The Effect of Submicron Grain Size on Thermal Stability and Mechanical Properties of High-Entropy Carbide Ceramics

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Introduction

- High-entropy ceramic materials have shown special physical properties. For example, the recent research on high-entropy carbides (HECs) has revealed low thermal conductivity, high hardness, and an improved oxidation resistance.
- In ceramic materials, a decrease in grain size to sub-micrometers or nanometers can significantly improve the mechanical strength, fracture toughness, hardness, radiation resistance, and induce super-plasticity at high temperatures.
- The promising properties of high-entropy ceramics have been attributed to the compositional complexity, significant lattice distortion, and sluggish diffusion. However, the fundamental mechanisms about the relation between the high-entropy effects and the physical and chemical properties of ceramic materials remain poorly understood.
- The objective of this research is to investigate the effect of submicron grain size on the thermal stability and mechanical properties of HEC.

Methods

- HfC, TiC, TaC, NbC, and ZrC powders were mixed at an equimolar ratio with stainless steel grinding balls (ball-to-powder ratio: 5:1), followed by ball milling using a planetary ball mill under Ar atmosphere.
- Spark plasma sintering (SPS) of the ball-milled powders was conducted on an SPS system under vacuum. The SPS conditions for coarse-grained $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ were 2000°C for 5 minutes at a pressure of 30 MPa. The fine-grained $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ was synthesized by SPS using the two-step sintering process.
- The phase composition of $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ samples was analyzed by X-ray diffraction on a diffractometer.
- Scanning electron microscopy (SEM) of microstructures was conducted on a FIB/SEM dual-beam workstation using the secondary electron imaging mode.
- The Vickers hardness was measured on a hardness tester with a 9.8 N load and a 15 sec dwell time. The bending strength was measured by the three-point bending test. The fracture toughness was measured by the single-edge notched beam (SENB) method.

Table 1. The spark plasma sintering (SPS) conditions, measured density, relative density, grain size, and mechanical properties of $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ samples. C1 is the coarse-grained sample, while F-1 to F-3 are the fine-grained samples

Sample #	SPS conditions	Density (g/cm^3)/ relative density	Grain size (μm)	Hardness (GPa)	Bending strength (MPa)	Fracture toughness (MPam$^{1/2}$)
C-1	2000°C (5 min)	8.45/94.9%	16.5 ± 4.2	16.21 ± 1.04	318 ± 25	4.9 ± 0.5
F-1	2000°C (0.5 min) + 1800°C (15 min)	8.25/92.7%	0.578 ± 0.217	17.07 ± 0.54	400 ± 27	5.9 ± 0.7
F-2	1800°C (0.5 min) + 1600°C (15 min)	7.75/87.1%	0.421 ± 0.138	10.00 ± 1.12		
F-3	1600°C (3 min) + 1400°C (40 min)	7.64/85.8%	0.412 ± 0.149	9.79 ± 0.66		

Phase Composition

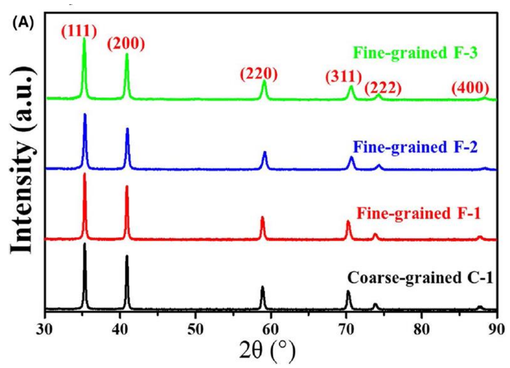


Figure 1. Phase characterizations of $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ samples. X-ray diffraction of the coarse- (C-1) and fine-grained samples (F-1 to F-3)

All coarse- and fine-grained samples show the formation of a single-phase structure. No secondary phase was observed.

Microstructure

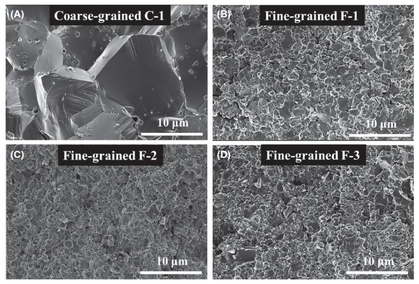


Figure 2. SEM images of the fracture surfaces

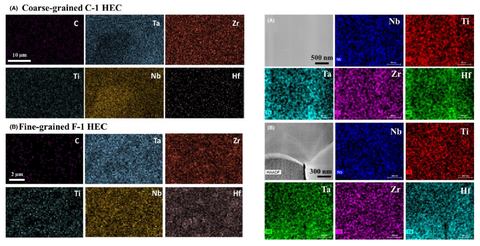
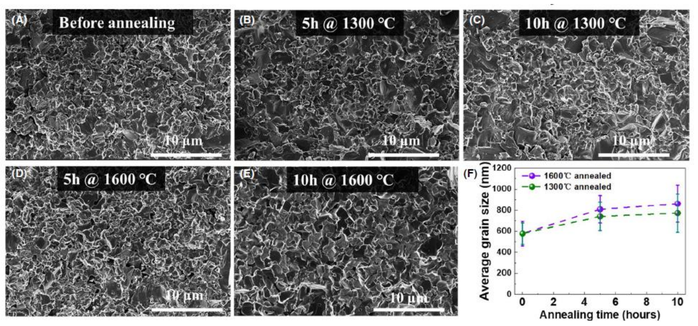


Figure 3. Energy-dispersive X-ray spectroscopy (EDS) mapping

- The grain sizes of fine-grained samples range from 400 to 600 nm. the average grain size of the coarse-grained sample is 16.5 μm.
- The combination of EDS analysis in SEM and TEM covered the scale of element distribution from micrometer to nanometer, in which no element segregation was observed.

Thermal Stability



The average grain size increased slightly from 0.57 μm before annealing, to 0.77 μm after annealing at 1300°C for 10 hours, and to 0.86 μm after annealing at 1600°C for 10 hours (F).

The grain growth at 1300 and 1600°C was small, suggesting that the fine-grained $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ sample has superior thermal stability at high temperatures.

Figure 4. SEM images of the grain morphology in fine-grained F-1 $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ sample: (A) before annealing, (B) after annealing at 1300°C for 5 h, (C) after annealing at 1300°C for 10 h, (D) after annealing at 1600°C for 5 h, and (E) after annealing at 1600°C for 10 h. (F) the average grain size as a function of annealing time at 1300 and 1600°C, respectively.

Conclusion

- HECs with submicron grain sizes of 400 to 600 nm were fabricated by SPS using the two-step sintering process. The SPS fabricated sample with a single phase of rock salt structure was confirmed by X-ray. No secondary phase or element segregation was observed.
- The grain growth kinetics in the fine-grained HECs is small at 1300 and 1600°C, indicating it has superior thermal stability at high temperatures.
- The fined-grained HECs showed higher cracking resistance to Vickers indentation than the coarse-grained one. The bending strength and fracture toughness of fine-grained HECs are 25% and 20% higher, respectively, than the coarse-grained HEC.

Mechanical Properties

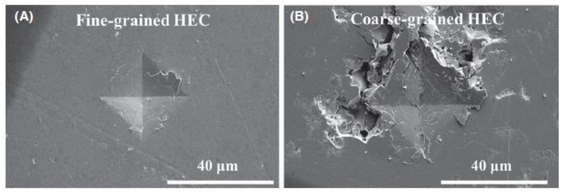


Figure 5. SEM image of the Vickers indentation of (A) fine grained F-1 and (B) coarse-grained C-1 $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ samples

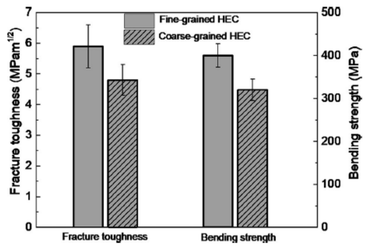


Figure 6. Comparison of fracture toughness and bending strength of the fine-grained F-1 and coarse-grained C-1 $(Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C$ samples

- The fine-grained sample has higher cracking resistance and fracture toughness than the coarse-grained sample.
- The bending strength and fracture toughness of fine-grained HECs are 25% and 20% higher, respectively, than the coarse-grained HEC.

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