

Synthesis and mechanical and tribological characterization of alumina–yttria stabilized zirconia (YSZ) nanocomposites with YSZ synthesized by means of an aqueous solution–gel method or a hydrothermal route

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Abstract

In the present study, yttria stabilized zirconia (YSZ) nanoparticles, prepared by means of an aqueous solution–gel method or a hydrothermal route, are incorporated in a matrix of submicron alumina particles by wet mechanical milling. The microstructural characteristics and the mechanical and tribological properties of the obtained alumina–YSZ nanocomposites are evaluated as a function of different processing conditions like milling time, YSZ amount, sintering procedure and synthesis method of YSZ.

It is noticed that the synthesis procedure and the agglomeration degree of the YSZ nanoparticles seriously affect the densification process of the alumina–YSZ nanocomposites and also their mechanical and tribological properties.

The most probable cause for the difference is that the hydrothermally prepared YSZ nanoparticles are not as homogeneously distributed in the alumina matrix as the solution–gel prepared nanoparticles. Moreover the former nanoparticles have surface groups which release undesired gases during sintering. Thus to obtain a dense sample, nanocomposites with these nanoparticles require a higher sintering temperature and this has a negative effect on the mechanical and tribological properties of these materials.

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1. Introduction

Zirconia or yttria stabilized zirconia (YSZ) particles are frequently employed as a toughening agent for alumina [1–4]. Although the toughness of alumina is indeed enhanced by introducing zirconia particles, the improvement of toughness may, depending on crack control or transformation control, be accompanied by a decrease in strength [1]. Thus, the

optimization of all the mechanical properties is widely studied for alumina–zirconia composites [1,2,4,5].

As discussed in literature, the transformation toughening ability of zirconia is based on fracture energy absorption by the tetragonal to monoclinic zirconia phase transformation [2,3,6]. To achieve the maximum benefit of this effect, the distribution of the ZrO₂ or YSZ particles in the alumina matrix must be uniform and the size should be as small as possible [2]. All mechanical properties of such alumina–zirconia composites are affected by, e.g. the powder characteristics, the processing methods and the variation of the ZrO₂ or YSZ content.

Another driving force for the development of composites is the fact that they can possess good wear resistance and are

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hence potential candidate materials for a number of tribological applications. The friction and wear properties of composites depend on material parameters (matrix, reinforcement chemistry and volume, hardness, toughness), counterbody material, operating parameters (sliding speed, load, humidity, etc.) and are system dependent [7,8].

In this study, a commercial alumina powder, used as the matrix material, is mixed with a second phase of freshly synthesized YSZ nanoparticles, either prepared via an aqueous solution–gel method or a hydrothermal route. By freshly synthesizing YSZ nanoparticles in different ways parameters like particle size, particle size distribution and surface characteristics can be varied. It is believed that the characteristics of the nanopowders, which are influenced by, e.g. the synthesis mechanism and the starting materials, can affect the sintering and densification mechanisms of the nanocomposites. The purpose of this work is not only to detect and explain possible differences in the microstructure or in the densification mechanism of alumina–YSZ nanocomposites, but also to evaluate the possible influence of the YSZ preparation method, the sintering conditions, the YSZ amount, etc. . . on the mechanical and tribological properties of these alumina–YSZ nanocomposites.

2. Experimental procedure

2.1. Synthesis of YSZ nanoparticles by means of an aqueous solution–gel method

The following starting materials are used for the synthesis of YSZ nanoparticles via an aqueous solution–gel route: zirconium(IV) propoxide solution ($C_{12}H_{28}O_4Zr$, ~70% in propanol, Fluka), yttrium(III) oxide (Y_2O_3 ; 99.99%, Acros), acetic acid ($C_2H_4O_2$, glacial, p.a., Acros), citric acid ($C_6H_8O_7$, 99%, Aldrich), hydrogen peroxide (H_2O_2 , 35wt% in H_2O , p.a., stabilized, Acros) and ammonia (ammonium hydroxide volumetric standard; 4.98N solution in water, Aldrich). The synthesis is based on earlier work [9], but, in this study, zirconia is stabilized with yttria.

At first, precursor solutions of the separate metal ions are synthesized as shown in Fig. 1. The exact concentrations of the monometallic precursor solutions are determined by ICP-AES (Perkin-Elmer, Optima 3000). The monometallic solutions are mixed in the desired proportion, according to the ratio 3 mol% Y_2O_3 and 97 mol% ZrO_2 , and stirred for 1 h.

The thus obtained combined precursor solution is then poured out in a petri-vessel and the solvent (water) is evaporated in an air-flushed oven at 60 °C in order to allow gelation. The obtained gel is calcined in a tube furnace (heating rate 20 °C/min; dry air) at 700 °C for 30 min to form yttria stabilized ZrO_2 , further on called YSZ_{SG} .

2.2. Synthesis of YSZ nanoparticles via a hydrothermal route

The hydrothermal synthesis of YSZ nanoparticles is already described in previous work [10]. First, an aqueous solution (0.25 M) of $ZrO(NO_3)_2 \cdot xH_2O$ (zirconyl nitrate hydrate, 99.9%, Aldrich) is prepared. A suitable amount of $Y(NO_3)_3 \cdot 6H_2O$ (yttrium(III) nitrate hexahydrate, +99%, Merck) is added, according to the ratio 3 mol% Y_2O_3 and 97 mol% ZrO_2 . After stirring for 30 min, a diluted solution of ammonia (ammonium hydroxide volumetric standard; 4.98N solution in water, Aldrich) is slowly added until a pH of about 7.5 is reached. Under the present conditions, both metal ions are present as hydroxides, forming a gelly precipitate. This precipitate is filtered and repeatedly washed with water to remove remaining nitrates. The thus obtained washed precipitate is put into a Teflon-lined Parr® (120 ml) pressure-vessel together with water (70 ml), and hydrothermally treated in an oven at 200 °C for 2 h. After the hydrothermal treatment a suspension of YSZ particles (or YSZ_{HT}) is obtained.

2.3. Preparation of alumina–YSZ nanocomposites

YSZ nanoparticles, either synthesized by means of an aqueous solution–gel technique (YSZ_{SG}) or via a hydrothermal method (YSZ_{HT}), are incorporated in a matrix of commercial

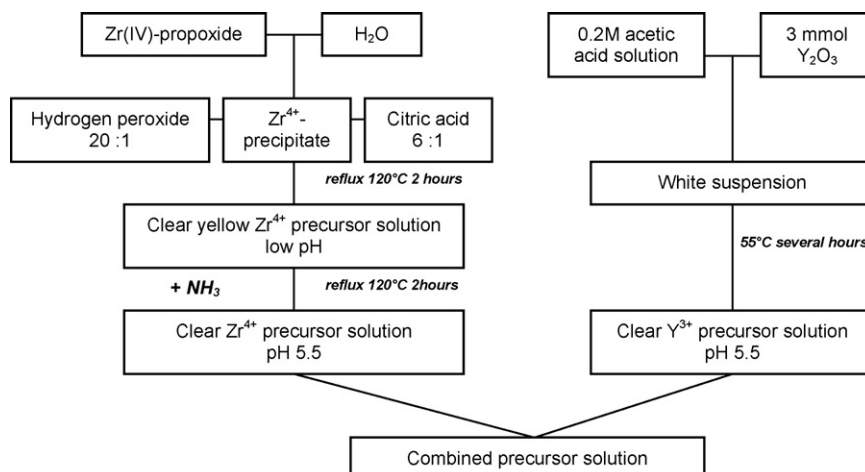


Fig. 1. Overview of the synthesis of a clear precursor solution consisting of a Zr^{4+} solution and a Y^{3+} solution.

alumina particles (AKP-30, 0.3–0.5 μm , Sumitomo Chemical Co., Japan) by planetary ball milling (Fritsch, level 8) for several hours (ranging from 1 to 8 h). The mechanical milling is performed in polyamide containers using zirconia balls and distilled water as the milling medium. Different compositions are prepared by varying the YSZ amount from 0 up to 5 vol%.

After milling, the obtained suspension is freeze dried, resulting in a dry powder in which the YSZ nanoparticles are distributed in the submicron alumina matrix.

The powder mixtures are uniaxially pressed (300 MPa) and conventionally sintered (1 h at 1400, 1500 or 1600 $^{\circ}\text{C}$; heating rate of 2 $^{\circ}\text{C}/\text{min}$ and cooling rate of 5 $^{\circ}\text{C}/\text{min}$) or hot pressed (15 min at 1400 $^{\circ}\text{C}$, 15 min at 1450 $^{\circ}\text{C}$ or 10 min at 1500 $^{\circ}\text{C}$; heating and cooling rate of 50 $^{\circ}\text{C}/\text{min}$) under a mechanical load of 28 MPa. Rectangular specimens (with dimensions of approximately 3 mm \times 4 mm \times 45 mm) are pressed for mechanical testing and large discs (30 mm diameter, 5 mm thickness) are elaborated for tribological testing. The surfaces of the nanocomposites are polished with diamond paste to a 1 μm finish before they are submitted to mechanical tests.

The bulk densities of the sintered samples are measured by the Archimedes method. The relative densities of the composite materials are calculated on the basis of the theoretical densities of 3.98 and 6.05 g/cm^3 for $\alpha\text{-Al}_2\text{O}_3$ and tetragonal YSZ, respectively.

2.4. Characterization techniques

The crystal structure of the nanoparticles is determined by means of powder X-ray diffraction (XRD) using a Siemens D-5000 diffractometer (Cu K α radiation). The particles are visualized by transmission electron microscopy (TEM) (Philips CM12) to determine their morphology and their size.

The YSZ_{HT} nanopowders are studied by means of Fourier transformed infrared spectroscopy (FTIR) (Bruker IFS 66, 2% (w/w) samples in KBr) in order to detect possible functional groups remaining from the synthesis process.

The particle size distribution of aqueous suspensions of the YSZ nanoparticles is measured by photon correlation spectroscopy (ZetaPALS with BI-MAS particle sizing option, Brookhaven Instruments Corporation). Therefore, a small amount of nanopowder is ultrasonically dispersed in water and the pH is adjusted with a diluted solution of NaOH.

The shrinkage behaviour during sintering of both the alumina matrix and the alumina–YSZ nanocomposites is followed by dilatometry (Netzsch dil 402C) at a constant heating rate of 2 $^{\circ}\text{C}/\text{min}$ up to 1650 $^{\circ}\text{C}$ in dry air.

For microstructural observation, the polished samples are thermally etched at their sintering temperature for 10 min to reveal the grain boundaries. After depositing a Pd/Pt layer, the etched surface is examined using a field emission gun scanning electron microscope (FEGSEM, type JEOL JSM-6340F). Via image analysis (KS400, C. Zeiss) the area of each grain is measured, from which the diameter of a circle of the same area is found. This way the average grain sizes of the Al_2O_3 matrix (dark grey grains in SEM pictures) and the YSZ inclusion particles (white grains) are determined. The average value is

obtained based on the analysis of at least 100 grains which were selected from several SEM micrographs of the specimen.

The elastic modulus, E , of the nanocomposites is measured on rectangular specimens by the resonance frequency method using a Grindo-Sonic (J.W. Lemmens, Elektronika, N.V.) apparatus.

The bending strength of the bars is evaluated by three-point bending on an Instron 4467 apparatus (Instron Corporation) at room temperature with a span of 20 mm and a crosshead speed of 0.1 mm/min. The fracture strength results are averaged over 3 to 4 specimens.

The hardness is measured by an indentation test using a Vickers pyramid diamond hardness testing apparatus (Zwick hardness tester). The applied load was 10 kg with a loading time of 15 s. At least five indentations are made per sample. After the diagonal length measurement, the values of the Vickers hardness (H_v) are calculated, by the following equation:

$$H_v = 1.8544 \left(\frac{P}{d^2} \right) \quad (1)$$

where H_v is Vickers hardness (kg/mm^2), P the indentation load (kg) and d the arithmetic mean of the diagonal length (mm).

The fracture toughness, K_{Ic} , is determined using the direct crack measurement method. In this procedure, the crack measurement is carried out after the indentation. This technique correlates K_{Ic} with the length of cracks emanating from the Vickers indentation corners. The K_{Ic} values are calculated according to the formula of Anstis et al. [11]:

$$K_{Ic} = 0.016 \left(\frac{E}{H_v} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (2)$$

where K_{Ic} is fracture toughness ($\text{MPa m}^{1/2}$), E the elastic modulus, H_v the Vickers hardness, P the indentation load and c the radius of the cracks (i.e. the length of the crack + the semi diagonal of the indentation).

The wear of the alumina–YSZ nanocomposites is determined by means of fretting. For the fretting tests WC–Co balls (10 mm diameter) are used and two different normal loads are evaluated (5 and 8 N). The displacement and the frequency of the movement are respectively 200 μm and 10 Hz. This tribological test is conducted in air at 23 $^{\circ}\text{C}$ with a relative humidity of 50%.

3. Results and discussion

3.1. Characterization of YSZ nanoparticles

It is well known that the tetragonal phase of zirconia gives rise to better mechanical properties than the monoclinic one [12]. Yttria is added to zirconia because it is able to stabilize the tetragonal phase. Indeed, the ZrO_2 nanoparticles stabilized with 3 mol% Y_2O_3 , which are either synthesized via an aqueous solution–gel method and calcined at 700 $^{\circ}\text{C}$ during 30 min (YSZ_{SG}) or hydrothermally synthesized at 200 $^{\circ}\text{C}$ for 2 h (YSZ_{HT}), consist completely of the tetragonal phase. In a

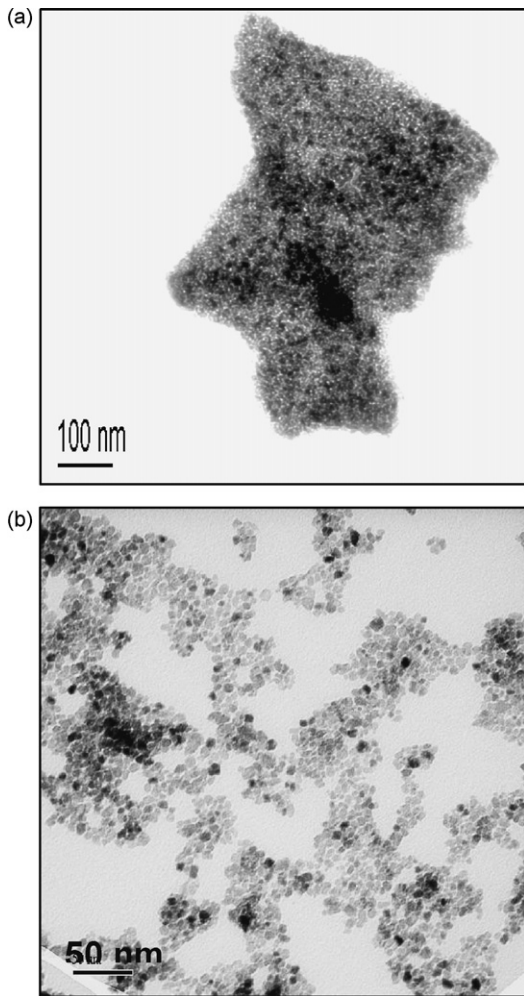


Fig. 2. (a) TEM-image of aqueous solution-gel prepared tetragonal YSZ nanoparticles, calcined at 700 °C during 30 min in dry air. (b) TEM-image of hydrothermally synthesized (200 °C during 2 h) YSZ nanoparticles.

typical TEM-image of the calcined YSZ_{SG} powder (Fig. 2a), it is seen that the sample contains densely packed agglomerates consisting of small YSZ nanocrystallites. The crystallite size is about 15 nm. On the contrary, a typical TEM-picture of the YSZ_{HT} nanoparticles (Fig. 2b), suggests that the individual nanoparticles are loosely packed. The YSZ_{HT} nanoparticles have a spherical morphology and the mean diameter of the separate crystallites is approximately 15 nm.

Both powders have also been characterized by means of photon correlation spectroscopy. The PCS study shows that the mean agglomerate diameter of YSZ_{HT} is larger than that of YSZ_{SG} at neutral and alkaline pH. Although, it has to be said that the isoelectric point of YSZ_{HT} is around a neutral pH, while the isoelectric point of YSZ_{SG} is around pH 4, as was concluded from previous zeta potential measurements [10]. So, because of the lower zeta potential in this pH region, it is plausible that the YSZ_{HT} agglomerates are larger.

When the TEM and PCS are united, one can deduce that the YSZ_{HT} agglomerates are larger but more loosely packed, compared to the YSZ_{SG} agglomerates. The YSZ_{SG} particles in the agglomerates are probably more strongly bound to each other.

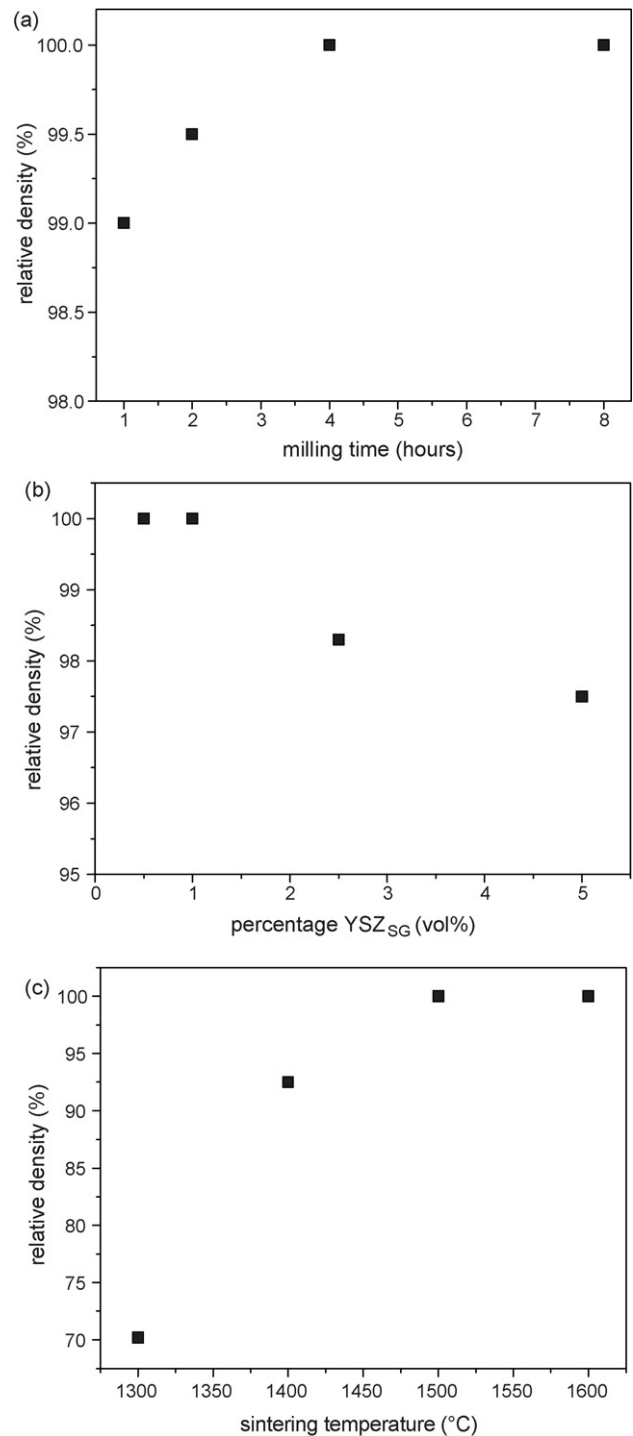


Fig. 3. (a) Relative density as a function of milling time for the alumina-YSZ nanocomposites with 1 vol% YSZ_{SG} , conventionally sintered at 1500 °C during 1 h. (b) Relative density as a function of percentage YSZ_{SG} for the alumina-YSZ nanocomposites, milled during 4 h and conventionally sintered at 1500 °C for 1 h. (c) Relative density as a function of sintering temperature for the alumina-YSZ nanocomposites with 1 vol% YSZ_{SG} , 4 h milling time and 1 h conventional sintering.

3.2. Microstructure and densification of the alumina-YSZ nanocomposites

For the fabrication of alumina based nanocomposites either YSZ_{SG} or YSZ_{HT} is incorporated in the alumina matrix. The

influence of several processing parameters on the microstructure and on the densification process of the nanocomposites as well as the difference between both kinds of alumina–YSZ nanocomposites is discussed below.

3.2.1. Influence of milling time

In Fig. 3, the relative density of conventionally sintered alumina–YSZ nanocomposites with YSZ_{SG} is plotted as a function of different parameters. To reach full density (Fig. 3a) at a sintering temperature of 1500 °C, it is found necessary to use a milling time of at least 4 h. When applying a shorter milling time (e.g. 1 h), the nanoparticles are not homogeneously distributed in the matrix and several YSZ agglomerates can be observed. Most probably the residual porosity in the YSZ agglomerates causes the lower density of the compact. Using a 4 h milling time, the YSZ particles are homogeneously distributed in the matrix (as can be seen in Fig. 6b further on) and there are relatively more YSZ particles situated on the grain boundaries of alumina grains leading to grain growth limitation of the alumina matrix (this effect will be discussed further on). Out of image analysis results, it can be concluded that a milling time of at least 4 h is necessary, not only to mix the YSZ nanoparticles homogeneously in the matrix phase, but also to deagglomerate both the matrix grains and the YSZ particles.

3.2.2. Influence of YSZ amount

When comparing the densities of composites in which different amounts of YSZ_{SG} nanoparticles are incorporated in the alumina matrix (Fig. 3b), it can be seen that the sintered density decreases when the amount of YSZ_{SG} increases. The lower density of the nanocomposites with a higher amount of YSZ_{SG} is most probably due to agglomeration and to the fact that the YSZ particles are not homogeneously distributed in the alumina matrix. Tuan et al. [1] also reported that the presence of zirconia particles inhibits the densification of the alumina matrix.

The YSZ particles are mainly located at the grain boundaries of alumina, so the microstructure of alumina is refined due to a pinning effect exerted by the YSZ particles, which could be deduced from image analysis. The decrease of the mean size of the alumina grains upon a higher percentage of YSZ_{SG} is also noticed by Tuan et al. [1], who used commercial powders.

The influence of the YSZ amount on the density of the compact is also determined for alumina–YSZ nanocomposites with YSZ_{HT} . It is immediately noticed that the overall density of the compacts is significantly lower (approximately 95% of the theoretical density for a nanocomposite with 1 vol% YSZ_{HT}) than the one of alumina–YSZ nanocomposites with YSZ_{SG} . Moreover, in the microstructure of these nanocomposites a lot of porosity is detected. An origin for this porosity could be that during the sintering process some gases are released and trapped within the densifying matrix resulting in pores. From an FTIR analysis of the YSZ_{HT} powder (Fig. 4) it can be inferred that some nitrate (used as a start product for the hydrothermal synthesis) is adsorbed on the surface of the particles (absorption bond at $\pm 1380\text{ cm}^{-1}$). To remove the adsorbed species before sintering, and hence overcome the

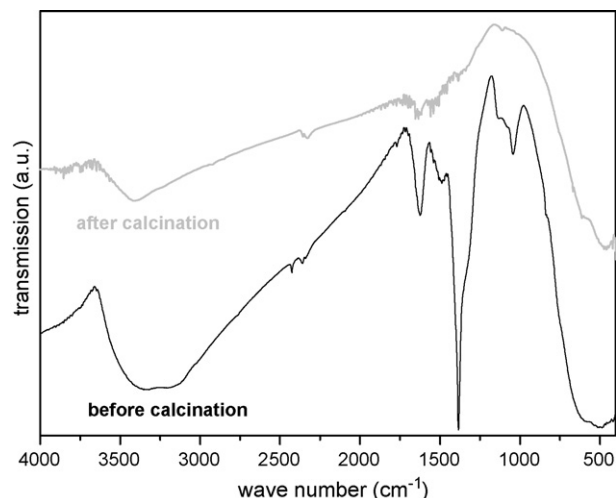


Fig. 4. FTIR spectrum of YSZ_{HT} , with or without calcination (5 min at 500 °C).

herewith related release of gases, the YSZ_{HT} nanoparticles are calcined at 500 °C during 5 min before incorporating them into the alumina matrix. The FTIR analysis in Fig. 4 shows that the nitrate impurity is removed from the surface of the YSZ particles after this calcination procedure. When these calcined YSZ_{HT} nanoparticles are subsequently incorporated in the alumina matrix, the densities of the nanocomposites are higher since there are no gases released during the sintering process. The trend of the curve showing the influence of the YSZ amount on the density is comparable to that of Fig. 3b: the density of the nanocomposite decreases as more YSZ_{HT} particles are incorporated. Although it has to be said that these nanocomposites are not completely dense (maximum 99.5 % relative density), probably because of residual impurities at the YSZ_{HT} surfaces and/or not fully deagglomerated YSZ_{HT} grains.

3.2.3. Influence of sintering temperature

The dynamic sintering curves up to 1650 °C of pure alumina, an alumina–YSZ nanocomposite with 0.5 vol% YSZ_{SG} and an alumina–YSZ nanocomposite with 0.5 vol% YSZ_{HT} (calcined at 500 °C) are presented in Fig. 5a. This dilatometer experiment proves that the densification of pure alumina starts at a lower temperature (± 1100 °C) than the alumina–YSZ nanocomposites (1250–1300 °C). Thus it can be concluded that adding YSZ nanoparticles to an alumina matrix hampers the densification process. It can also be seen that the compacts will be completely densified at 1500–1600 °C. Schehl et al. [13] have seen the same results when comparing the dynamic sintering curve of alumina and an alumina–zirconia nanocomposite with 5 wt% ZrO_2 : the densification of pure alumina starts around 1100 °C while the nanocomposite only starts to densify from 1300 °C on.

As a reference experiment, alumina–YSZ nanocomposites with 1 vol% YSZ_{SG} are conventionally sintered in a furnace for 1 h at different temperatures and each time the density is measured (Fig. 3c). Indeed, fully dense samples can be obtained at a temperature of 1500 °C by conventional sintering during 1 h. The same trend of the relative density of alumina–zirconia composites (with 15 wt% ZrO_2) is found by Rao et al. [4]: the

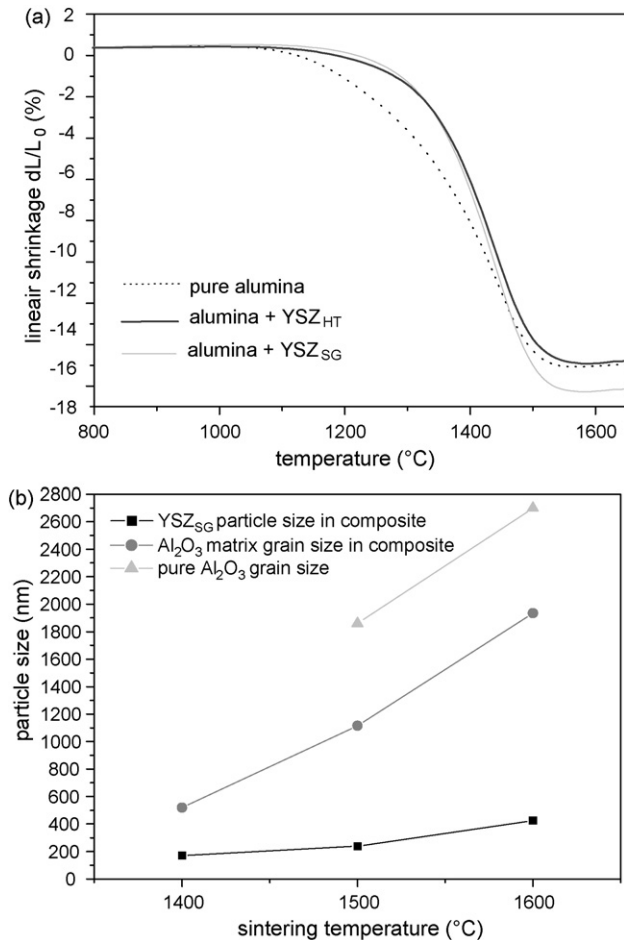


Fig. 5. (a) Dynamic sintering curve of pure alumina and alumina–YSZ nanocomposites with YSZ_{SG} or YSZ_{HT} (each time 0.5 vol% YSZ). The samples are heated up to 1650 °C in dry air with a constant heating rate of 2 °C/min. (b) Particle sizes, measured via image analysis, as a function of sintering temperature (sintering time 1 h). Image analysis is done on SEM microstructures of pure alumina or alumina–YSZ nanocomposites with 1 vol% YSZ_{SG} with a milling time of 4 h.

density increases rapidly with the sintering temperature. They obtain nearly fully dense samples (about 99% of the theoretical density) when sintering at 1450 °C for 2 h.

Via image analysis, the grain growth of both oxide phases is monitored with increasing sintering temperature and compared

with the mean grain size of pure alumina (Fig. 5b). The average size of the YSZ_{SG} nanoparticles at 1400 °C is 170 nm, whereas they have grown to 425 nm at 1600 °C. The grain growth of the matrix grains is obvious: at 1400 °C their size is about 500 nm, but after sintering at 1600 °C the mean size is almost quadrupled.

The densification process of alumina–YSZ nanocomposites with YSZ_{HT} is more difficult than for the nanocomposites with YSZ_{SG}. The former nanocomposites cannot be sintered to full density, not even at 1600 °C, and this is most likely due to the synthesis procedure of the YSZ nanoparticles. As discussed earlier, the hydrothermal route gives rise to residual impurities at the surface of the YSZ nanoparticles resulting in local pores during the sintering process.

The influence of the addition of a small amount of YSZ_{SG} nanoparticles to a submicron alumina matrix with regard to the grain growth of the alumina matrix is revealed by comparison with the microstructure of the pure alumina component, using the same submicron powder and milled and sintered at the same conditions as the nanocomposite (Fig. 6). The presence of YSZ nanoparticles impedes grain growth of the alumina matrix to a large extent. The average alumina grain size in the pure alumina component is around 1.88 μm at a sintering temperature of 1500 °C during 1 h. The average alumina grain size in the alumina–YSZ nanocomposite with 1 vol% YSZ_{SG} treated the same way, on the other hand, is approximately 1.1 μm. The refining of the matrix grain size is caused by the incorporation of the YSZ nanoparticles, which are uniformly distributed within the composite and are mostly located at the grain boundaries of alumina (Fig. 6b).

3.2.4. Reducing grain growth

Since conventional sintering unarguable leads to undesired grain growth, the alumina–YSZ nanocomposites are hot pressed in order to obtain a dense sample reducing the temperature and the time of sintering. Alumina–YSZ nanocomposites with 1 vol% YSZ_{SG} are dense after hot pressing at 1400 °C during 15 min. From the microstructure, it can be deduced that both the matrix grains and the nanoparticles remain considerably smaller than when conventionally sintered (e.g. 1 h at 1500 °C).

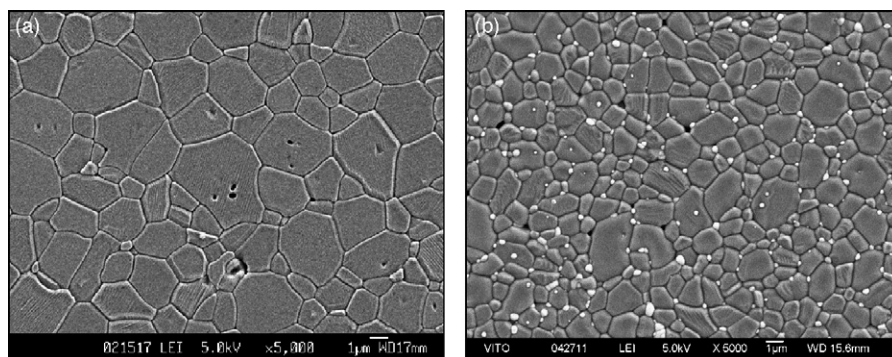


Fig. 6. Influence of YSZ incorporation on the microstructure of alumina. Both pure alumina (a) and the alumina–YSZ nanocomposite with 1 vol% YSZ_{SG} (b) are milled during 4 h and sintered at 1500 °C for 1 h.

3.3. Mechanical properties of alumina–YSZ nanocomposites

3.3.1. Elasticity modulus

The elastic modulus of pure alumina and the alumina–YSZ nanocomposites is measured because it is required for the calculation of the fracture toughness (see Eq. (2)). The elastic modulus of alumina is approximately 400 GPa (after conventional sintering at 1500 °C) and it decreases with increasing zirconia content in the nanocomposite (both for alumina–YSZ nanocomposites with YSZ_{SG} and YSZ_{HT}) to a value of about 380 GPa. The decrease is partially due to the lower elastic modulus of zirconia but probably mainly to minor microstructural defects such as local porosity and microcracks in the nanocomposites. Tuan et al. [1] and Boniecki et al. [14] also described the same phenomenon.

3.3.2. Vickers hardness

The Vickers hardness of the nanocomposite material with YSZ_{SG} as a function of the YSZ content (conventionally sintered at 1500 °C) is presented in Fig. 7a. Despite a large standard deviation, a typical evolution of the hardness can be observed: when a small volume of YSZ_{SG} is added to the

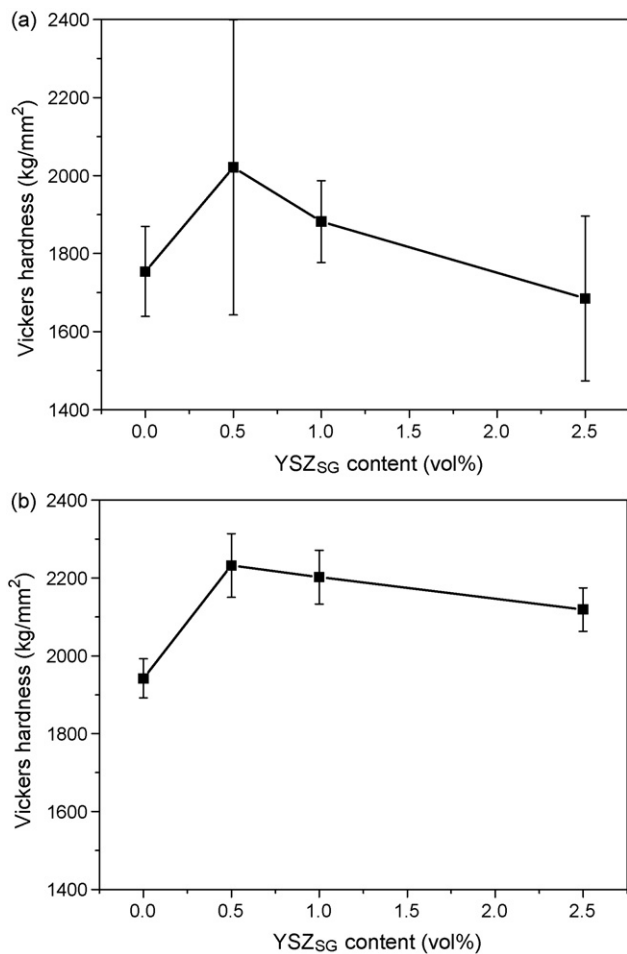


Fig. 7. Vickers hardness of alumina–YSZ nanocomposites with YSZ_{SG} as a function of YSZ content for nanocomposites conventionally sintered at 1500 °C during 1 h (a) or hot pressed at 1400 °C for 15 min (b).

alumina matrix the mean value of the hardness increases and with a higher YSZ content the mean hardness diminishes again. Also Boniecki et al. [14] observed this behaviour of the hardness as a function of the addition of increasing amounts of ZrO₂ in alumina–ZrO₂ nanocomposites. It is believed that the main cause for the rise of the hardness is the reduction of the particle size of the matrix grains in the composite when adding zirconia to the alumina matrix. In a report by Moraes et al. [15] it is seen that the hardness decreases when 5 wt% or more zirconia is added to the alumina matrix. The decrease of the hardness of composites when a considerable amount of ZrO₂ or YSZ is added to the alumina matrix is probably due to the presence of agglomerates and residual porosity.

When the alumina–YSZ mixtures are hot pressed instead of conventionally sintered, the absolute hardness of the nanocomposites is about 10% higher, however the trend of the hardness curve as a function of the YSZ content is comparable (Fig. 7b). This hardness increase is most probably due to the reduced grain growth of the alumina matrix particles caused by the hot press technique. The hardness of the

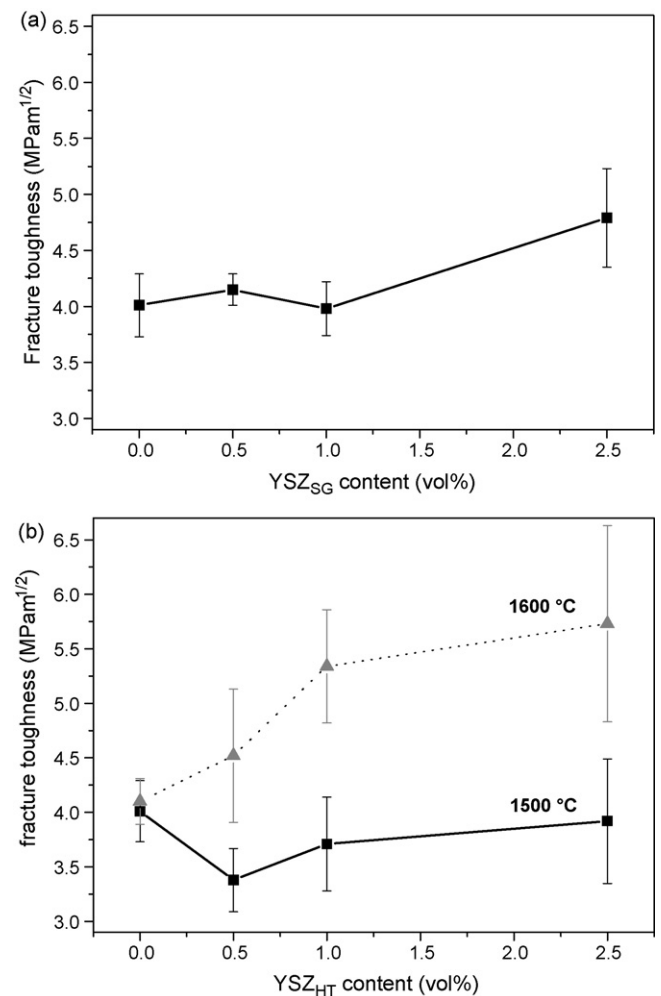


Fig. 8. (a) Fracture toughness as a function of YSZ content for the alumina–YSZ nanocomposites with YSZ_{SG}, conventionally sintered at 1500 °C during 1 h. (b) Fracture toughness as a function of YSZ content for the alumina–YSZ nanocomposites with YSZ_{HT}, conventionally sintered at 1500 °C or 1600 °C during 1 h.

nanocomposites with 1 vol% YSZ_{SG} is around 2200 kg/mm^2 , so these nanocomposites can be considered as very hard materials.

3.3.3. Fracture toughness

The YSZ addition also has a perceptible effect on the fracture toughness (Fig. 8). When an amount of 2.5 vol% YSZ_{SG} nanoparticles is added, the nanocomposite has, after conventional sintering at 1500°C , a fracture toughness of $4.8 \text{ MPa m}^{1/2}$, which is a significant increase compared with pure alumina ($K_{\text{Ic}} = 4.0 \text{ MPa m}^{1/2}$) (Fig. 8a). In Casellas et al. [3] and Moraes et al. [15] it is reported that the toughness of alumina diminishes as the grain size decreases due to the reduced load bridging capability of the smaller grain bridges. Thus, it is expected that the addition of YSZ will result in a decreased contribution of this mechanism to the total toughness of the material. However, such reduction of grain bridging extension can be compensated by the introduction of transformation toughening [1,3,15,16]. Hence, K_{Ic} changes with the addition of YSZ may be rationalized by the relative predominance of the two main acting toughening mechanisms, i.e. grain bridging and transformation toughening. Out of this study, it can be deduced that transformation toughening gets the upper hand when 2.5 vol% YSZ_{SG} is incorporated in the matrix because under these circumstances the fracture toughness obviously increases. Tuan et al. [1] and Boniecki et al. [14] also observed that the fracture toughness of alumina increases with the amount of ZrO_2 or YSZ.

The dependence of toughness on sintering temperature of alumina–YSZ nanocomposites with YSZ_{SG} is investigated (not shown). It appears that the fracture toughness is higher for the nanocomposites that are sintered at a higher temperature. This is most probably due to the larger grain size, resulting in a higher capability for grain bridging, but it is also partly attributed to transformation toughening and probably also to microcrack toughening [15].

The dependence of the sintering temperature on the fracture toughness is even more clear for alumina–YSZ nanocomposites with YSZ_{HT} (Fig. 8b). It is seen that the fracture toughness of these nanocomposites does not change very much when they are sintered at 1500°C because they are not completely dense under these circumstances. In contrast, when these nanocomposites are sintered at 1600°C , the same effect is observed as with the nanocomposites that contain YSZ_{SG} : the fracture toughness increases when the YSZ amount increases. The mean fracture toughness of the alumina–YSZ nanocomposite with 2.5 vol% YSZ_{HT} is even $5.7 \text{ MPa m}^{1/2}$ after conventionally sintering at 1600°C for 1 h.

When the nanocomposites are hot pressed instead of conventionally sintered, the curve of the fracture toughness as function of the YSZ percentage follows the same trend, but the values of the fracture toughness are substantially lower (about $3.5 \text{ MPa m}^{1/2}$ for nanocomposites with 2.5 vol% YSZ_{SG} , hot pressed at 1400°C for 15 min). The reason for that can be found in the decreased particle size and the higher hardness of such nanocomposites.

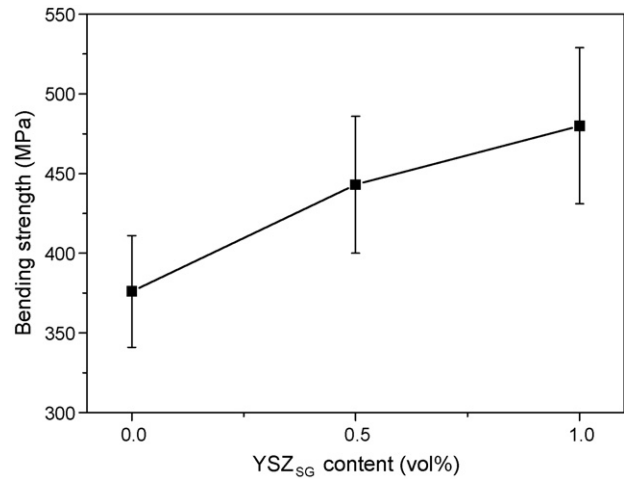


Fig. 9. Bending strength as a function of YSZ_{SG} content for the nanocomposites conventionally sintered at 1500°C during 1 h.

3.3.4. Bending strength

In Fig. 9, the average bending strength of the alumina–YSZ nanocomposites with YSZ_{SG} , conventionally sintered at 1500°C , is plotted as a function of YSZ amount. It can be noted that the mean value of the strength of the nanocomposites increases with increasing volume fraction of YSZ. The strengthening effect is partly attributed to the decrease of the matrix grain size, caused by the addition of YSZ_{SG} nanoparticles. According to Tuan et al. [1] and Spriggs et al. [16] the strength of ceramics is inversely proportional to the square root of the grain size. But it is also claimed that the microstructural refinement alone is not sufficient to account for the strength enhancement [1]. The strength also depends on the size of critical cracks and compressive stresses into the surface layer of the nanocomposites [1]. The same trend of the bending strength is published in Moraes et al. [15]. As for bending strength, the nanocomposite with 1 vol% YSZ_{SG} shows in this study the highest value with 480 MPa. This is a significant rise with respect to pure alumina, which has a bending strength of about 370 MPa with the same processing conditions.

3.4. Tribological properties of alumina–YSZ nanocomposites

The friction and wear properties of the pure alumina matrix and the alumina–YSZ nanocomposites are studied at fretting contacts against WC–Co. For all the materials, COF (coefficient of friction) values increase to a certain value in a running-in-period and then attains a steady state value. However, small variations in averaged steady state COF depending on the materials and load are observed. The experimental data obtained from tests carried out under 5 and 8 N are presented in Table 1. A slight decrease of the COF can be observed when the load of the WC–Co ball is higher. It is also seen that the nanocomposites with YSZ_{HT} have a little bit higher COF compared to the other materials. Besides that, it is noticed that the COF value of nanocomposites with 1 vol% YSZ is slightly lower than that of nanocomposites with

Table 1

Summary of the obtained averaged steady-state COF values measured while fretting against WC–Co at fretting conditions of 10 Hz frequency and 200 μm displacement

	Al ₂ O ₃	Al ₂ O ₃ + 1% YSZ _{SG}	Al ₂ O ₃ + 2.5% YSZ _{SG}	Al ₂ O ₃ + 1% YSZ _{HT}	Al ₂ O ₃ + 2.5% YSZ _{HT}
CS (1 h, 1500 °C)	0.28 0.26	0.30 0.28		0.35	
HP (15 min, 1400 °C)	0.29 0.26	0.30 0.27		0.34	
HP (15 min, 1450 °C)		0.28 0.27		0.30 0.27	
HP (10 min, 1500 °C)	0.32 0.29	0.28 0.29	0.32 0.30	0.31 0.30	0.31 0.31

The first number is the COF with a load of 5 N and the second bold number is the COF with a load of 8 N. CS: conventionally sintered, HP: hot pressed.

Table 2

Wear volume (in $10^3 \mu\text{m}^3$) of the materials measured via profilometry after the fretting test

	Al ₂ O ₃	Al ₂ O ₃ + 1% YSZ _{SG}	Al ₂ O ₃ + 2.5% YSZ _{SG}	Al ₂ O ₃ + 1% YSZ _{HT}	Al ₂ O ₃ + 2.5% YSZ _{HT}
CS (1 h, 1500 °C)	25 30	37 49		13	
HP (15 min, 1400 °C)	10 23	16 68		105	
HP (15 min, 1450 °C)		3 11		6 22	
HP (10 min, 1500 °C)	2.4 6.8	2.8 4.9	2.3 3.5	3.2 7.9	3.2 7.2

The first number is the wear volume with a fretting load of 5 N and the second bold number is the wear volume with a load of 8 N. CS: conventionally sintered, HP: hot pressed.

2.5 vol% YSZ, especially for YSZ from solution–gel origin, independently of the load. However, the differences observed in COF are very small and so should be considered with caution.

The severity of material removal from the fretting interface is assessed by measuring wear volume by means of profilometry. In Table 2 the measured wear volumes of the materials are presented. The values of Table 2 confirm that the wear volume increases with a higher fretting load, which is logical. It can also be deduced that the materials become more wear resistant when they are densified at a higher temperature. It has to be mentioned that the measured wear volumes of the alumina–YSZ nanocomposites with 1 vol% YSZ_{HT}, conventionally sintered at 1500 °C or hot pressed at 1400 °C, are not very reliable because these nanocomposites are not completely dense. The wear resistance is also to be related with the amount of porosity at the surface of the sample. Via image analysis the surface porosity is calculated and it seems that this has a big influence on the wear resistance, e.g. the surface porosity of nanocomposites with 1 vol% YSZ_{HT} hot pressed at 1400 °C is about 6% while it is less than 0.3% when hot pressed at 1450 °C with a wear volume of respectively 105×10^3 and $6 \times 10^3 \mu\text{m}^3$ at 5 N.

Another striking fact is that the nanocomposites that contain YSZ_{SG} tend to have a better wear resistance compared to the nanocomposites with YSZ_{HT}, pure alumina lying in between. There is a slight trend that the wear resistance of both types of nanocomposites would increase when the YSZ amount

increases from 1 to 2.5 vol%. However, it is to note that the measurement of such a small wear volume is very critical and so induces a relatively high uncertainty of the obtained value. The influence of the YSZ type, the YSZ concentration of nanocomposites hot pressed at 1500 °C for 10 min and the fretting load on the wear volume is plotted in Fig. 10. For the different tested materials, the wear volumes measured at a fretting load of 5 N are very similar. By increasing the load (8 N), the wear volume increase seems to become dependent on

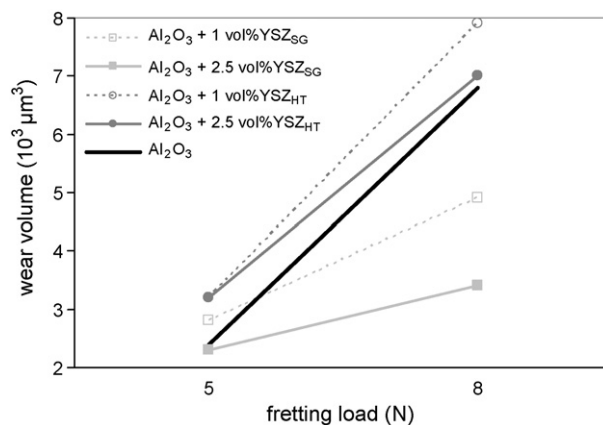


Fig. 10. Wear volume of alumina–YSZ nanocomposites as a function of the YSZ type, the YSZ concentration and the fretting load. All materials are hot pressed at 1500 °C for 10 min.

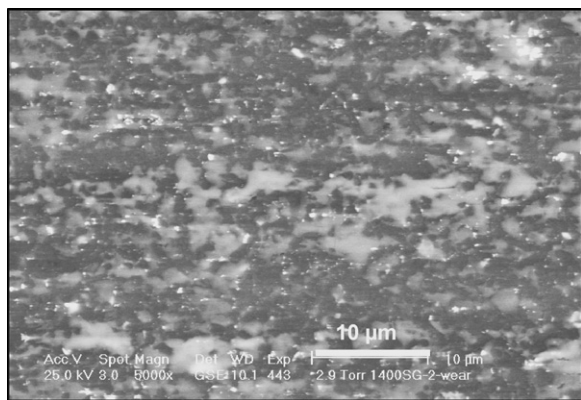


Fig. 11. Microstructure of the wear track (fretting load of 5 N) in an alumina–YSZ nanocomposite with 1 vol% YSZ_{SG}, hot pressed at 1400 °C (15 min).

the type of material. The slope of such a curve gives an idea about the change in wear resistance of a material relative to the fretting load. It can be deduced that the slope of the curve of alumina–YSZ nanocomposites with YSZ_{SG} is substantially less steep than the one of pure alumina. On the other hand, the slope of the curve of pure alumina is comparable with the one of nanocomposites that contain YSZ_{HT}. It means that the wear volume of alumina–YSZ nanocomposites with YSZ_{SG} is less influenced by the higher fretting load compared to pure alumina; the opposite is true for alumina–YSZ nanocomposites with YSZ_{HT}.

Fig. 11 shows a representative SEM picture of the wear track after the fretting test. Debris (light grey) is present in the state of a discontinuous layer on the surface of the sample with a relatively good adhesivity inside the wear track. Some loose debris is also formed at the edge of the wear track. An EDX analysis of the debris shows that it originates from the fretting ball (WC–Co). It seems that WC–Co pieces are spread out and the residual pores of the sample surface are filled up. This type of debris and debris distribution inside the wear track is observed for all the tested samples. This transfer of material from the ball to the samples is probably the cause for the similar coefficient of friction for all the materials.

The differences in wear resistance between the different samples are rather small. This can be caused by several reasons. From SEM pictures and image analysis it is seen that the surface of some materials still has porosity in various amounts, although the overall material can be considered as completely dense. As the amount of porosity has an important influence on the wear resistance, variation of this amount can generate differences in wear resistance that would overlap with the other investigated parameters (composition, sintering process) and could mask the effects of the latter. It is also noticed that the pure alumina matrix is contaminated with some ZrO₂ grains coming from the milling media. This explains why the difference in wear resistance between the pure alumina and the nanocomposites is not as big as expected. The lower wear resistance of YSZ_{HT} containing nanocomposites in comparison with YSZ_{SG} containing nanocomposites is probably caused by the fact that the YSZ_{HT} particles are not as homogeneously distributed in the

matrix as the YSZ_{SG} particles, as could be detected in SEM pictures.

4. Conclusion

By means of wet mechanical milling it is possible to homogeneously distribute a small quantity of YSZ nanoparticles, synthesized via an aqueous solution–gel method, in an alumina submicron matrix. After uniaxial pressing and conventional sintering at 1500 °C during 1 h an alumina–YSZ nanocomposite with 1 vol% YSZ_{SG} is completely dense. The incorporation of YSZ nanoparticles leads to a refinement of the alumina matrix.

The incorporation of hydrothermally synthesized YSZ nanoparticles in an alumina matrix experienced more difficulties. Most of the impurities at the surfaces of the nanoparticles, left behind after the hydrothermal synthesis, could be removed by calcination, but even then the nanocomposites were not as dense as the nanocomposites with YSZ_{SG} under the same circumstances.

So, it can be said that the characteristics of the nanopowder really influence the densification and the morphology of the nanocomposite. Not only the particle size and the particle size distribution of the nanoparticles are important parameters, but it is found that the agglomeration and the possible presence of impurities are even more important parameters which one has to keep in mind when synthesizing nanocomposites. Those characteristics are often stipulated by the synthesis procedure and the starting materials of the nanopowder.

The fact that YSZ_{HT} containing nanocomposites require a higher sintering temperature for densifying, has a by-effect on the mechanical properties of these nanocomposites. They are less hard and have a lower bending strength compared to alumina–YSZ nanocomposites with YSZ_{SG} (considered at the same sintering temperature).

Both types of nanocomposites also have a different wear resistance. When 2.5 vol% YSZ_{SG} is incorporated into alumina, the wear resistance slightly improves, whereas it does not get better when YSZ_{HT} is added. The most logical explanation for this behaviour is that the YSZ_{HT} nanoparticles are not as homogeneously distributed in the matrix compared to YSZ_{SG} and have more porous regions.

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