MODELING AND SYNTHESIS OF HIGH-ENTROPY REFRACTORY CARBIDES, NITRIDES, AND CARBONITRIDES

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It has been well demonstrated that, through entropic stabilization, many equiatomic multicomponent metallic compositions will form single-phase, complex solid solutions, often called high-entropy alloys. It is known for metallic systems that one can take advantage of the inherent favorable properties of these materials, including increased thermal stability and solid solution strengthening. In order to extend the field of high-entropy alloys into the ultra-high temperature realm, we investigate novel equiatomic, hexanery (5-metal + anion), high-entropy refractory carbides, nitrides, and carbonitrides of group IV, V, and VI transition metals via modeling and experimental synthesis routes. The CALPHAD technique enabled rapid screening of a vast number of material systems to find likely candidates for formation of truly single-phase high-entropy ultra-high temperature ceramics (UHTCs). Compositions that exhibited broad, single-phase solubility across a large temperature region were selected, making processing possible at reasonable temperatures (≤2500°C). For further screening of compositions, a novel, first-principles materials design method was developed. The theory follows that for low temperature single-phase formation, the different configurations should have similar energies to increase the number of thermodynamically accessible states. A partial occupation method was implemented within AFLOW to automate the generation and calculation of the different configurations. The energy distributions were then used to construct a descriptor to predict the formation of high-entropy materials. Following model predictions, bulk samples were synthesized using a combination of high-energy ball milling (HEBM), spark plasma sintering (SPS) at 2200°C, and hot press (HP) annealing at 2500°C. Phase determination was done via x-ray diffraction techniques as well as TEM microscopy, while chemistry was evaluated via energy dispersive x-ray spectroscopy and STEM-EDS. Many of the carbide compositions, including $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}Zr_{0.2})C$, $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}V_{0.2})C$, $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}W_{0.2})C$, and $(Nb_{0.2}Ta_{0.2}Ti_{0.2}V_{0.2}W_{0.2})C$ demonstrated virtually single-phase, solid-solution compounds and were sintered to greater than 95% theoretical density. Figure 1 shows the experimental X-ray diffraction patterns for a sample of composition $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}V_{0.2})C$ following each processing step. The material progresses into the desired single cubic NaCl structure following complete processing. Work on single-phase determination in nitride and carbonitride systems is ongoing. This work demonstrates the extension of entropic-stabilization principles into refractory interstitial ceramics and development of new classes of high-entropy ceramic materials for high-temperature applications.

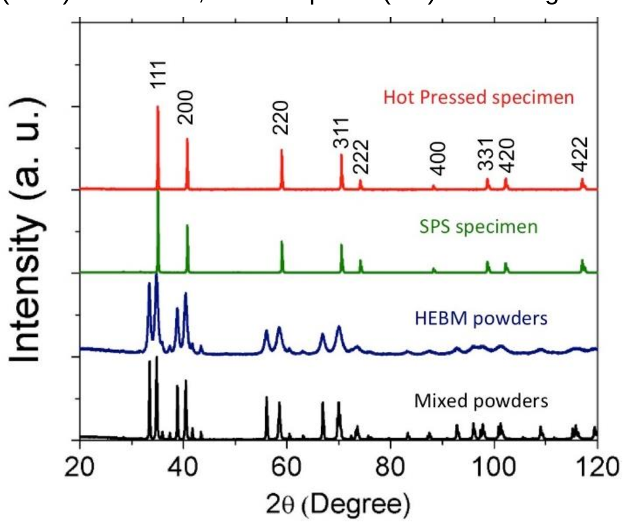

Figure 1 – Experimental X-ray diffraction patterns of a $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}V_{0.2})C$ following each processing step, starting with hand mixed powder, to high-energy ball milled powder, to sintered specimen, and finally hot press annealed specimen, demonstrating the progression into a single phase.

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