Surface Analysis of Additive Manufacturing Materials

Overview

Additive manufacturing, the process of building one layer at a time, allows parts with complex geometry to be constructed quickly and with little waste compared to traditional manufacturing techniques. Uniquely shaped objects and prototypes can be readily modified, functionally graded, and optimized for reduced weight and performance. For these reasons, additive manufacturing is rapidly gaining popularity in application spaces such as aerospace, automotive, biomedical, and many more. Recently copper alloys have been explored as ideal materials for the additive manufacturing of aerospace engine combustion chamber components because of their high thermal and good electrical conductivity, high strength, and corrosion resistance.

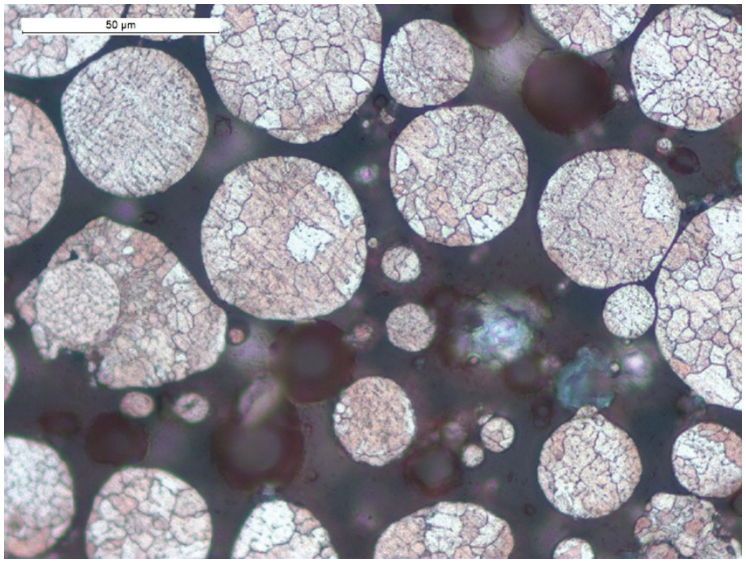

Figure 1: *Optical image of CuCrZr 3D printing powder particles. Particles have been embedded in epoxy and polished to reveal grains.*

Here, a CuCrZr alloy powder used in the laser-powder bed fusion process of 3D printing will be analyzed for grain boundary diffusion and for chemical variation among different particle sizes. The investigation of such defects is a critical step in optimizing the quality of the final 3D printed product.

Sample Measurements

Auger electron spectroscopy (AES) experiments were conducted using a PHI 710 Scanning Auger Nanoprobe. The primary beam was operated with an accelerating voltage of 10-20 kV and a target current of 10 nA producing an analytical probe size of approximately 10 nm. The PHI 710 is equipped with a Ga^+ LMIG FIB and EDS detector. A UHV environment of $<5x10^{-10}$ torr was maintained throughout the analysis. X-ray photoelectron spectroscopy (XPS) and hard X-ray photoelectron spectroscopy (HAXPES) experiments were conducted using a lab-based PHI Quantes XPS/HAXPES microprobe. An ~8 µm Al X-ray source was used to produce X-ray induced secondary electron imaging (SXI) images and small-area XPS spectra from individual particles, and a ~14 µm Cr X-ray source was used to acquire small-area HAXPES spectra from individual particles.

Results

The distribution of the particle sizes present within the 3D printing powder ranged from 13 µm to 47 µm in diameter. Particles of different sizes were selected for AES analysis: 26 µm diameter and 47 µm diameter.

AES Analysis - 26 µm Diameter Particle

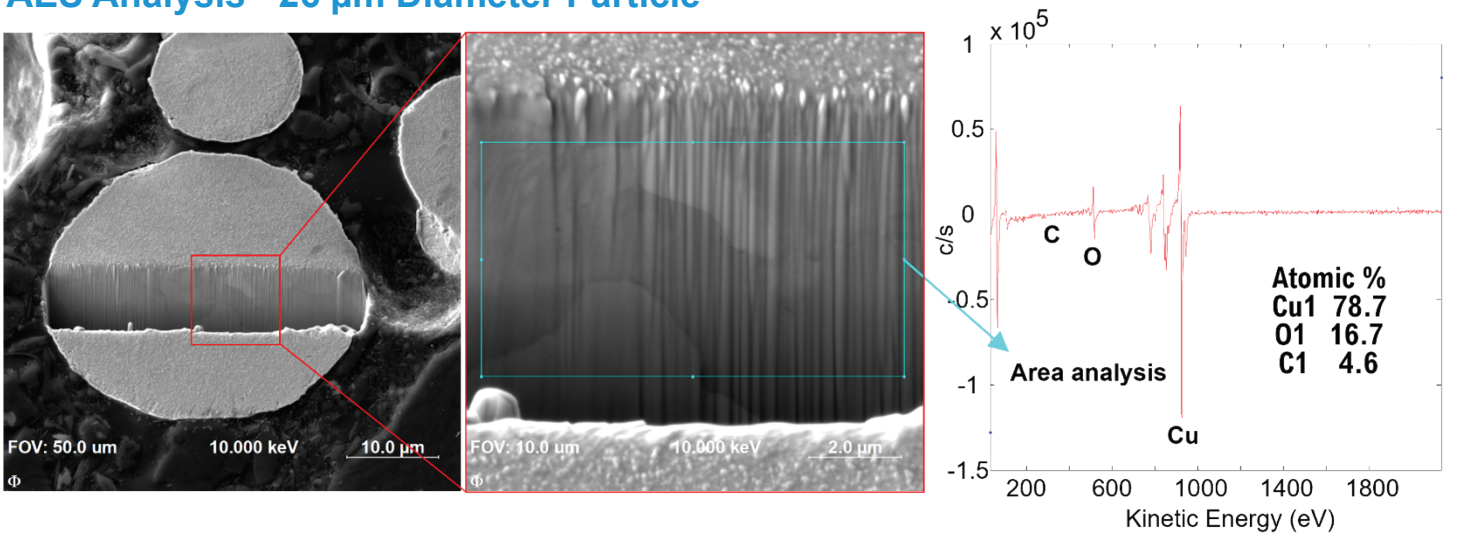

Figure 2: *SEM images of a 26 µm diameter particle embedded in epoxy after FIB cut (left) and a magnified image of the FIB face (center) with the Auger spectrum extracted from the blue region of interest (right).*

A FIB cut conducted on a 26 µm particle revealed regions of varying contrast, likely indicative of grain boundaries. A region of interest on the FIB face was analyzed with AES and revealed to contain ~79 at. % copper, ~17 at. % oxygen, and ~5 at. % carbon (Figure 2)

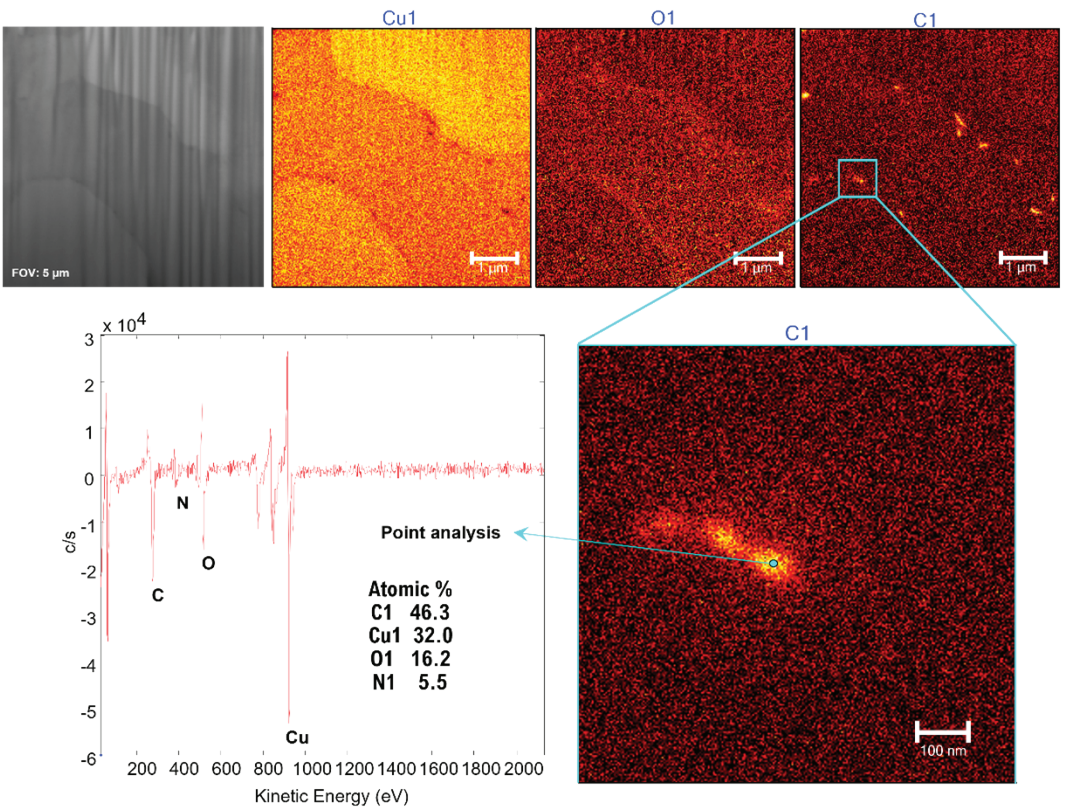

Figure 3: *SEM images and AES elemental maps of the FIB face of the 26 µm diameter particle shown in Figure 2 with a point spectrum acquired on a high carbon concentration region.*

AES elemental mapping at a smaller 5 µm FOV (Figure 3) reveals that the light grains in the SEM image have a higher copper concentration than the darker grains. Grains consisting of lower copper concentration correspond to a higher concentration of oxygen as seen in the maps. The carbon map of the FIB face shows grain boundary segregation. At 1 µm FOV, the carbon grain boundary diffusion is clearly visible in the AES C map. AES point analysis of a high concentration of carbon at the grain boundary detects ~46 at. % carbon concentration, almost 10 times the amount of carbon observed over the large area survey (Figure 2).

AES Analysis - 47 µm Diameter Particle

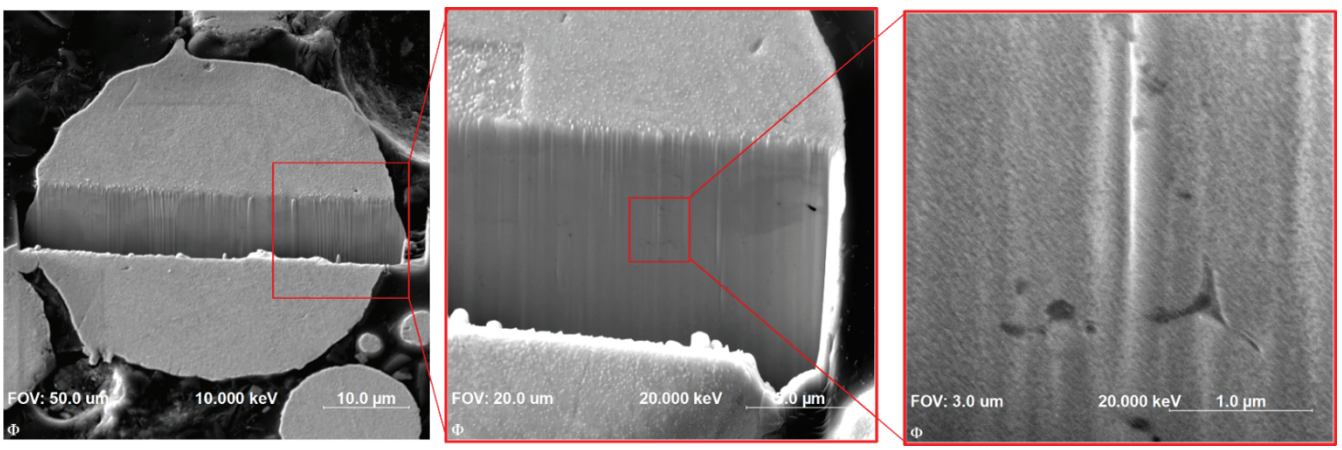

Figure 4: *SEM images of a 47 µm diameter particle embedded in epoxy after FIB cut (left) with the magnified FIB face (center and right).*

As with small- and medium- sized particles, the FIB cross section of the 47 µm particle revealed regions of patchy discoloration which are likely indicative of grain boundary diffusion (Figure 4). Two points of interest were selected based on features observed in the SEM image of the FIB face at 3 µm FOV. AES spectra of both points show similar chemistries; high concentration of carbon, and lower concentrations of Zr, N, and Cr (Figure 5).

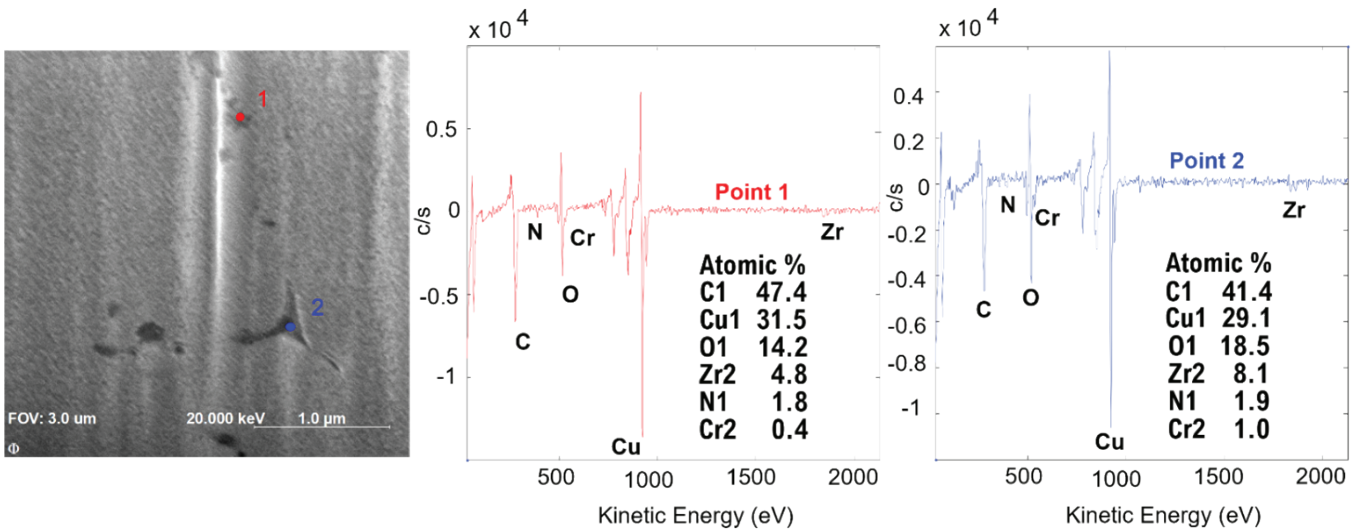

Figure 5: *SEM image at 3 µm FOV of the 47 µm diameter particle after FIB cut (left) and Auger spectra extracted from two points of interest (center and right).*

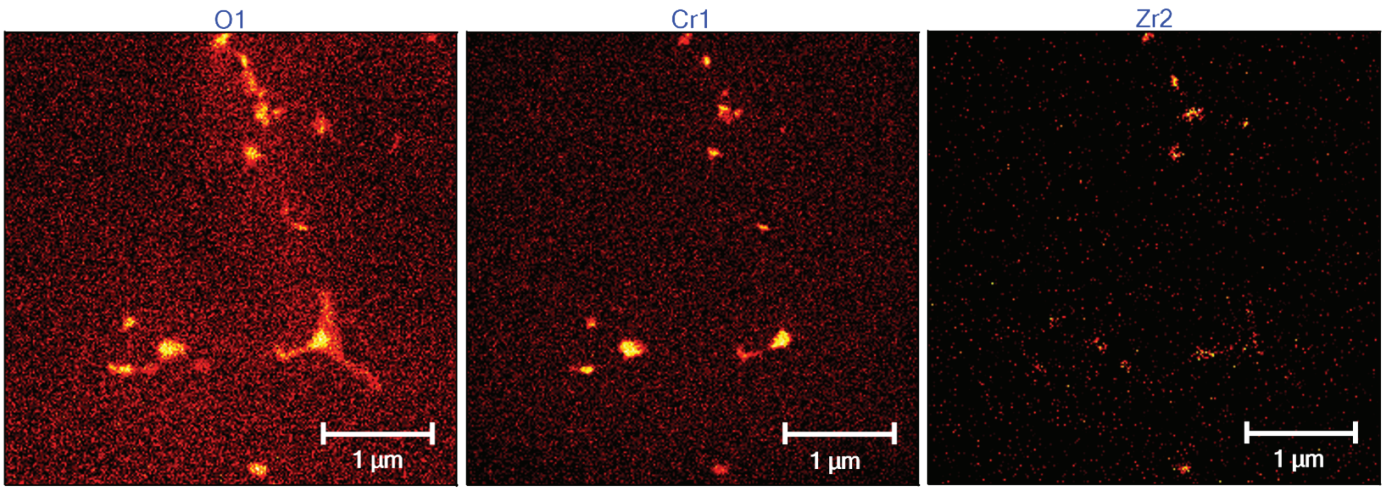

Figure 6: *AES elemental maps at 3 µm FOV of the 47 µm diameter particle after FIB cut acquired from the same region shown in Figure 5.*

XPS/HAXPES Analysis

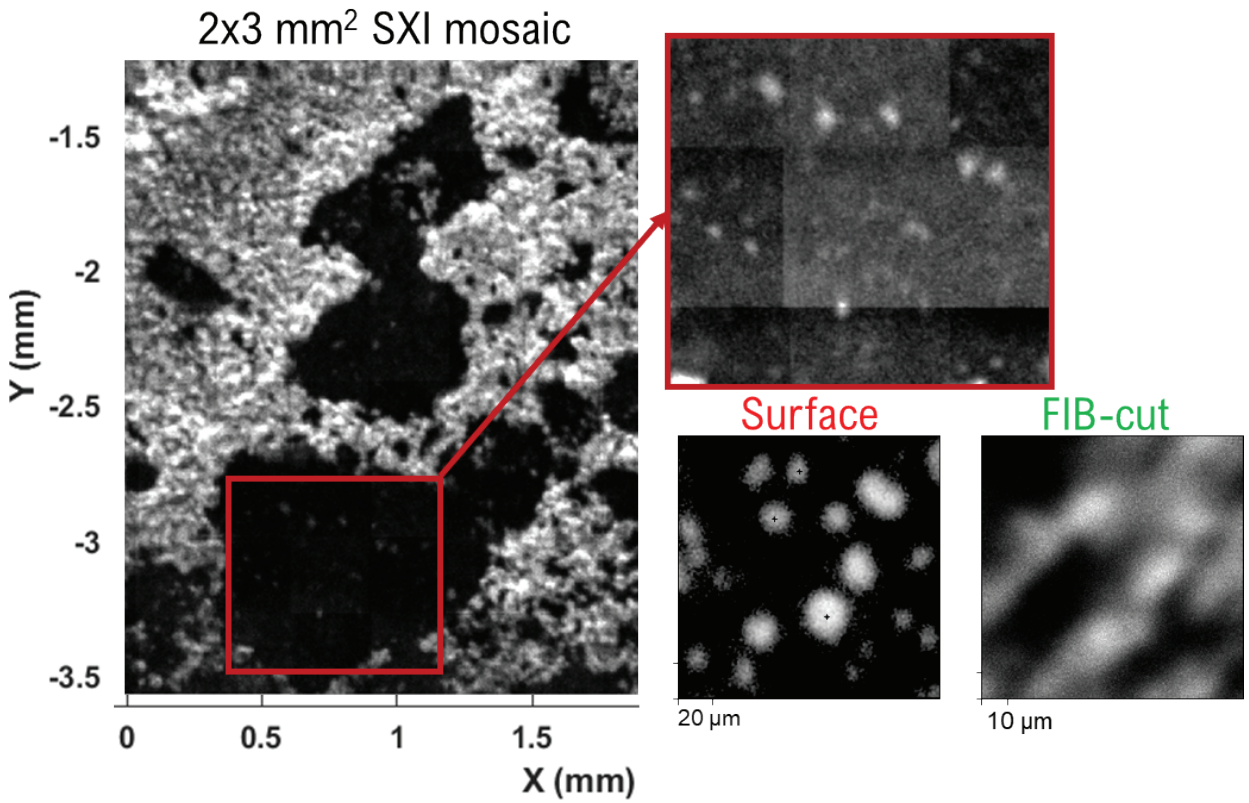

Figure 7: *Large area mosaic mapped SXI image (left) with smaller FOV regions extracted (right) showing individual particles.*

X-ray induced Secondary Electron image (SXI) mosaic allows large areas of the sample surface to be quickly imaged (Figure 7). Within the 2 x 3 mm^2 image, individual particles of varying sizes can clearly be distinguished from agglomeration of particles. Furthermore, the morphology of the particles as received and after FIB cutting can be observed in the SXI image. This type of imaging allows for rapid detection of individual 3D printing powder particles over large areas. While the information depth of XPS is shallow (~5 nm), the analysis depth of HAXPES is roughly 3 times deeper, allowing for comparison of surface chemistry versus the more bulk-like chemistry in the depth (Figure 8).

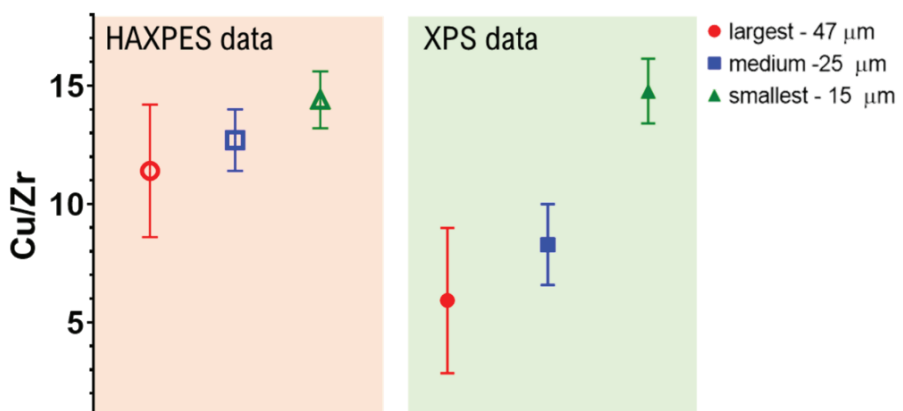

Figure 8: *Cu/Zr ratios for three particles sizes calculated using HAXPES and XPS.*

The availability of both techniques on one instrument leads to the following observations:

- Much larger difference in chemistry between different-size particles is observed at the surface (XPS) than in bulk (HAXPES)
- Largest difference in surface and bulk composition is observed for larger particles
- The smallest particles have the smallest amount of Zr on the surface
- FIB-cut particles are only composed of Cu pointing out that Zr and Cr are located on the outer surface of particles
- The smallest particles have the largest amount of oxygen detected by XPS due to larger surface area and a larger amount of oxides

Conclusions

In this study, Auger electron spectroscopy was used in conjunction with FIB and XPS/HAXPES to characterize CuCrZr particles used in additive manufacturing. The *in-situ* FIB and subsequent AES analysis allowed for grain boundaries within the powder particles to be revealed and analyzed with elemental quantification at a spatial resolution of ~8 nm. The unique co-axial geometry of PHI's cylindrical mirror analyzer (CMA) allows for line-of-sight analysis of these highly topographical powder materials. Furthermore, the coaxial geometry of the CMA allows for easy, user-friendly analysis of FIB cuts with little sample prep or stage manipulation. The variation in chemistry among the particles indicates grain boundary diffusion, potentially impacting final device performance. XPS and HAXPES measurements support this finding, revealing the variation of chemical composition as a function of particle size and demonstrating that Zr is surface enriched.

Acknowledgment

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