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The influence of percolation during pulsed electric current sintering of ZrO_2–TiN powder compacts with varying TiN content

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Abstract

A series of ZrO_2–TiN composite powder compacts with varying TiN content was densified using the field assisted sintering technique, also known as spark plasma sintering or pulsed electric current sintering (PECS). The TiN content was varied between 35 and 90 vol.% in order to obtain an electrical conductive composite material that can be shaped by electrical discharge machining. The influence of the TiN content on the densification behaviour was investigated experimentally, whereas its influence on the temperature and current distribution in the PECS tool set-up was simulated using a previously developed finite element model. The predicted temperature distribution was confirmed experimentally using a double pyrometer set-up, one focusing on the outer die wall surface and one on the bottom of a borehole in the upper punch. The changing thermal and electrical properties of the sintering ZrO_2–TiN powder compacts were calculated using mixture rules. Using a double pyrometer set-up, a clear relationship could be verified experimentally between the changing electrical properties of the sintering compact and the temperature redistribution in the punch/die/sample set-up during the PECS process. The homogeneity of sintering inside the PECS equipment is discussed in detail and suggestions are made in order to promote a more homogeneous sintering process. Carbon felt, acting as a thermal insulator, was placed around the die in order to minimize the radiation heat losses and to minimize the thermal gradients during heating and the dwell period at maximum temperature. The mechanical and electrical properties of the different composite materials are discussed as functions of the TiN content.

Keywords: Pulsed electric current sintering (PECS); Spark plasma sintering (SPS); Ceramic composites; Thermo-electrical properties; Temperature and current distribution

1. Introduction

During the last decade, the applicability of zirconia to induce toughening by the stress-induced transformation of the tetragonal to monoclinic ZrO_2 phase in the stress field of propagating cracks, a phenomenon known as transformation toughening [3,4], has been intensively investigated. Recent developments in zirconia composites are focused not only on the improvement of toughness, strength and hardness, but also on the possibility for mass production and manufacturing cost reduction. A successful approach is to incorporate electrically conductive reinforcements such as TiB_2 [5], WC [6], ZrB_2 [7], TiC [8], TiCN [8] and TiN [11] into the zirconia matrix. The incorporation of a certain content of these conductive reinforcements makes the composite electrically conductive enough to be machineable by electrical discharge machining (EDM), thus avoiding the expensive cutting and grinding operation for component shaping. Electrical resistivity threshold values for EDM are reported to be in between 100 and 300 Ω cm [9,10].

Traditionally, these composites are densified by hot pressing [11]. This study investigates the possibility to process ZrO_2–TiN composites by PECS. In a previous study [2], it was pointed out that the changing thermal and electrical properties of a sintering ZrO_2–TiN (60/40) composite powder compact should be taken into account in order to

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be able to get a realistic idea of the temperature distribution in the tool and sample during PECS processing.

The goal of the present work is to investigate and evaluate (a) how the TiN content, varying between 35 and 90 vol.%, influences the densification behaviour of the ZrO_2–TiN composite powder compacts; (b) how it influences the temperature and current distribution during the heating stage, when the main part of the densification takes place; and (c) how it influences the temperature distribution in the sample during the final dwell time after full densification has been reached. Using this information, an adjusted sinter set-up was used to improve the homogeneity of sintering. Finally, the influence of the TiN content on the mechanical and thermo-electrical properties of the fully dense materials is discussed in more detail.

2. Experimental procedure

Yttria-stabilised ZrO_2–TiN composites with 35–90 vol.% TiN were investigated. Details on the commercial starting powders are given in Table 1. The commercial powders are yttria-free monoclinic ZrO_2 (Tosoh grade TZ-0, Tokyo, Japan) and TiN (H.C. Starck grade C, Laufenburg, Germany). Y_2O_3-stabiliser (2 mol.%) was incorporated in the composites by means of colloidal coating of the monoclinic ZrO_2 starting powder [12].

The powder mixtures were ball milled in a multidirectional Turbula mixer (type T2A, Basel, Switzerland) in ethanol in a polyethylene container of 250 ml for 24 h at 60 rpm. Zirconia milling balls (250 g; Tosoh grade TZ-3Y, Tokyo, Japan) with a diameter of 15 mm were added to the container to break the agglomerates in the starting powder and to enhance powder mixing. The ethanol was removed after mixing using a rotating evaporator.

Table 1
Starting powders

Powder	Grade	Supplier	Crystal size*
ZrO_2	TZ-0	Tosoh (Japan)	27 nm
ZrO_2	TZ-3Y	Tosoh (Japan)	27 nm
TiN	C	Starck (Germany)	1.2 μm

* According to the supplier datasheets.

The dry powder mixture was sieved and inserted into a graphite die/punch set-up (inner diameter 40 mm; outer diameter 56 mm), as shown in Fig. 1. All samples were PECS sintered (Type HP D 25/1, FCT Systeme, Rauenstein, Germany, equipped with a 250 kN uniaxial press) in vacuum (~0.05 Pa) for 2 min at 1500 °C under a load of 56 MPa, applying a heating rate of 200 °C/min. The pressure was increased gradually from 5 to 28 MPa at 1050 °C within a period of 1 min and from 28 to 56 MPa within a period of 1 min upon reaching the sintering temperature, as shown in Fig. 2. After 2 min, the current was switched off and followed by a natural cooling with a cooling rate of about 250 °C/min.

The density of the samples was measured in ethanol, according to the Archimedes method (BP210S balance, Sartorius AG, Germany). The Vickers hardness (HV_{10}) was measured on a hardness tester (Model FV-700, Future-Tech, Japan) with an indentation load of 10 kg. The indentation toughness, K_{IC}, based on the crack length measurement of the radial crack pattern produced by Vickers HV_{10} indentations, was calculated according to the formula of Anstis et al. [13]. Vickers hardness profiles, containing at least 10 indentations, were obtained from polished cross-sections of 40 mm diameter discs. The elastic modulus (E) of the ceramic specimens was measured using the resonance frequency method. The resonance frequency was measured by the impulse excitation technique (Model Grindo-Sonic, J.W. Lemmens N.V., Leuven, Belgium). X-ray diffraction (Seifert 3003 T/T, Ahrensburg, Germany) analysis was used for phase identification and calculation

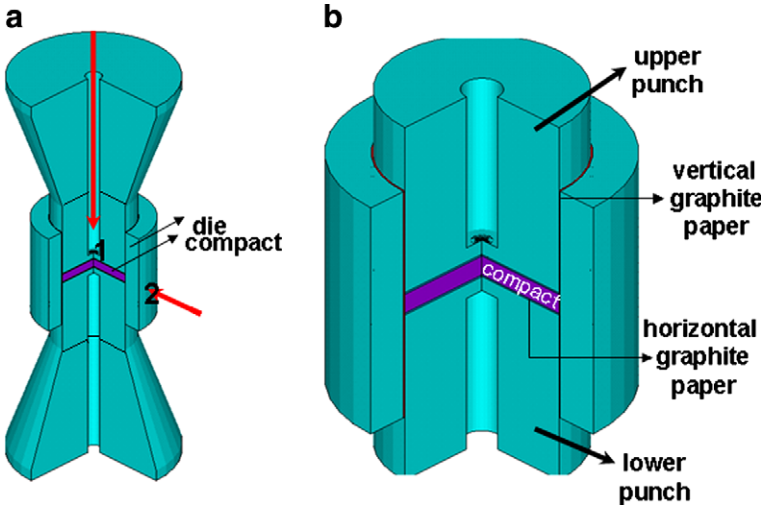

Fig. 1. Overview of the PECS tool set-up (a). The focusing point of the central pyrometer (CP) (1) and of the external pyrometer (EP) (2) is indicated by an arrow. When full density was reached the sample dimensions were 40 mm diameter and 5 mm height. A detailed sketch shows the presence of the vertical and horizontal graphite papers (b).