Mater. Res. Soc. Symp. Proc. Vol. 1735 © 2015 Materials Research Society
DOI: 10.1557/opl.2015.155

Spark Plasma Sintering of Yttria-Stabilized Zirconia/Titanium Nitride Composites

Paulo S. M. Silva and Fabio C. Fonseca
Nuclear and Energy Research Institute – IPEN, São Paulo, SP, 05508-000, Brazil.

ABSTRACT

Composites of 8 mol% yttria-stabilized zirconia (YSZ) and titanium nitride (TiN) were obtained by mechanical mixing of commercial powders. High-density samples of (1-*x*) YSZ / *x* TiN, with *x* = 0, 25, 50, and 75 wt.%, were obtained by spark plasma sintering (SPS) at 1450 °C for 5 min. Surface contamination with carbon from the SPS was eliminated by diamond sawing of parallel surfaces. X-rays diffraction analyses showed that samples are composed by a mixture of the initial phases, without appreciable reaction as inferred from calculated lattice parameters. dc 4-probe electrical measurements in the 100-850°C under showed that samples have a metallic behavior, indicating that the percolation threshold was attained for the sample with the lowest content of the TiN (*x*=25 wt.%), which corresponds to ~27 vol.%.

INTRODUCTION

High-performance materials are required for different applications at high-temperatures such as for replacing conventional metal parts on special structural and electronic devices and for manufacturing complex shape ceramic components by electric discharge machining (EDM) [1]. Among different types of ceramics, composites having oxides and covalent phases have been investigated for applications requiring unique mechanical and electrical properties [2-7]. Previous studies have studied the properties of composites having partially-stabilized zirconia and a covalent phase, such as TiC, TiN, and TiB_2, aiming at enhanced mechanical properties [2]. However, relatively less attention has been given to the electrical properties of such zirconia-based composites [2-7]. More recently, yttria-stabilized zirconia (YSZ) and WC composites have been investigated as solid oxide fuel cell aiming at carbon-resistant anode [7]. TiN has been pointed out as a high melting temperature (2950 °C) material with good conductivity and high resistance to corrosion and oxidation [3]. Nevertheless, sintering of such composites can be a hard task. Therefore, to fabricate composites with high density and fast processing, with reduced temperatures to avoid undesired reactions and microstructural evolution, requires advanced sintering techniques [2-6,8]. In the present study we have investigated the properties of YSZ-TiN composites fabricated by spark plasma sintering (SPS) aiming at good electrical properties at high temperatures.

EXPERIMENTAL

Starting materials were 8 mol% yttria-stabilized zirconia (Tosoh, Japan) and TiN (Sigma-Aldrich). Batches of 5 g of powders were mixed in a ball mill using ethanol and partially-stabilized zirconia grinding media (4 mm diameter) for 80 min to obtain (1-*x*) YSZ / *x* TiN samples, with *x* = 0, 25, 50, and 75 wt.% (YSZ / *x* TiN). After ball mill, the slurry was dried under constant magnetic mixing, followed by homogenization of the dry powder in agate mortar. Cylindrical pellets were sintered by pulsed electric field (spark-plasma sintering, SPS1050 Dr.

Sinter, Syntex) at 1450°C for 5 min, with heating rate of 100°C/min and 46 MPa load up to 1250°C and 93 MPa for higher sintering temperatures[11]. Graphite dies and punches were isolated from the composite powders by using a graphite foil (~0.4 mm thick). Final dimensions were ~14 mm diameter and 1 mm thick. Samples were characterized by X-ray diffraction (XRD) using Cu K_α radiation in the 20-90° 2θ range with a step size of 0.05° and 2 s counting time. Apparent densities were calculated by the Archimedes method. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were performed in the 20-1200°C temperature range with 10 °C/min heating rate under synthetic air or argon flow. Fractured surfaces were observed by scanning electron microscopy (SEM) in a field-emission gun FEI Inspect F50. The electrical resistivity was measured in bar-shaped samples, cut with a diamond saw from the central portion of sintered pellets, painted with silver contact pads. Measurements were performed in the 100-850°C temperature range with 3 °C/min heating rate in an air tight resistive furnace under argon flow (pO_2 ~5.10^{-6} atm). Temperature was measured by a type K thermocouple positioned close to the sample and room temperature was monitored by a temperature sensor close to the thermocouple reference. Electrical resistivity was determined with a Lakeshore 370N resistance bridge with applied current in the 0.1-1 mA range.

DISCUSSION

Figure 1 shows simultaneous TG/DTA in air of TiN starting powder and YSZ / 25 TiN sample. Both materials display a pronounced mass gain in the ~470-800 °C temperature range in air, corresponding to the oxidation of the TiN to TiO_2. The theoretical mass increase for the TiN oxidation (~27%) is in reasonable agreement with the experimental data (29%). The YSZ / 25 TiN sample shows a ~8% mas increase between ~500 °C and 790 °C, which is in agreement with the expected value (7%), indicating good homogeneity of the sample and total oxidation of sintered samples. The oxidation of YSZ / 25 TiN under argon extends over a wider temperature range and completes at ~1170°C.

Figure 2 shows the X-rays diffraction data for the YSZ / *x* TiN composites. In Fig. 2a the most pronounced peaks were indexed as graphite, while the remaining peaks, corresponding to the composite phases, have a much lower relative intensity. Carbon contamination resulting from SPS process is usual and it is typically eliminated by heat treatments at ~900 °C in oxidizing atmosphere [13]. However, the temperature required for carbon oxidation is higher than that of TiN oxidation. The TG/DTA results (Fig. 1) evidenced that removing carbon by thermal treatments would result in oxidation of the nitride phase. Thus, carbon removal was carried out by grinding in a diamond wheel, which removed ~300 μm from each parallel surface of samples. The XRD data of samples after grinding step is shown in Fig. 2b. X-rays diffractograms display only the peaks indexed to both YSZ and TiN. Relative intensity of peaks varies according to the relative fraction of phases and the position of the peaks is not significantly changed indicating no relevant reaction between YSZ and TiN.

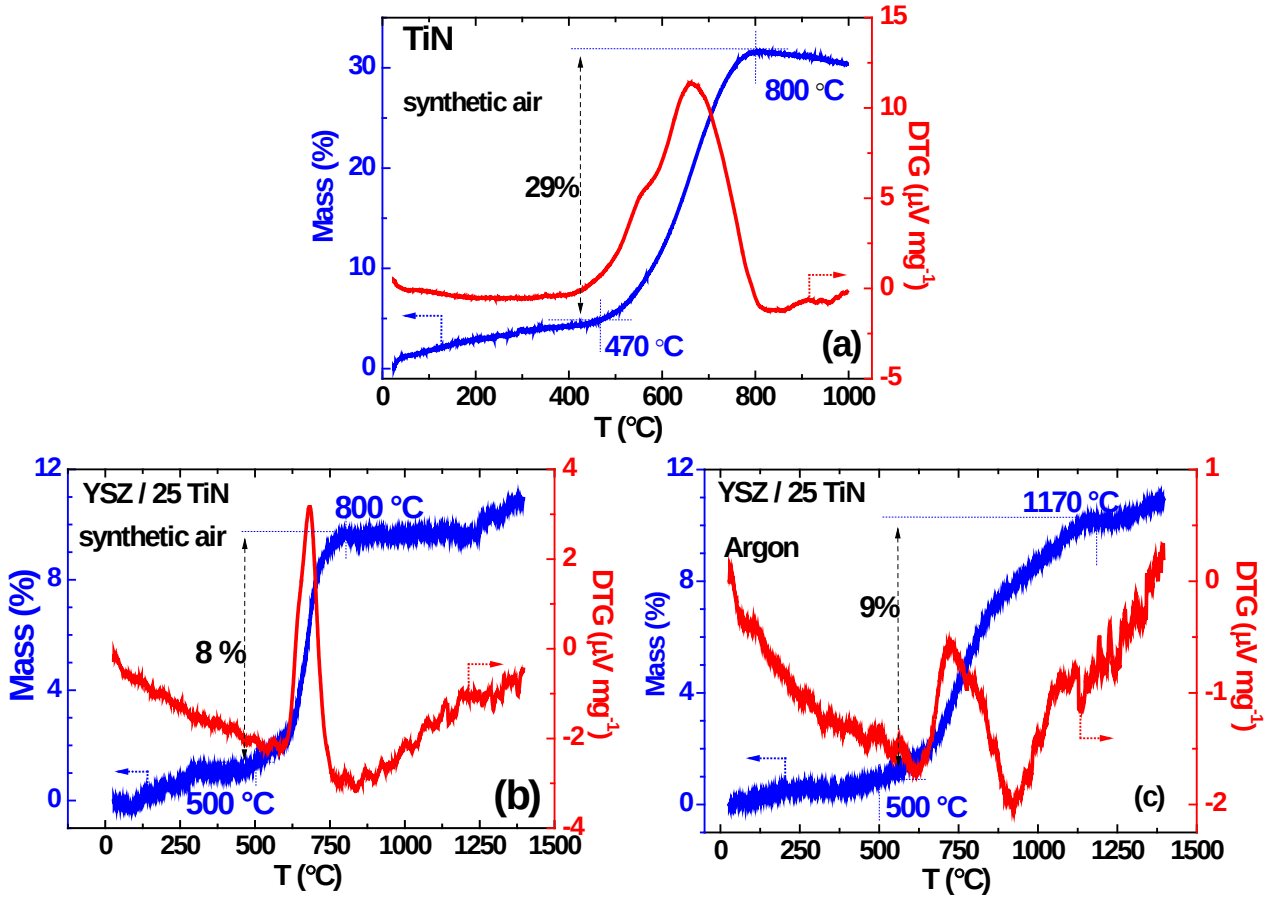

Figure 1. TG/DTA analyses of TiN (a) starting powder and YSZ / 25 TiN in both synthetic air (b) and argon (c) flow.

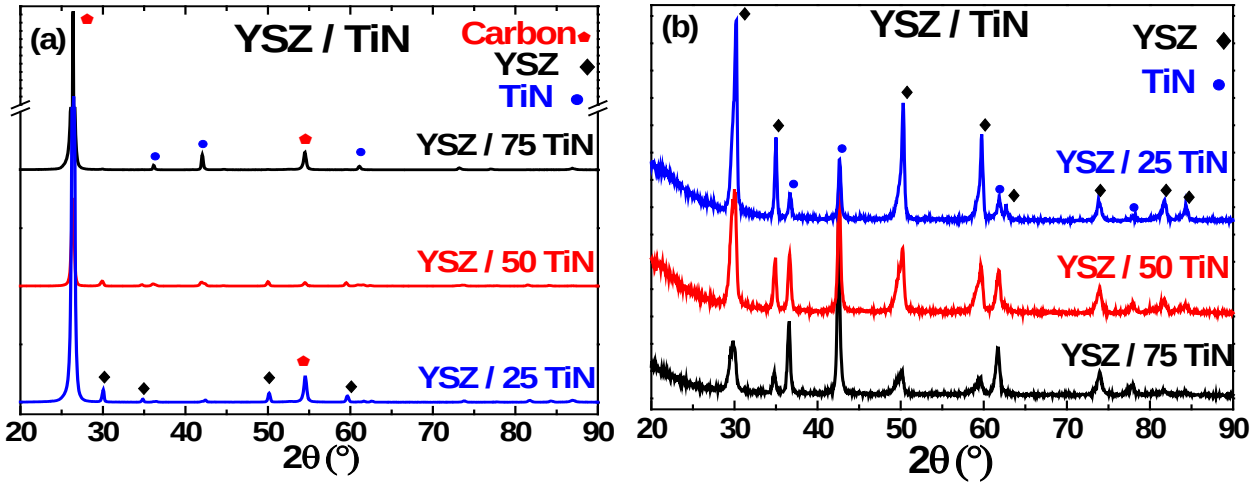

Figure 2. X-rays diffraction data for the YSZ / *x* TiN composites (a) as sintered in SPS at 1450 °C and (b) after diamond wheel grinding for surface carbon removal.

The microstructure of the composite was observed by SEM analyses. Fig. 3 shows secondary electron images of fractured cross sections of YSZ / *x* TiN. Images reveal low phase contrast, samples with high density, and average grain size roughly estimated in the 1μm range.

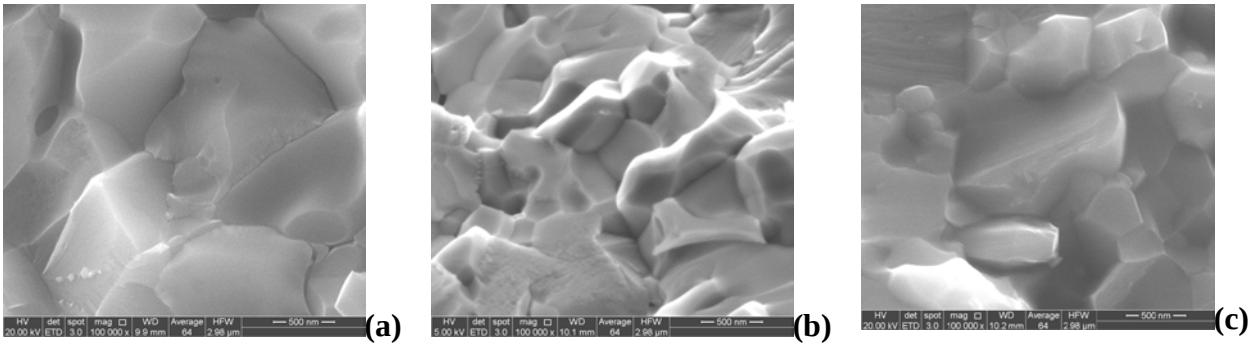

Figure 3. FEG-SEM images of the YSZ / *x* TiN composites (a) *x* = 25 wt.%, (b) *x* = 50 wt.%, (c) *x* = 75 wt.%.

Table I lists values of apparent density (ρ) determined by Archimedes' method, the theoretical density calculated by the rule of mixture and lattice parameters (*a*) of the cubic structure of both phases calculated from XRD data. Composite samples exhibited lattice parameters close to the reported ones and high apparent densities (> 92% of the theoretical value), indicating that SPS process was efficient.

Table I. Apparent density (ρ), theoretical density calculated by the rule of mixture (ρ_{RM}), and lattice parameters (*a*).

Sample	*a* TiN* (nm)	*a* YSZ* (nm)	ρ (g cm^{-3})	ρ_{RM} (g cm^{-3})	ρ/ρ_{RM} (%)
YSZ / 25 TiN	0.4241	0.5137	5.72	5.85	98
YSZ / 50 TiN	0.4242	0.5134	5.20	5.69	92
YSZ / 75 TiN	0.4244	0.5131	5.26	5.54	95

The electrical resistivity of the YSZ / *x* TiN composites was measured as a function of the temperature in argon flow (pO_2 ~5.10^{-6} atm), as shown in the Fig. 4. Increasing *x* decreases the electrical resistivity; however, as compared to TiN composites exhibit larger resistivity values. At to room temperature, the resistivity of the YSZ / 50 TiN sample is approximately one order of magnitude larger than that of TiN [4]. Moreover, composites display a metallic behavior, with increasing resistivity with increasing temperature. The metallic behavior indicates that composite samples attained the percolation threshold at $x \leq 25$ wt.% (corresponding to ~27 vol.%).

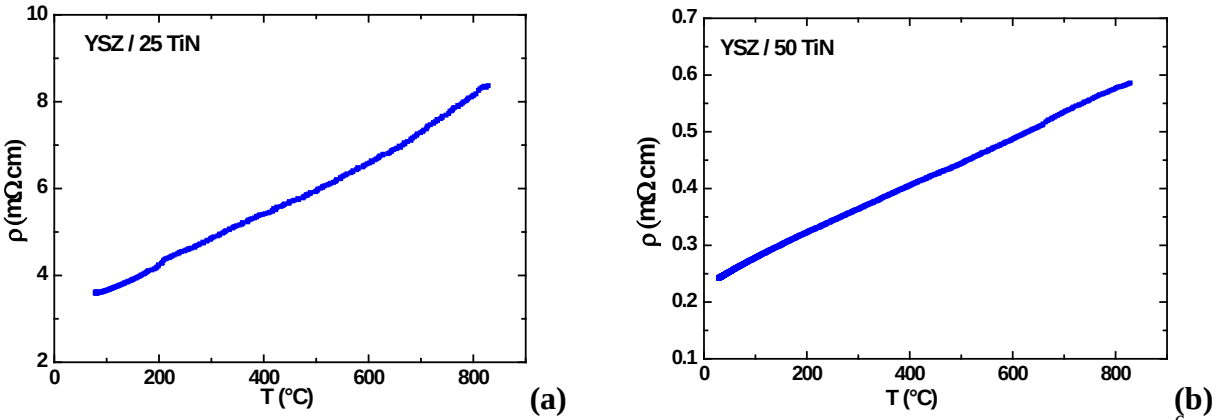

Figure 4. Temperature dependence of the electrical resistivity under argon flow (pO_2~5.10^{-6} atm) for samples (a) YSZ / 25 TiN and (b) YSZ / 50 TiN.

CONCLUSION

Composite samples of YSZ / TiN prepared by spark plasma sintering showed high relative densities (> 92% of the theoretical density) and homogeneous distribution of the phases, without significant reaction after sintering at 1450 °C. High electrical conductivity and metallic behavior was measured for the sample with lowest TiN fraction x = 25 wt% (~27 vol.%). Such features indicate that the YSZ / TiN composite is a promising material for high temperature applications.

ACKNOWLEDGMENTS

Thanks are due to Dr. I. F. Machado (POLI-USP) for SPS, Dr. R. Muccillo (IPEN) for SEM analyses and to the partial financial support of IPEN-CNEN/SP and CNPq.

REFERENCES

1. J. Kozak, K. P. Rajurkar and N. Chandarana, *J. Mat. Proc. Tech.* **146**, 266 (2004)
2. J. Vleugels and O. Van der Biest, *J. Am. Ceram. Soc.* **82**, 2717 (1999).
3. J. G. Li, L. Gao and J. K. Guo, *J. Eur. Ceram. Soc.* **23**, 69 (2003).
4. S. Salehi , O. Van der Biest and J. Vleugels, *J. European Ceramic Soc.* **26**, 3173 (2006).
5. S. Salehi , O. Van der Biest and J. Vleugels, *Materials Science Forum* **554**, 135 (2007).
6. S. Ran and L. Gao, *Ceramics International* **38**, 4923 (2012).
7. A. Torabi, T. H. Etsell, N. Semagina and P. Sarkar, *Electrochimica Acta* **67**, 172 (2012).
8. J. E. Garay, *Annual Review of Materials Reserch* **40**, 445 (2010).