Ceramics International 42 (2016) 15610–15617

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Surface microstructural changes of spark plasma sintered zirconia after grinding and annealing

Latifa Melk [a,b,c,d,*], Johanne Mouzon [e], Miquel Turon [a,b], Farid Akhtar [c], Marta-Lena Antti [c], Marc Anglada [a,b]

[a] CIEFMA-Department of Materials Science and Metallurgical Engineering, ETSEIB, Universitat Politècnica de Catalunya, 08028, Barcelona, Spain
[b] CRnE, Campus Diagonal Sud, Edifici C', Universitat Politècnica de Catalunya, 08028, Barcelona, Spain
[c] Department of Engineering Sciences and Mathematics, Luleå University of Technology, 97187 Luleå, Sweden
[d] Department of Materials Science and Engineering/ETSEIB, Diagonal 647., 08028, Barcelona, Spain
[e] Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, 97187 Luleå, Sweden

ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
1 July 2016
Accepted 2 July 2016
Available online 4 July 2016

Keywords:
Zirconia
SPS
Grinding
Annealing
Grain size
Low temperature degradation

ABSTRACT

Spark plasma sintered zirconia (3Y-TZP) specimens have been produced of 140 nm 372 nm and 753 nm grain sizes by sintering at 1250 °C, 1450 °C and 1600 °C, respectively. The sintered zirconia specimens were grinded using a diamond grinding disc with an average diamond particle size of about 60 μm, under a pressure of 0.9 MPa. The influence of grinding and annealing on the grain size has been analysed. It was shown that thermal etching after a ruff grinding of specimens at 1100 °C for one hour induced an irregular surface layer of about a few hundred nanometres in thickness of recrystallized nano-grains, independently of the initial grain size. However, if the ground specimens were exposed to higher temperature, e.g. annealing at 1575 °C for one hour, the nano-grain layer was not observed. The resulted grain size was similar to that achieved by the same heat treatments on carefully polished specimens. Therefore, by appropriate grinding and thermal etching treatments, nanograined surface layer can be obtained which increases the resistance to low temperature degradation.

1. Introduction

Yttria stabilised tetragonal polycrystalline zirconia (3Y-TZP) has a wide range of applications, especially in the medical sector, because of its biocompatibility and very good mechanical properties, such as strength and toughness. The local and constrained phase transformation from tetragonal (*t*) to monoclinic (*m*) structure generates compressive stresses at the crack tip which enhances toughness. However, 3Y-TZP suffers from surface spontaneous *t-m* transformation in humid atmosphere, often referred to as hydrothermal degradation, aging or low temperature degradation (LTD), which is accompanied by formation of near surface microcracks and loss of surface mechanical properties [1–4].

During the processes of final shaping and surface finishing, 3Y-TZP may be subjected to different machining processes (cutting, polishing, grinding, and milling). The damage induced by machining affects structural integrity and reliability of the material. Therefore, machining zirconia is considered as a critical step in the manufacturing of long lasting and strong 3Y-TZP components.

Previous investigations have shown that grinding influences the surface integrity and the flexural strength of 3Y-TZP materials [5]. Therefore, most of the studies on ground zirconia have focussed on characterizing surface microstructural changes that may affect the chemical and mechanical behaviour. The main changes frequently observed in the X-ray diffraction (XRD) spectrum are the following: (1) *t–m* phase transformation; (2) asymmetrical broadening of the (1 1 1) tetragonal peak at $\approx 30°$ (2θ); (3) intensity reversal of the tetragonal doublet at 34.64° and 35.22° (2θ) corresponding to the (0 0 2) and (2 0 0) planes [6–10]. On the other hand, a TEM investigation of the ground surface by Munoz et al. [11] reported the existence of three different regions from the ground surface towards the bulk: (1) a recrystallized zone, exactly at the surface, where the grains have a diameter in the range 10–20 nm; (2) a plastically deformed zone; (3) a *t-m* transformed zone, which is mainly responsible for the formation of compressive residual stresses that usually increase the flexure strength and the apparent fracture toughness of ground specimens [11].

The near surface monoclinic phase formed during machining operations can be reversed to tetragonal by annealing. The operation of grinding and the time and temperature of annealing have an influence on the resistance to LTD., which can be inhibited

* Corresponding author at: Department of Materials Science and Engineering/ ETSEIB, Diagonal 647. 08028, Barcelona, Spain.
E-mail address: melk.latifa@gmail.com (L. Melk).

http://dx.doi.org/10.1016/j.ceramint.2016.07.014
0272-8842/

Table 1
Density and grain size of the SPS zirconia specimens before and after annealing.

Temperature/Grain size							
Specimen	Density (g cm^{-3})	1100 °C POL (nm)	1100 °C GRD (nm)	1200 °C POL (nm)	1200 °C GRD (nm)	1575 °C POL (nm)	1575 °C GRD (nm)
SPS1250	6.00 ± 0.03	140 ± 10	59 ± 7	144 ± 16	105 ± 9	611 ± 93	602 ± 153
SPS1450	5.99 ± 0.09	372 ± 50	66 ± 15	386 ± 29	149 ± 22	699 ± 79	896 ± 167
SPS1600	6.05 ± 0.04	753 ± 60	67 ± 11	658 ± 76	±	856 ± 57	708 ± 97

Table 2
Vickers hardness and indentation fracture toughness of the SPS zirconia samples.

Specimen	Vickers hardness (HV10) (GPa)	Indentation K_{IC} (Niihara) (MPa m$^{1/2}$)	Indentation K_{IC} (Anstis) (MPa m$^{1/2}$)
SPS 1250	14.7 ± 0.2	5.2 ± 0.1	3.9 ± 0.2
SPS 1450	13.8 ± 0.1	5.1 ± 0.1	3.8 ± 0.1
SPS 1600	13.6 ± 0.2	5.2 ± 0.1	4.0 ± 0.1

or delayed [12]. The evolution of the resistance to LTD of specimens of initially 330 nm grain size subjected to grinding and annealing at 1200 °C for different times (1 min, 10 min and 1 h) was analysed by Muñoz et al. [13]. The results showed that LTD of ground 3Y-TZP was supressed due to the formation of a recrystallized nano-grain layer on the surface. Moreover, the resistance to LTD was decreasing during long time annealing at 1200 °C after that grain size reached grew beyond the initial surface grain size of 330 nm. The effect of different high annealing temperatures in the range 1200–1600 °C on the surface microstructure of ground zirconia was recently studied by Roa et al. [14]; they also found the recrystallized surface nano-grain layer after annealing at 1200 °C by milling a small cross section of the near surface region by FIB/SEM, while at 1600 °C the near surface microstructure was composed of larger grain sizes than the grain size of the bulk material.

To the best of our knowledge, previous studies of the effect of grinding has been carried out only on 3Y-TZP with grain size around 330 nm sintered using conventional methods. However, the aim of this work is to study the of surface microstructural changes after grinding and annealing on grains in the range of 140–370 nm produced by Spark Plasma Sintered (SPS) at 1250 °C and 1600 °C, respectively.

2. Experimental

2.1. Material processing

Zirconia powder stabilized with 3 mol% of yttria (TZ-3YSB-E, Tosoh, Tokyo, Japan) with a crystalline size of 36 nm was sintered using spark plasma sintering (SPS) at 1250 °C, 1450 °C and 1600 °C for 5 min. The pressure maintained during the sintering cycle was 55 MPa and the heating rate was 100 °C/min.

The final samples were ceramic discs (50 mmx3 mm). The average grain size was determined using the line intercept method on SEM images and the density was measured by the Archimedes method.

The samples were ground using a new diamond grinding disc

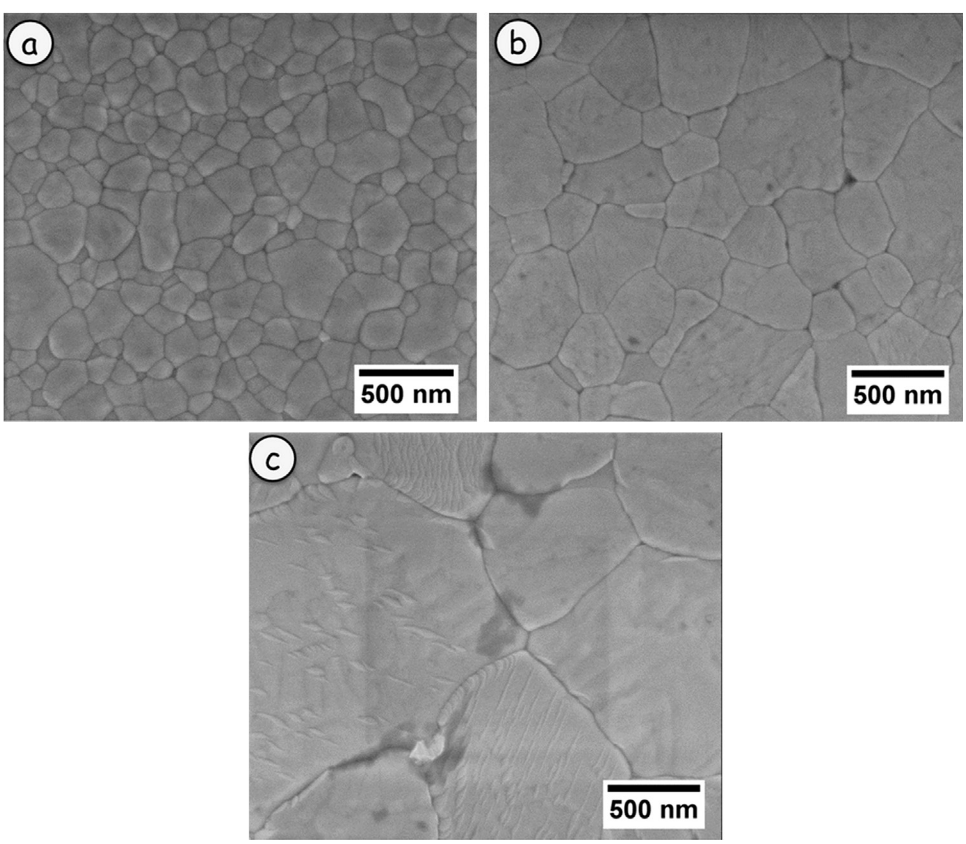

Fig. 1. SEM images showing the microstructure of POL after thermal etching at 1100 °C for 1 h: (a) SPS 1250 (b) SPS1450 and (c) SPS1600.