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Application of ζ-factor Microanalysis to Measure Phase Compositions in Ultrahard Ceramics and Complex Concentrated Alloys

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ζ-factor microanalysis is a (scanning) transmission electron microscopy ((S)TEM) X-ray energy dispersive spectroscopy (XEDS) quantification method that corrects for specimen thickness effects [1]. It has been recently extended to compositionally characterize ultrahard ceramics [2] and complex concentrated alloys [3]. This talk will review ζ-factor microanalysis, then describe the difficulties and subsequent strategies to characterize ultrahard ceramics and complex concentrated alloys.

Ultrahard ceramics (e.g. boron carbide) are used for high-strength applications. Methods to improve their performance focus on engineering their microstructure across multiple length-scales, particularly modifying bulk stoichiometry, incorporating nanoscale phases, developing stacking faults, and engineering grain and phase boundaries [4]. The approach of tailoring nanoscale phases and interfaces requires high-resolution techniques (e.g. (S)TEM). However, there are significant challenges of analyzing ultrahard ceramics using (S)TEM XEDS, namely poor detectability and high absorption loss of soft X-ray lines, native surface oxide layers, hydrocarbon contamination, etc. In combination, these analytical difficulties often result in inconclusive (S)TEM XEDS results. ζ-factor microanalysis has the capability to overcome these experimental difficulties because of its inherent absorption correction capability.

The first task was to determine the ζ-factors associated with the EDS detector in our JEOL ARM-200CF instrument. K-family ζ-factors were initially determined or estimated using a NIST SRM-2063a thin film. Wedged SiB_6, SiC, and GaN thin specimens were also used to directly determine B, C, and N K-line ζ-factors [2]. Figure 1a shows the ζ-factors generated during this work. Most notably, direct measurement of B, C, and N K-line ζ-factors revealed that indirect estimation methods underestimate their true value. Next, the B and C K-line ζ-factors were validated by analyzing three standard boron carbide specimens having different B/C ratios, namely $B_{10.0}C$, $B_{7.4}C$, and $B_{4.1}C$, where the standard boron carbide compositions were independently determined via titration and combustion gas measurements [5]. STEM XEDS spectrum-imaging datasets were acquired from each bulk sample to efficiently collect thousands of individual spectra from different specimen thicknesses. Acquisition of spectra from different specimen thicknesses was conducted to confirm that ζ-factor microanalysis can accurately, and precisely, determine boron carbide stoichiometry despite specimen thickness effects. Figure 1b shows histograms of B/C concentration ratios obtained from each boron carbide specimen. Overall, the ζ-factor results agreed well with the known boron carbide stoichiometries, thus proving ζ-factor microanalysis as a viable method of determining stoichiometries of ultrahard ceramics [2].

Complex concentrated alloys (CCAs) oftentimes exhibit unpredictable microstructures that are highly dependent on synthesis/processing methods. In some cases, CCAs exhibit multi-phase microstructures that consist of intentional metallic phases as well as unintentional impurity ceramic phases. Therefore, there is a need to confidently identify microstructural phases in CCAs in order to elucidate mechanical properties. Similar to ultrahard ceramics, difficulties associated with analyzing ceramic phases in CCAs via STEM XEDS are poor detectability and high X-ray absorption of soft C, N, and O K-line X-rays. In addition, poor detectability of very hard metallic X-ray lines (e.g. Nb Kα and Mo Kα) and overlapping X-ray peaks also add to the difficulty. Considering the challenges of XEDS characterization of CCAs, a refractory NbMoTaW alloy

that contains multiple impurity nitride phases was chosen as a model alloy to showcase the capabilities of ζ-factor microanalysis.

The NbMoTaW alloy was synthesized by cryogenic ball milling and combustion gas methods determined that the alloy contained 25 at.% N. Impurity nitrogen was introduced by milling with LN_2. The alloy was then annealed at 1200 °C for 100 hours to induce grain growth. An XEDS spectrum-image was acquired and the results are shown in Figure 2. Maps of specimen thickness and all atomic concentrations of the major intentional and unintentional alloying elements were extracted. The specimen thickness map shows that the sample was roughly 100 nm thick towards the top left of the image but nearly 10-20 nm towards the bottom. Despite the great range of specimen thicknesses, and thereby differences in varying absorption losses for each element, the atomic concentration maps do not show a dependence on specimen thickness. The N and Nb atomic fraction maps, shown in Figure 2c and 2e, respectively, clearly show that two nitride phases precipitated: one enriched with N-Nb-Ta (marked by white circles) and another enriched with N-Fe-Nb-Ta (marked by while triangles). The experimentally determined nitrogen concentrations in the two nitrides were 14.6 ± 0.6 and 31.3 ± 0.9 at.% N, respectively. Atomic-resolution STEM imaging was also conducted to aid in the nitride phase identification. Images were taken from several low index zone axes and it was determined that nitride phases were cubic and hexagonal. Upon considering the nitrogen concentrations and crystal structures, the nitride phases were determined to be a M_6N η-nitride and a M_2N heminitride. Their theoretical nitrogen concentrations of 14.3 and 33.3 at.% N, respectively, were in close agreement with the ζ-factor measurements. Overall, ζ-factor microanalysis enabled full phase identification which would otherwise have been difficult due to severe X-ray absorption [3].

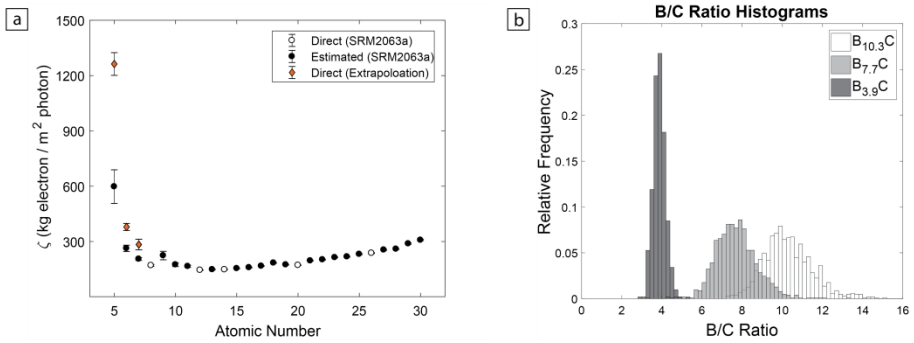

Figure 1. (a) Experimentally determined ζ-factors and (b) determined boron carbide stoichiometries of three bulk samples.

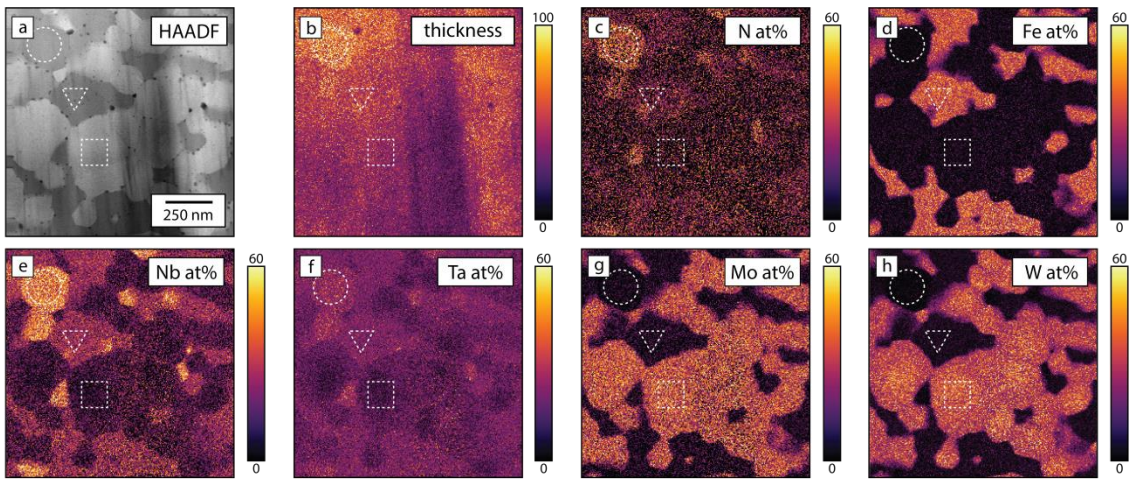

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Figure 2. STEM-XEDS spectral image of a mechanically alloyed NbMoTaW CCA after annealing at 1200 °C for 1000 hours: (a) HAADF micrograph, (b) thickness (nm), (c) N at.%, (d) Fe at.%, (e) Nb at.%, (f) Mo at.%, (g) Ta at.%, and (h) W at.%. The microstructure contained a W(Mo) BCC solid solution (square), Fe-Ta-Nb-rich M6N η-nitride (triangle), and a Nb-Ta-rich M2N heminitride (circle). Mo and W were correlated just as Ta and Nb were correlated.

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