PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

Segregation of Impurities to Interphase Boundaries in Ductile Iron

Overview: Grain boundary embrittlement and high temperature grain boundary instability are important factors in the quest for higher performance metals for many industrial applications. Of particular importance is the composition of interphase boundaries (the interface between separate phases) in these metals. Scanning Auger spectroscopy combined with *in situ* facture analysis provides a unique technique to expose the surfaces of the interphase boundaries and provide compositional analysis and elemental mapping of these surfaces. An earlier study provided a wealth of information about the effects of different additives on the eutectic transformation of ductile iron[1]. This earlier study utilized *in situ* fracture analysis with a PHI 590 Scanning Auger with a spatial resolution of 200 nm. The dramatic improvement in spatial resolution afforded with the Field Emission electron gun column of the PHI 700Xi Scanning Auger Nanoprobe can now provide a spatial resolution down to 8 nm. This Note illustrates the improved imaging for the analysis of the interphase boundaries and nanostructures from *in situ* fractured metallurgical samples.

Results:

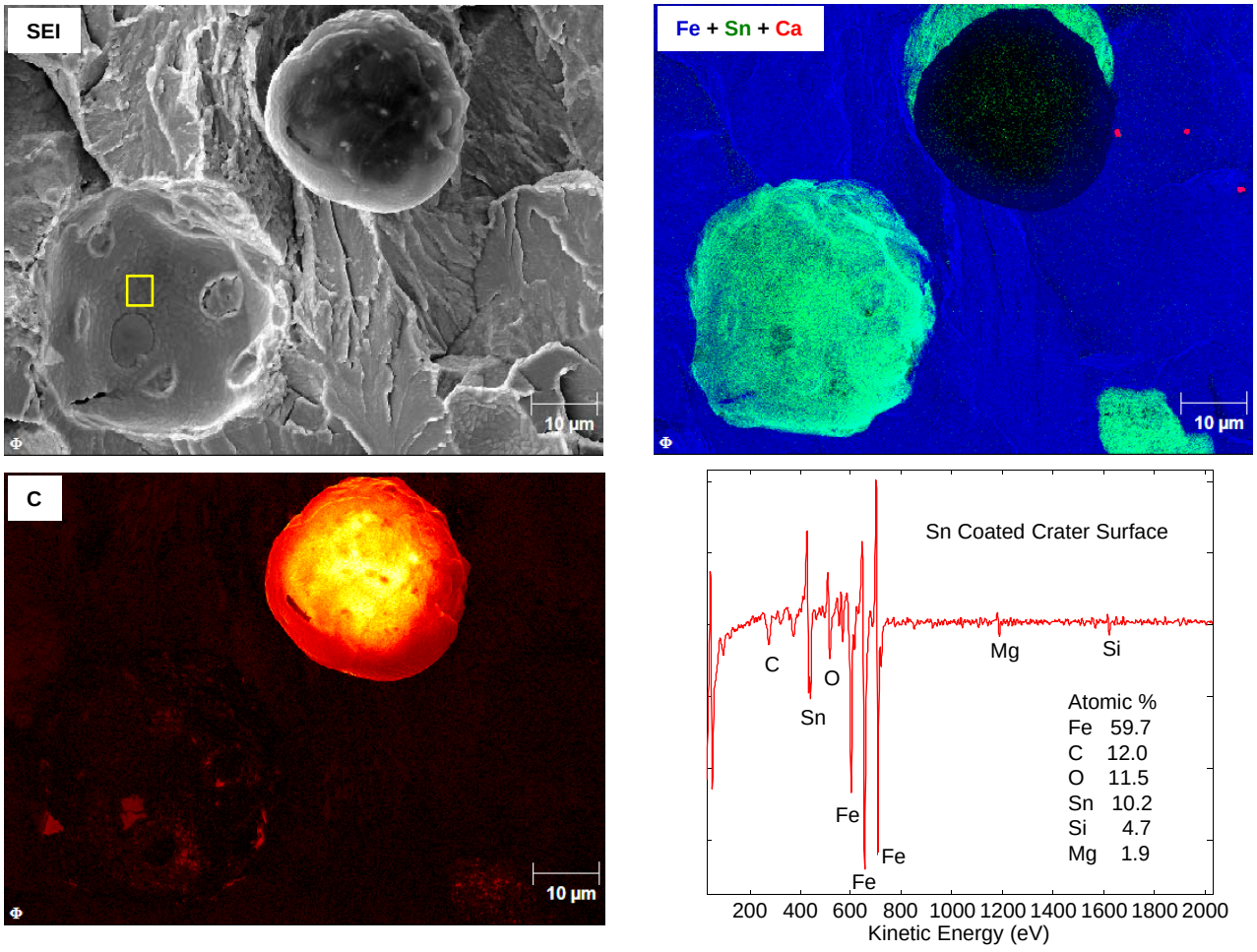

Figure 1. *Upper left panel shows the Secondary Electron Image (SEI) of a 0.11% Sn fractured iron sample. Upper right shows Sn (green), Fe (blue), Ca (red), Fe+Sn (light green) Auger color overlay maps. Lower left shows the C map displayed in thermal pseudo color. Lower right shows Auger compositional analysis on the Sn coated crater from the area indicated in yellow on the SEI.*

A ductile iron sample with 0.11% Sn was fractured *in situ* and analyzed in a PHI 700Xi Scanning Auger Nanoprobe. For higher sensitivity, all analyses were performed with a 20 kV beam at 10 nA with a resulting beam size of 12 nm. Auger spectra and maps were acquired with a Cylindrical Mirror Analyzer (CMA) with an eight channel detector operating at 0.5% energy resolution. Ultrahigh vacuum conditions (less than 7 x 10^{-8} Pa or 5 x 10^{-10} Torr) were maintained during the fracture and analysis to prevent contamination of the freshly exposed surfaces.

Figure 1 shows the results from a fracture that occurred along the graphite/metal interface. The upper left panel shows a secondary electron image (SEI) revealing a surface with extremely high topography. A graphite/iron nodule is observed at the upper right of the SEI. A crater is observed in the lower left of the SEI. The color overlay scanning Auger maps of the area shown in the SEI for Sn (green), Fe (blue), Ca (red) and *Fe+Sn (light green)* are shown in the upper right panel. The overlay maps clearly show that the crater has a surface composition of Sn that has segregated to the boundary of the graphite/iron nodule that was removed from the crater by the fracture process. This is further reinforced by the Sn coated iron crater that is visible under the graphite/iron nodule in the upper right of the SEI image and in the overlay maps shown in the upper right panel. The carbon Auger image shown in the lower left panel confirms that the nodule is a graphite/iron nodule. The Auger spectrum, shown in the lower right panel, was acquired from a raster scanned area, noted in yellow on the SEI image, in the area of the iron crater. The atomic concentrations noted on the Auger spectrum confirm the segregation of Sn as well as Si, Mg and O at the interphase boundary with the graphite nodules.

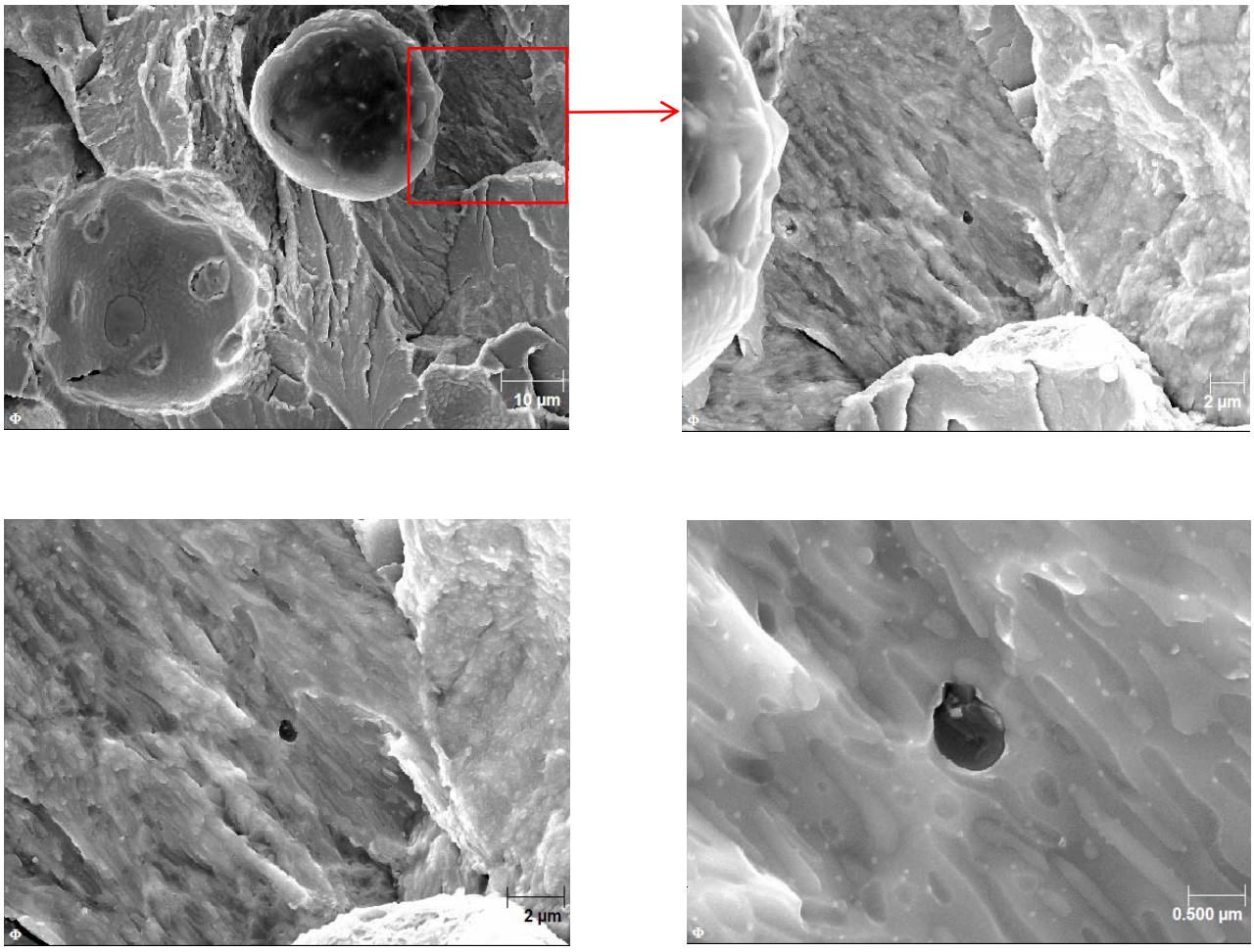

Figure 2. SEI image (also shown in Figure 1) with progressively higher magnification from upper left panel, upper right panel, lower left panel and lower right panel. The lower right panel shows the area of a suspected precipitate with Ca that was indicated in the color overlay maps (upper right Figure 1).

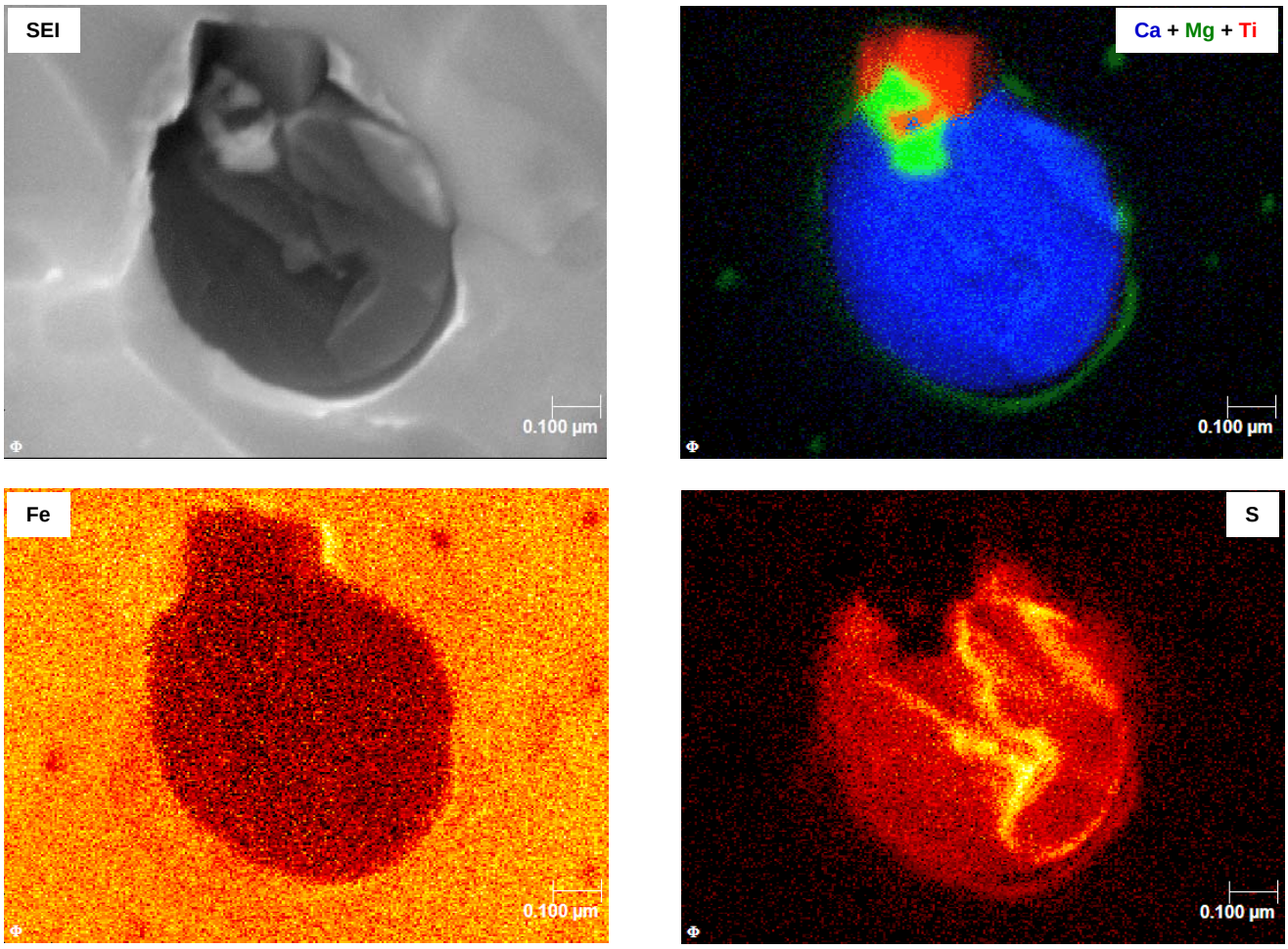

Figure 3. Upper left shows a high resolution SEI image of a ~ 500 nm precipitate at the location of the high Ca observed in the Figure 1 upper right panel. The upper right panel of this figure shows Auger color overlay maps of Ca (blue), Mg (green) and Ti (red). The lower left panel shows the Fe Auger map. The lower right panel shows the Auger map of S. The Fe and S maps are displayed in thermal pseudo color.

The Auger color overlay maps shown in the upper right panel of Figure 1 shows 3 very small regions of high intensity Ca. Progressively higher spatial resolution SEI images, shown in Figure 2, were used to locate one of these high Ca regions. SEI and Auger maps were acquired with a 20 kV, 1 nA electron beam to achieve the highest spatial resolution of 8 nm. The SEI is shown in the upper left panel of Figure 3. An Auger survey spectra, not shown, was acquired within the entire region of this feature to identify appropriate elements for Auger mapping. The color overlay map of Ca (blue), Mg (green) and Ti (red), shown in the upper right panel of Figure 3, shows three distinct phases: Ca rich, Ti rich, and Mg rich phases. In addition, a thin rim with higher intensity of Mg encircles most of the feature. The Fe Auger map, shown in the lower left panel, shows the iron matrix surrounding the 500 nm feature. In addition, six areas of higher Mg intensity with a feature size smaller than 50 nm are observed in both the Mg and Fe maps. The S map, displayed in the lower right panel of Figure 3 shows S to be coincident with Ca.

To confirm the elemental compositions of the three phases noted in the upper right panel of Figure 3, multiple Auger point survey spectra, not shown, were acquired from each of the three phases. The phase associated with high Ca also contained higher amounts of S, Mg, and O. The phase with highest Mg contained very high O, and low amounts of Ca and Ti. The phase with the highest Ti had very high intensity C as well as lower intensity O, Ca, S and Mg. Fe peaks, potentially from the matrix, were also observed in the spectra from the three phases.

Conclusion: The PHI 700Xi Scanning Auger NanoProbe combined with an *in situ* fracture stage is a unique instrument for the analysis of interface boundaries in iron. The 8 nm spatial resolution of this state-of-the art scanning Auger facilitates comprehensive analysis of the smallest features. This spatial resolution, when combined with software controlled image registration, allows high sensitivity Auger mapping of multiple phases observed within 500 nm craters. The CMA allows full Auger mapping of all nodules and craters produced during the fracture analysis without any observed topographical shadowing. The Auger analysis confirms that the graphite nodules separate at the interface with the interphase boundaries that form as a result of segregation of minor constituents in the iron such as Sn, Ca, S, Mg, O and Ti. This surface analysis capability should have extensive applications in the continued development of new high strength metallurgical materials.

Reference:

1. W. C Johnson and B. V. Kovacs, *Metallurgical Transactions A,* **9A** 219-229 (1978).

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