Scanning Nano-Structure Electron Microscopy - Hidden Potential for Evolving Systems

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In recent years, Electron Diffraction, and especially the 4D-STEM [2] is growingly becoming a routine part of structural characterizations of materials at the nano-scale. Its un-matched spatial resolution (down to sub-nm) enables the exploration of local variations within a sample, which alternatively is averaged over the entire irradiated sampled area, when explored, for example, by x-rays. As often shown in electron microscope, samples are often heterogeneous, and consequently their local properties, which then reflect on the average behavior of the material, composite, or device. Besides morphology and composition, the local structural order can vary, especially in evolving systems. In this study, we explore how far we can take electron diffraction when the interest is in the evolution of materials.

We challenge ourselves with mapping the local structure in a composite of crystalline Ni and amorphous Zr-Cu-Ni-Al Bulk Metallic Glass (BMG) that was fused into a composite via hot-rolling [2]. Using a fast camera looking through the fluorescence screen, we captured diffraction patterns in a 4D-STEM modality, where we captured diffraction patterns coupled with beam precession with 3 nm step size in a Ni/BMG/Ni cross-section sample that was cut from the composite - in total 131x289 diffraction patterns. Using the collected diffraction patterns and tailoring automated data reduction and analysis pipelines, such as auto-masking, azimuthal-integration, Fourier-transformation to get the electron Pair Distribution Function (ePDF) and various fittings of the PDF, we were efficiently deriving a large set of physically meaningful scalars, which we generalize as Quantities of Interest, or QoI of a scanning nano-structure electron microscopy (SNEM).

Using different QoI's (see Figure)- those derived directly from the images, such as virtual-dark-field and mostly from ePDF's, we could map out most clearly Ni/BMG boundaries, visualize inter-diffusion between Ni and BMG, extract regions of formed nano-crystals within the BMG, follow compositional changes via the average bond-distance (verified with EELS from the same area) and extract the distribution of atomic pairs. We were also able to map the deviation of each pixel within the BMG from an expected structural model, which exposed the BMG/Ni inter-diffusion front. Finally, we could estimate the effective local structure of the nano-crystalline inclusions within the BMG as FCC structures.

Using an assembly of these results we could learn that nano-crystalline inclusions within the BMG are located in regions where Cu is deficient and Zr is in excess. Most importantly, we learn the origin of success in forming the Ni/BMG composite via hot-rolling, which is nonetheless, a challenging goal. Hot rolling is found to be a challenging process due to the excessive formation of nano-crystallites at the Ni/BMG interface. Here, however, the assembly of SNEM results suggested that the metallic Ni amorphized instead of the BMG--Ni crystallize at the BMG/Ni interface. These results emphasize the richness SNEM experiments hide, and with the assistance of automated (and in the future - autonomated) pipelines can expose the story of evolving systems.

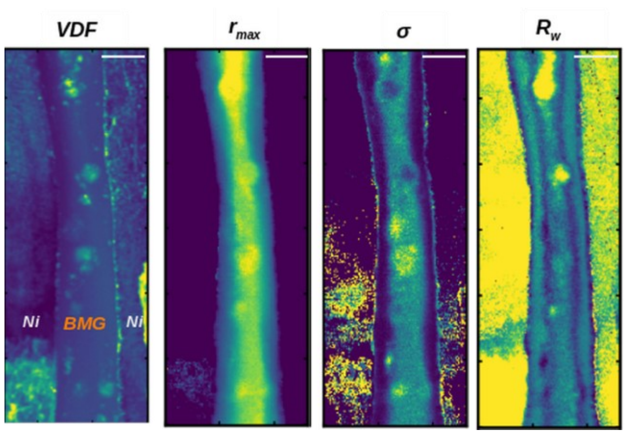

Figure 1: QoI maps of the Ni/BMG/Ni sandwich (BMG is the central vertical layer). From left to right: virtual dark-field (VDF) from the annulus of the amorphous diffraction ring. The bright spots indicate for presence of crystallites; the r-value of the first PDF peak (r_{max}) indicating the average interatomic distance; the peak width of the first interatomic distance, σ, indicating the distribution of the inter-atomic-pair distances; the goodness of fit of the PDF at each pixel to an exponentially-decaying sine wave, R_w which the structural fit at each pixel to perfectly randomly distributed amorphous material. The scale that is represented by the white vertical bar is 100 nm.

[1] Xiaoke Mu, Andrey Mazilkin, Christian Sprau, Alexander Colsmann, Christian Kübel, (2019). *Microscopy.* **3554,** 301
[2] Sina Shahrezaei, Douglas C. Hofmann, Suveen N. Mathaudhu (2019). *JOM.* **71**, 2

Keywords: Electron Pair Distribution Function, Electron Diffraction, 4D-STEM, Bulk Metallic Glass

SB and YR thank the support from the U.S. National Science Foundation through grant DMREF-1922234.