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Characterization of Modulated Nanostructure in Au-Pt Alloy using Aberration Corrected STEM

Ronit Sawant[1*] and R W Carpenter[2]

[1.] Materials Science and Engineering, Arizona State University, Tempe, AZ, United States.
[2.] School of Molecular Sciences, Arizona State University, Tempe, AZ, United States.
* Corresponding author: rpsawant@asu.edu

Modulated nanostructures are short-range periodic composition fluctuations observed in metals, semiconductors, and ceramic alloys. The presence of such a structure is often attributed to spinodal decomposition (1). The early stages of the reaction consist of small composition fluctuations in the matrix whose amplitude and wavelength increase as the reaction proceeds to system equilibrium. Typical wavelength of the modulations range from 5 nm to 15 nm (2). A review paper by Bentley (3) provides useful information about the wavelength and strain fields in the structures using the diffraction/strain contrast imaging technique, but little regarding the amplitude of the fluctuations. To study the reaction kinetics, direct measurement of the composition amplitude is necessary. The development of field emission guns (4), aberration correctors (5), and ADF imaging for STEM, have provided us with the necessary resolution to resolve the diffused interface of the modulations. This should give us for the first time a direct measurement of the amplitude and wavelength of the structure required to study the reaction kinetics.

Here we analyze an Au-Pt alloy system with a symmetrical solid-state miscibility gap at about 60wt%Pt and 1275°C, respectively. A 60%Pt-20%Au alloy was homogenized at 1280°C for 60 min and then aged at 552°C for 100 min. This provided the alloy with the necessary driving force to decompose by spinodal decomposition. The sample was then made by the focused ion beam (FIB) lift-out technique. The electron backscatter diffraction (EBSD) method was used to map the grain orientation. The sample was lifted-out in FIB such that the orientation was close to the [100] zone axis. We then analyzed the alloy in an aberration-corrected JEOL ARM 200F STEM microscope. Energy-dispersive X-ray spectroscopy (EDS) was used to measure the amplitude of composition fluctuation. The imaging was done along the [100] zone axis. Figure 1 shows a low magnification high angle annular dark-field (HAADF) image of the modulated structure along the [100] zone axis orientation. The images showed that modulations are multidirectional and are not uniform across the region. The average wavelength obtained from the images is about 10.1±1.2 nm, which agrees with the X-ray diffraction (XRD) data (2). The dark regions on the HAADF image are Pt-rich, and the bright areas are Au-rich. Figure 2a show a high magnification HAADF image of the modulated structure. Figure 2b shows the composition variation of the modulated structure along the [100] direction using an EDS line scan. From the plot, we see the Pt-rich region has a composition of about 85At%Pt and about 71At%Au is the composition for the Au-rich region. As the reaction proceeds to equilibrium, the amplitude of the fluctuations should increase and reach the equilibrium composition at the end of the tie line at the selected aging temperature. The equilibrium composition of the alloy at the aging temperature is 99At%Pt for Pt-rich and 83At%Au for the gold-rich region. The results indicate this specimen is far from equilibrium. Additional aging is required for the alloy at the 552°C temperature to reach equilibrium. The diffused interface between the regions has a composition change of about 18 At%/nm. These results show that we can analyze the structure down to the atomic level with the development of an aberration-corrected STEM microscope. With EDS spectroscopy, we can directly measure the amplitude of the fluctuations. The main objective of this work is to compare the composition amplitude with the aging time. This will give us a direct comparison of experimental aging kinetics with the spinodal rate theory (1).

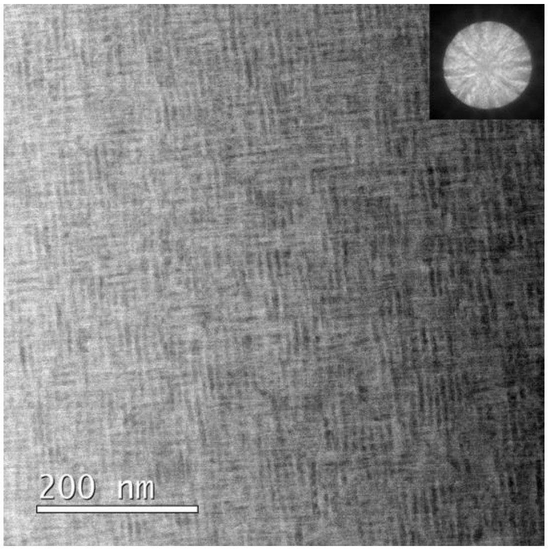

Figure 1. Low magnification HAADF STEM image of the modulated structure along the [100] zone axis in 60%Pt-40%Au alloy aged at 552°C for 100min. The modulations are two-dimensional in some regions. Note that the structure is not uniform all over the specimen. Although the entire specimen volume is modulated there are variations in wavelength and composition amplitude throughout the specimen volume. The insert shows [100] zone axis orientation.

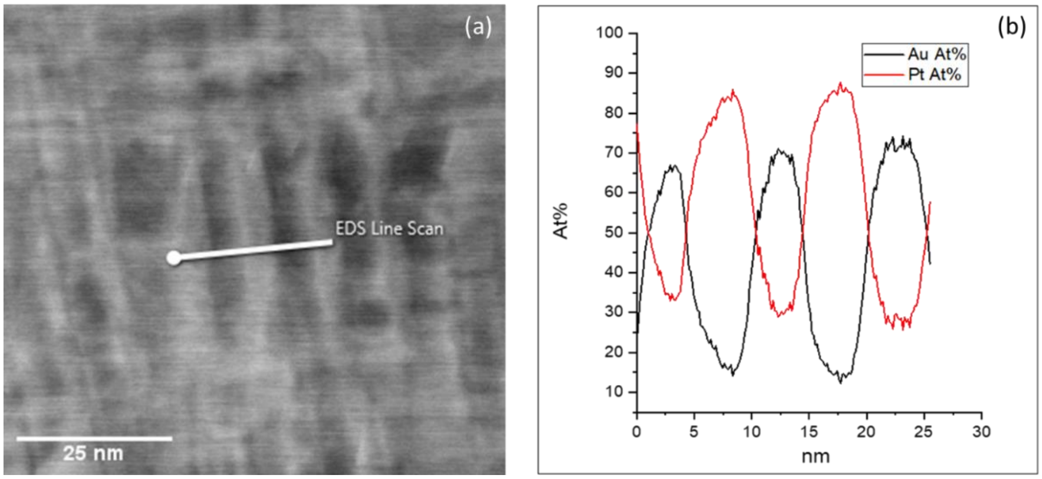

Figure 2. (a) High magnification HAADF STEM image showing a 1D modulated structure along [100] direction. The dark region is Pt-rich, while the bright part is Au-rich. (b) EDS line scan across the modulated structure along the [100] scan direction. The vertical axis shows the relative composition of the alloy in At%.

References:

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