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

Lianbing Zhong,1 Guihong Geng,2 Yujin Wang,1 Feng Ye,1 and Limeng Liu1,2

1School of Materials Science and Engineering, Harbin Institute of Technology, Xidazhi Street 91, Harbin 150001, China
2School of Materials Science and Engineering, North Minzu University, Wenchangbei Street 204, Yinchuan 750021, China

Correspondence should be addressed to Limeng Liu; llm681@sina.com

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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], B4C [9, 10], SiC [11, 12], TaSi2 [13, 14], MoSi2 [13, 15], TaB2 [9, 10, 16], and Si3N4 [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.
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) and 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 (Ta, Zr)C, 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$_2$O$_5$ and 0.388 wt% ZrO$_2$, respectively, in the TaC + ZrC + Cu powder compact. The glassy phase was formed by eutectic reaction between Ta$_2$O$_5$ and ZrO$_2$ at the sintering temperature of 1900°C, because eutectic temperature is less than 1887°C in the Ta$_2$O$_5$-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$_2$O$_5$ 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.

3.2. 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 to any phase in the ceramic. Neither O nor Cu was detected in the (Ta, Zr)C ss grains.

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 and Ta cations to form (Ta, Zr)C solid solution (ss). Metallic Cu also helped increase mechanical properties [2, 17]. The enhanced densification of the investigated composition relative to pure TaC was due to mutual diffusion of Zr and Ta cations to form (Ta, Zr)C solid solution (ss). Metallic Cu also helped increase mechanical properties [2, 17]. The enhanced densification of the investigated composition relative to pure TaC was due to mutual diffusion of Zr and Ta cations to form (Ta, Zr)C solid solution (ss). Metallic Cu also helped increase mechanical properties [2, 17].
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 conjunctions in the TaC ceramic. This combination of high hardness and exceptional properties makes (Ta, Zr)C nanoceramics promising candidates for various high-performance applications.
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.

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**References**


