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Live EDS Mapping of the Precipitation and Annealing Cycle of Alloys in the TEM Generated Through *in Situ* Heating

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In situ experimentation allows for the direct observation of a sample in a dynamic environment. This has been facilitated by the introduction of a range of sample holders including heating, biasing, gas injection and liquid cell [1]. The ability to chemically characterise a sample, using energy dispersive x-ray spectroscopy (EDS), as it is evolving within these dynamic environments has proven to be challenging. For *in situ* heating experiments this is due to the large quantities of infrared (IR) and ultra violet (UV) radiation released as a sample is heated and the geometry of the sample holders. IR and UV are both forms of electromagnetic radiation, like x-rays, and are detected in an EDS system as low energy noise. At high temperatures, the combined IR/UV input rate can be more than 2 orders of magnitude greater than the x-ray input from a sample and can saturate the EDS detector.

These challenges have been overcome through improvements to the EDS detector electronics, allowing higher levels of signal throughput, preventing the EDS detector from becoming saturated by the IR and UV radiation [2]. This has also been aided by the introduction of MEMs based heating holders, in which the sample is mounted on top of a SiN chip giving the sample greater exposure to the EDS detector [3]. Here we report continuous *in situ* heating EDS mapping and characterisation experiments of Au nanoparticle agglomeration and Cu precipitation and annealing from Al_2Cu [4].

A DENSsolutions *lightning* sample holder was used to perform the heating experiments on two simultaneous biasing and heating nano-chips. One containing a SiN membrane with sputtered Au nanoparticles, the other a FIB prepared TEM lamella lifted out from a bulk Al_2Cu alloy. They were analysed using a 200 kV aberration-corrected JEOL-ARM200F at the University of Warwick equipped with an Oxford Instruments EDS system with a 100 mm^2 windowless silicon-drift detector. The Au nanoparticles were heated at a constant ramp rate of 50ºC a minute and held at 1000ºC. The Al_2Cu lamella was heated at a constant ramp rate of 45ºC a minute and held at 450ºC.

The effects of high temperature EDS acquisition are explored through the analysis of Au nanoparticles and the associated EDS spectra acquired at elevated temperatures. Figure 1 compares EDS spectra acquired at room temperature and 900ºC. This highlights the two orders of magnitude increase in low level radiation generated by IR and UV emitted from the sample and heating filament. The magnitude of the low energy noise peak is directly related to the temperature. The low atomic number energy lines become unresolvable against this low energy noise, however the latest low noise, high throughput detectors can still resolve the N kα (0.392 keV) energy line from this noise at 900ºC. Figure 2 shows the formation and annealing of a Cu precipitate from the Al_2Cu bulk alloy. This was acquired in one continuous EDS mapping experiment with no pausing during the sample heating for EDS acquisition. Cu is seen to precipitate out of the bulk at ≈ 300ºC in the live image and X-ray map before annealing back into solution at 450ºC.

This study has shown the advantages and disadvantages of live continuous EDS mapping with respect to *in situ* heating experiments. It has also allowed us to study in detail the adverse effects of acquiring EDS data at high temperatures and its influence on spectral resolution.

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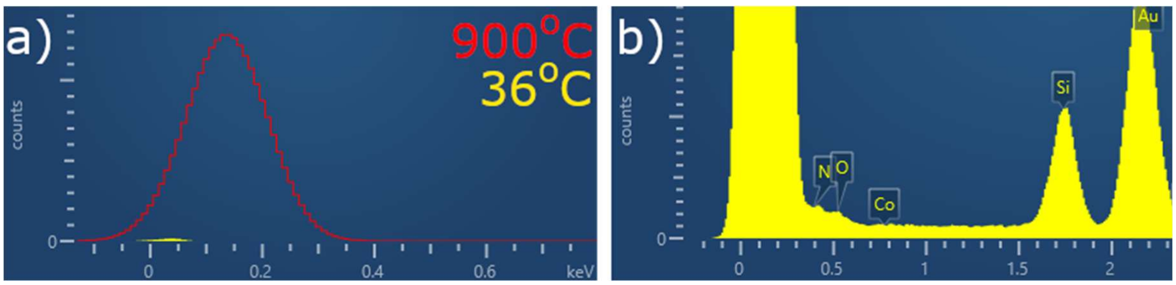

Figure 1. a) Low energy noise generated by *in situ* heating holders at 36ºC (yellow) and 900ºC (red). b) Spectra collected from Au particles on a SiN substrate at 900ºC.

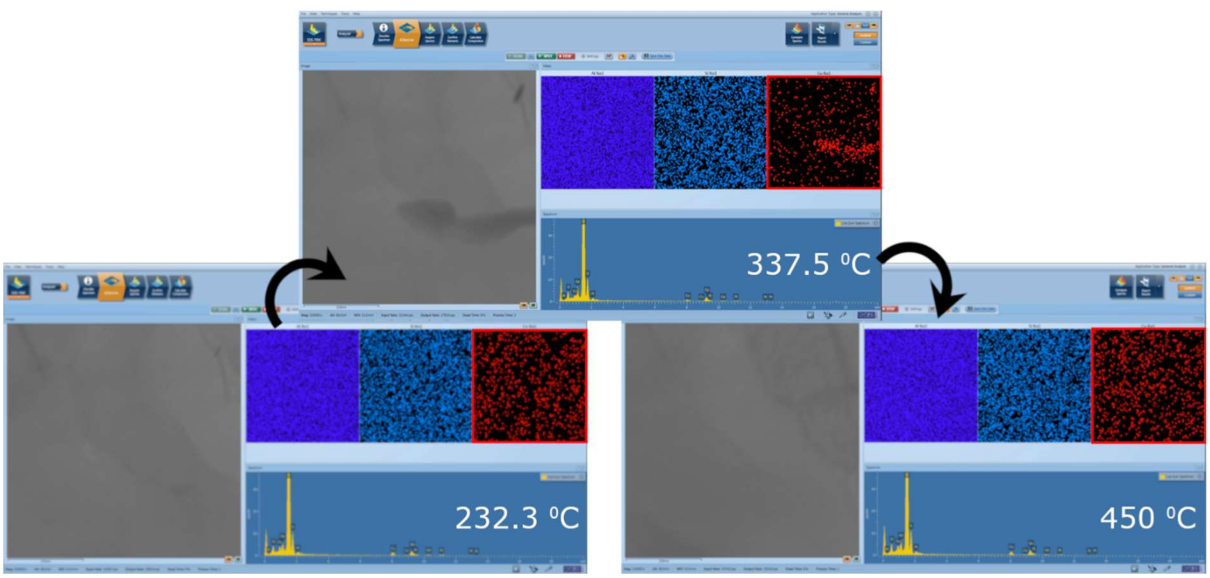

Figure 2. Three frames from a video of continuous EDS mapping in which Cu is seen precipitating and annealing at 337.5ºC and 450ºC respectively.

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