Effect of ageing on scratch resistance of 3Y-TZP

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Abstract

Effect of low-temperature degradation of 3Y-TZP ceramics (polycrystalline zirconia stabilized by 3 mol% of yttria) on dry sliding wear behaviour and contact damage resistance has been studied applying scratch testing technique. Scratching by sharp (Vickers) and blunt (spherical) indenters was performed. Friction properties and damage mechanisms have been investigated for various degrees of hydrothermal ageing, i.e. for different grain sizes and crystallography, and for different thickness of the degraded surface layer. The 10 hours degradation did not lower the scratch resistance but led to intensified fine debris production. The contact damage micromechanisms corresponding to various degrees of degradation have been studied in detail by interferometry and microscopy. The onset of plastic damage, catastrophic cracking, grain pull-out, spalling and chipping due to the degraded layer debonding have been identified. It was shown that 60 hours long ageing significantly degraded the surface damage resistance of the material. The critical load leading to such material's surface layer destruction was found to be around 80 N.

Key words: ceramics, biomaterials, oxides, wear, grain growth

1. Introduction

Tetragonal zirconia ceramics doped with various concentrations of yttria is a promising material for a number of industrial and biomedical applications thanks to its relatively high fracture toughness when compared to other ceramics [1]. This property is a consequence of its crystallographic structure. The tetragonal phase is at room temperature a metastable one and it is usually stabilized by dopants like magnesia, ceria, and yttria. Such stabilized tetragonal zirconia grains can transform back to monoclinic phase in presence of stresses, connected to external loads, cracking and/or damage. The transformation is accompanied by 4 % increase of volume [2]. Thus the transformed grains expand and introduce compressive stresses to surrounding microstructure and can also cause closing of propagating cracks.

The main concerns in fully tetragonal zirconia are connected to durability and reliability issues because over time of service in presence of humidity, the tetragonal zirconia grains are prone to spontaneous transformation to the stable, monoclinic phase [3]. This ageing is accompanied by embrittlement, microcracking and loss of structural integrity and reliability. The process is called hydrothermal or low temperature degradation (LTD) [4] and it has been a major problem for biomedical applications such as hip prostheses [5]. Therefore, thorough knowledge of conditions leading to LTD is of great interest and importance.

According to Guo et al. [6] the environmentally driven LTD occurs by the removal of oxygen vacancies by water near the surface until the concentration is reduced to the extent that the tetragonal phase is not longer stable. The degradation begins in isolated grains at the surface, then it spreads and with time it continues into the bulk of the piece, forming a growing surface layer of degraded material.

The effects of LTD on the near surface mechanical properties of 3Y-TZP have been studied mostly in

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terms of hardness response to nanoindentation of materials with different grain sizes and degradation times [7–10]. There, the effects of depth and microstructure of the surface degraded layer on microcracking, elastic modulus and hardness have been studied. The indentation studies, however, cannot be fully generalized for understanding the impact damage behaviour of pieces in conditions of scratching and wear.

The objective of this work is to study the impact damage resistance of near surface layer of biomedically graded 3Y-TZP in terms of scratch behaviour in correlation with various degrees of LTD.

2. Experimental material

The experimental material was zirconia stabilized by 3 mol% yttria (3Y-TZP). It was prepared using a commercial powder TZ-3Y-SB, by TOSOH Corp. The powder was cold isostatically pressed at 200 MPa during 3–5 minutes, then pressurelessly sintered at 1450 ℃ for 2 hours in air. The samples were cut by diamond saw, then ground and polished with 3 μm diamond paste and later with colloidal silica to ensure roughness lower than 0.02 μm *Ra*. Finally, they were annealed at 1300 ℃ for 1 hour in air. This material is hereafter denoted as the as-sintered (AS). Some samples were subsequently subjected to the hydrothermal degradation, which was performed in autoclave, at 131 ℃, 100 % steam atmosphere at 0.2 MPa of pressure during 10 and 60 hours, respectively, and these specimens will be referred to as D10H and D60H, respectively. Chevalier et al. [11] found that 1 h of this treatment corresponded roughly to 4 years in body conditions. If this is the case, then D10H corresponds to 40 years of use, which is probably more than would be necessary for a typical biomedical implant.

3. Experimental method

Scratch testing was carried out using an Automatic Scratch Tester, CSEM-REVETEST, Neuchatel (Switzerland). Sharp (Vickers) and blunt (spherical) indenters were used. To study very high-localized stresses scratches by Vickers diamond indenter at different constant loads (3 N, 5 N and 10 N) were made over 8 mm sliding distance, at sliding speed of 5 mm min^{-1} in air. In order to mimic typical (blunt) contact wear a diamond spherical indenter with radius of 200 μm was used. In this case, the scratches were made in progressive loading mode at initial load of 20 N, which monotonically increased up to 130 N over 6 mm sliding distance at sliding speed of 5 mm min^{-1}. In all experiments both normal and tangential forces as well as the acoustic emission signal were measured and recorded.

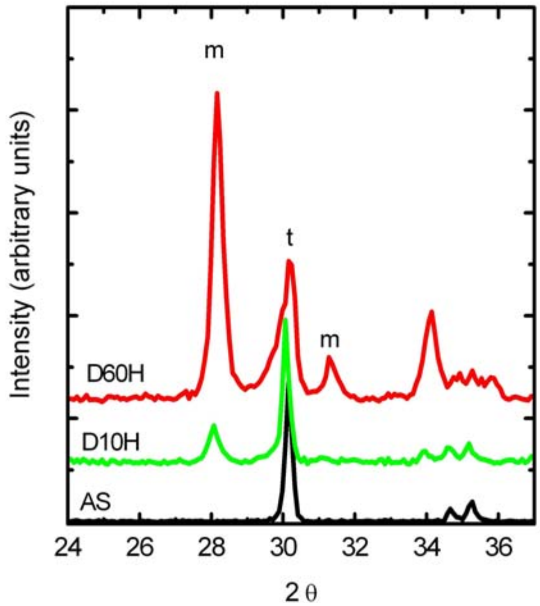

Fig. 1. XRD patterns of 3Y-TZP after sintering and ageing.

3D images of the scratch grooves were constructed and measured with an interferometer Wyko NT9300 (Veeco Instruments) in order to obtain an estimate of the volume removed per unit of sliding distance. To identify the surface response to impact and the damage mechanisms the character of the tested surface was investigated using scanning electron microscopy.

4. Results and discussion

Microstructure of the experimental materials has been studied in detail elsewhere [12]. The character and thickness of the degraded layer depend strongly on the initial material. X-ray diffraction patterns obtained for three materials (AS, 10H, 60H) are shown in Fig. 1. It is clear that AS sample had full tetragonal structure after sintering. Monoclinic phase is observed in both 10H and 60H. The amount of monoclinic varies with the time of ageing. The initial material (AS) had a fine-grained microstructure (grain size ∼ 300 nm) with density > 99 % of the theoretical one. It was shown that the degradation produced a surface layer with high amount of monoclinic Y-TZP whose thickness increased with time. The kinetics of its growth depends strongly on the initial material. In general, with larger initial grains and with presence of some cubic grains the thickening of the degraded layer is faster [10]. From nanoindentation measurements and from its measurement after long times, it was suggested that it grows approximately linearly [10]. In the present case, the thickness of the layer is of the order of a micron for D10H and about 12 μm for D60H [12].

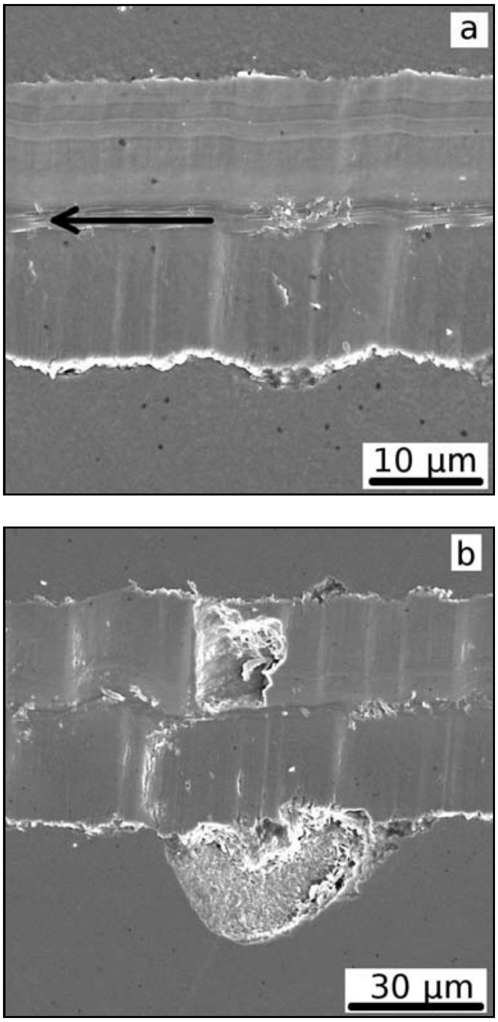

Fig. 2. Scratch grooves in AS: (a) 3 N load, (b) 10 N load. The arrow indicates the scratch direction (movement of the indenter tip).

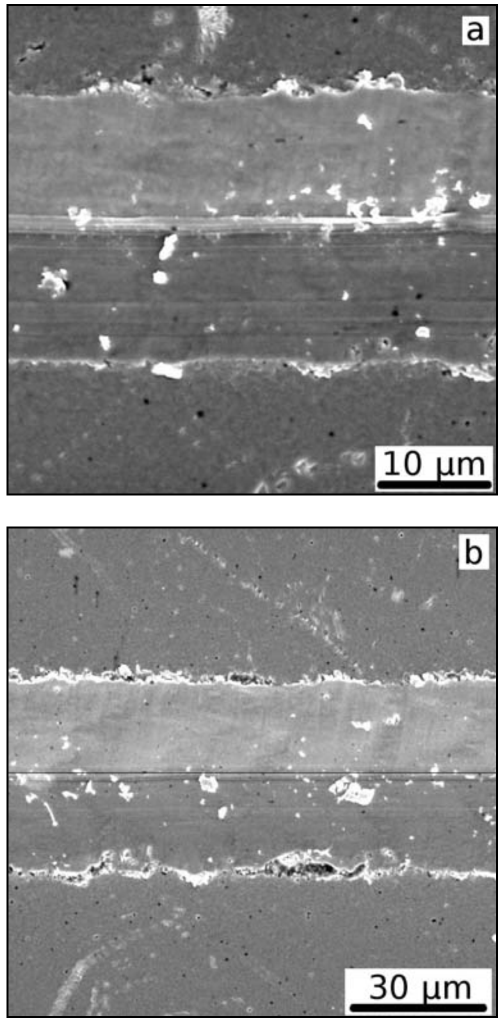

Fig. 3. Scratch grooves in D10H: (a) 3 N load, (b) 10 N load.

However, when the layer becomes thicker, one can observe a gradient in the amount of monoclinic phase at the boundary between the degraded layer and the bulk, so there is not a sharp transition.

4.1. Scratching by sharp indenter

Figures 2–4 show the Vickers scratch grooves in all experimental materials made by 3 N and 10 N normal loads. The scratch direction (direction of the indenter tip movement) in all photographs was the same as shown by the arrow in Fig. 2a (from right to left).

The AS material under 3 N deforms smoothly, only continuous plastic deformation is appreciable, with little pile-up around the groove edges. It exhibited similar behaviour under 5 N. With 10 N loading the groove was still generally smooth, but occasionally also some brittle fracture accompanied by large pull-out was observed, as it is shown in Fig. 2b. This is probably a result of the deformation energy being released at some larger technological defect that acted as a stress concentrator. Sometimes also large flakes of the material outside the groove chipped out (Fig. 2b). These were caused by initially invisible subsurface lateral cracks that grew sideways until they reached the free surface. They can not be associated with interlayer debonding, as in this material no degraded layer was present. This sort of chipping is frequently observed in indentation of very brittle materials.

The material degraded for 10 hours (D10H) showed slightly different picture. Generally, its scratch resistance was comparable to that of the AS but even under low loads an appreciable amount of debris (individual grains) was observed inside the scratch grooves (white particles in Fig. 3). Apart from this, however, the scratch profile geometry was practically identical to that of the non-degraded specimen and no significant detrimental effect of the degradation was visible. Moreover, even at the highest load the scratching was accompanied only by debris production and moder-

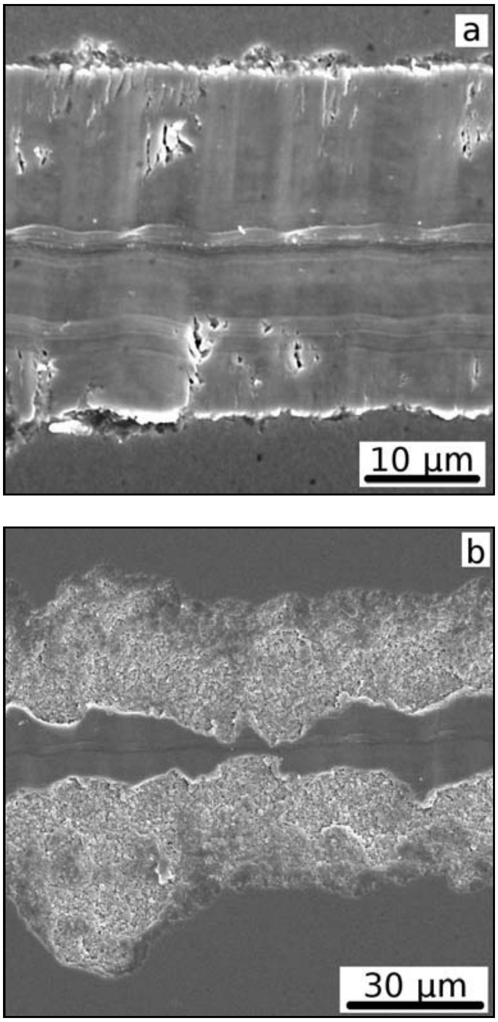

Fig. 4. Scratch grooves in D60H: (a) 3 N load, (b) 10 N load.

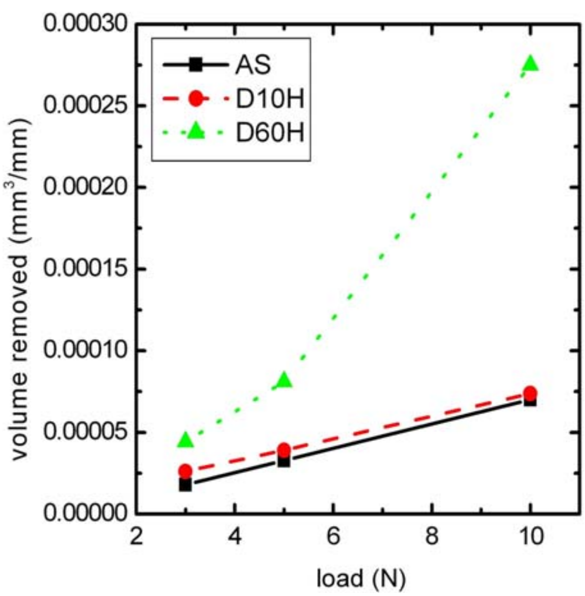

Fig. 5. Volume removed by scratching at various loads.

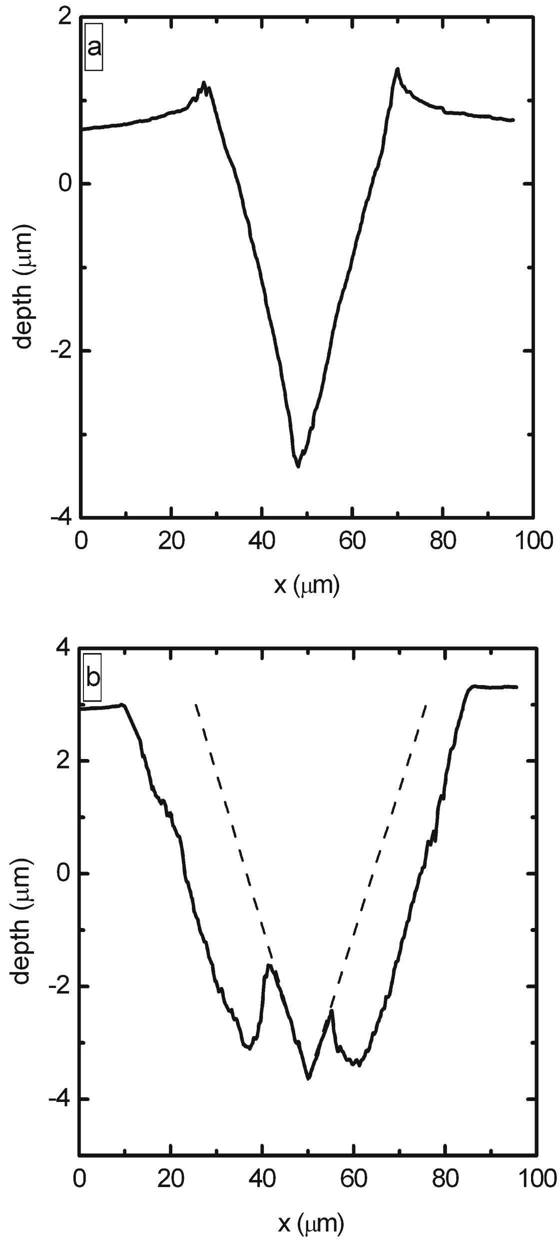

Fig. 6. The profile of the scratch groove: (a) D10H, 10 N load, (b) D60H, 10 N load. The dotted lines illustrate the original indenter profile.

ate grain pull-out from the groove edges (Fig. 3b). No lateral cracking was observed. It seems that the microcracking, which produces the debris, dissipates the excess of deformation energy and releases the stress. In this respect it seems that little superficial degradation might have beneficial effect on the damage resistance. However, one has to keep in mind that at repeated wearing the situation would be very different as the debris would most probably act as an abrasive and would contribute to more damage.

The material degraded for 60 hours (D60H) had in every respect the lowest damage tolerance. Even at

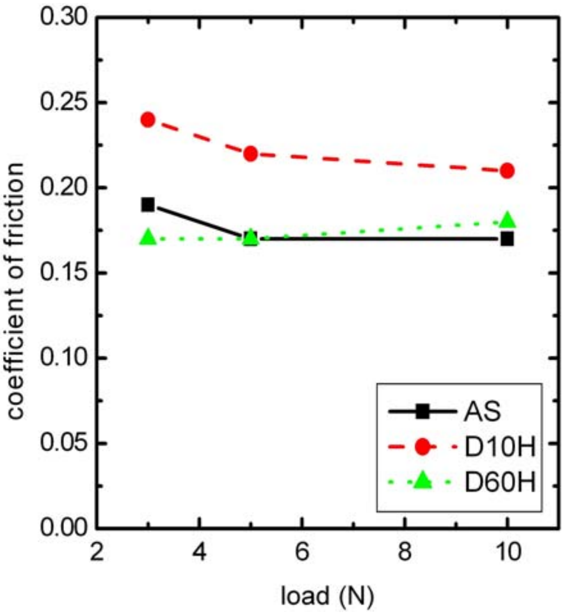

Fig. 7. Coefficient of friction for scratching by Vickers indenter as a function of load.

3 N load the depth (and width) of scratch was clearly greater than in the other two materials (Fig. 4a). The plastic deformation was accompanied by creation of relatively large cracks perpendicular to the sliding direction in the outer (upper) part of the groove. These cracks are related to the damage of the uppermost, most brittle part of the degraded, monoclinic--rich, layer. Profilometry showed that the cracking here reached down to about 2 μm depth. With increasing load intensity of damage increased, at 5 N the volume removal was much more intense than in the other two materials (Fig. 5) due to frequent surface flaking and spalling. Loading by 10 N produced additional damage mechanisms – massive chipping out of the groove walls. Figure 4b shows that in this case only the central part, close to the indenter tip, remained. This again is analogous to the indentation of brittle materials, but here it is probably connected to the presence of the degraded layer and to the interlayer debonding between the surface (degraded monoclinic ZrO_2) and "substrate" (healthy tetragonal ZrO_2). Clearly, the volume removal had intensified dramatically, as it is also illustrated by the plot in Fig. 5.

Figure 6a,b shows the profiles of the two degraded materials scratched by 10 N load. It illustrates the difference between D60H and the other two materials. The extent of the chipping of the material outside the indenter area is clearly visible.

Figure 7 shows the coefficient of friction measured for different normal loads. The increase of load had very little effect on the friction coefficient, as was noted also in literature [13]. The D10H exhibited consistently slightly higher friction, which might be related to the presence of debris in the trough. This higher friction, however, did not lead to higher damage. On the other hand, the D60H had the friction coefficient equal to that of AS despite much greater surface damage.

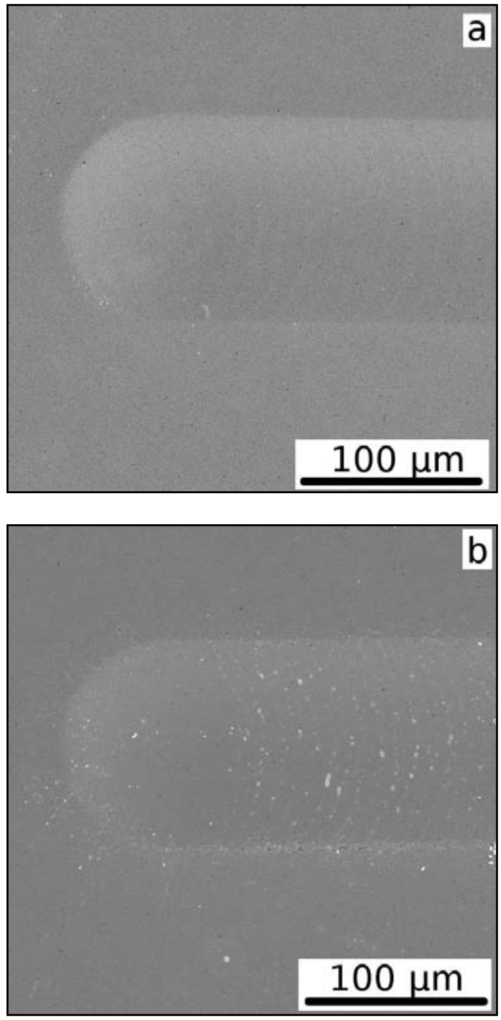

Fig. 8. End of the scratch marks made by spherical indenter by load up to 130 N. (a) AS, (b) D10H, pull-out of individual grains around ring cracks and groove edges.

4.2. Scratching by spherical indenter

Even though the normal loads reached much higher values (from 20 N up to 130 N) the scratch behaviour is in these cases significantly different from that under Vickers indenter as contact area is much larger and stress concentrations generally do not reach very high levels. Figures 8 and 9 show the micrographs of the end of scratches for all three materials, i.e. the places where the applied load reached 130 N. Again, in the materials AS and D10H only plastic deformation can be appreciated. In the case of AS (Fig. 8a) whole

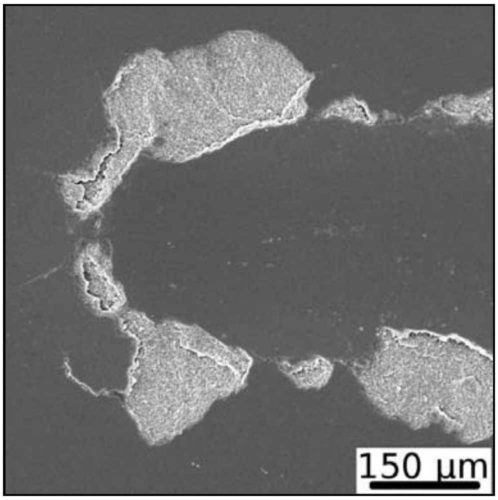

Fig. 9. Scratching of material D60H by spherical indenter. Intense chipping out and microfracturing of the groove edges.

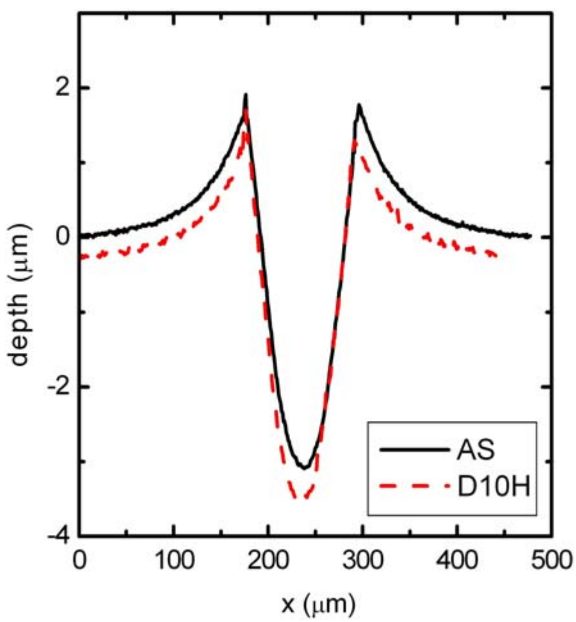

Fig. 10. Profile of the scratch produced by spherical indenter – material AS and D10H. Effect of piling-up around the groove visible.

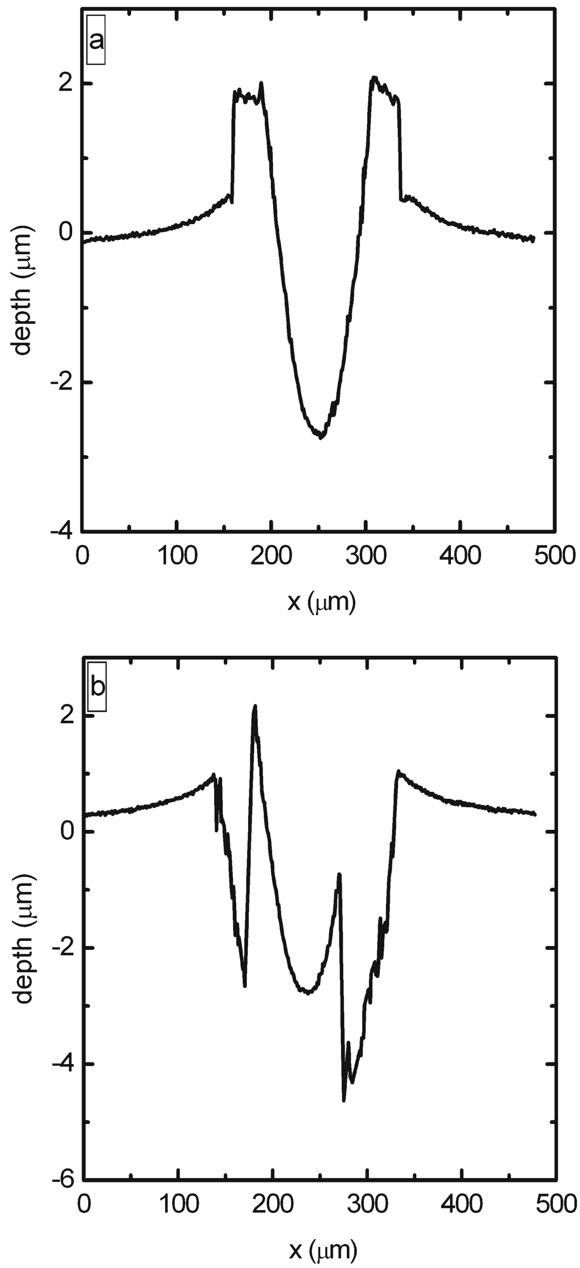

Fig. 11. Profiles of the scratch produced by spherical indenter – material D60H – corresponding to various places in Fig. 8. First, lateral cracking raises the surface layer (a), subsequently its chipping out follows (b).

groove is very smooth with only very faint markings inside the groove hinting the initiation of Hertzian ring cracks, similarly as observed in [14]. In D10H (Fig. 8b) the ring crack formation is more visible because it is accompanied by grain pull-out. Also, the grain pull-out is appreciable around the edges of the scratch, i.e. in places with highest surface tensile stresses. This corresponds to the behaviour observed in D10H under Vickers indenter. The geometry of the grooves observed for these two materials is illustrated in Fig. 10. For both cases the profile is virtually identical, elliptical in shape, accompanied by smooth pile-up around the edges.

The nature of damage of the material degraded for 60 hours differs from the former two samples. Again, at lower loads, only plastic deformation and very little grain pullout is observed along the groove edges. But when the load reaches around 75–80 N, first, rising of the groove edges due to subsurface lateral cracking can be seen, as illustrated by Fig. 11a. Later severe

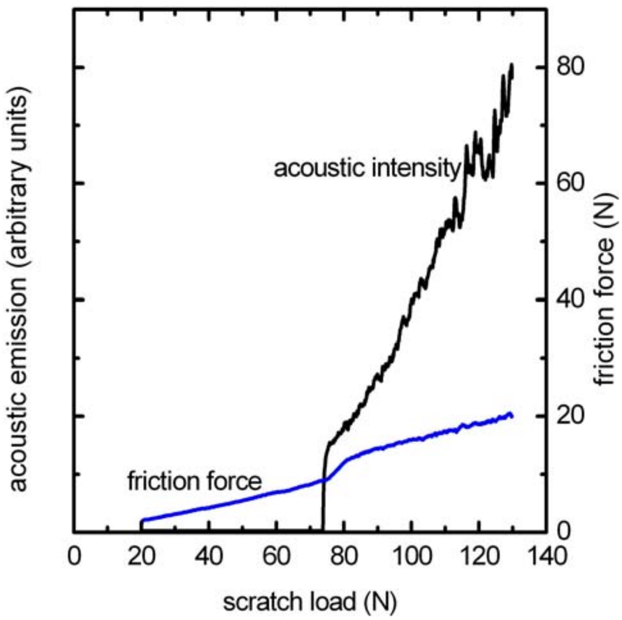

Fig. 12. Acoustic signal intensity and frictional force as a function of increasing scratch load, material D60H.

chipping associated with grain boundary microfracture (Fig. 9) is observed. With further increase of load the material removal continued to intensify and depth of the chipping out even exceeded the depth of the scratch groove (Fig. 11b). Acoustic emission measurements also found a sharp increase in acoustic signal around 75–80 N load, corresponding to increase in measured frictional force (Fig. 12). This corroborates that under applied load/geometry conditions such loads are critical for material removal in D60H samples, which is in agreement with findings of Lee [15].

5. Conclusions

Contact damage resistance of zirconia ceramics degraded to various degrees was studied by scratch testing. It was observed to depend on a degree of low temperature degradation. The results show that the 10 hours long degradation (corresponding to 40 years usage *in vivo*) might not be too detrimental, it caused more debris but neither massive pull-out nor lateral cracking was observed. The debris production even seemed to help releasing the stress energy. However, this debris could cause problems in repeated contact, where it can act as an abrasive. The 60 hour long ageing significantly decreased the surface resistance, the monoclinic surface layer started to crack at low loads and at 10 N extensive interlayer debonding and surface removal took place. Similar comparison can be made for scratching by spherical indenter, where the AS and D10H materials up to 130 N load underwent only limited plastic deformation, whereas D60H at loads above 80 N suffered catastrophic damage and surface layer delamination.

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References

[1] GARVIE, R. C.—HANNINK, R. H. J.—PASCOE, R. T.: Nature, *258*, 1975, p. 703.
[2] GREEN, J.—HANNINK, R. H. J.—SWAIN, M. V.: Transformation Toughening of Ceramics. Boca Raton (Florida), CRC Press Inc. 1989.
[3] LAWSON, S.: J. Eur. Ceram. Soc., *15*, 1995, p. 485.
[4] CHEVALIER, J.—GREMILLARD, L.—DEVILLE, S.: Annu. Rev. Mater. Res., *37*, 2007, p. 1.
[5] CHEVALIER, J.: Biomaterials, *27*, 2006, p. 535.
[6] GUO, X.—SCHOBER, T.: J. Am. Ceram. Soc., *87*, 2004, p. 746.
[7] CATLEDGE, S. A.—COOK, M.—VOHRA, Y. K.—SANTOS, E. M.—McCLENNY, M. D.—MOORE, K. D.: J. Mater. Sci. Mat. Med., *14*, 2003, p. 863.
[8] GUICCIARDI, S.—SHIMOZONO, T.—PEZZOTTI, G.: Advanced Engineering Materials, *8*, 2006, p. 994.
[9] GUICCIARDI, S.—SHIMOZONO, T.—PEZZOTTI, G.: J. Mater. Sci., *42*, 2007, p. 718.
[10] GAILLARD, Y.—JIMÉNEZ-PIQUÉ, E.—SOLDERA, F.—MÜCKLICH, F.—ANGLADA, M.: Acta Materialia, *56*, 2008, p. 4206.
[11] CHEVALIER, J.—DROUIN, J. M.—CALES, B.: Bioceramics, *10*, 1997, p. 135.
[12] MARRO, F. G.—CHINTAPALLI, R.—HVIZDOŠ, P.—SOLDERA, F.—MÜCKLICH, F.—ANGLADA, M.: Int. J. Mat. Res., *100*, 2009, p. 92.
[13] SUH, M.-S.—CHAE, Y.-H.—KIM, S.-S.: Wear, *264*, 2008, p. 800.
[14] SIVAKUMAR, R.—JONES, M. I.—HIRAO, K.—KANEMATSU, W.: J. Eur. Ceram. Soc., *26*, 2006, p. 351.
[15] LEE, S. K.—TANDON, R.—READEY, M. J.—LAWN, B. R.: J. Am. Ceram. Soc., *83*, 2000, p. 1428.