

MODELING AND SYNTHESIS OF HIGH-ENTROPY REFRACTORY CARBIDES

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Bulk samples of equiatomic, hexanery (5-metal), high-entropy refractory carbides were fabricated using a combination of high-energy ball milling (HEBM), spark plasma sintering (SPS), and hot pressing (HP) annealing. To select candidate composition that are likely to form single phase high-entropy materials at lower processing temperatures (<2500°C), 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 of Entropy Forming Ability (EFA) to predict the formation of high-entropy materials. CALPHAD results were found to agree with the configuration energy range descriptor for each composition, and these carbides exhibited broad, single-phase solubility across each system, making processing possible at reasonable temperatures. Many of the complex carbide compositions, including $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Zr}_{0.2})\text{C}$, $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{V}_{0.2})\text{C}$, $(\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{W}_{0.2})\text{C}$, and $(\text{Nb}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{V}_{0.2}\text{W}_{0.2})\text{C}$ demonstrated virtually single-phase, solid-solution compounds with the NaCl crystal structure as determined by x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS), while some compositions, including $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ta}_{0.2}\text{W}_{0.2}\text{Zr}_{0.2})\text{C}$ and $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{V}_{0.2}\text{W}_{0.2}\text{Zr}_{0.2})\text{C}$, exhibited multiple phases. Results were found to be in good agreement with the *ab initio* based formulation of entropic stability, where the compositions with the highest EFA values were found to form a single rocksalt structure and compositions with the lower EFA values were found to exhibit multiple phases. Further, among the systems that were found to form single phase materials at 2500°C, artificial segregation was introduced via lower processing temperatures. In these artificially segregated samples, the extent of mixing was analyzed via peak broadening in XRD according to the formulation of Williamson and Hall [1] and compositional mapping in EDS. Results of artificially segregated samples provide continued support for the viability of the EFA formulation, where broadening was found to be more pronounced (i.e. more chemical segregation) in samples that were determined to have a lower EFA value. This work demonstrates the extension of entropic-stabilization into refractory interstitial carbides, paving the way for development of an entirely new class of UHTCs.

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[1] G.. Williamson, W.. Hall, X-ray line broadening from filed aluminium and wolfram, Acta Metall. 1 (1953) 22–31. doi:10.1016/0001-6160(53)90006-6.