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Processing and Spark Plasma Sintering of zirconia/titanium cermets

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Abstract

This study focuses on the preparation of zirconia/titanium ceramic–metal composites. Three different metal contents (25 vol%, 50 vol% and 75 vol% Ti) have been selected from the entire range. First, to obtain stable and well-dispersed suspensions that will lead to optimum mechanical features, a rheology study has been performed by shifting two critical parameters: solid content and defloculant volume. Once the optimum conditions were selected, the powders obtained have been prepared to be sintered using Spark Plasma Sintering in order to reach the highest densities in the compacts. Microstructure and mechanical properties (bending strength, Vickers hardness and fracture toughness) of the different compositions have been studied, presenting in some cases values higher than expected by the rule of mixtures. X-ray diffraction studies have been performed throughout the work to optimise the parameters related to the sintering process, the system reactivity and mechanical response.

Keywords: A: Suspensions; B: Composites; C: Mechanical properties; D: ZrO2

1. Introduction

It has been widely tested shown that the combination of dissimilar materials can show superior properties compared with their pure counterparts [1]. One of the most successful examples for this purpose is the group of ceramic-metal composites or "cermets". The most obvious advantage of cermets is that they can favourably combine the dissimilar properties of ceramic and metal components in one material. One of the most commonly used ceramics is tetragonal zirconia polycrystalline partially stabilised with 3 mol% Y_2O_3, because of its bending strength and high toughness values. Of the metals, titanium is one of the most used because of its relatively low density compared with other metals.

Different preparation processes of ceramic–metal composites can be found in the literature [2–4]. In particular, a wet processing route has been used in this work and, therefore, in order to avoid the segregation of metal and ceramic particles, it is necessary to study the rheological behaviour of the suspensions. The selection of an appropriate solid content and the correct amount of dispersant will provide the steric and electrostatic stabilisation that will lead to homogeneous sintered compacts.

The aim of the present work was to prepare zirconia/titanium composites using the following steps: first, study of the behaviour of zirconia/titanium particulate suspensions to adjust the rheological parameters in order to avoid the segregation of the components; second, sintering dense compacts with a homogeneous microstructure; and, third, evaluation of the mechanical response.

2. Materials and methods

2.1. Starting materials

The following commercially available powders have been used as raw materials: (1) tetragonal zirconia polycrystalline

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(Y-TZP 3 mol%; TZ-3Y-E, Tosoh Corp., Japan), with an average particle size of $d_{50} = 0.26 \pm 0.05$ μm and BET specific surface area of 6.7 m^2/g; (2) titanium powder (Goodfellow, UK, 99.5% purity), with an average particle size $d_{50} = 150$ μm.

2.2. Sedimentation and rheological study

Different 3Y-TZP/Ti suspensions of 70 wt% and 80 wt% solid content were prepared using distilled water as liquid media and a 1- and 3-wt% addition of an alkali-free organic polyelectrolyte as surfactant (*Dolapix CE*64) with a relative proportion of metal of 50 vol% Ti. This metal concentration was considered as representative of the other suspensions prepared with different metal contents. The mixtures were homogenised by milling with zirconia balls in polyethylene containers at 150 rpm for 24 h.

The sedimentation behaviour was performed in glass test tubes at room temperature up to 24 h. Viscosity measurements were performed with a rotational rheometer (*Haake Mars III*, *Thermo Fisher Scientific*, Karlsruhe, Germany). The temperature was maintained constant at 20 °C. A cylinder sensor system, Z40DIN (DIN53019/ISO3219) for the Haake rheometer was used. The general flow behaviour of the suspensions was measured following a cycle in three steps: (1) up sweep increasing the shear stress, τ, continuously until a maximum of 100 Pa in 100 s; (2) maintenance of the maximum shear stress reached in step 1 for 60 s; (3) down sweep decreasing continuously from the maximum value to near zero in 100 s.

2.3. Powder processing and sintering process

Based on the sedimentation and rheological study, three different suspensions with 80 wt% solid content and 3 wt% surfactant *Dolapix CE*64 were prepared using water as liquid media. The powders were homogenised by milling with zirconia balls in polyethylene containers at 150 rpm for 24 h and then dried at 90 °C for 24 h. The resulting powders were milled in an agate mortar and passed through a 180-μm sieve. The relative concentrations of Ti in each suspension were 25 vol%, 50 vol% and 75 vol%, denoted Z-25Ti, Z-50Ti and Z-75Ti, respectively. For comparative purposes, a similar experimental procedure was used to prepare pure zirconia samples.

The resulting powders were spark plasma sintered (SPS, *FCT Systeme GmbH*, HPD 25, Germany) under vacuum at 1350 °C, 80 MPa, 10 min, with a heating rate of 100 °C/min. These conditions were selected considering the melting point of titanium (1668 °C), in order to enable the densification of the material in an inert atmosphere.

2.4. Microstructures and density

The microstructures of fired specimens were studied on diamond polished surfaces down to 1 μm by scanning electron microscopy (*Hitachi* Tabletop microscope *TM*3000, Japan). The bulk densities of all the samples were measured using the Archimedes method, with water as the immersion medium.

2.5. Mechanical properties

Bending strength, σ_f, was determined by biaxial bending test using at least 10 discs of 20 mm for each composition. The tests were performed at room temperature using a universal testing machine (*Instron* E10000). The specimens were loaded to failure with a cross-head speed of 1 mm/min (ISO 6872:2008). The Vickers hardness, H_v was measured using a Vickers diamond indenter (Leco 100-A, St. Joseph, MI) on surfaces polished down to 1 μm, with applied loads of 49 N. The corresponding indentation sizes were determined using an optical microscope (Leica DMRM). The fracture toughness of the rectangular samples was determined by single-edge pre-cracked beam (SEPB) test method using the three-point bend test with 20-mm span between the two supports and the cross-head speed of 1 mm/min. Pre-cracks were incised in the middle of the samples along the top using a 0.2 mm width circular saw. The pre-crack length was 0.40 W, where W is the height of the test specimen. K_{IC} was calculated according to ISO 6872:2008.

3. Results and discussion

3.1. Sedimentation and rheology

Several suspensions were prepared to study the influence of different parameters on the stability of the mixture in order to find the conditions that lead to homogeneous microstructures. The results obtained from the sedimentation study of the suspensions are summarised in Table 1. The metal content was 50 vol% Ti in all suspensions and only one parameter was changed in each case: either the solids content or the surfactant content.

In slurries A and C the metallic phase segregated from the ceramic and, eventually, deposited on the bottom of the tube. Although the metal particles have a lower density than zirconia (4.5 g/cm^3 and 6.1 g/cm^3, respectively), they settle faster than the ceramic particles due to the large difference between grain sizes. Therefore, it seems that 1 wt% of deflocculant addition is not enough to stabilise the titanium particles. When deflocculant concentration rises to 3 wt% (suspensions B and D), no segregation is

Table 1
Rehological data of the suspensions prepared. The best behavior was presented by the conditions B, being selected to prepare the slurries for subsequent studies.

Suspension	Solid content (wt%)	Dolapix (wt%)	τ_0 (Pa)	dv/dx_{max} (s^{-1})	η (mPa s)
A	80	1	4	1741	52
B	80	3	40	788	127
C	70	1	< 1	1725	23
D	70	3	4	1688	31

observed. However, in the suspension D, due to the higher water content, part of this water is removed from the suspension. This effect is not observed in suspension B, where the water content has been reduced producing a higher deflocculant activity and reducing the distance between particles that leads to a higher particle interaction. Therefore, according to the sedimentation study, suspension B (80 wt% solid content, 3 wt% deflocculant) presented the best homogeneity.

In order to quantify the study, the flow curves corresponding to the four suspensions were obtained (Fig. 1). Suspensions A and C display a pseudoplastic behaviour (Fig. 1A and Fig. 1C). The low surfactant-content prevents the dispersion of the aggregates, leading to the sedimentation of the particles. Moreover, in slurry C, with a 70 wt% solid content, the interaction between particles is even lower than in slurry A, which explains the observation of a faster sedimentation of the bigger particles and, therefore, an important segregation.

As shown in Fig. 1D, slurry D presents a slightly plastic behaviour. In this case, the deflocculant content promotes the dispersion of the particles creating an attractive interparticle force that gives rise to the formation of a three-dimensional network of particles. The formation of this network prevents the sedimentation of the particles and will produce homogeneously dispersed microstructures in the final materials. The yield stress (τ_0) can be a representative value of the strength of the particle network. The higher the yield stress, the stronger the particle interaction and the higher the strength of the particle network. As can be observed, the yield stress in slurry D is quite low (about 4 Pa), close to the pseudoplastic behaviour observed in slurries A and C. No sedimentation is observed in suspension D, but the creation of a supernatant shows the tendency of the slurry to eliminate water. This situation does not occur in suspension B (Fig. 1B), where the higher solid content and deflocculant content have led to the formation of a stable structure with a high yield stress (40 Pa) that prevents the slurry from sedimentation and the formation of supernatant. Therefore, suspension B presented the best behaviour, and the corresponding parameters (80 wt% solid content, 3 wt% deflocculant) were selected to prepare the samples for subsequent studies.

3.2. Microstructure and density

The three different concentrations were prepared under the same conditions as slurry B, and subsequently sintered by SPS under vacuum at 1350 °C, 80 MPa, 10 min, with a heating rate of 100 °C/min. Fig. 2 shows the corresponding SEM microstructures. The darker and brighter phases are titanium and zirconia grains, respectively. As can be observed, the fired samples present metallic particles homogeneously dispersed throughout the ceramic matrix. The 3Y-TZP/Ti interface is well bonded and no microcracks are observed. Table 2 shows the results of the density measurements. In all cases the relative densities of the sintered composites were found to be very close to the theoretical values (> 99%th.).

3.3. Mechanical properties

The bending strength values for the Z-25Ti, Z-50Ti and Z-75Ti composites (Table 3) were found to be 60%, 75% and 80% lower than pure zirconia, respectively. This fact has been related to the formation of new phases at the

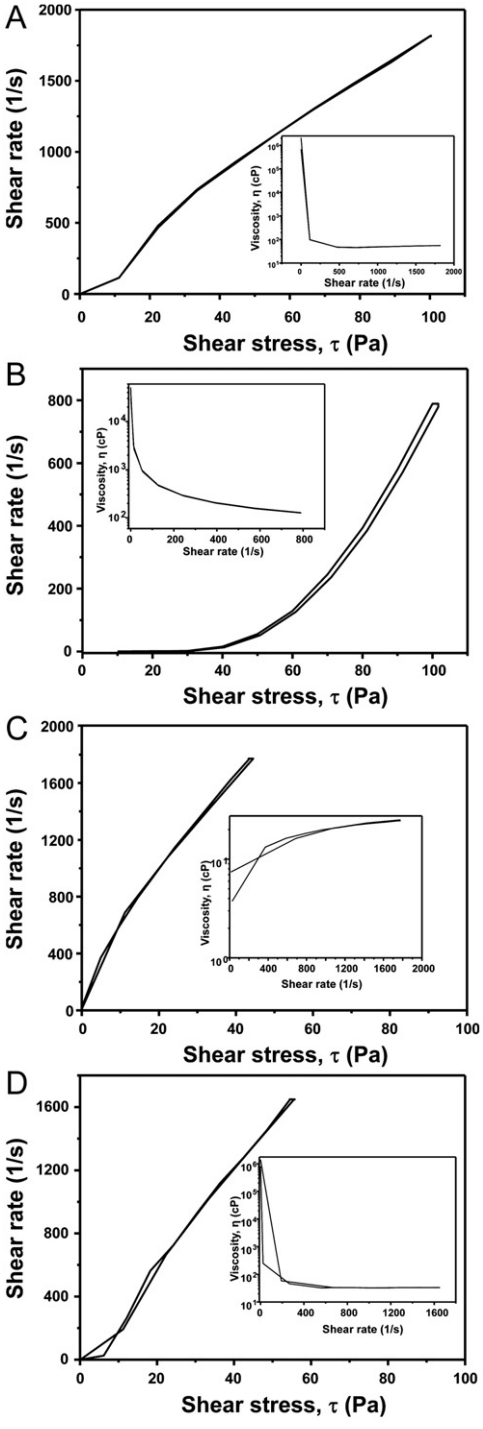

Fig. 1. Flow curves for the different prepared suspensions.

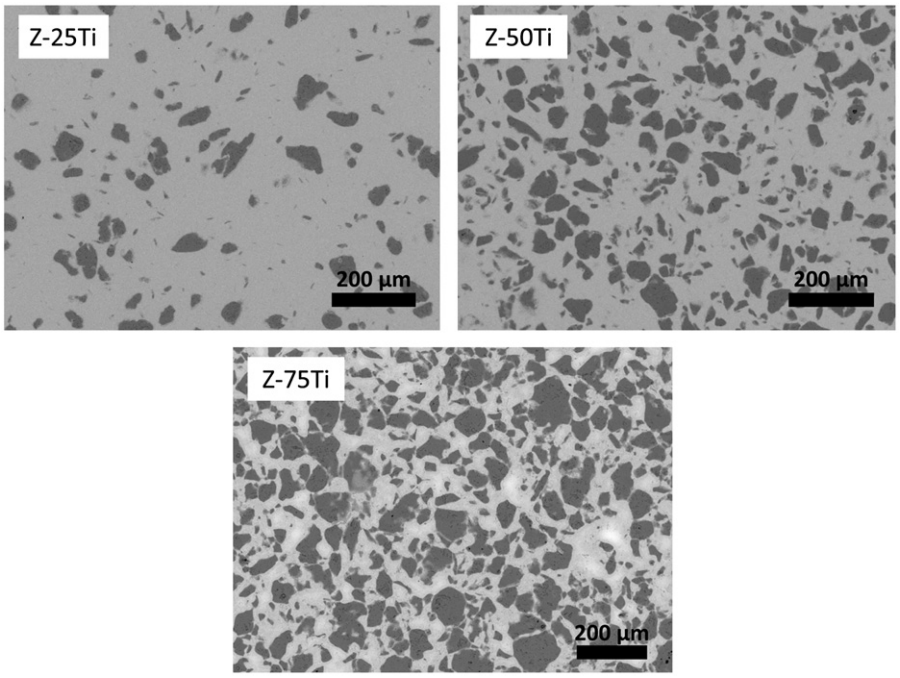

Fig. 2. Microstructure SEM images of the three composites obtained after the Spark Plasma Sintering process.

Table 2
Densities of the sintered compacts (SPS in vacuum at 1350 °C, 80 MPa, 10 min, with a heating rate of 100 °C/min) for all Ti contents, processed starting from suspensions prepared in the conditions of suspension B (80 wt% solid content, 3 wt% deffoculant).

Sample	Density (g/cm^3)	Theoretical density (g/cm^3)	% Theoretical density
Z-25Ti	5.69	5.71	99.7
Z-50Ti	5.30	5.32	99.6
Z-75Ti	4.90	4.93	99.4

Table 3
Mechanical properties of the composites and pure zirconia.

Sample	Bending strength σ_f (MPa)	Fracture toughness K_{IC} (MPa $m^{1/2}$)
Z-0Ti	800 ± 112	6.0 ± 0.2
Z-25Ti	310 ± 35	5.1 ± 0.3
Z-50Ti	200 ± 50	3.3 ± 0.2
Z-75Ti	155 ± 25	2.0 ± 0.1

ceramic-metal interface. Fig. 3 shows the formation of new phases with platelet and globular shapes, which have been identified as a zirconium–titanium oxide (Ti_2ZrO), and yttrium titanium oxide ($Y_2Ti_2O_7$) structures [5].

The results for Vickers hardness are plotted in Fig. 4. The hardness of all three composite materials is higher than that predicted by the rule of mixtures (continuous line), considering the Ti Vickers hardness (≈ 1 GPa) [6]. It can also be seen that the deviation from the rule is higher

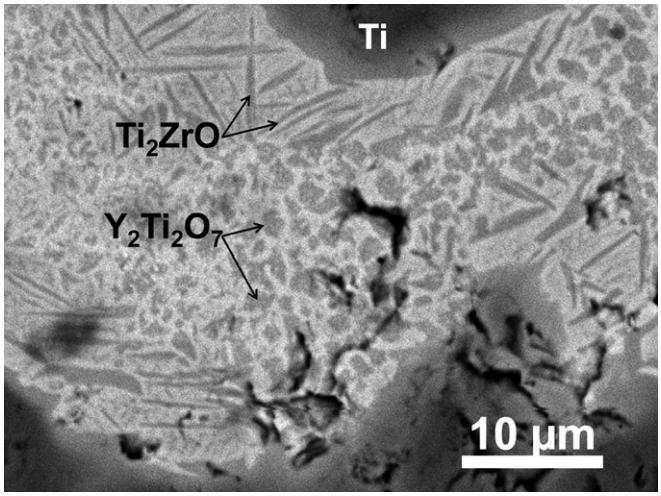

Fig. 3. SEM image of the interface between zirconia and titanium for the Z-75Ti composite. Reactions products are marked with arrows.

when the titanium content increases in such a way that the hardness measured for Z-75Ti (8.6 GPa) doubles the value predicted by the rule of mixtures (4.2 GPa). Therefore, as the formation of the reaction products increases with the titanium concentration, these reaction products seem to be responsible for the hardness deviation [7].

In the case of the fracture toughness (Table 3), it decreases with the metal content. Fig. 5 shows a fracture surface of the Z-75Ti composite, where the fracture of the titanium particles occurred predominantly by cleavage and there was no evidence of debonding at the metal–ceramic interface. This behaviour is typically associated with brittle fracture [8]. Due to the absence of ductile deformation of

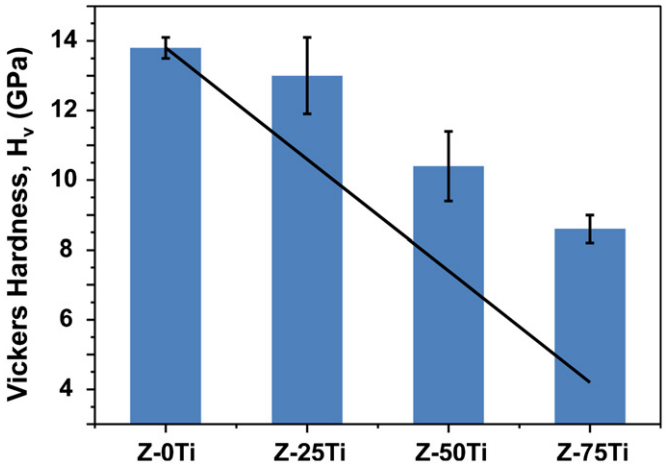

Fig. 4. Hardness measurements for the three composites. Continuous line represents values predicted by the rule of mixtures.

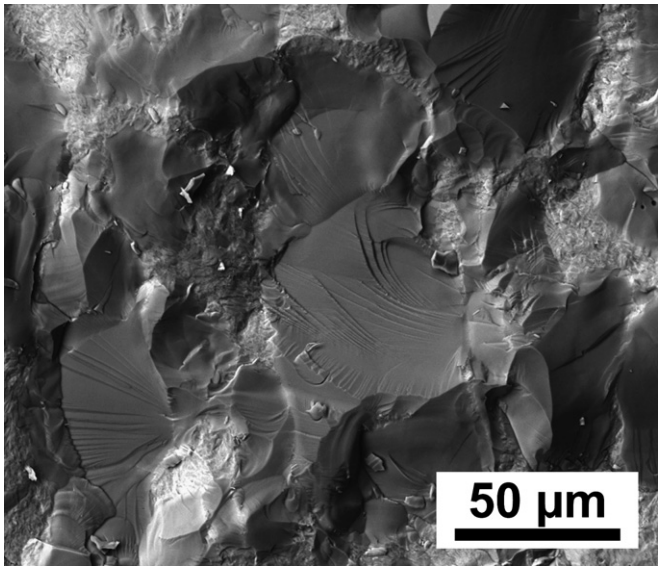

Fig. 5. SEM micrograph of the fracture surface of Z-75Ti composite.

the metal particles, no increase in the toughness is expected. Moreover, the reactivity between components and the difference between ceramic and metal particle sizes may be responsible for this behaviour.

Fig. 6 shows two XRD diffractograms for the Z-50Ti material. Diffractogram (a) was performed after a conventional sintering process under an inert argon atmosphere at 1350 °C. A diffractogram (b) was performed after the SPS sintering process as described in paragraph 2.3. There are two main differences between them. First, the formation of a new reaction product only observed in the material sintered by SPS that matches a zirconium titanium oxide structure (Ti_2ZrO). The formation of this new product was previously detected and reported in Fig. 3. In conventional sintering (Fig. 6a), peaks corresponding to monoclinic zirconia phase appear as a consequence of zirconia destabilisation. In this case it is believed that, due to

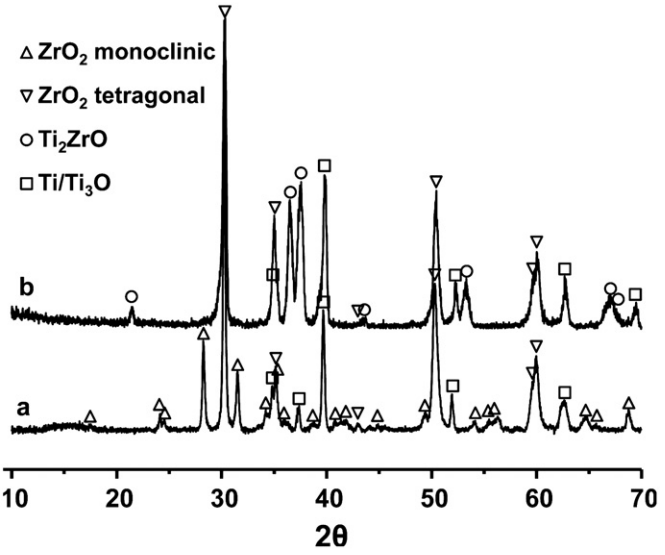

Fig. 6. XRD diffractograms of the sintered Z-50Ti composite. (a) After a conventionally sintering process in argon atmosphere at 1350 °C. (b) After spark plasma sintering at 1350 °C.

a longer sintering, the products formed during this process may have time to be dissolved into the ceramic matrix forming a solid solution. The amount of titanium forming a solid solution in the zirconia has not been measured but it has been observed that the composite structure collapses because of this destabilisation. In both cases, it appears that titanium is slightly oxidised because there is a slight displacement of the peaks of pure titanium towards higher angles. This is related to the existence of a Ti_3O structure whose peaks, slightly displaced to right with respect to the Ti ones, almost overlap.

4. Conclusions

A complete study of the rheological behaviour of the 3Y-TZP/Ti system in the entire range of metal content has been performed. The use of the Spark Plasma Sintering (SPS) technique has been adequate, leading to high densities in the compacts. The materials processed present interesting mechanical features in terms of bending strength, Vickers hardness and fracture toughness, presenting in some cases values higher than expected.

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