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Spark plasma sintering of TiC ceramic with tungsten carbide as a sintering additive

Lixia Cheng, Zhipeng Xie *, Guanwei Liu

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

By adding a small amount of tungsten carbide (WC) as sintering aids, nearly fully dense TiC ceramics were obtained by spark plasma sintering at 1450–1600 °C. The results show that the densification temperature of TiC ceramic was significantly decreased with the addition of 3.5 wt% WC. Compared with the monolithic TiC, the densification temperature of TiC–3.5 wt% WC is lower by ~150 °C and no deterioration of mechanical properties is observed. The TiC composite sintered at 1600 °C exhibits full density, a Vickers hardness of 28.2 ± 1.2 MPa, a flexural strength of 599.5 ± 34.7 MPa and a fracture toughness of 6.3 ± 1.4 MPa $m^{1/2}$.

Keywords: TiC; WC; Spark plasma sintering; Densification; Mechanical properties

1. Introduction

Titanium carbide (TiC) is not only an attractive potential candidate for cutting tool materials because of its excellent wear-resistance, perfect chemical stability, low friction coefficient to metals and superior thermal deformation resistance[1–4] but also a promising candidate of inert matrix fuels to retain fission products used in fuels for gas-cooled fast reactor (GFR) due to its high melting temperature, high thermal conductivity, high hardness, good corrosion resistance and low neutron absorption cross-section.[5,6] However, because of its strong covalent bond, it is difficult to obtain fully dense samples using traditional sintering technologies without substantial amounts of sintering aids and at temperatures lower than 2000 °C.[7] In order to reduce the sintering temperature, previous investigations usually added large amounts of metals (Ni,[4,8] Co)[9] or alloys (Ni–Mo)[10,11] as sintering binders. Generally speaking, the lower melting temperature of these metals or alloys could unfavorably affect the high temperature performances. In addition, the core temperature of the GFR may reach as high as 1600 °C in minutes and remain there for hours in accidental scenarios.[5,12] Therefore, the possible extreme temperature necessitates a kind of fuel that can not only withstand such high temperature for extending periods of time, but also remain structurally intact and retain fission products. If TiC is used as an inert matrix fuel for GFR, the impact of metals or alloys binders on the high temperature performance is undesirable.

Additionally, the inert matrix fuel was considered to include a certain amount of easily decomposed and evaporated materials (such as AmN)[5,13] at high temperature. It means that high temperature and long time heating treatment is not acceptable for sintering process. Therefore, rapid densification method for the inert matrix materials has been desired. Moreover, spark plasma sintering (SPS) is an advanced sintering technology for rapid densification of metal or ceramic powders at relatively low temperature. The outstanding advantage of SPS is that highly dense samples can be obtained within just a few minutes under mechanical pressure and large electric current. Therefore, SPS technology has been widely applied in the preparation of Nitides,[13] transparent nanoceramics[14] and carbides[15,16] in previous investigations.

WC added as secondary carbide to enhance wettability and sinterability, inhibit grain growth and improve the mechanical properties of Ti (CN)-based composites has been widely investigated in Ti ($C_{0.7}N_{0.3}$)–WC–Ni,[17] (Ti, W)(CN)–Ni and (Ti, W)C–Ni[4] as well as Ti ($C_{0.5}N_{0.5}$)–WC–Mo–Ni[10] systems, while only a limited number of investigations are available in previous literatures on the properties of binderless TiC–WC composites.

* Corresponding author. Tel.: +86 10 6279 9031; fax: +86 10 6277 1161.
E-mail address: xzp@mail.tsinghua.edu.cn (Z. Xie).

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Although Mas-Guindal et al.[18] and Kim et al.[19] investigated TiC–WC composites without any binders, a large content of WC (>20 mol%) were added. For example, Kim et al.[19] studied the WC-based composites with TiC as an additive, at least 50 at.% WC was used. Moreover, most of the TiC-based cermets or Ti(CN)-based composites as mentioned above were prepared by conventional sintering techniques rather than SPS methods.

In order to reduce the sintering temperature and avoid deteriorating the high-temperature properties of TiC, the densification evolution and mechanical properties of TiC with a small amount of WC sintered by SPS were investigated in our present work. The experimental results demonstrated that fully dense of TiC-based composites without any deteriorated mechanical properties could be obtained at a lower temperature.

2. Experimental procedures

Commercially available TiC powder (99% purity, particle size ~2 μm supplied by ST-nano Science & Technology Co., Ltd., Shanghai, China) and WC powder (97% purity, particle size ~3 μm supplied by CW-nano Science & Technology Co., Ltd., Shanghai, China) were used as starting materials. The powder mixtures of TiC–WC were prepared in a polyurethane jar using a planetary ball mill (MQ-3SP2, Nanjing University Instrument Plant, Nanjing, China) for 6 h with the milling rotation speed of 300 rpm, using absolute alcohol and tungsten carbide balls as milling mediums, subsequently dried in a rotary evaporator at 70 °C. The weight ratio of powder to balls was 1:10. The dried mixtures were sieved through a 100-mesh and then placed into a graphite die (30 mm in diameter) inserted with graphite sheets to avoid reaction between the powders and the die during sintering process. The samples were sintered with Dr. Sinter SPS-1050T spark plasma sintering system (SPS, Sumitomo Coal Mining Co. Ltd., Japan) in vacuum and an infrared thermometer was used to measure the temperature. All samples were densified at temperatures from 1450 °C to 1600 °C with ~120 °C min^{-1} heat rate and 5 min holding time. The applied uniaxial pressure was 50 MPa and maintained for 5 min during the final sintering temperature.

The particle size and microstructure of mixture powders were characterized by transmission electron microscope (H-800, Hitachi Ltd., Japan). The bulk density was determined by the Archimedes method using distilled water. The change of crystalline phase compositions of the samples before and after sintering was identified by X-ray diffraction (XRD) using Cu Kα radiation (Dmax-2500 diffractometer, Rigaku, Japan). Rietveld refinement was used to calculate the lattice parameters of TiC ceramic from the XRD data. The microstructures were observed by field-emission scanning electronic microscope (FESEM, LEO-1530, Germany) and transmission electron microscope (TEM, JEOL 2011, Japan). Average grain size of the sintered specimens was estimated on FESEM micrographs of the polished and etched surface by image analysis techniques, measuring at least 150 grains. The Vickers indentation test (HV-120; Laizhou Hardness Tester Manufactory, China) was used to evaluate the hardness of sintered specimens, using a load of 49 N with a dwell time of 15 s. Fracture toughness (K_{IC}) was calculated using the equation given by Anstis et al.,[20] measuring at least 9 points. The equation as following,

$$K_{IC} = \frac{0.016(E/H)^{1/2}P}{c^{3/2}} \quad (1)$$

where E is the Young's modulus obtained by the ultrasonic velocity measurements, P is the applied load, c is the average crack length, and H is the Vickers hardness calculated by the expression,

$$H = 1.8544\,\mathrm{P}\ \mathrm{d}^{-2} \quad (2)$$

where P is the applied load, d is the diagonal of the indentation. The flexural strength (σ_b) was evaluated by three-point bending using a universal testing machine (AG-IC; Shimadzu, Kyoto, Japan) on 3 mm × 4 mm × 22 mm specimens. At least six specimens were performed for each sintering temperature.

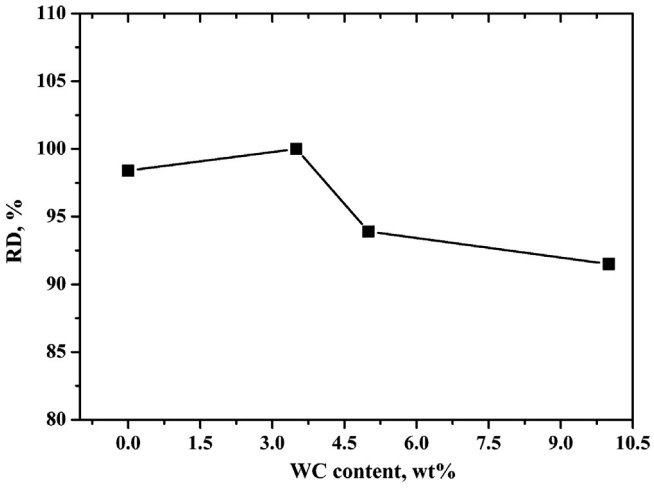

Fig. 1. Effects of WC content on the densification of TiC ceramic at 1600 °C.

3. Results and discussion

To explore the effects of WC amount on the densification and mechanical property of TiC ceramic, different amounts of WC (0, 3.5 wt%, 5 wt% and 10 wt%) were introduced in TiC matrix. The relative density of TiC with various contents of WC sintered at 1600 °C for 5 min is presented in Fig. 1. The density first increased from 98% to 100% with a small amount of WC (3.5 wt %) added, and then decreased to 91% with further additions of WC (10 wt%), as shown in Fig. 1. Hence 3.5 wt% is adopted as the optimal content in the following discussion.

Representative TEM image of the TiC–3.5 wt% WC milled powder microstructure is shown in Fig. 2, which displays that the morphology of TiC–3.5 wt% WC is irregular and the range of particle size from ~20 nm to ~3.5 μm. Table 1 shows the composition of pure TiC and TiC–3.5 wt% WC powder characterized by X-ray fluorescence spectrometry (XRF, XRF-1800, Shimadzu, Japan). Little contamination can be found in TiC–3.5 wt% WC powder except trace Na and K elements. Fig. 3 exhibits the X-ray diffraction patterns of TiC–3.5 wt% WC original powder mixture and bulk TiC–3.5 WC ceramics