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Bulk TiC_xN_{1-x}–15%Co cermets obtained by direct spark plasma sintering of mechanochemical synthesized powders

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ABSTRACT

TiC_xN_{1-x}–15 wt.%Co cermets were obtained by a mechanically induced self-sustaining reaction (MSR) and sintered by spark plasma sintering (SPS) technique at different temperatures (1200–1400 °C) for 1 min in vacuum under a uniaxial load of 80 MPa. The evolution of microstructure and mechanical properties was investigated. SPS allowed high densification with limited grain growth at a relatively low temperature. Material sintered at 1300 °C showed a good combination of mechanical properties with Vickers hardness of 17.1 ± 0.5 GPa, fracture toughness of 5.51 ± 0.29 MPa $m^{1/2}$ and bending strength of 904 ± 12 MPa. Lower sintering temperature resulted in a decrease in bending strength due to poor cohesion between the ceramic and binder phases. An increase in sintering temperature would allow tailoring the cermet microstructure and, therefore, adjusting the Vickers hardness/fracture toughness relation.

1. Introduction

Ceramic–metal composites combining a hard ceramic phase and a binding metallic component are commonly known as "cermets". Modern cermets are normally based on titanium carbonitride, Ti(C, N). Various carbides, nitrides as well as metal binders are used as raw materials for preparing Ti(C, N)-based cermets. These systems exhibit a complex microstructure according to the type of binary carbide used [1]. They have been employed since decades in different engineering applications such as cutting tools or wear resistant parts [2,3].

A key aspect to achieve high mechanical performance is to control the ceramic–metal bond during sintering [4]. For that reason, a number of additives such as WC and Mo_2C are currently used in this process [5]. Moreover, the selection of suitable raw materials and adequate synthesis methods are essential to obtain high quality cermet powders, but also the correct choice of the sintering method is crucial to obtain composites with improved properties through microstructure control.

Recently, the mechanochemical process denoted as a mechanically induced self-sustaining reaction (MSR) has been successfully employed in the accurate synthesis of complex carbonitride phases. This process has allowed the synthesis of powdered cermets in a short time with nanometric characteristics, good stoichiometric control and low energetic cost [6]. Furthermore, non-conventional fast sintering technique, spark plasma sintering (SPS), has been proved to be a promising option for producing completely dense materials [7]. This technique can work at heating rates as large as hundreds of degrees per minute, combining high pressure and temperature in a short time [8]. These features allow the achievement of microstructures unattainable by other sintering methods and, therefore, mechanical properties superior to those obtained using conventional techniques. Thus, the improvement in cermet properties can be pursued following two approaches, formulation of new compositions and/or adjustment of microstructure features.

The aim of this work is to report the examination of the microstructure and mechanical properties of TiCN–15%Co cermets first synthesized by MRS and, subsequently, sintered through SPS technique at different temperatures (1200–1400 °C). The possibility of obtaining fully dense cermets at very low temperature is studied. The mechanical properties, such as bending strength, Vickers hardness and fracture toughness were investigated.

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2. Experimental

Powdered cermets with a starting nominal composition of 85 wt.%$TiC_{0.5}N_{0.5}$ and 15 wt.%Co were synthesized by MSR from elemental powder mixtures of Ti (99% in purity, <325 mesh, Strem Chemicals), graphite (<270 mesh, Fe ≤0.4%, Merck) and Co (99.9% in purity, <100 mesh, Sigma) in a nitrogen atmosphere (H_2O and O_2 ≤3 ppm, Air Liquide). This method takes advantage of the strong exothermic character of the titanium carbonitride formation from the elements to promote self-propagating reactions during milling. As this synthesis process is carried out from elemental components, the control of the powder composition can be easily accomplished.

Fifteen tempered steel balls (d = 20 mm, m = 32.6 g) and 46.5 g of the elemental Ti/C/Co powder mixture were placed in a 300 ml tempered steel vial (67 HRC) and milled under 6 atm of N_2 using a modified planetary ball mill (Planetary Mill Pulverisette 4, Fritsch). The powder-to-ball mass ratio (PBR) was ~1/10.5, and a spinning rate of 400 rpm for both the rotation of the supporting disc and the superimposed rotation in the direction opposite to the vial was employed. The planetary mill allowed for operation at a constant gas pressure and the detection of self-propagating reactions during milling [6]. After 42 min of treatment in the planetary mill, the ignition of the self-propagating reaction associated with the formation of the carbonitride ceramic phase was observed. The milling continued for 30 min after ignition to ensure the completion of the reaction and the homogenization of the powdered cermet.

Powdered cermets were sintered using an SPS apparatus HP D25/1 (FCT Systeme GmbH, Rauenstein, Germany) at temperatures from 1200 to 1400 °C and 80 MPa of pressure. In each test, 5 g of material were used, which were introduced into a 20 mm diameter graphite die. The tests were carried out under vacuum at a heating rate of 100 °C min^{-1} with a 1 min dwelling time at the maximum temperature. The density was measured by the Archimedes method (ISO-3369). Relative densities were estimated in accordance with the real density of the powder measured by Helium picnometry (5.18 g cm^{-3}).

Sintered cermets were longitudinally cut in half cylinders with a diamond saw and polished (Struers, model RotoPol-31) with diamond to 1 μm roughness. The Vickers hardness value, Hv, was determined using a conventional diamond pyramid indenter with a load of 5 N for 10 s (Buehler, model Micromet 5103) and using the standard specification ASTM E92-72. The indentation fracture toughness value, K_{IC} [9], was obtained by the method of Niihara et al. [10] from 294 N Vickers indentations that created Palmqvist cracks. The bending strength was measured at room temperature in the universal machine Instron (Model 856) with a cross-head displacement speed of 0.002 mm s^{-1} using biaxial testing and the equations of Kirstein and Woolley [11], Vitman and Pukh [12], and the standard specification ASTM F394-78. The fracture surface sections of the sintered samples have been observed using a field emission gun scanning electron microscope (FESEM, HITACHI S-4800, SCSIE of the University of Valencia, Spain). The crystalline phases of the bulk ceramic composites were determined by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The measurements were performed in the 30–70° range and the step size and time of reading were 0.02° and 0.3 s, respectively.

3. Results and discussions

Piston speed and displacement as a function of temperature for the sample sintered up to 1300 °C are shown in Fig. 1. In this cycle, the maximum pressure (80 MPa) was applied between 600 and 700 °C, which produced the compaction of the powder. Once the maximum pressure had been reached it was held up to the each final temperature. After the first piston displacement, it was observed that sintering process started at 750 °C and the material was completely dense at temperatures as low as 1225 °C, approximately.

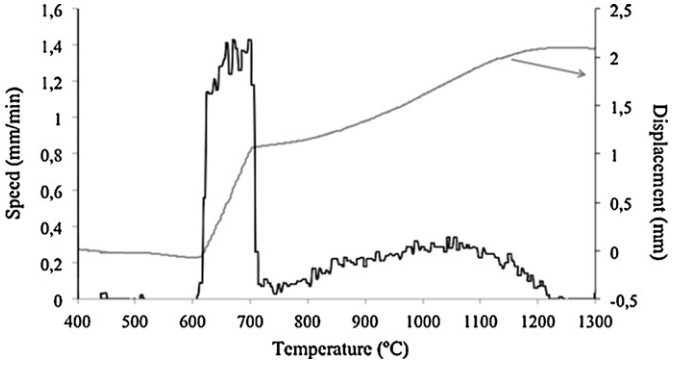

Fig. 1. Piston speed and displacement during spark plasma sintering of TiC_xN_{1-x}–15%Co cermet at 1300 °C.

In this work, three final temperatures were chosen for sintering the cermets: a low temperature at which the material is not completely sintered (1200 °C), a temperature at which densification is finished (1300 °C), and a higher temperature comparable with that used in pressureless process (1400 °C) described in a previous work for cermets with similar composition [13].

The relative densities of the TiC_xN_{1-x}–15%Co cermets sintered by SPS at 1200, 1300 and 1400 °C were 98.5, >99.0 and >99.0% t.d., respectively. The high densification at relatively low temperatures is consequence of the optimum homogenization and distribution of the ceramic and binder phases obtained by MSR process and the sintering conditions applied during SPS. With this sintering technique, the material can be densified fairly quickly because of the high heating rate employed and the pressure applied during the process.

The XRD patterns of starting powder and samples sintered at 1200, 1300 and 1400 °C are shown in Fig. 2, where peaks for TiC_xN_{1-x} and metallic binder phase are identified. The binder phase detected in the XRD diagrams was not elemental Co, but a TiCo intermetallic compound. This intermetallic was already observed in the powdered cermet and was obtained during the milling process. It has been previously shown that the formation of this intermetallic phase was triggered by the heat released during the self-propagating reaction involved in the carbonitride phase formation [6].

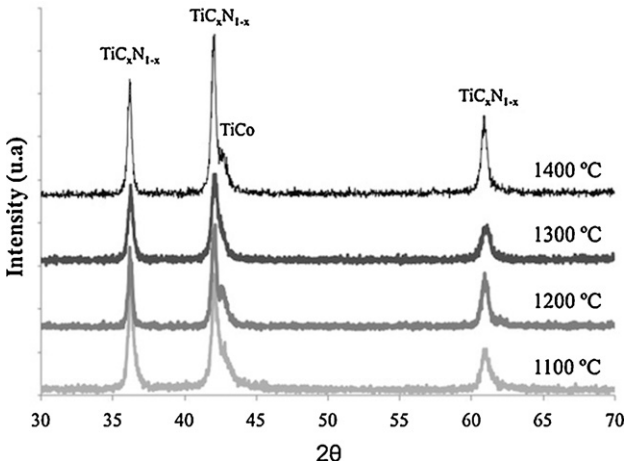

Fig. 2. X-ray diffractograms of the TiC_xN_{1-x}–15%Co powdered material and after sintering at 1200 °C, 1300 °C and 1400 °C by SPS.