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ScienceDirect
Ceramics International 36 (2010) 351–355
CERAMICS INTERNATIONAL
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Properties and rapid consolidation of nanostructured TiC-based hard materials with various binders by a high-frequency induction heated sintering

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Received 1 June 2009; received in revised form 6 July 2009; accepted 20 August 2009
Available online 22 September 2009

Abstract

The densification of hard TiC–10 vol.% binder (Co, Ni, Fe) materials was accomplished within 2 min using a high-frequency induction heated sintering (HFIHS) method. The advantage of this process is not only rapid densification to almost the theoretical density but also the prevention of grain growth of the nano-structured materials. Highly dense TiC–binder (Co, Ni, Fe) composites with a relative density of up to 99.9% were obtained within 2 min by HFIHS under 80 MPa. The average grain size of TiC in the TiC–10 vol.% Ni composite was approximately 44 nm. The hardness and fracture toughness of the dense TiC–10 vol.% binder (Co, Ni, Fe) composite produced by HFIHS were also investigated.

Keywords: A. Sintering; B. Nanocomposites; C. Hardness; Hard materials; Fracture toughness

1. Introduction

Titanium carbide has many attractive properties, such as high hardness, low density, and relatively high thermal and electrical conductivity. TiC is also very stable with a melting temperature of 3100 °C, and does not undergo a phase transformation. These properties have seen it being used extensively in cutting tools and abrasive materials in composites with a binder metal, such as Ni. However, the high cost of Ni has generated interest in alternative binder phases.

The mechanical properties and stability of cemented carbides could also be improved by changing the microstructure, such as grain size refinement [1,2]. However, the conventional powder metallurgy (PM) preparation of cemented carbides with a refined grain structure can result in residual porosity due to localized agglomeration of the powders [3]. Moreover, the use of conventional methods to consolidate nanopowders often leads to grain growth [4]. Grain growth can be minimized by sintering at lower temperatures and for shorter periods. In this regard, a high-frequency induction heated sintering (HFIHS) method can be effective in achieving this goal [5,6]. When a high pressure is applied, lower temperatures and shorter times are needed for the overall compaction process due to the increase in driving force for densification.

This paper reports the sintering of TiC–10 vol.% binder (Co, Ni, Fe) composites using a rapid sintering process, high-frequency induction heated sintering (HFIHS), with the simultaneous application of an induced current and high pressure. The aim of this study was to produce a dense and nanostructured TiC–10 vol.% binder (Co, Ni, Fe) hard materials in a very short sintering time (<2 min). In addition, the effect of the Co, Ni and Fe binder on the mechanical properties of the TiC hard materials was investigated.

2. Experimental procedure

The TiC powder (particle size, 2 μm; purity, 99.5%) used in this study was supplied by Alfa. Co (~3 μm, 99.7% pure,

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0272-8842/$36.00
doi:10.1016/j.ceramint.2009.09.005

Sigma–Aldrich), Ni (<2 μm, 99.8% pure, Sigma–Aldrich), and Fe (<10 μm, 99.9% pure, Alfa) were used as the binder materials. Three different specimens, TiC–10 vol.% Co, TiC–10 vol.% Ni, and TiC–10 vol.% Fe, were examined. The TiC powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm and 10 h. Tungsten carbide balls (5 mm in diameter) were placed in a sealed cylindrical stainless steel vial under an argon atmosphere. The ball-to-powder weight ratio was 30:1. Fig. 1 shows XRD patterns of the raw powders and milled TiC powder. The full width at half-maximum (FWHM) value obtained from the XRD pattern of the milled powder was larger than that of the raw powder due to internal strain and a decrease in grain size. The grain size and internal strain were calculated using Suryanarayana and Grant Norton's formula [7]. The average grain sizes of the milled TiC powder was determined to be 25 nm.

The TiC–10 vol.% Co, TiC–10 vol.% Ni and TiC–10 vol.% Fe starting powders were mixed in a universal milling machine at a ball-to-powder weight ratio of 6:1. Milling was performed by planetary ball milling using polyethylene bottles with zirconia balls and at a horizontal rotation velocity of 300 rpm for 24 h.

The powders were placed in a graphite die (external diameter, 45 mm; internal diameter, 20 mm; height, 40 mm) and then introduced into a High-frequency Induction Heating Sintering (HFIHS, Eltek Co., Republic of Korea) apparatus [5,6]. The HFIHS apparatus included a 15 kW power supply, which provides an induced current through the sample, and a 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. An induced current was then activated and maintained until the densification rate

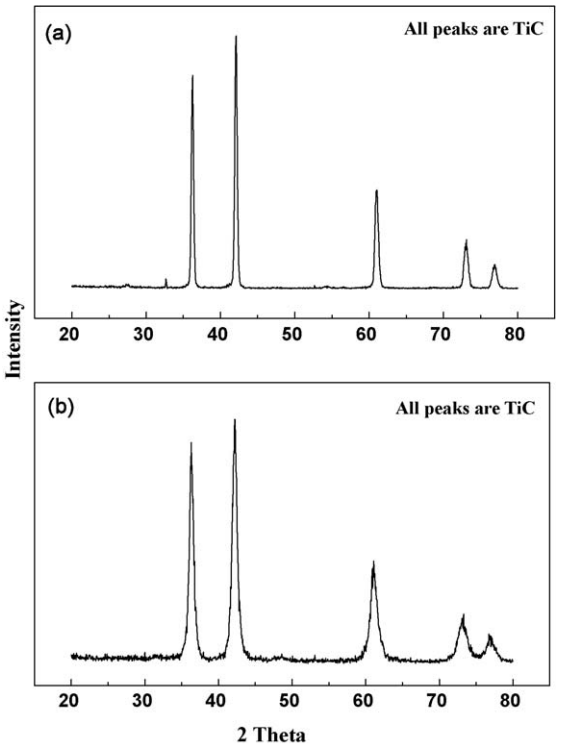

Fig. 1. XRD patterns of TiC: (a) raw powders and (b) milled powder.

was negligible, as indicated by the real-time output of sample shrinkage. The level of shrinkage was determined by measuring the vertical displacement using a linear gauge. The temperature was measured using a pyrometer focused on the surface of the graphite die. The temperature gradient from the surface to the center of the sample is dependent on the heating rate, the electrical and thermal conductivity of the compact, and its relative density. The heating rates in the process were approximately 1000 K min^{-1}. At the end of the process, the induced current was turned off and the sample was cooled to room temperature. The process was carried out under a vacuum of 4×10^{-2} Torr.

The relative density of the sintered sample was measured using the Archimedes method. Microstructural information was obtained from the product samples, which had been polished and etched using Murakami's reagent (10 g potassium ferricyanide, 10 g NaOH, and 100 mL water) for 1–2 min at room temperature. Compositional and microstructural analyses of the products were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and field emission scanning electron microscope (FE-SEM). The Vickers hardness was measured by indentation at a load of 20 kg_f and a dwell time of 15 s.

3. Results and discussion

3.1. Densification behavior and microstructure

Fig. 2 shows the changes in shrinkage and temperature with the heating time during the sintering of WC–10 vol.% Co, WC–10 vol.% Ni and WC–10 vol.% Fe by HFIHS under an 80 MPa pressure. As the induced current was applied, the shrinkage displacement increased gradually with temperature up to approximately 850 °C, and then increased abruptly as the temperature was increased further. When the temperature

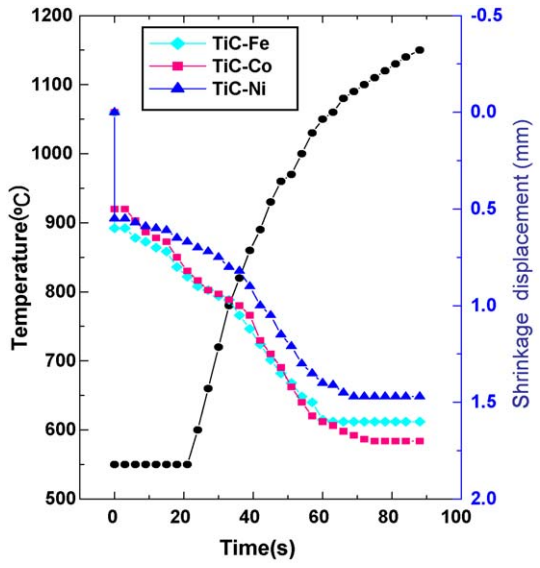

Fig. 2. Changes in temperature and shrinkage displacement with heating time during the sintering of TiC–10 vol.% binder (Co, Ni, Fe) hard materials produced by HFIHS.

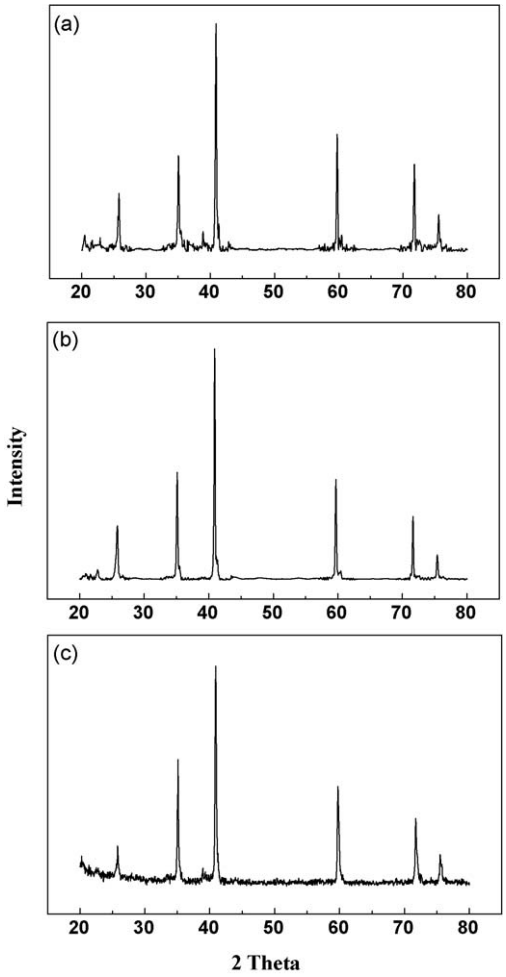

Fig. 3. XRD patterns of (a) TiC–10 vol.% Co, (b) TiC–10 vol.% Ni, and (c) TiC–10 vol.% Fe hard materials produced by HFIHS.

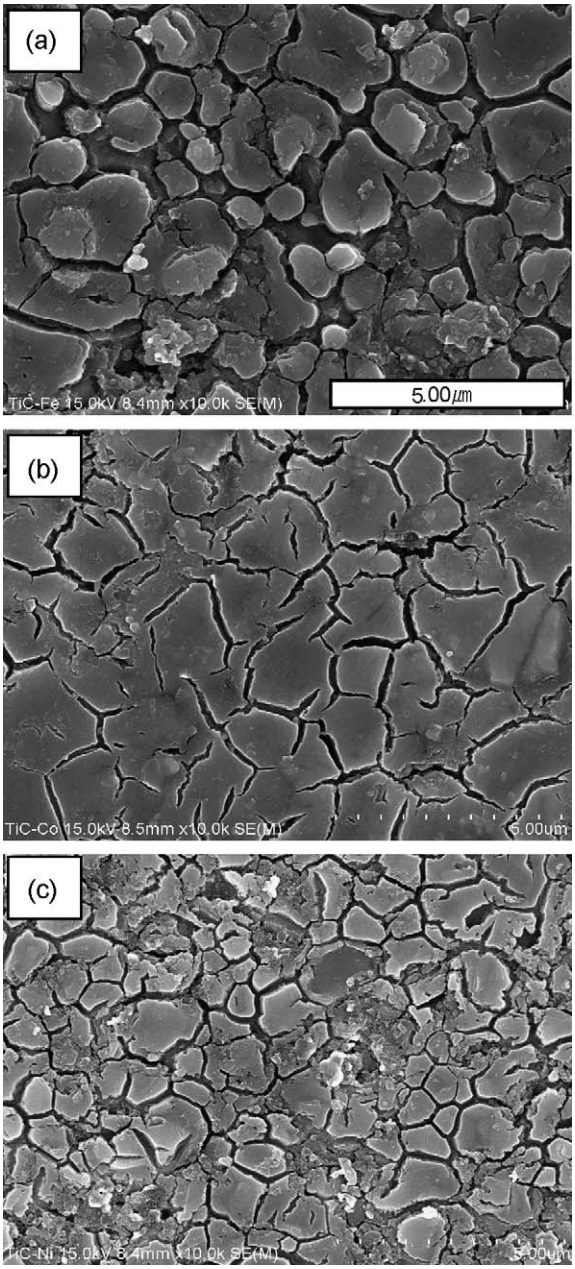

Fig. 4. Back scattered electron images of TiC–binder (Co, Ni, Fe) hard materials produced by HFIHS: (a) TiC–10 wt.% Co, (b) TiC–10 wt.% Ni, and (c) TiC–10 wt.% Fe.

reached approximately 1150 °C, the densification rate became almost negligible. The samples densified to 98%, 98% and 99.9% of the theoretical density within approximately 90 s. In the case of binderless TiC hard materials, densification was obtained at approximately 1350 °C [8]. The densification temperature of TiC was reduced remarkably by the addition of Co, Ni and Fe because they would be molten during the sintering process. The main densification mechanism involves the rearrangement of carbide particles, enhancement of diffusion, and viscous flow of the binder [9]. The TiC–Fe sample, which is cheaper than TiC–Co and TiC–Ni, had the highest relative density of the three composites.

Fig. 3 shows XRD patterns of the TiC–Co, TiC–Ni and TiC–Fe composites after HFIHS. In all cases, only TiC peaks were detected. Fig. 4 shows the back scattered electron images of the etched samples after sintering to approximately 1150 °C. Fig. 5 shows FE-SEM images of the TiC–Co, TiC–Ni and TiC–Fe sintered from milled powder. The sintered TiC–10 vol.% binder consisted of a nanophase. The average sizes of the TiC in all the almost fully dense TiC–10 vol.% Co, TiC–10 vol.% Ni and TiC–10 vol.% Fe composites were determined to be approximately 61, 44 and 80 nm, respectively, using Suryanarayana and Grant Norton's formula [7]. Therefore, ultrafine microstructures can be obtained without grain growth during HFIHS.

Although the densification mechanism under induced current heating and pressure is unclear, the accelerated densification by HFIHS may be due to a combination of electrical discharge, resistance heating and pressure application effects. When an electric induced current is applied, energy emission may be concentrated on the particle contacts that achieve high temperatures. These concentrated heat effects at the particle surfaces may cause surface melting and oxide breakdown in a similar manner to the surface effects in the electrodischarge machining (EDM) process [10]. Despite the relatively short time, the samples sintered by the HFIHS

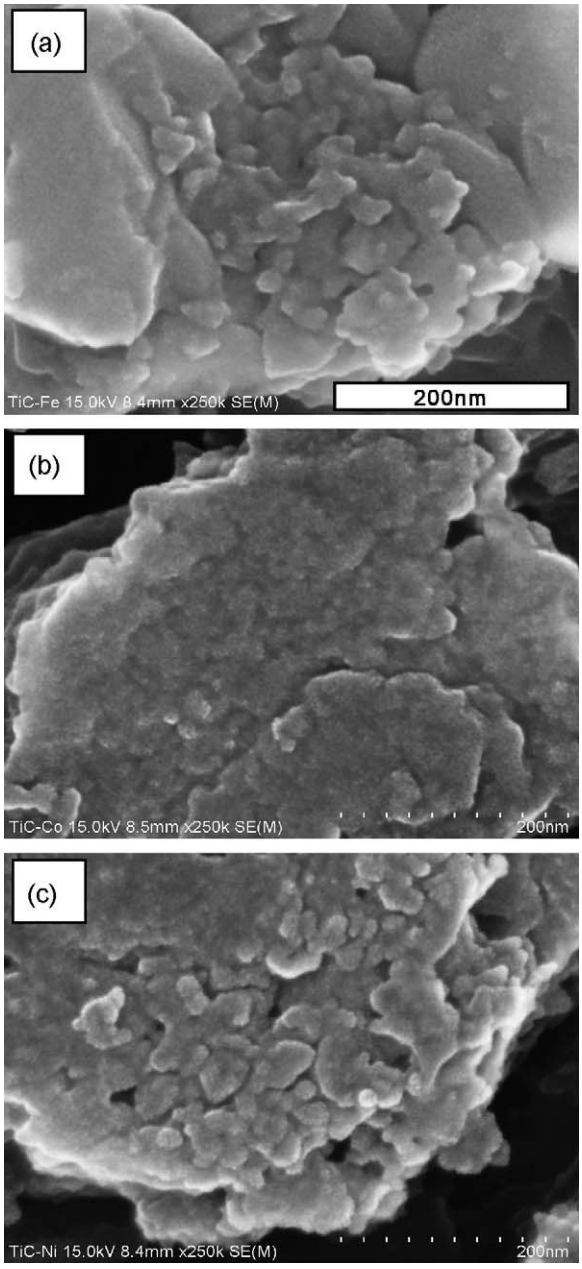

Fig. 5. Field emission scanning microscopy electron images of TiC–binder hard materials produced by HFIHS: (a) TiC–10 vol.% Fe, (b) TiC–10 vol.% Co, and (c) TiC–10 vol.% Ni (250,000×).

method were exposed to high temperatures and pressures. Meanwhile, the effect of the electrical induced current on rapid densification could also be explained by the rapid heating rate due to Joule heating, and the intrinsic contribution of the current to mass transport [11]. Therefore, accelerated HFIHS densification may be attributed to a combination of fast heating rates and intrinsic effects on mass transport.

3.2. Physical and mechanical properties

The Vickers hardness measurements were carried out on polished sections of the TiC–Co, TiC–Ni and TiC–Fe composites using a $20\,kg_f$ load and a 15 s dwell time. Indentations with sufficiently large loads produced radial cracks emanating from the corners of the indent. The fracture toughness of the material can be estimated from the length of these cracks using the Anstis et al. expression [12]:

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

where E, H, P and C are the Young's modulus, indentation hardness, indentation load, and trace length of the crack measured from the center of indentation, respectively. Typically, one to three additional cracks were observed to propagate radically from the indent. In the same manner as the hardness, the toughness was derived from an average of ten measurements. The calculated fracture toughness and hardness of TiC–Co, TiC–Ni and TiC–Fe composites produced by HFIHS were 8.3 MPa $m^{1/2}$ and 1780 kg/mm^2, 8.6 MPa $m^{1/2}$ and 1822 kg/mm^2, 8.5 MPa $m^{1/2}$ and 1905 kg/mm^2, respectively. There was a slight difference in fracture toughness between the three compounds. However, the hardness of TiC–Fe was higher than that of TiC–Ni or TiC–Co. These results are promising given the lower cost in the WC–Fe case.

4. Summary

The rapid consolidation of TiC–10 vol.% Co, TiC–10 vol.% Ni and TiC–10 vol.% Fe hard materials was accomplished using high-frequency induction heated sintering (HFIHS). Almost fully dense TiC–binder (Co, Ni, Fe) composites could be obtained within 2 min. The densification temperature of TiC was reduced remarkably by the addition of Co, Ni and Fe. The grain size of the TiC–10 vol.% Co, TiC–10 vol.% Ni and TiC–10 vol.% Fe hard materials were approximately 61, 44 and 80 nm, respectively. The fracture toughness and hardness of the WC–10Co, WC–10Ni and WC–10Fe composites synthesized by HFIHS at a pressure of 80 MPa were 8.3 MPa $m^{1/2}$ and 1780 kg/mm^2, 8.6 MPa $m^{1/2}$ and 1822 kg/mm^2, 8.5 MPa $m^{1/2}$ and 1905 kg/mm^2, respectively. The hardness of TiC–Fe was higher than that of TiC–Co or TiC–Ni without any decrease in fracture toughness.

Acknowledgements

This study was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-20002-0).

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