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Research Article

Nano-(Ta, Zr)C Precipitates at Multigrain Conjunctions in TaC Ceramic with 10 mol% ZrC and 5 mol% Cu as Sintering Aid

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A fully dense TaC ceramic was prepared by hot pressing using 10 mol% ZrC plus 5 mol% Cu as a sintering aid. Formation of (Ta, Zr)C solid solution (ss) by reaction between TaC and ZrC facilitated densification. Addition of Cu refined the microstructure and consequently improved flexural strength of the TaC ceramics. TEM investigation found ubiquitous precipitation of nanocrystallites at multigrain conjunctions. The nanocrystallites were (Ta, Zr)C solid solution with uniform dispersion in an oxygen-rich glassy matrix. Although formation of nanoprecipitates may not much affect the mechanical properties of the TaC ceramic, the structure suggested a new type of nanoceramic worth further research.

1. Introduction

Tantalum carbide (TaC) is one of the ultrahigh temperature ceramics (UHTC) [1] as it has high melting point (~3983°C), good electrical and thermal conductivity, and relatively good mechanical properties. Because TaC ceramics are extremely hard to densify [2], sintering aids such as C [3–6], Si [7, 8], B_4C [9, 10], SiC [11, 12], $TaSi_2$ [13, 14], $MoSi_2$ [13, 15], TaB_2 [9, 10, 16], and Si_3N_4 [17] were used to increase densification. In a previous work, TaC ceramics were hot pressed with ZrC plus Cu as sintering aids [18]. Herein, secondary phases in the TaC ceramics were detailed by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) to show precipitation of nanocrystallites in a continuous glassy phase at multigrain conjunctions. The structure at the multigrain conjunction was very similar to a glass ceramic in terms of precipitation of crystallites in a glass matrix. Considering the good physiomechanical properties of the TaC and the ZrC compound, the intergranular composition of the TaC ceramics may suggest a new type of nano-(Ta, Zr)C ceramic of good electrical and thermal conductivities.

2. Experimental

TaC (Ningxia Orient Tantalum Industry, Yinchuan, China), ZrC (Aladdin Reagent Company, Shanghai, China), and Cu (Aladdin Reagent Company, Shanghai, China) powders were used as starting materials. A powder mixture with a TaC : ZrC : Cu molar ratio of 1.00 : 0.10 : 0.05 was homogenized and was hot pressed in a graphite furnace (15 t Hot Press Furnace, Materials Research Furnaces, Inc., USA) at 1900°C for 30 min under 30 MPa pressure in an Ar flux with a flowing rate of 2.0 L/min. Density was measured and relative density was calculated. Crystalline phases were detected by XRD (X-ray diffraction, XRD-6000, Shimadzu, Japan). Polished-and-thermally etched surfaces parallel to the hot pressing direction were observed by SEM (Electron Scanning Microscopy, SSX-500, Shimadzu, Japan). A thin piece was sliced along diameter of the sample, followed by manual thinning and ion milling to prepare foil for TEM observation (Tecnai G2 F30, FEI Co., Oregon, USA). Chemical compositions of interested areas were detected by Energy Dispersive Spectroscopy (EDS, Bruker Nano GmbH, Berlin, Germany) operating at an excitation voltage of 200 kV.

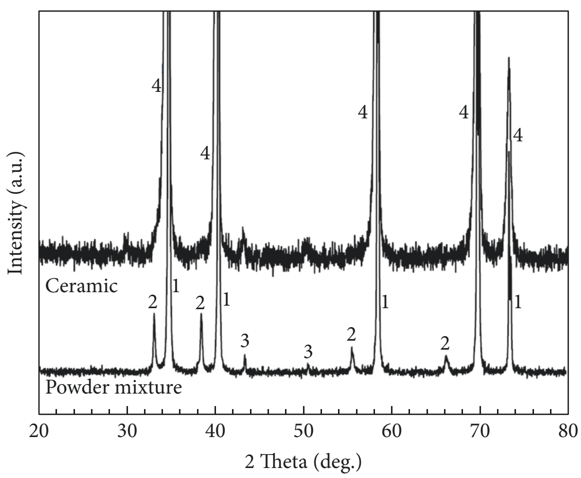

FIGURE 1: XRD pattern of the TaC-20 mol% ZrC-5 mol% Cu powder mixture and the consolidated ceramic.

Selected area electron diffraction (SAED) was preformed to identify the phases.

3. Results and Discussion

3.1. General Observation. The consolidated TaC ceramic reached a relative density value of 97.6% to give good flexural strength of 589 ± 47 MPa and fracture toughness of 5.0 MPa·m$^{1/2}$. In comparison, pure TaC without using any sintering aid showed low values of relative density and mechanical properties [2, 17]. The enhanced densification of the investigated composition relative to pure TaC was due to mutual diffusion of Zr^{4+} and Ta^{4+} cations to form (Ta, Zr)C solid solution (ss). Metallic Cu also helped increase densification of the TaC ceramic. XRD patterns for both the powder mixture and the consolidated ceramic are shown in Figure 1. Diffractions of Cu were barely observable, while ZrC phase was absent in the consolidated ceramic. The dominant XRD peaks from the consolidated ceramic were indexed by TaC with significant broadening and shift towards lower 2θ positions, indicating formation of a (Ta, Zr)C ss [18, 19]. SEM of the polished-and-thermally etched surface (not shown) revealed uniform equiaxed grains having an average diameter from ~0.9 to 6.4 μm.

3.2. Formation of Nano-(Ta, Zr)C at Multigrain Conjunctions. A typical TEM micrograph of the ceramic is shown in Figure 2(a). SAED of the predominant phase (Figure 2(d)) was consistent with (Ta, Zr)C ss. EDS (Figure 2(e)) revealed Zr in addition to Ta and C, which is in agreement with formation of (Ta, Zr)C ss as revealed by XRD. Mo and Cr signals occasionally detected by EDS were due to effects of the TEM sample holder, not belonging toany phase in the ceramic. Neither O nor Cu was detected in the (Ta, Zr)C ss grains.

Pockets containing secondary phases existed at multigrain conjunctions. A SAED pattern of the phase at a multigrain conjunction is shown in Figure 2(c). The continuous ring diffraction pattern (DP, Figure 2(c)) indicated nanocrystallites. HRTEM image (Figure 2(b)) of the same area evidenced nanocrystallites with average grain size less than 10 nm. Interplanar spacings of the nanocrystals (i.e., d_{hkl} values) were calculated by the ring DP to be in agreement with TaC, with slightly larger d_{hkl} relative to pure TaC, which could be explained by incorporation of Zr into TaC lattice to form (Ta, Zr)C ss.

EDS result of the nanocrystallites (Figure 2(e)) showed predominant Ta, Zr, and C, consistent with (Ta, Zr)C ss. Significant amount of O was also detected, indicating other phases rich in O in equilibrium with the (Ta, Zr)C ss. In the HRTEM image, Figure 2(b), completely disordered regions were presented in neighbor of the nano-(Ta, Zr)C crystallites. The TaC and ZrC powder contained O impurity to estimate 1.23 wt% Ta_2O_5 and 0.388 wt% ZrO_2, respectively, in the TaC + ZrC + Cu powder compact. The glassy phase was formed by eutectic reaction between Ta_2O_5 and ZrO_2 at the sintering temperature of 1900°C, because eutectic temperature is less than 1887°C in the Ta_2O_5-ZrO_2 system. TaC and ZrC presumably dissolved in the eutectic liquid at high temperatures and subsequently precipitated nano-(Ta, Zr)C upon cooling, while the eutectic liquid was quenched to form the glassy matrix.

Formation of nano-(Ta, Zr)C at multigrain conjunctions in the TaC ceramic was ubiquitous. Analysis for another intergranular pocket is shown in Figure 3. Chemistry and SAED (Figures 3(b) and 3(d)) both evidenced nano-(Ta, Zr)C ss, the same as shown in Figure 2. Metallic Cu was identified here and there by SAD (Figure 3(c)) and EDS (Figure 3(b)). Small concentrations of C, O, Ta, and Zr were also detected in combination with Cu due to effect of the neighboring (Ta, Zr)C grains. Cu did not react with either Ta_2O_5 or ZrO_2 from room temperature to 2000°C, according to thermodynamics calculation. The intergranular metallic Cu may form a liquid at high temperature to facilitate nano-(Ta, Zr)C formation.

3.3. Brief Discussion on the Nanoprecipitates. In summary, nano-(Ta, Zr)C was ubiquitously observed for the first time at multigrain conjunctions in the TaC ceramic with 10 mol% ZrC plus 5 mol% Cu as the sintering aid. Formation of nanoprecipitates may not much affect room-temperature mechanical properties of the TaC ceramic [17], while thermal-physical properties such as thermal shock resistance could shift due to possible changes in thermal conductivity and interfacial structure, though investigation of such thermal-physical properties was out of the scope of this paper. Nevertheless, this observation may suggest a composition possibly for a new nanoceramic with a uniform dispersion of (Ta, Zr)C nanoparticles less than 10 nm in size in a continuous O-rich glassy matrix. Polycrystalline nanomaterials are expected

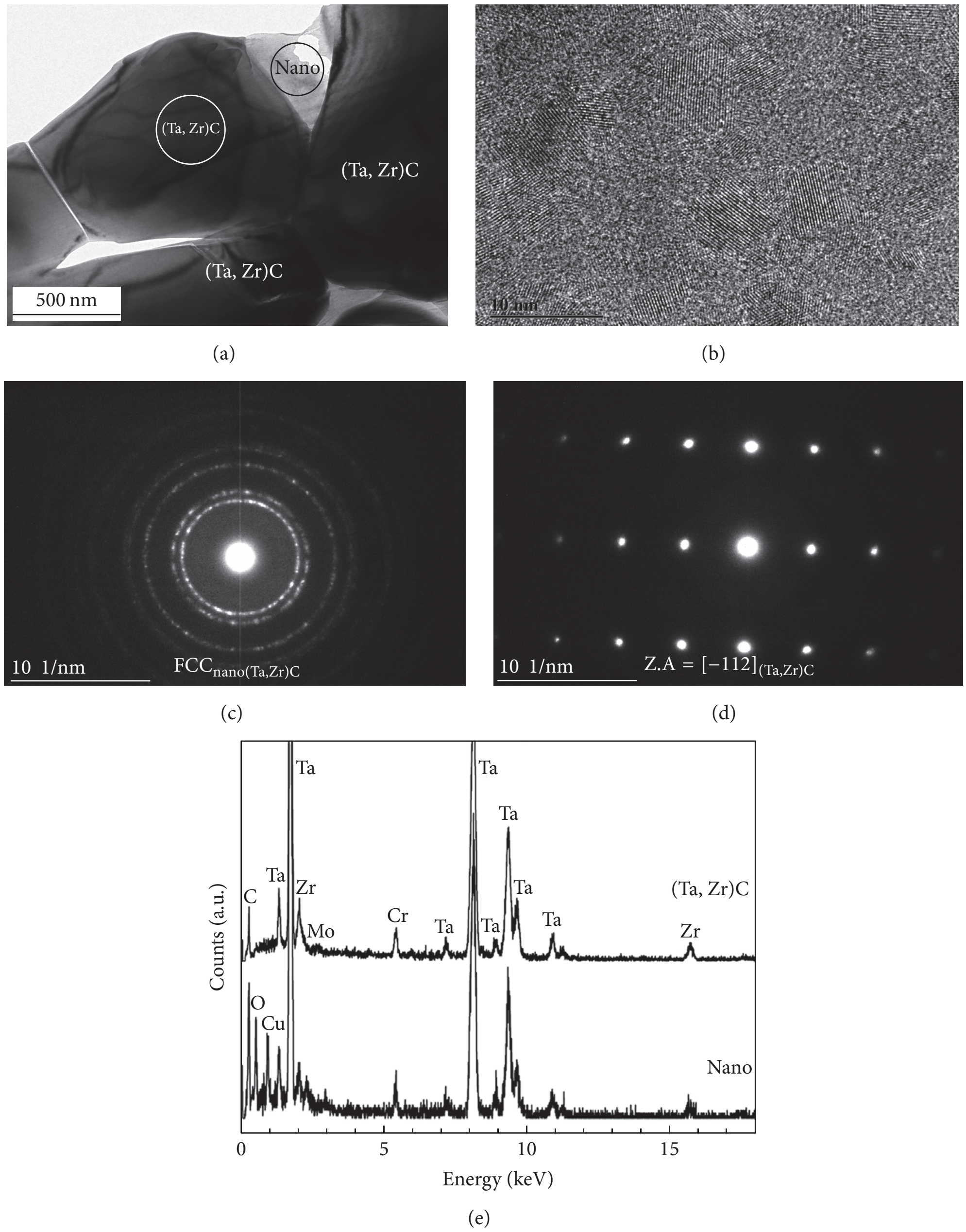

Figure 2: TEM of the consolidated TaC ceramic with 10 mol% ZrC plus 5 mol% Cu as sintering aid (a). HRTEM (b) and ring DP (c) of the circled area at multigrain conjunction evidenced formation of polycrystalline nano-(Ta, Zr)C. (d) DP of the circled (Ta, Zr)C grain, and (e) EDS of the circled area at multigrain conjunction and the (Ta, Zr)C grain.

to show extraordinary properties but are extremely hard to synthesize. One possible route to fabricate nanoceramics is via controlled crystallization of glass ceramics. Dispersion of nano-(Ta, Zr)C crystallites in the glassy phase at multigrain conjunctions in the TaC ceramic indicated such a glass ceramic system, though further works on optimizing the composition and the processing parameters are needed in order to successfully develop such a conceptual (Ta, Zr)C nanoceramic.

4. Conclusion

Microstructure of the TaC ceramic with 10 mol% ZrC plus 5 mol% Cu as a sintering aid was investigated by means of TEM, HRTEM, SAED, and DES. TaC and ZrC reacted to form a (Ta, Zr)C solid solution, while metallic Cu remained at multigrain conjunctions. Uniform dispersion of nano-(Ta, Zr)C crystallites less than 10 nm in size in a continuous O-rich glassy matrix was observed ubiquitously at multigrain

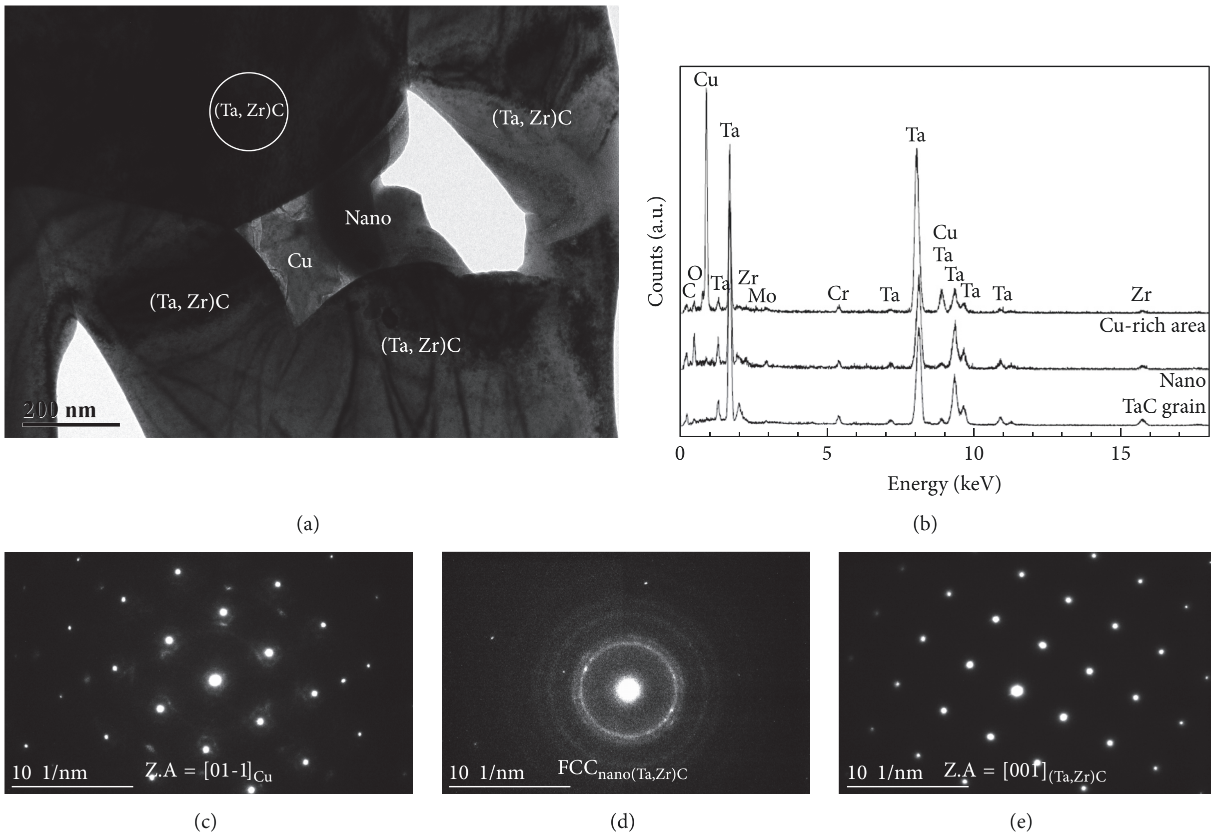

FIGURE 3: TEM of the consolidated TaC ceramic with 10 mol% ZrC plus 5 mol% Cu as sintering aid (a). EDS (b) and DP (c) evidenced metallic Cu. And again (d) ring DP showed polycrystalline nano-(Ta, Zr)C in neighbor of Cu and (e) DP of the circled (Ta, Zr)C grain.

conjunctions. Effects of such nanoprecipitates on properties of the TaC ceramic are not clear yet.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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