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Analysis of Microwave-Induced Plasma Composition Using Optical Emission Spectra for High-Entropy Carbides

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Introduction

- High-entropy materials demonstrate high tensile strength, high resistance to fracture, corrosion, and oxidation, and high temperature stability.
- Applications in hypersonic flight, nuclear reactors, and jet engines.[1,2]
- Synthesis of metal carbide and high-entropy carbides with low-temperature microwave (MW) plasma.
- Utilization of optical emission spectroscopy (OES) to determine the degree of single-phase synthesis achieved.
- Rapid processing time, decreased sintering temperatures, and improved physical and mechanical properties from MW plasma sintering.[3]
- High-entropy carbides possess a face-centered cubic crystal structure composed of a uniquely random assortment of five transition metals.

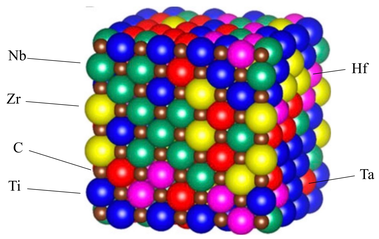


Figure 1[4]**.** Face-centered cubic (FCC) lattice structure of a high-entropy carbide (HEC).

Materials and Methods

X-Ray Diffraction

- A thin film scan of each pellet was performed to determine the elemental composition and crystal structure.
- Goal is the formation of a single-phase metal carbide and high-entropy carbide after annealing.

Scanning Electron Microscope

- Scans of each pellet were performed using a scanning electron microscope with energy dispersive x-ray spectroscopy (SEM/EDX).
- Presented additional information regarding the elemental composition and physical structure of the pellets.
- Analysis performed to determine the progress of the reduction from metal oxide + graphite to metal carbide.

Powder Processing & Microwave Plasma Sintering

- Five transition metal oxide (Hf, Nb, Ta, Ti, and Zr) powders were separately (and collectively) mixed with graphite powder and milled with a high energy ball mill.
- Resulting powder was pressed into pellets under ~1.2 ton using a hydraulic pellet press.
- Pellets were annealed using low-temperature MW plasma in a chemical vapor deposition (CVD) machine with a fiber optic cable for OES.

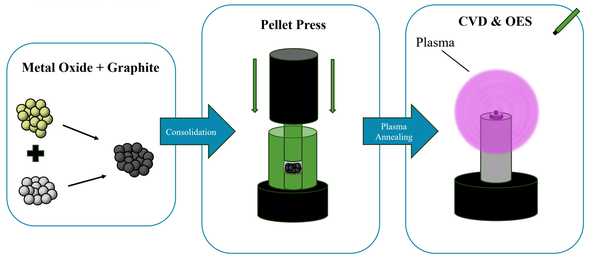
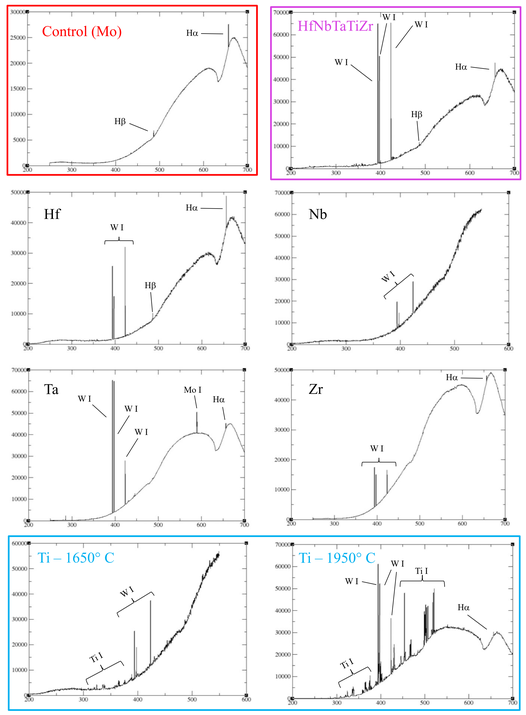


Figure 2. Schematic representation of pellet formation using high energy ball milling followed by consolidation of the powder into a pellet using a hydraulic press and finally annealing using a CVD machine.

Results and Discussion

200 nm – 700 nm



700 nm – 1050 nm

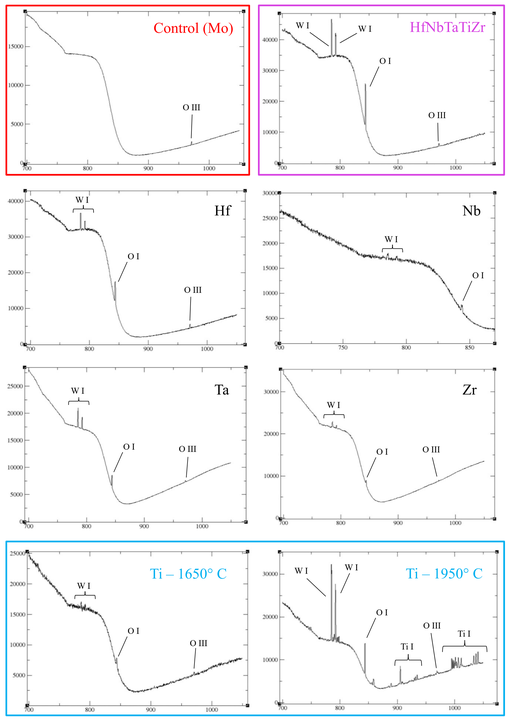


Figure 3. OES spectra peaks for (*from left to right going down*) the molybdenum control screw, HfNbTaTiZr oxide + graphite pellet, and the Hf, Nb, Ta, Zr, and Ti metal oxide + graphite pellets for the temperatures range of 1500° C – 1650° C and wavelength ranges of 200 nm – 700 nm and 700 nm – 1050 nm. TiO_2 + graphite pellet OES spectra for a temperature of 1950° C is also shown for both wavelength ranges.

- Ubiquitous peaks present in each pellet at 394 nm, 397 nm, 423 nm, 785 nm, and 792 nm have been linked to tungsten impurities. An 844 nm peak has been linked to atomic oxygen.
- Expected metal peaks were not clearly observed except for titanium.
- The molybdenum control screw presented with no impurity peaks and only with Hγ, Hβ, and Hα, peaks at 434 nm, 486 nm, and 656 nm, respectively, and with an atomic oxygen peak at 971 nm. All these peaks were present in each pellet.
- SEM/EDX scans showed a significant decrease in the oxygen concentration relative to the metal only for the metal oxide + graphite pellets, and the presence of tungsten impurities on all the pellets.

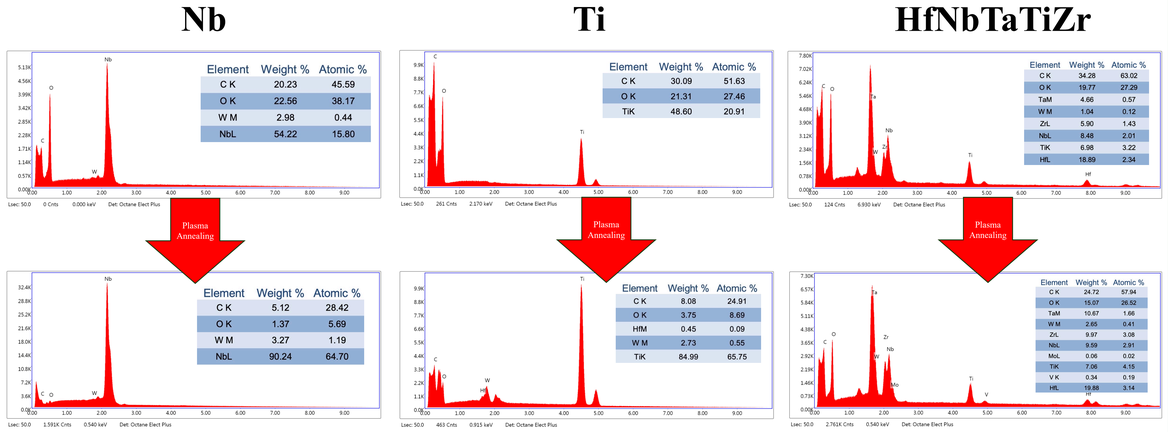


Figure 4. SEM/EDX data regarding the elemental composition percentage of the precursor metal oxide + graphite pellets for niobium oxide (*top left*), titanium oxide (*top middle*), and the HfNbTaTiZr oxide + graphite pellet (*top right*) as well as the elemental composition percentage of the pellets after annealing for niobium oxide (*bottom left*), titanium oxide (*bottom middle*), and the HfNbTaTiZr oxide + graphite pellet (*bottom right*).

Results and Discussion (Cont.)

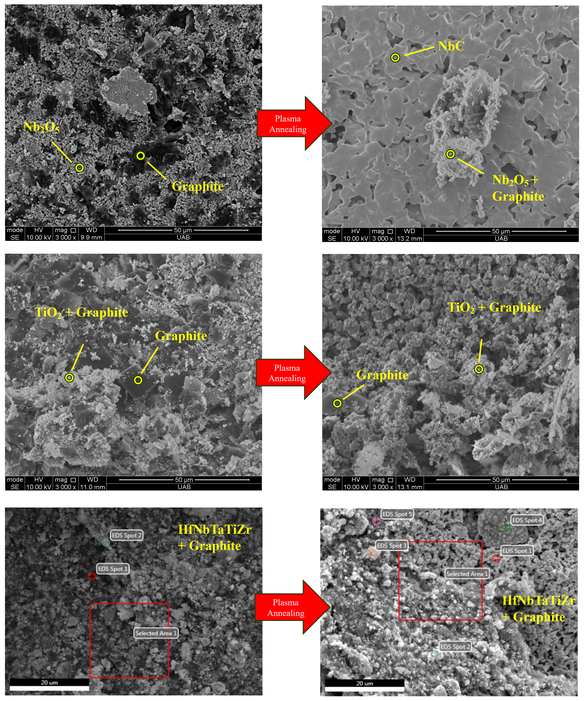


Figure 5. SEM images of niobium oxide + graphite, titanium oxide + graphite, and the HfNbTaTiZr oxide + graphite pellets before annealing *(left)* and after *(right)*.

- Significant conversion of Nb_2O_5 + graphite into NbC.
- No significant conversion of TiO_2 + graphite into TiC indicative of no single-phase synthesis.
- No significant conversion of HfNbTaTiZr oxide + graphite into TiC indicative of no single-phase synthesis.

Conclusion & Future Work

- No significant contrast between oxygen intensity at lower and higher temperatures with OES data indicates it is an imperfect measurement of molecular reduction.
- Lack of OES peaks indicates that metals are not appearing in the plasma composition, possibly due to annealing into metal carbides with stronger atomic and molecular bonds. Additional SEM/EDX scans on Zr, Ta, and Hf precursors are needed to determine if metal carbide synthesis is occurring.

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The author has no conflicts of interest to disclose.

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