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ScienceDirect

Ceramics International 40 (2014) 10517–10522

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mechanical properties of nanocrystalline TiC–ZrC solid solutions fabricated by spark plasma sintering

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Received 18 February 2014; received in revised form 6 March 2014; accepted 6 March 2014
Available online 17 March 2014

Abstract

Nanocrystalline TiC–ZrC solid solutions ($Ti_xZr_{1-x}C_{1-\delta}$) with densification of ~100% have been successfully prepared by spark plasma sintering. Due to the difference in ionic radii of Ti and Zr, the required sintering temperature for single-phase solid solutions exhibits an asymmetric dependence on x, being highest at $x=0.7$. At a temperature lower than the consolute one, the two-phase solid solution is formed, exhibiting the ability of grain size refinements to nanoscale. Due to the alternate reinforcements and the grain size refinements in TiC–ZrC solid solutions, the mechanical properties of Vickers hardness and fracture toughness are significantly increased when compared to TiC and ZrC.

Keywords: C. Mechanical properties; D. Carbides; Solid solutions; Spark plasma sintering

1. Introduction

Zirconium carbide (ZrC) is an important refractory ceramic. Similar to the other refractory carbides, ZrC exhibits many interesting physical properties such as high melting temperature (3400 °C) [1], high hardness [2], high thermal and electrical conductivity [3], good corrosion and oxidation resistance [4]. Thereby, it is considered as the suitable material in many technological applications such as cutting tools [5], wear guides [6], rocket propulsion systems [7], etc. Moreover, owing to the excellent property of low neutron cross section, ZrC is being considered as a potential material in nuclear reactor systems [8]. Unfortunately, practical applications of ZrC have been prevented by the poor fracture toughness (<4 MPa $m^{1/2}$) [9]. With addition of Nb, W, Mo, TiC and carbon nanotubes, for examples, ZrC-based ceramics have been intensively investigated for improvement of the sinterability and fracture resistance [10–18].

TiC and ZrC have the same cubic structure. The formation of TiC–ZrC solid solutions has been investigated by first-principle calculations of Adjaoud et al. [19]. It is expected that the physical properties of TiC–ZrC solid solutions can be optimized via the adjustment of the Ti and Zr compositions. However, owing to the difference in ionic radii of the exchangeable Ti and Zr, the formation of a complete solid solution is difficult to obtain. Generally, high sintering temperature is required. Experimentally, Mroz [20] successfully prepared the solid solutions of $Ti_xZr_{1-x}C$ ($x=0.3$, 0.5 and 0.7) by pressureless (2100 °C) and hot-press (21 MPa, 1900 °C) sintering of mixed TiC and ZrC powders (several microns in size). Measurements of Vickers hardness (at the load of 500 g) and fracture toughness (at the load of 2 kg) indicate that compared to the pure TiC and ZrC, the hardness and fracture resistance are significantly improved for the solid solutions.

For carbides, it is known that their mechanical properties could be well improved via the grain size refinement [21,22]. In the present work, similar to our previous preparation of the nonstoichiometric TiC_x and ZrC_x [23,24], the nanocrystalline

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http://dx.doi.org/10.1016/j.ceramint.2014.03.024
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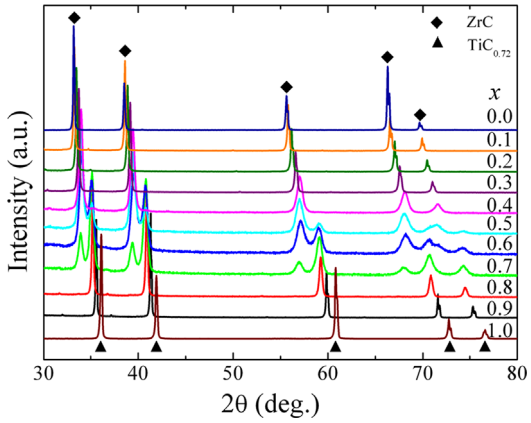

Fig. 1. XRD patterns at room temperature for the SPS-sintered solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$ at 1800 °C.

TiC–ZrC solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$ are fabricated by two steps: (i) synthesis of nanoparticles by high-energy ball milling of mixed Ti and Zr metallic powders in toluene; (ii) consolidation by spark plasma sintering (SPS). By changing atomic ratio of Ti to Zr or x, a series of solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$ have been prepared, and investigations have been performed on their mechanical properties.

2. Experimental procedure

2.1. Synthesis

The synthesizing process of TiC–ZrC solid solutions ($Ti_xZr_{1-x}C_{1-\delta}$) was divided into two steps, i.e. preparation and SPS sintering of the starting materials, similar to that of Ti (Zr) carbides in our previous investigations [23,24]. In a glove box filled with highly pure argon gas, mixed Ti and Zr powders (−325 mesh, purity 99%, China) in a desired ratio, WC balls and toluene were loaded into a WC vial and sealed. The weight ratios of WC balls and toluene to mix metallic powder were 10:1 and 3:1, respectively. The high-energy ball milling was performed in a planetary ball mill (P4, Fritsch, Germany). The rotation speed was set at 400 rpm. After milling for 25 h, the as-milled product in a mash state was collected in a glove box under Ar atmosphere. After being dried at 100 °C for 20 h in a vacuum chamber ($\sim 10^{-3}$ Pa), the obtained nanopowder was pressed into a pellet and inserted into a graphite die of 20 mm in diameter. The pellet was then sintered in a SPS 1030 system (Sumitomo Coal Mining, Japan). In the sintering process, a compressive pressure of 50 MPa was first applied, and then heating at a rate of 100 °C/min was performed up to 800 °C. After dwelling at 800 °C for 30 min, the heating was continued to the final desired temperature and kept at that temperature for 5 min. After the sintering, the applied current was first shut off, and then the compressive pressure was released. The sintered sample remained in the vacuum chamber to cool down to room temperature. The SPS-sintered sample was finally polished to remove any carbon contamination on the surface.

2.2. Characterization

The structures of SPS-sintered TiC–ZrC solid solutions were characterized by X-ray diffraction (XRD) (Smartlab, Japan. Cu Kα radiation of λ=1.5418 Å at 200 mA and 40 kV). Field-emission scanning electron microscopy (SEM) (Model S4800, HITACHI, Japan) was used to check the morphologies of fracture surfaces and mechanically polished surfaces after etching in a solution of HF, HNO_3 and H_2O in a ratio of 10:45:45. Carbon contents of the SPS-sintered TiC–ZrC solid solutions were determined by the complete oxidation in air to TiO_2 and ZrO_2 at 1100 °C using a homemade quartz-tube furnace. The densities were measured using Archimedes' method. Vickers hardness tests were performed with a loading time of 10 s under a series of loads (KB 5 BVZ, Germany). Fracture toughness was determined by the Vickers indentation method with a load of 2 kg. The elastic modulus was obtained from nanoindentation measurements with a Berkovich indenter at a peak load of 5 mN (Hysitron TI 950 TriboIndentor, America).

3. Results and discussion

3.1. XRD analyses of SPS-sintered solid solutions

The SPS-sintering of TiC–ZrC solid solutions ($Ti_xZr_{1-x}C_{1-\delta}$) was performed at a series of temperatures. Fig. 1 shows the XRD patterns for the SPS-sintered TiC–ZrC systems at 1800 °C. Close to the TiC and ZrC ends, complete solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$ are obtained. For the Ti composition of x in the range of $0.4 \le x \le 0.7$, however, the sintering temperature of 1800 °C is not high enough to realize the complete solid solutions. From the XRD spectra, it is identified that the two-phase solid solutions are actually produced: the Ti and Zr-rich solid solutions. Higher sintering temperatures are thus required for the formation of single-phase solid solutions (see Fig. S1 in Supplementary materials). Fig. 2 displays the consolute temperatures required for SPS sintering of the single-phase solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$. As theoretically predicted [19], the consolute sintering temperature is highly related to the atomic ratio of Ti to Zr from the ZrC to TiC ends, the consolute temperature increases gradually up to a maximum at the Zr composition of 0.3, and then decreases. Clearly, the consolute temperature exhibits an asymmetric dependence on the atomic ratio of Ti to Zr. This asymmetric feature can be directly correlated with difference in ionic radii of the exchangeable cations [19]. Relatively, the SPS sintering of TiC–ZrC solid solution is easier close to the ZrC end than that close to the TiC end, because the replacement of larger Zr ions by smaller Ti ones is easier than vice a versa.

For SPS-sintered single solid solutions of $Ti_xZr_{1-x}C_{1-\delta}$, their lattice parameters were determined by Rietveld refinement of the XRD patterns. The inset of Fig. 2 shows the determined lattice parameter as a function of Zr composition. In the range of $0 < 1-x < 1$, the increase of Zr composition leads to a linear expansion of the lattice parameter a (see the red solid fitting line). However, the linear fitting line is found