

Spark plasma and conventional sintering of ZrO₂-TiN composites: A comparative study on the microstructure and mechanical properties

Yuri Pristinskiy^{1, *}, Nestor Washington Solis Pinargote¹ and Anton Smirnov¹

¹Moscow State University of Technology “STANKIN”, Vadkovskij per. 1, Moscow, 101472, Russian Federation

Abstract. Spark plasma sintering (SPS) is an extremely fast solidification technique for compounds that are difficult to sinter within the material group metals, ceramics or composites. SPS uses a uniaxial pressure and a very rapid heating cycle to consolidate these materials. This direct way of heating allows the application of very high heating and cooling rates, enhancing densification over grain growth promoting diffusion mechanisms allowing maintaining the intrinsic properties of nanopowders in their fully dense products. The ZrO₂-TiN cermets prepared by SPS processing achieves the enhanced mechanical properties with the hardness of 15.1 GPa and the fracture toughness of 9.1 MPa·m^{1/2} in comparison to standard reference ZrO₂-TiN material.

1 Introduction

For many high demanding applications in the industry and biomedical field technical ceramics (e.g.: Al₂O₃, SiC, B₄C, Si₃N₄, etc.) provide solutions, because of their mechanical properties such as: high Young’s modulus, superior abrasion resistance, chemical resistance, high melting point and dimensional stability [1].

Usually, these materials processed by mechanical methods, which include the processing of a diamond cutting tool. However, ceramics is a slight material, and therefore it is very difficult to process it mechanically. An alternative to the mechanical method is EDM.

Although there are some setups which allow EDM (electrical discharge machining) processing of nonconductive materials [2], standard EDM processes do require the work piece to be electrically conductive [3].

Zirconium oxide (ZrO₂), known to the general public for its use in the biomedical industry, has a good fracture toughness. However, this material cannot be machined using the conventional EDM setup, as it is one of the worst electro-conductive materials. Also, zirconium oxide has a low hardness, which limits its use in wear conditions [4].

To date, several composites such as ZrO₂-WC, ZrO₂-TiB₂, ZrO₂-ZrC, ZrO₂-SiC, ZrO₂-TiN, and ZrO₂-TiCN have been fabricated aiming to achieve an unique combination of high hardness, high strength, and high fracture toughness [5-10].

* Corresponding author: y.pristinskiy@gmail.com

As of today, ZrO₂-TiN samples are conventionally made by such methods as hot pressing and hot isostatic pressing [11]. However, these methods have a number of drawbacks like low sintering rate, high equipment costs, low reproducibility of the output, etc. From this perspective, spark plasma sintering seems a very promising method [12].

Spark plasma sintering (SPS) or pulsed electric current sintering (PECS) is a sintering technique utilizing uniaxial force and a pulsed (on-off) direct electrical current (DC) under low atmospheric pressure to perform high speed consolidation of the powder. This direct way of heating allows the application of very high heating and cooling rates, enhancing densification over grain growth promoting diffusion mechanisms allowing maintaining the intrinsic properties of nanopowders in their fully dense products [13,14]. The heating rate during the SPS process depends on the geometry of the container/sample ensemble, its thermal and electrical properties, and on the electric power supplier. Heating rates as high as 1000 °C/min can be achieved. As a consequence, the processing time typically takes some minutes depending on the material, dimensions of the piece, configuration, and equipment capacity.

The purpose of the present study was to investigate the dependence of the basic SPS processing parameters, such as temperature and time on the mechanical properties of ZrO₂-TiN composites.

2 Materials and characterization

2.1 Raw materials

Commercially available nanopowder ZrO₂ stabilized by 3mol% of Y₂O₃ (3Y-ZrO₂) and TiN (Plasmotherm, Moscow, Russia). with an average ZrO₂ particles size from 40 to 75nm and average TiN particle from 40 to 75 nm was used as an initial material.

2.2 Powder processing and sintering

Three suspensions of ZrO₂-20vol%, ZrO₂-30vol% and ZrO₂-40vol% were prepared using a colloidal method . Slurry of powder was prepared using distilled water as liquid media via dry ball mill (ML-1, Kaluga, Russia), containing zirconia balls, in polyethylene containers at 150 rpm during 24 h. Then, in freeze-drying system the suspension was dried at the collector temperature of $-50 \pm 2^\circ\text{C}$. Furthermore, the shell temperature and the chamber pressure were kept at $+23 \pm 2^\circ\text{C}$ and 0.02 ± 0.01 mbar, respectively, during the entire process. Powder densification was performed by SPS KCE-FCT-H-HP-D25-SD (FCT Systeme GmbH, Rauenstein, Germany) at a maximum temperature of 1300-1500°C (increments of 100°C), reached under vacuum at a heating rate of 100°C/min, and an applied pressure of 80 MPa. The final temperature and pressure were maintained for 3 min. The sintered specimens had diameters of 20 mm and thicknesses of 3 mm.

2.3 Microstructural and mechanical characterization

XRD analyses (Empyrean diffractometer, PANalytical, Almelo, Netherlands, Cu-K α radiation, wavelength 1.5405981 Å, accelerating voltage 60 kV, beam current 30 mA) of the sintered samples were conducted in a step scanning mode at diffraction angles 2θ ranging from 25° to 100° (step size 0.05°).

Scanning electron microscopy characterization was carried out on polished down to 1 μm surfaces by VEGA 3 LMH (SEM Tescan, Brno, Czech Republic).

The density of the sintered samples (ρ) was measured in distilled water using Archimedes' principle and was compared with the theoretical value, calculated according to the rule of mixtures.

In order to quantify the ZrO₂ average grain size, the sintered and polished samples were thermally etched in vacuum oven (Thermionic, Podolsk, Russia) for 30 min at a temperature of 25% lower than the sintering temperature, and the linear intercept method (LIM) was used [15].

Vickers hardness, H_V , was measured on polished surfaces using a Vickers diamond indenter (Qness A10 Microhardness Tester, Salzburg, Austria), applying a load of 1 kg and an indentation time of 10 s. The hardness results were averaged over 10 indentations per specimen.

Fracture toughness (K_{Ic}) was determined from Vickers indentations obtained with a load of 10 kg for 10 seconds. The sizes of the corresponding indentations and crack lengths were measured using SEM. The H_V and K_{Ic} of reference materials were measured using the same equipment and under the same testing conditions. The method and formulas for calculating H_V and K_{Ic} have been reported elsewhere [16].

3 Results and discussion

3.1 XRD analyses

X-ray diffraction was carried out for the sintered sample (1400°C / 3 min / 80 MPa) (Fig.1). XRD analysis revealed the presence of zirconium oxide (■) and titanium nitride (●) phases, without any additional peaks appearing.

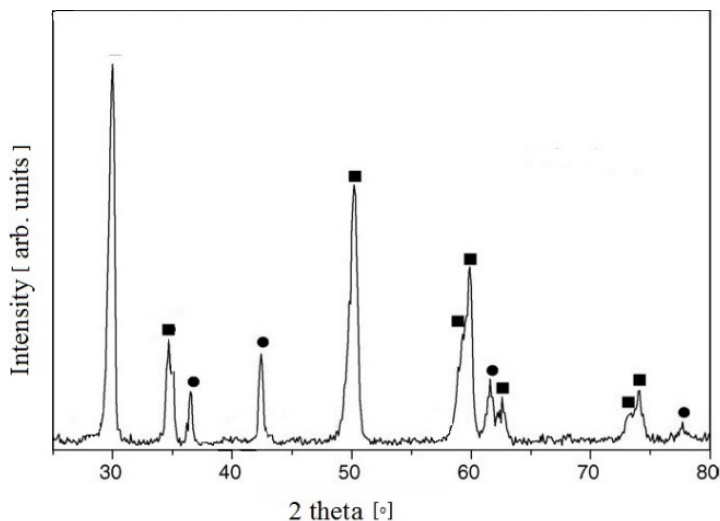


Fig. 1. XRD patterns of SPS sintered (1400°C/3min/80MPa) sample.

3.2 Microstructure characterization

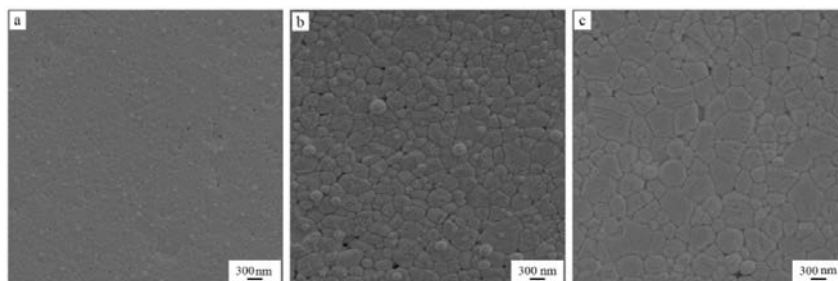


Fig. 2. SEM images of polished and thermally etched sections of SPS sintered (1300°C (a), 1400°C (b) and 1500°C (c)) ZrO₂ composites.

The microstructure of ZrO₂ sintered in the following sintering regimes: sintering temperature-1300 ° C (a), 1400 ° C (b) and 1500 ° C (c) is shown in Fig. 2. Microstructure images were obtained after thermal etching of samples in a vacuum oven.

It can be seen that a granular structure with an average grain size of $0.3 \pm 0.2 \mu\text{m}$, $0.5 \pm 0.2 \mu\text{m}$ and $0.7 \pm 0.2 \mu\text{m}$ was obtained for samples whose sintering temperature was 1300 ° C, 1400 ° C and 1500 ° C, respectively.

3.3 Mechanical properties

The influence of sintering temperature on density, hardness and fracture toughness of sintered composites presented on Fig.3-5.

At a sintering temperature of 1300 ° C all the samples achieve low density (95-96%), but when the temperature is raised to 1400 ° C, the density values reach their maximum (99.5-99.8%). This is presented in Fig. 3.

It can be seen from Fig. 4 that the hardness values reach their maximum (for 20% TiN-15.1 GPa, for 30% TiN-14.5 GPa, for 40% TiN-13 GPa) at a sintering temperature of 1400 ° C. When the temperature is raised to 1500 ° C, the hardness and fracture toughness decrease. This is due to the fact that at a higher temperature the growth of the grain increases significantly (Fig. 2). For comparison, the hardness of a sample made by hot pressing is 13.7GPa.

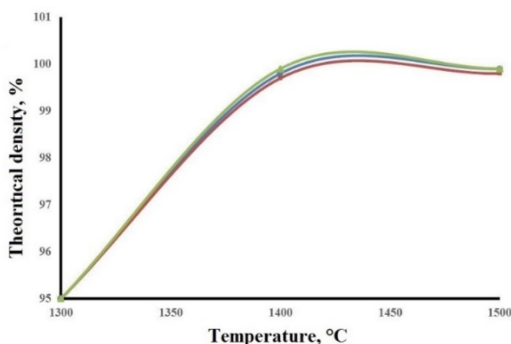


Fig. 3. Evolution of density of ZrO₂-20vol%TiN (—), ZrO₂-40vol%TiN (—) and ZrO₂-20vol%TiN (—) composites sintered at 1300°C, 1400°C and 1500°C, respectively with dwelling time 3 minutes under 80MPa pressure.

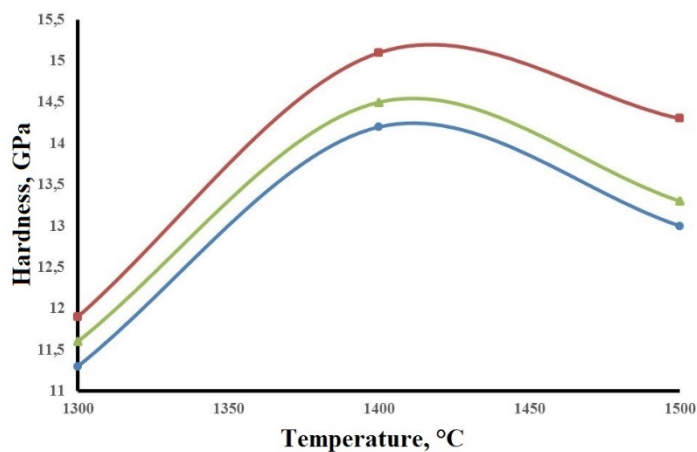


Fig. 4. Evolution of hardness of ZrO₂-20vol%TiN (—), ZrO₂-40vol%TiN (—) and ZrO₂-20vol%TiN (—) composites sintered at 1300°C, 1400°C and 1500°C, respectively with dwelling time 3 minutes under 80MPa pressure.

In an earlier published paper [17], it was shown that the mechanical properties of the samples are also affected by the sintering pressure. In this regard, the optimum pressure of 80 MPa was chosen, at which all the samples were sintered. In addition, it was selected due to the strength of graphite matrix.

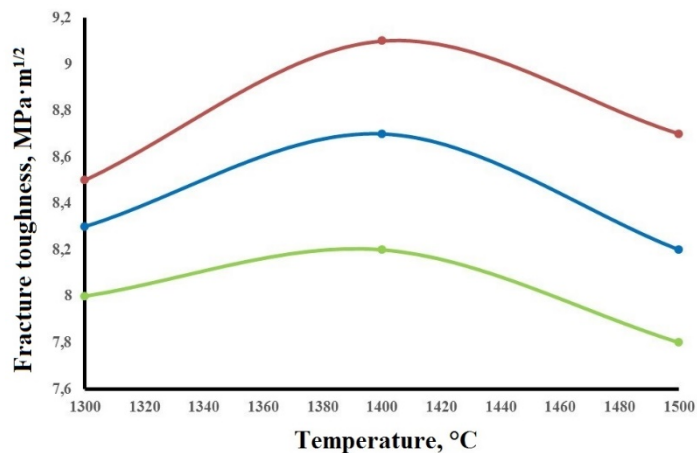


Fig. 5. Evolution of fracture toughness of ZrO₂-20vol%TiN (—), ZrO₂-40vol%TiN (—) and ZrO₂-20vol%TiN (—) composites sintered at 1300°C, 1400°C and 1500°C, respectively with dwelling time 3 minutes under 80MPa pressure.

Graphs of the dependence of fracture toughness on temperature during sintering is shown on the Fig. 5.

Greatest value of fracture toughness (9.1 MPa · m^{1/2}) is achieved on a sample with a 20vol%TiN. It is also seen that the highest values of fracture toughness on all samples are achieved at a sintering temperature of 1400 °C, then this index decreases due to grain growth.

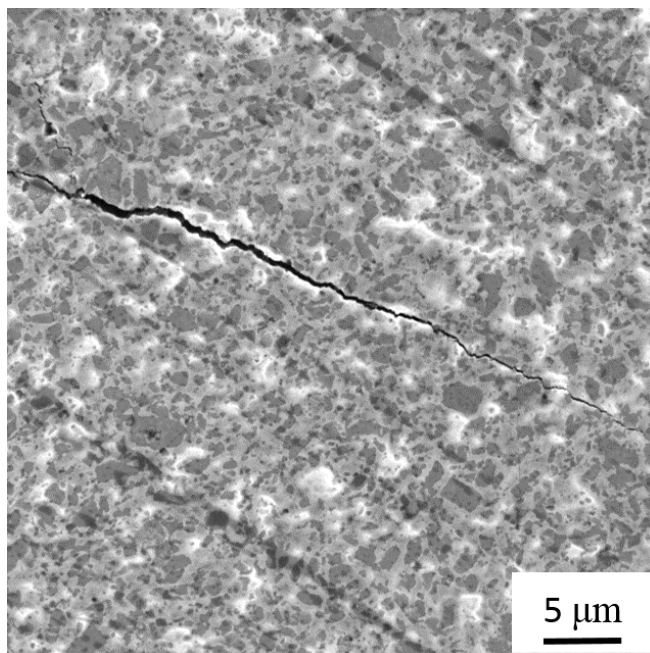


Fig. 6. Vickers indentation cracks induced on the surfaces of SPSeD composite.

Fig. 6 shows the Vickers indentation cracks induced on the surfaces of ZrO_2 -30vol% TiN. Fig. 6 shows a crack path that is mainly comprised of transgranular fractures. Which indicates that this sample has a good fracture toughness.

The electrical resistivity was also measured. The material with 20vol% TiN resistivity was $15 \pm 1 \Omega \cdot m$, with 30vol%TiN- $7.7 \pm 1 \Omega \cdot m$, with 40vol% TiN- $4 \pm \Omega \cdot m$.

In samples with a TiN content of 30% and 40%, sufficient electrical resistance was found to be processed by EDM. However, for a sample with a TiN content of 20% this index was insufficient, which makes it impossible to process this material with the aid of EDM.

In connection with the foregoing, the optimum content of titanium nitride should be considered 30vol%, as it provides not only increased hardness and fracture toughness, but also makes it possible to apply EDM to this material.

4 Conclusion

ZrO_2 -TiN cermets have been successfully fabricated by Spark Plasma Sintering. Results showed that all free basic sintering parameters (temperature, time) have a significant effect on the mechanical performance of sintered materials. The optimum percentage of TiN should be considered to be 30vol%, since with this additive the sample has an increased hardness (14.5 GPa), fracture toughness ($8.2 \text{ MPa} \cdot \text{m}^{1/2}$), and sufficient conductivity, which allows processing of products from of this material by EDM. With respect to the same sample made by the hot pressing, the samples produced by the spark plasma sintering showed an increase in hardness by 10%, and an increase in crack resistance by 16%.

We would like to thank the Ministry of Education and Science of the Russian Federation for supporting this work under contract No. 14.577.21.0288, unique identifier of contract RFMEFI57718X0288.

References

1. F. Vogeler, B. Lauwers, E. Ferraris, *ScienceDirect*. **42**, 268-273 (2016);
2. N. Mohril, Y. Fukuzawal, T. Taniz, N. Saitol, K. Furutani, *CIRP Annals – Manufacturing Technology*. **45**, 201-204 (1996).
3. W. König, DF Dauw, G. Levy, U. Panten, *CIRP Annals - Manufacturing Technology*. **37**, 623-631.
4. J. Vleugels, O. Van der Biest, *J. Am. Ceram. Soc.* **82**, 2717-2720 (1999).
5. D.T. Jiang, O.V.D. Biest, J. Vleugels, *J. Eur. Ceram. Soc.* **27**, 1247-1251 (2007).
6. B. Basu, J. Vleugels, O.V.D. Biest, *J. Eur. Ceram. Soc.* **25**, 3629-3637 (2005).
7. Y.G. Xu, Y.G. Liu, Z.H. Huang, M.H. Fang, X.Z. Hu, L.Yin, J.T. Huang, *Mater. Res. Bull.* **48**, 7-11 (2013).
8. K. Bonny, P.D. Baets, J. Vleugels, A. Salehi, O.V.D. Biest, B. Lauwers, W. Liu, *Wear*. **265**, 1884-1892 (2008).
9. C. F. Gutierrez-Gonzalez, N. W. Solis Pinargote, S. Agouram, P. Y. Peretyagin, S. Lopez-Esteban and R. Torrecillas, *Mechanics & Industry*. **16**, 703 (2015).
10. R.S. Khmyrov, V.A. Safronov, A.V. Gusarov, Obtaining crack-free WC–Co alloys by selective laser melting, *Phys.Procedia*. **83**, 874–881 (2016).
11. N. W. Solís, P. Peretyagin, R. Torrecillas, A. Fernández, J. L. Menéndez, C. Mallada, L. A. Díaz, J. S. Moya, *Electroceram.* **38**, 119 (2017).
12. C.F. Gutiérrez-González, M. Suarez, S. Pozhidaev, S. Rivera, P. Peretyagin, W. Solís, L.A. Díaz, A. Fernandez, R. Torrecillas, *J. Eur. Ceram. Soc.* **36**, 2149 (2016)
13. D. I. Yushin, V. Smirnov, N. Solis Pinargote, P. Yu. Peretyagin, V. A. Kuznetsov and R. Torrecillas, *Rus. Ing. Res.* **36**, 410 (2016).
14. S. S. Pozhidaev, A. E. Seleznev, N. W. Solis Pinargote and P. Yu. Peretyagin, *Mechanics & Industry* **16**, 710 (2015)
15. J.C. Wurst, J.A. Nelson, *Ceram. Soc.* **55** (2), 109 (1972).
16. A. Smirnov, H. D. Kurland, J. Grabow, F. A. Müller, J. F. Bartolomé, *J. Eur. Ceram. So.* **35**, 2685 (2015)
17. Y. Pristinskiy, N. Peretyagin, N.W. Solis Pinargote, *MATEC Web of Conferences*. **129**, 02028 (2017).