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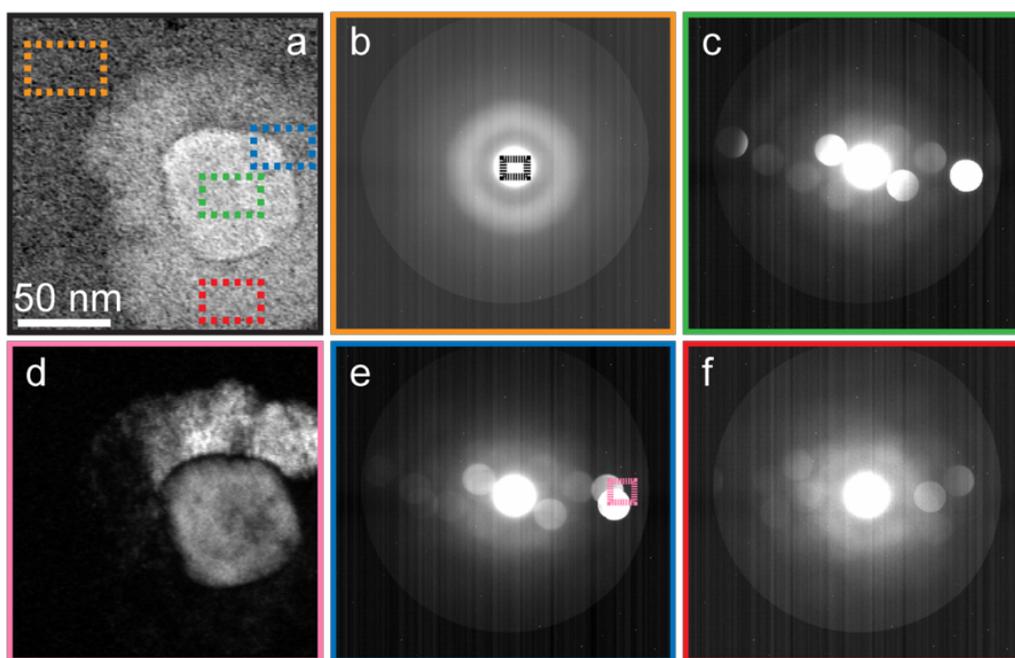


Figure 1. a) Virtual bright field image from the aperture shown in b), with color coded virtual selected area apertures. b,c,e,f) Virtual selected area diffraction patterns. d) Virtual dark field image from e), showing the orientation relationship between different crystalline phases.

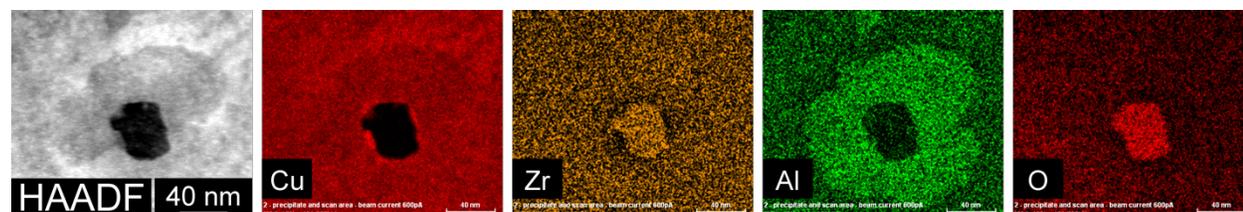


Figure 2. HAADF and EDS maps of crystalline and amorphous region from Fig. 1. Note the chemical segregation between the central Zr and O-rich region, and the Al-rich outer crystalline region.