Coefficient of friction and wear resistance of zirconia-CNT composites

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Abstract

Conventional powder processing and spark plasma sintering (SPS) have been used to prepare composites of 3 mol. % yttria-doped tetragonal zirconia (3Y-TZP) with up to 2 wt. % multiwalled carbon nanotubes with theoretical densities between 99.4 and 97.4 %, respectively. The 3Y-TZP grain size decreases from 174 to 148 nm with the addition of carbon nanotube (CNT). The effect of CNT on the coefficient of friction (COF) was studied by scratch testing at increasing loads with a Rockwell indenter, while both the COF and the wear rate were investigated in reciprocating sliding against a zirconia ball under a load of 5 N. It is shown that in both tests the COF decreases with CNT content. However, with a Rockwell indenter under increasing loads, brittle fracture sets in at lower load when increasing CNT content. The wear resistance changes slightly for less than 1 wt. % CNT, but it increases strongly for 2 wt. % CNT under the conditions studied. The results are discussed in terms of material properties.

Keywords: nanocomposites; carbon nanotubes; zirconia; spark plasma sintering; coefficient of friction, wear resistance, scratch resistance.

1. Introduction

Tetragonal zirconia doped with 3 mol. % yttria (3Y-TZP) has an excellent combination of high hardness, strength and fracture toughness. Regarding the tribological properties, there is experimental evidence that the tribological couple 3Y-TZP /3Y-TZP has high wear rate in comparison to other ceramic pairs like alumina/alumina [1], [2]. This fact has been associated to surface fracture induced by microcracking during tetragonal (t) to monoclinic (m) phase transformation [3] and to the low thermal conductivity of zirconia [4].

It has been found that the addition of carbon nanotubes (CNT) or carbon nanofibers (CNF) to 3Y-TZP matrix lowers the friction coefficient (COF). Hvizdos et al. [5] studied the friction and wear behavior of ZrO_2 + 1.07 wt.% CNF composite and monolithic ZrO_2 using the ball (alumina)-on-disk geometry under unlubricated condition and at room temperature. They found that the COF of the composite was significantly lower compared to monolithic zirconia, but the wear rate was slightly higher. The main wear mechanism in the nanocomposite was abrasion accompanied with pull-out of the carbon nanofibers which acted in the interface as a sort of lubricating media. Recently, Kaperski et al. [6] have also reported lower COFs for 3Y-TZP/CNT composites with more than 1.86 % CNTs while for smaller contents the COF does not change significantly with respect to the matrix. A similar study of the effect of CNTs and CNFs on Si_3N_4, ZrO_2 and Al_2O_3 has shown a decrease in wear resistance in most cases, with the exception of 5 wt. % CNT [7].

The purpose of the present contribution is to reveal the effect of CNTs on the friction and wear behavior of SPSed 3Y-TZP/CNT nanocomposites by conducting scratch and wear testing.

2. Experimental

Composites with four different amounts of CNTs (0, 0.5, 1 and 2 wt. %) were prepared. The starting materials were high purity (99.9 %) zirconia powder (TZ-3YSB-E, Tosoh, Japan) with crystalline size of 36 nm and CNTs (Graphistrength C100, Arkema, France) sintered by SPS (SPS FCT HP D25I, FCT System Gmβh, Germany). The details of the processing route used and preparation of specimens are described elsewhere [8].

The average grain size was determined using the line intercept method on scanning electron microscopy (SEM) images and the density was determined by the Archimedes method.

One method used to assess the response to contact loading was by means of macro-scratch testing using a sliding Rockwell indenter with a diamond spherical tip radius of 200 μm (automatic Scratch Tester, CSM-Instruments, Switzerland). Both normal and tangential forces were recorded. Applied load ranged from 1 to 150 N over a sliding distance of 7.5 mm at a sliding speed 5 mm/min.

Tribology tests were performed on an automatic tribometer (Wazau TRM1000, Germany) in reciprocating sliding conditions, using ball on disc geometry, at ambient temperature and pressure. A zirconia ball with 10 mm diameter was used as a counterpart. All the tests were done at a constant normal load of 5 N and by keeping the sliding velocity of 300 rpm with 4 mm stroke. The total sliding distance was 100 m. At least four tests were performed for each condition and data represent their average. The tribology tests were performed in reciprocating dry sliding conditions.

The COF was calculated by taking the ratio of the tangential and normal forces and it is reported versus the sliding distance. The volume removed was measured using a stylus profilometer where a hundred profiles along the width of the track were recorded. The wear rate, W, was calculated in terms of the volume loss divided per distance and applied load. The worn surface morphology of the wear tracks was analyzed using a Scanning Electron Microscope (SEM) to examine the wear behaviour.

3. Results

Main properties of the composites together with code designation are given in Table 1. The CNTs diminish the final density from 99.4 % for 3Y-TZP to 97.4 % for 2 wt. % CNT. Regarding the grain size, SPSed ZM0 has an average size (177 nm) which is about half of that of 3Y-TZP (330 nm) conventionally sintered at 1450 °C [9]. In the composites, the average grain size of the zirconia matrix decreases slightly with CNT content down to 148 nm for ZM2.

The Vickers indentation response in terms of hardness and indentation fracture toughness has been studied elsewhere [10]. Hardness diminishes and indentation fracture toughness increases with CNT content making the material more tolerant to damage by contact loading (Table 1). However, we have recently shown that the true fracture toughness measured in SENB specimens with a very sharp notch induced by ultra-short laser pulses does not change with CNT content [10], [11].

The results of the COF from macro-scratch testing with a sliding Rockwell indenter at increasing loads are shown in Fig. 1. It is clearly seen that below about 40 N the COF is clearly smaller for the composites with higher CNT content; beyond a critical load, about 120, 95 and 80 N for ZM0.5, ZM1 and ZM2 respectively, it shows strong oscillations except for ZM0.

SEM pictures of the macro-scratch track are shown in Fig. 2 where the load is increasing from right to left. It is observed that brittle fracture debris are hardly observed in ZM0 near the scratch tip, while for the composites ZM1 and ZM2 brittle fracture is present at the tip as well as along the track in the region above the critical load. The beginning of brittle fracture is located at distances from the scratch tip of about 2.75 mm (80 N, for ZM2) and of 3.5 mm (95 N, for ZM1), which are the places where oscillations in the COF start to appear as can be seen in Fig. 1.

Table 1: Main properties of the composites studied.

Specimen code	Composition	E_{Berk}(GPa)	H_{Berk}(GPa)	$(E_{Berk}/H)^{1/2}$	K_{Ic}^{*} (MPa√m)	K_{Ic} (MPa√m)
ZM0	3Y-TZP	263 ± 5	20.0 ± 0.4	4.30±0.02	3.57±0.09	2.67
ZM0.5	3Y-TZP+0.5 wt.% CNT	224 ± 4	15.9 ± 0.4	4.15±0.02	4.02±0.05	2.71
ZM1	3Y-TZP+1 wt.% CNT	215 ± 7	15.9 ± 0.7	4.36±0.02	4.56±0.08	2.76
ZM2	3Y-TZP+2 wt.% CNT	181 ± 6	12.7 ± 0.7	4.36±0.02	4.97±0.06	2.82

*Indentation method of Anstis *et al.* [12]

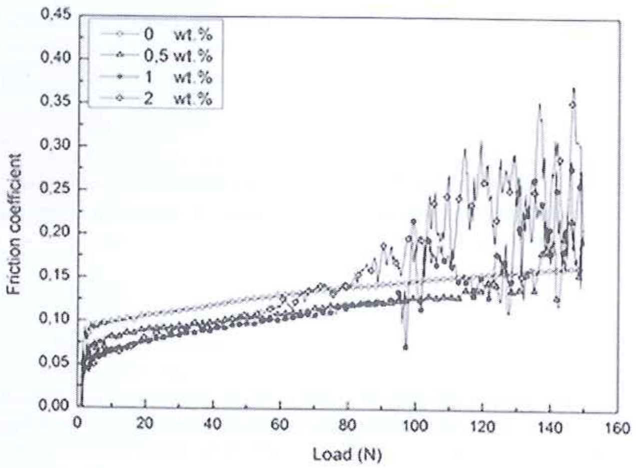

Fig. 1: COF of the macro-scratch test under an incremental load (1-150 N)

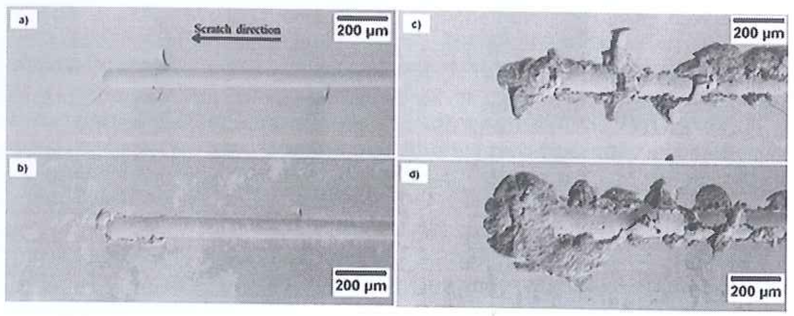

Fig. 2: Tracks of the Rockwell scratch tests: a) ZM0; b) ZM0.5; c) ZM1; d) ZM2.

During reciprocating sliding conditions, where a ball on disc geometry and zirconia ball as a counterpart were used, the COF increases with the sliding distance as can be seen in Fig. 3a). On the first 20 m sliding distance, the average value of the COF for all compositions is ~ 0.45 and the differences on this range among all composites are small, with the exception of the 3Y-TZP matrix for which the COF increases from 0.36 to 0.54. With further sliding, during the next 30 meters, there is a strong raise in the COF for all compositions, followed by a slight increase afterwards. It is remarkable that after 100 meters sliding distance, the smaller COF corresponds to ZM2 (the highest CNT wt. %) as can be also appreciated in Fig. 3b, where the average values of the COFs are plotted for different sliding distance intervals. It is concluded that the COFs are ranged between 0.85 and 0.57 for ZM0 and ZM2 respectively. In addition, the COF of conventionally sintered 3Y-TZP (~330 nm grain size) is larger than the COF of ZM0 with lower grain size.

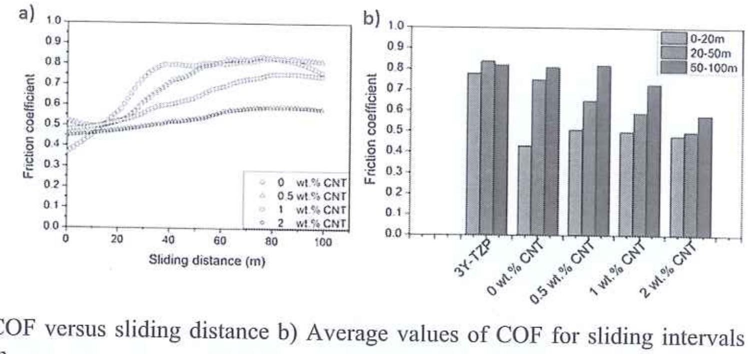

Fig. 3: a) COF versus sliding distance b) Average values of COF for sliding intervals in terms of composition.

With respect to the wear rate, the effect of CNTs is clearly visible in the measured track profiles at half-track length where more material is removed (Fig. 4a)). Once the wear rate is calculated and plotted (Fig. 4b) it is observed that the wear rate for ZM0.5 and ZM1 very slightly increase with respect to ZM0 while a strong decrease takes place for ZM2.

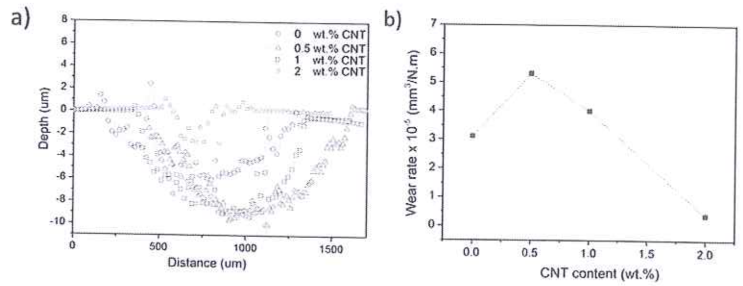

Fig. 4: a) Track profiles measured at half-track length b) Wear rate of the studied composites.

The appearance of the surface of the track in the SEM at higher magnification is shown in Fig. 5. The main difference observed is the presence of grain pull out and debris of ZM0 while the addition of MWNTs results in a smeared carbon based-transferred film. The carbon film is more apparent along the wear track of ZM2 where there is a high carbon content. The presence of such a film was reported before by Hvizdos et al. [5] and Kasperski et al.[6] where it was explained that it permits easy shear and provides a lubricating effect that lowers the friction coefficient.

4. Discussion

Regarding the COF in contact with zirconia, the main results can be summarized as that the COF for ZM0 is lower than for conventionally 3Y-TZP under the currently studied load. Similarly, the addition of CNT diminishes the COF of ZM0. The COF values obtained for the composites are in the range 0.52 and 0.73 as compared to 0.45-0.6 [6] and to ~0.4-0.5 for 3Y-TZP-1.07 % CNF [5] where for both cases an alumina balls was used as a counterpart. Concerning, the different analysed sliding distances, the COF of ZM1 after 25 m sliding is still far away from reaching a saturation value. It is also observed that there is a progressive deterioration of the material that increases the COF with sliding distance, except for compositions ZM0 where no CNT are present and for ZM2 where a certain percolation is reached. This may be related to a decrease in abrasion by an increase in thermal conductivity with percolation and/or the rate of formation of a tribo-film.

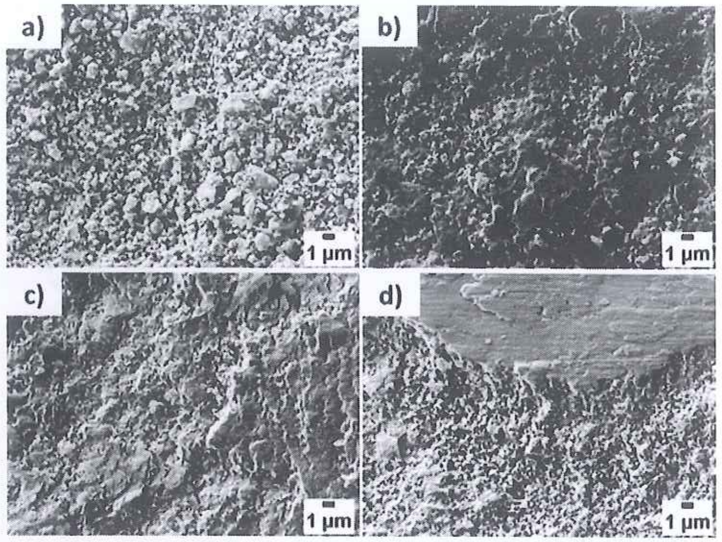

Fig. 5: SEM images of the wear tracks for a) ZM0 b) ZM0.5 c) ZM1 d) ZM2.

During the scratch test, the load at which the COF increases with CNT content coincides with the appearance of brittle fracture on the scratch track. The lower value of COF for the composite with higher CNT content may be understood by the lubricating effect of CNTs trapped just below the tip of the indenter, but no carbon tribofilm has been detected.

It is interestingly seen that the composite with the lowest resistance to fracture in the macroscopic scratch test (ZM2) has the highest resistant to cracking under Vickers static indentation [10]. This may be associated to the high tensile stress perpendicular to the surface generated behind the scratch test while in Vickers indentation the tensile stresses near the surface at the contact are small. Therefore, the tensile stress easily propagates the lateral cracks preferably formed by the presence of more CNT agglomerates in the highest composition.

Hvizdos et al. [5] also detected a small increase in the wear rate by using an alumina ball as counterpart when adding 1 wt. % CNF to zirconia, however, the absolute values of the wear rate were lower than in the present investigation.

The decrease in wear rate for ZM2 under the conditions studied here has not been reported before in 3Y-TZP-CNT composites. The reason for this behavior cannot be associated to an increase in

mechanical properties of the composites since the fracture toughness measured by the SEVNB beam technique does not suffer significant changes with the addition of CNTs [10]. Also hardness and elastic modulus decrease with increasing CNT content, and their ratio is practically constant if the expression developed by Evans for W is considered [11]:

$$W = a\frac{F^{1/8}}{K_{Ic}^{1/2}H^{5/8}}\left(\frac{E}{H}\right)^{4/5} \qquad \text{Equation (1)}$$

where F is the applied load, K_{Ic} the fracture toughness, H the hardness, a is a constant independent of material type. As E/H and K_{Ic} practically do not change and H decreases with increasing CNTs, one should expect a higher W in the composites, which is opposite to the present findings. Therefore, the reason for this behavior should lie in the change in other parameters that may affect the wear behaviour. One of these factors is the higher thermal conductivity of the material for ZM2 since the percolation value is reached and higher amount of heat transfer is possible, giving a smaller tendency to *t-m* transformation also because of the smaller grain size and the existence to a large amount of tribo-film.

5. Conclusion

From the study of the COF and wear of spark plasma sintered 3Y-TZP with up to 2 wt. % MWNTs it is concluded that these composites have lower COF and similar or higher wear resistance than 3Y-TZP SPSed under the same conditions.

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Session 4

Processing