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Pseudoplastic deformation pits on polished ceramics due to cavitation erosion

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Abstract

In a previous study, pseudoplastic deformation pits created by cavitation exposure were reported in silicon nitride and zirconia. In this research, further comparison of the size and number of pits between several silicon nitride and zirconia materials is carried out. The pits are larger and much more numerous in silicon nitride than in zirconia although silicon nitride is harder than zirconia. An explanation of this phenomenon is given. Also, in the previous study it was reported that apparently a partially stabilized zirconia with yttria oxide developed a delay in the phase transformation from tetragonal to monoclinic after being exposed to cavitation. In this research, further experiments related with this phase transformation delay are carried out. Also, the phase transformation is verified with X-ray diffraction analysis. It is concluded that the ‘‘activation’’ of the partial stabilized zirconia happens regardless of the oxide used to stabilize it.

Keywords: C. Plasticity; C. Toughness and toughening; D. Si_3N_4; D. ZrO_2

1. Introduction

The use of technical ceramics materials has increased in the last decades within a wide range of applications from electronics to mechanical parts and hip prosthesis. One of the main reasons for that is the improvement of the fracture toughness that allows the ceramic material to perform better when it is subjected to the operating conditions. However, there are operating conditions that can produce cavitation erosion on technical ceramics, for example during the operation of bearings, injectors or valves. Hence, the study of the cavitation erosion mechanisms of technical ceramics is of importance to improve their performance in real applications.

Silicon nitride and zirconia are reported as the technical ceramics with the best cavitation erosion resistance in the literature [1–3]. The erosion mechanism of silicon nitride subjected to cavitation exposure has been studied. Previous authors have reported that a larger grain size leads to a larger erosion rate [2,4]. The cracking is mainly intergranular although some cracks are visible within big or elongated grains. These cracks produce erosion pits, most of them showing microcracks extension at the boundaries. This produces pits bridging or coalescence, removing successively more pits [5].

Recently, a study of the relationship of cavitation erosion with rolling wear in silicon nitride has been published. Bearings in rocket engines can undergo cavitation due to the huge pressure variations and the lubrication with liquid oxygen or liquid nitrogen. It has been concluded that the combination of both mechanisms produces a blistering on the surface of the rolling silicon nitride element that leads to pit proliferation and wear [6].

In a previous study, the appearance of pseudoplastic deformation pits on the surface of polished ceramics was reported. The volume and size of these pseudoplastic pits were measured for four commercially available silicon nitrides and one zirconia. However, no explanation was given about how the pseudoplastic deformation pits were produced. Also, a transformation of the surface topography of the zirconia after being exposed to cavitation was reported. This topographic change of the surface happened when the zirconia sample was

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stored at room conditions for several weeks or months. It was ascribed to a transformation phase from metastable tetragonal phase to monoclinic phase induced mainly by residual stresses, but no further investigation was performed on this [7].

In the present article, further investigation about the pseudoplastic deformation pits is presented; an explanation of the pseudoplastic deformation pits is given; and the delay in the phase transformation of zirconia is investigated in detail in another five commercially available zirconias with different compositions.

2. Experimental procedures

The fluid dynamic system of the experimental methodology used here to produce ultrasonic cavitation is explained in detail somewhere else [8]. The parameters and geometry of the cavitation erosion test are summarised in Fig. 1 and are the same as in [7].

The tested samples are commercially available balls made of silicon nitride or zirconia and their properties are presented in Table 1. The silicon nitrides "G" and "H" are bearing balls. The zirconia materials "I", "J", "K", "L" and "M" are commercial ceramic balls. Zirconia "I", "J" and "M" are bearing balls while zirconia "K" and "L" are milling balls for chemistry and forensic laboratories. Zirconia "I" is magnesia (magnesium oxide) partially stabilized, while zirconia "J" is yttria (yttrium oxide) partially stabilized. Zirconia "K" has an unknown but important percentage of hafnium oxide and five percent yttria. Zirconia "L" has 3.2 percent magnesia; this amount of magnesia should be enough to warranty a partially stabilized tetragonal phase but it is unknown if it has followed the heat treatment and quench process that allows the tetragonal phase to remain as metastable. Zirconia "K" and "L" are milling balls. The transformation toughening in a milling ball is not as important as in a bearing ball since they do not need to stand high loads in its working condition. The composition of zirconia "M" is unknown but it is a ball bearing for leisure industry. All the samples are cut with a precision cutting machine and polished until they achieve a roughness < 10 nm.

In order to study the pseudoplastic deformation pits, the polished samples are exposed to cavitation erosion for 30 s to count the number of pits produced during this time; for 4 min to measure the size of the biggest pits; for 10 and 40 min to study the phase transformation delay in zirconia.

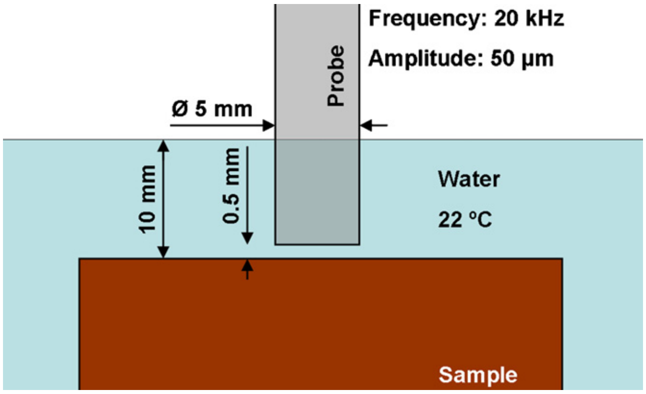

Fig. 1. Ultrasonic cavitation erosion test.

The phase transformation can be detected by means of X-ray diffraction. Different phases have different interatomic plane distances giving different X-ray diffraction angles. The type of X-ray used here is monochromatic Cu Kα radiation (1.5418 Å). The scanned angle range is from 26° to 32°. It is expected to have a peak of tetragonal at around 30.3° and two peaks of monoclinic at 28.5° and 31.5° [9–11]. The irradiated volume depends on the collimator chosen. In this case the irradiated volume is approximately a regular hexahedron of 1.5 mm × 1 mm × 0.01 mm. This volume allows the measurement of the diffraction angle of the surface region that is eroded by cavitation exposure.

Apart from the cavitation erosion, the surface of zirconia samples is subjected to other wear mechanisms in order to obtain a similar stress state of the surface and to check if this leads to phase transformation delay. The wear mechanisms are polishing, lapping and indentations.

3. Results

3.1. Pseudoplastic deformation pits

In the previous work, the size of the largest plastic deformation pits were reported for silicon nitride and zirconia [7]. The size of the zirconia pits was much smaller than the size

Table 1
Commercially available silicon nitride and zirconia balls. Properties.

	Nickname						
	G	H	I	J	K	L	M
Material	Si_3N_4	Si_3N_4	MgPSZ	YTZP	ZrO_2	ZrO_2	ZrO_2
Composition			3% MgO	$\sim$%Y_2O3	5% Y_2O3, $\sim HfO_2$	3.2% MgO	
Hardness (kg/mm^2)	1500 H_V20	1500	80–84 HRa	1270	1290 H_V1	17 GPa Knoop (100 g)	1250
Elastic modulus (GPa)	310	320	200				211
Poisson's ratio	0.29						
Flexural strength (GPa)	1.1	1					
Tensile strength (GPa)			0.41				5.48
Density (g/cm^3)	3.24	3.2			6.06	5.9	6.062
Fracture indentation toughness (MPa$\sqrt{m}$)	7	6					

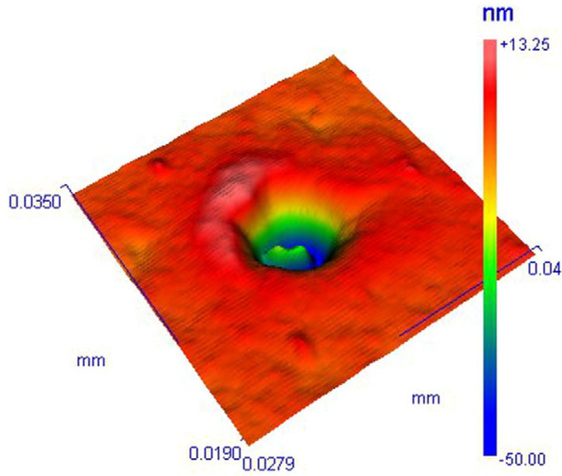

Fig. 2. Pseudoplastic deformation pit in zirconia "I" produced by cavitation erosion.

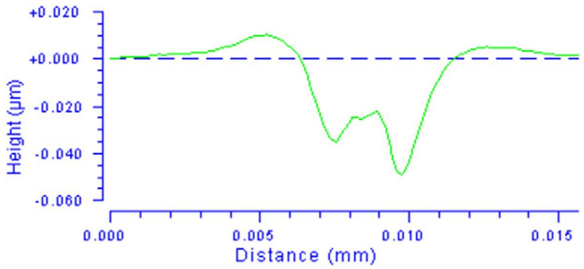

Fig. 3. Profile of pseudoplastic deformation pit in zirconia "I" produced by cavitation erosion.

found on different silicon nitride materials. Although it is not commented there, this result was unexpected because zirconia is softer than silicon nitride. Hence, the size of the biggest plastic deformation pits in zirconia after 4 min of cavitation exposure are measured for other zirconia materials. An example is provided in Fig. 2. The results are presented in Table 2. The volume of the pits in zirconia ranges from 0.6 to 1.5 μm^3 while in silicon nitride it ranges from 1.7 to 3.3 μm^3. Also, as zirconia is softer than silicon nitride it was expected that the collapsing of bubbles would damage the surface of zirconia more than the surface of silicon nitride, however the amount of pits in zirconia is significantly smaller than in silicon nitride. This phenomenon is clearly visible in all the zirconia materials tested here and Table 2 presents the amount of pits for zirconia "I" and "J". The result is that typically the number of pits in zirconia is around 4–7 pits per 30 s while in silicon nitride it is 62–89. The number of pits created changes linearly with the exposure time.

Although in Fig. 2, the pseudoplastic deformation pit appears quite deep with respect to the horizontal dimensions, this is due to the use of different vertical and horizontal scales. This effect is also present in the profile in Fig. 3. A study of the tilt of the walls of the pits reveals that the inclination of the walls is around 1–4°.

On the other hand, silicon nitride and zirconia suffer permanent deformation when subjected to cavitation erosion, as demonstrated with the measurement of the pits. Furthermore, it is expected that the grains have suffered plastic deformation, although it is unclear if the glassy boundary has developed fracture. This is discussed later. According to previous studies, when a grain of a ceramic is plastically deformed, there is dislocation movement and multiplication. This effect produces in the grain a work hardening effect that increases the hardness of the grain. This is due to the dislocations interaction. When dislocations intersect, jogs are formed and they pin the dislocations [12].

The hardness of the surface deformed by cavitation erosion has been measured for silicon nitride. Although it is expected to be increased by the plastic deformation it is in fact reduced. In order to study this apparent softening effect on the surface statistically, the hardness of silicon nitride "H" is measured before and after 4 min of cavitation exposure. The measurement of hardness is made in the same region with 65 indentations before cavitation and 64 indentations after cavitation. The indentations are separated by 70 µm to make sure there is no interaction between indentations. Those indentations made after cavitation exposure that are close to previous indentations are not taken into account. The indentation load for Vickers hardness is 25 g. This load produces an indentation with a diagonal of around 5 µm and a depth of around 1 µm, which is of the same order as the grain size.

From the statistical point of view, the two groups of indentation measurements are studied as samples of two populations. The Kolmogorov–Smirnov test is used to verify that they follow a standard distribution. The values of hardness and their probability density function are plotted in Fig. 4. The Vickers hardness for silicon nitride "H" before cavitation is 1493 kg/mm^2 and its standard deviation is 139 kg/mm^2, the

Table 2
Measurement averages of pseudoplastic deformation pits with profiler interferometer.

	Diameter (µm)	Volume (μm^3)	Depth (µm)	Amount in 30 s
Silicon nitride "A" from [7]	8–12	1.7	0.05	62
Silicon nitride "C" from [7]	8–12	2.0	0.06	89
Silicon nitride "D" from [7]	8–12	2.2	0.08	77
Silicon nitride "B" from [7]	8–12	3.3	0.09	62
Zirconia from [7]	3–6	0.6	0.03	4
Zirconia "I"	6–7	1.1	0.10	4
Zirconia "J"	7–9	1.5	0.07	7

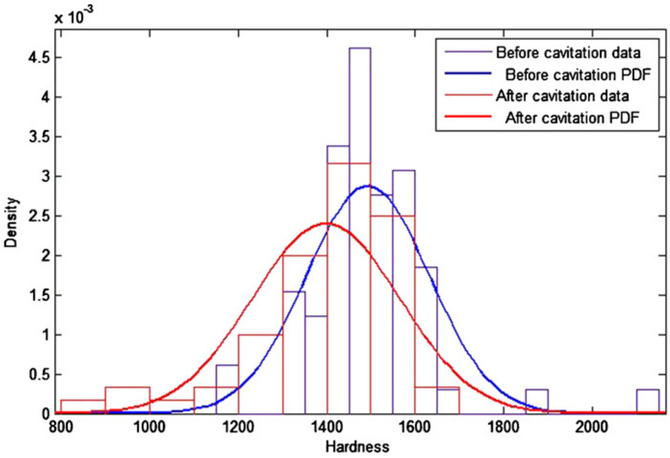

Fig. 4. Probability density function (PDF) of Vickers hardness (25 g) of silicon nitride ‘‘H’’ before and after 4 min of cavitation exposure.

hardness after 4 min of cavitation exposure is 1398 kg/mm^2 and its standard deviation is 166 kg/mm^2.

As it is possible to see in Fig. 4, although the standard deviation of the indentation values is larger after cavitation, the probability of obtaining a value of 1600 kg/mm^2 after cavitation is smaller than before cavitation. The same situation happens for any value bigger than 1493 kg/mm^2. This means that there is no work hardening effect on the surface, although a very slight damage is produced on the surface with 4 min of cavitation exposure. Similar results are obtained for silicon nitride ‘‘G’’.

When subjecting silicon nitride to cavitation exposure, although the surface presents some deformation, there is no apparent work hardening effect. It is clear that no work hardening has occurred, and, in fact, an apparent softening effect has taken place. The explanation is that the cracks associated with cavitation exposure that are created at the grain boundaries, allow the movement of the dislocations, produce regions where the grains can move with respect to one another, create stress risers that facilitate deformation and weaken the surface. Although it is likely that the dislocations have produced work hardening in the grain itself, the surface, as a set of grains, grain boundaries and cracks, is weakened.

3.2. Transformation delay in zirconia

One important aspect of this investigation is to verify if the phase transformation delay occurs with other types of partially stabilized zirconia or it is just an isolated characteristic of the zirconia used in [7]. For this reason, five types of commercial zirconia materials are studied in detail. The ‘‘activation’’ of the surface effect is clearly shown in zirconia ‘‘I’’, ‘‘J’’ and ‘‘M’’. This is also shown in zirconia ‘‘K’’, but in a smaller amount than in ‘‘I’’, ‘‘J’’ and ‘‘M’’. Zirconia ‘‘L’’ does not present the ageing effect. To illustrate this, an image composition with the five different materials is presented in Fig. 5. The samples are exposed to cavitation erosion for 40 min. Then, micrographs of the eroded surface are taken and the samples are kept in a cupboard, at room temperature for one month. After that time, new micrographs of the same surfaces are taken. Fig. 5 shows

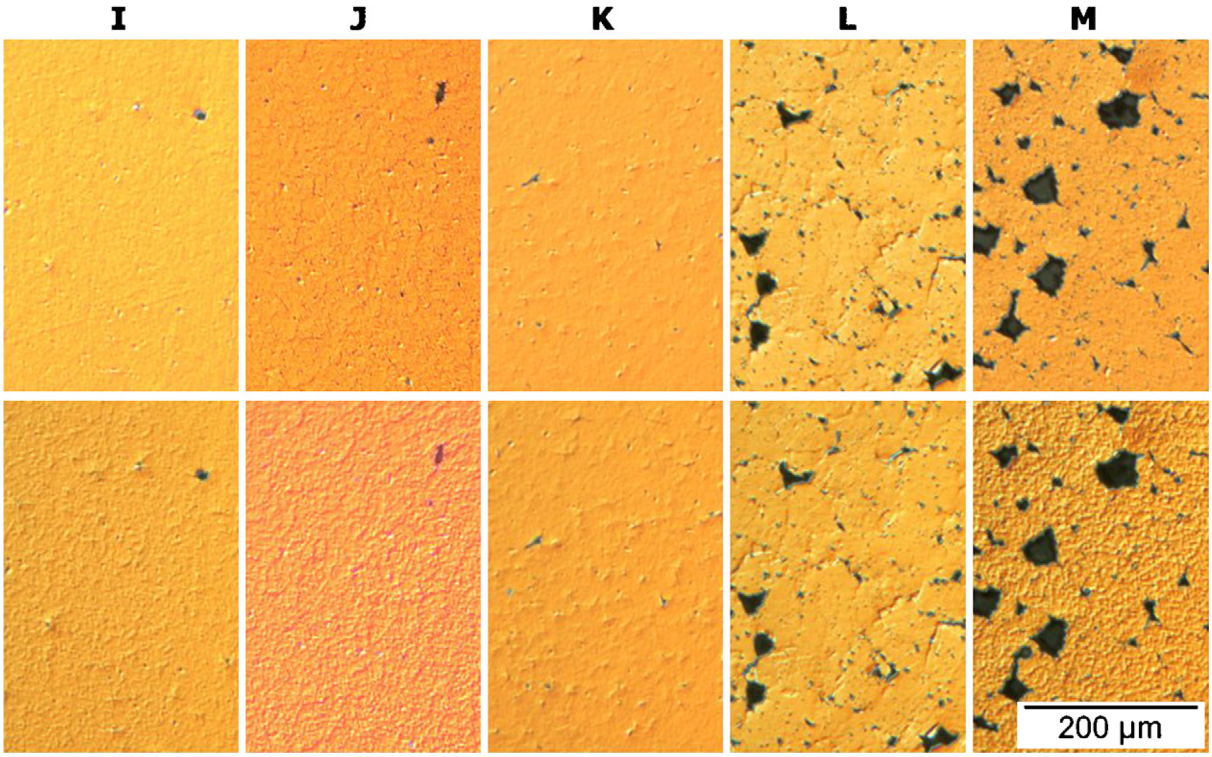

Fig. 5. Ageing of zirconia after 40 min of cavitation erosion. Micrographs from first row are taken after the experiment and those from second row one month after the experiment.

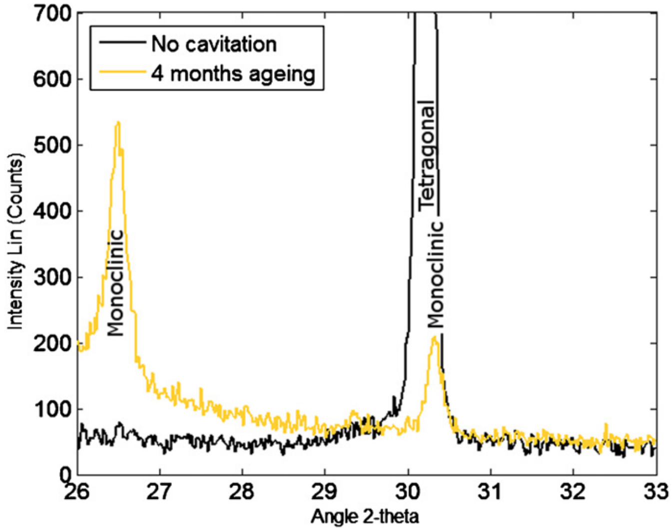

Fig. 6. X-ray diffraction intensity versus angle for zirconia "I" after 40 min of cavitation exposure and 4 months of ageing, and without cavitation.

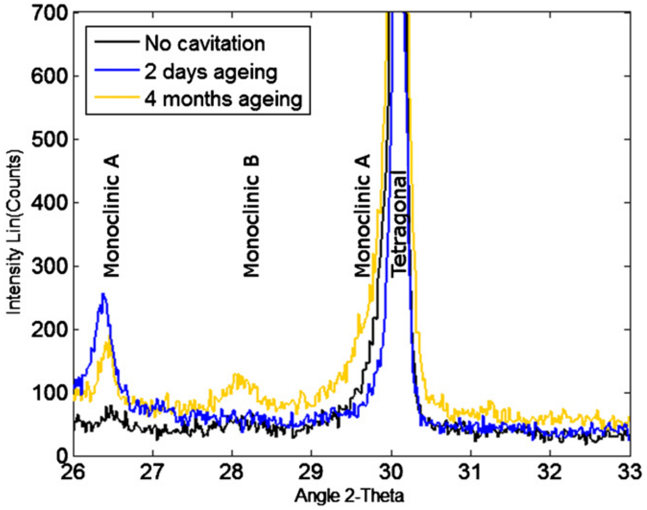

Fig. 7. X-ray diffraction intensity versus angle for zirconia "J" with no cavitation exposure; after 40 min of cavitation exposure and 2 days of ageing; and after 40 min of cavitation exposure and 4 months of ageing.

the micrographs immediately after the exposure to cavitation in the first row and one month later in the second row.

Materials "I" and "J" present clear ageing. Material "M" presents clear ageing also but the loss of material due to cavitation erosion is bigger. Material "K" presents ageing also but in a smaller amount than the others probably due to the presence of hafnium oxide in its composition. Material "L" does not present the ageing phenomena.

Previous studies published about the ageing of zirconia have subjected the samples to high temperature (above 95 °C) and high humidity, sometimes even soaked in water, to obtain some phase transformation [10,13,14]. In order to clarify whether there is an influence of humidity on the change from tetragonal to monoclinic phase of zirconia, the eroded sample is isolated with grease from the ambient humidity. The grease is spread on the eroded surface just after the experiment and sealed with a sheet of acetate to isolate it from humidity. The ageing effect is unchanged with the presence of grease. This indicates that the effect of the ambient humidity is not relevant for the ageing effect when the surface is "activated" by cavitation exposure.

X-ray diffraction measurements are performed in order to confirm that there is phase transformation on the zirconia surface. The diffraction angle of the X-ray depends on the distance between atomic planes.

Fig. 6 shows the X-ray diffraction angles for zirconia "I" without cavitation exposure and after 40 min of cavitation exposure and 4 months of ageing. Zirconia "I" without cavitation exposure shows only tetragonal phase. Conversely, zirconia "I" with cavitation exposure shows only monoclinic phase. This result demonstrates clearly that cavitation produces change of phase in partially stabilized zirconia. In order to understand what is happening during the ageing process, X-ray diffraction measurements are taken after 40 min of cavitation, either 2 days or 4 months after the cavitation exposure for zirconia "J". Fig. 7 shows that originally zirconia "J" was tetragonal. After the exposure to cavitation erosion, some tetragonal zirconia is transformed into monoclinic A. The delay in the transformation of zirconia is demonstrated with the appearance of another monoclinic phase in the sample that has 4 months of ageing. This other monoclinic phase is shown as monoclinic B in Fig. 7. Both monoclinic phases are identified in the data base of the software of the X-ray machine. It is concluded that in zirconia "J" the exposure to cavitation erosion produces monoclinic phase A, mainly by the stress caused by the impact of the collapsing bubbles. Also, it is concluded that the partially stabilized tetragonal zirconia transforms into monoclinic phase B spontaneously with the ageing.

On the other hand, zirconia samples have been subjected to other wear processes that may create a similar surface state to that created by cavitation erosion. Polishing may create residual stresses in the polishing lines with some cracks. Lapping wear may create large amount of deformation and residual stresses with the third body abrasion. A distribution of indentations along the surface may have similar results. However, although these experiments are performed within various conditions, no evidence of phase transformation delay is detected with the optical microscope.

4. Discussion

4.1. Discussion of pseudoplastic deformation pits

The linear behaviour of the creation of pits with the time indicates that the pits are created by the impact of a single bubble collapsing close to the surface.

In steel, the softer the surface, the larger is the plastic deformation pit [7]. In ceramics this is not true. The typical Vickers hardness of the silicon nitride tested here is 1500–1600 kg/mm^2 while the typical hardness of the zirconia is 1250–1270 kg/mm^2. However the pseudoplastic deformation pits are much larger in silicon nitride than in zirconia. This leads to conclude that the mechanism that produces the pits is different from just deformation of the surface due to the impact as it is in steel. Here, this mechanism is discussed.

It is known that plastic deformation of a single ceramic crystal produces work hardening. It is demonstrated that there is a permanent deformation of the surface after cavitation exposure. However the surface is softer rather than harder after cavitation exposure as seen in Section 3.

On the other hand, it is known that the cavitation erosion process of ceramics is mainly caused by intergranular crack growth due to fatigue and detachment of the grains [2–4]. Consequently, there must be a moment when these cracks appear and start to grow. Furthermore, some of the impacts of the collapsing bubbles should produce high enough stress on the surface to create a crack, or several of them, that in subsequent impact would grow and finally, in time, detach a grain.

The softening effect on the surface due to cavitation erosion with the evident need that there must be a moment when the cracks are created to eventually produce the dislodging of a grain, suggests that the surface is cracked from the very beginning of the damaged. No evidence of plastic deformation, without softening effect is observed. This indicates that the plastic deformation of the surface is linked to crack initiation. Also, the plastic deformation pits are linked to crack creation. For this reason, as the plastic deformation pits are always related to crack creation they are referred to, in this research, as pseudoplastic deformation pits.

It is not possible to see these small cracks on a ceramic surface with the optical microscope. Further, the SEM images taken did not show the cracks. Even the corner cracks of indentations that are used to measure the fracture indentation toughness could not be seen. This is due to the lack of contrast in the SEM images; the difficulty related to the fact that ceramics are not conductive and need coating; and the small size of the cracks. It is not possible to see these small cracks with the dye penetrant liquids technique used here, again, due to the small size of the cracks.

In order to understand the mechanism of plastic deformation within silicon nitride, the surface of ball bearing samples is subjected to extreme high loads in rolling contact using a four-ball machine. Despite the use of interferometry to detect small changes of the surface with a height as small as 5 nm, no plastic deformation is detected. The glassy boundary prevents the movement of dislocations and constrains the slip planes. In the same way, it could be expected that no deformation can happen when the ceramic surface is exposed to cavitation. However, the permanent deformation that is obvious in the pseudoplastic deformation pits implies a different mechanism to withstand the pressure than the one to withstand high pressure contact between balls.

The hardness indentation of ceramic surface is a good example of pseudoplastic deformation on the silicon nitride and zirconia surfaces. The grain size is shown in the figures of [7] where it is possible to see the intergranular phases. The size of the grains are submicron for silicon nitride "A", "B", "C" and zirconia according to [7], and coarser for silicon nitride "D". The diameter of pseudoplastic cavitation pits for zirconia are 3–6 μm and for silicon nitride 8–12 μm [7]. Consequently the size of the pit is not directly related to the size of the grain since one pit covers a good number of different grains and grain boundaries. Furthermore, the size of the pseudoplastic pit is similar within silicon nitrides despite the fact that the grain sizes are dissimilar containing the finest and the coarsest grains among the samples. The zirconia from [7] has the smallest pseudoplastic deformation pit while the grain size is medium with respect to the silicon nitride grain sizes.

The best explanation for the creation of pseudoplastic deformation pits coherent with the experimental results and the established knowledge is that a pit is created when the surface is deformed by the impact of one bubble in a severe enough grade to create cracks in the intergranular phase. Then these cracks release the slip systems in the crystals, allowing a small plastic deformation within the grains that will remain after the impact.

This explanation addresses the questions related to the pseudoplastic deformation pits: (1) Why are the pits larger in silicon nitride than in zirconia although zirconia is softer?; and (2) Why is the number of pits smaller in zirconia than in silicon nitride? The answer to the first question is that the creation of cracks in zirconia is harder and the same impact creates less amount and smaller size of cracks in the intergranular phase of zirconia than in silicon nitride. Then the amount of plastic deformation allowed is smaller in zirconia since the size and number of slip planes released is smaller. The answer to the second question is that the threshold to create cracks in zirconia is higher than in silicon nitride, then, the number of collapsing bubbles that pass that threshold is smaller in zirconia than in silicon nitride. Further, this explanation is consistent with the softening effect of the surface exposed to cavitation erosion. The creation of cracks reduces the apparent hardness of the surface.

Figs. 8–11 show the explanation for the creation of pseudoplastic deformation pits. Fig. 8 represents a section of the original surface; Fig. 9 shows the possible slip planes that are released when some cracks, represented by double line, are created. The presence of cracks release slip planes in the individual grains of the material and allow them to deform plastically. Slip planes are planes defined by the atomic crystal structure where the relative movement of the two parts of the grain divided by the plane is possible due to dislocations. Often, the slip planes are not completely planar and are called slip surfaces. In Fig. 8 the slip planes are constrained and no plastic deformation is possible. When the collapsing bubble impacts the surface, the surface is elastically deformed (Fig. 10). This

Fig. 8. When there is no crack, the slip planes are constrained by the intergranular phase.

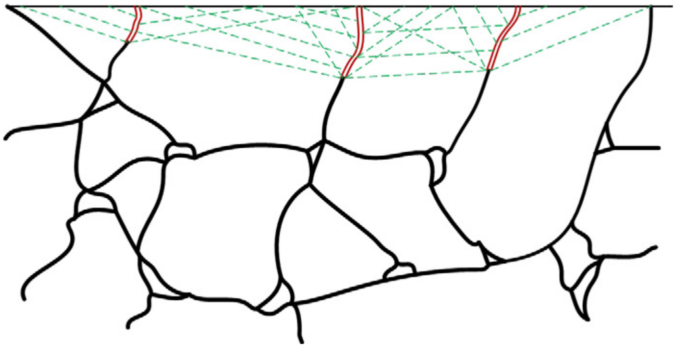

Fig. 9. The cracks in the intergranular phase release the slip planes.

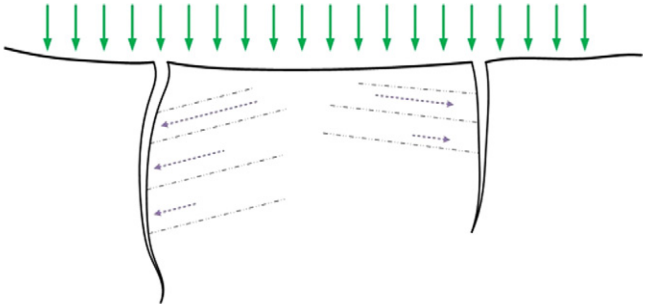

Fig. 11. The water pressure deforms plastically the grains when the slip planes are released by the cracks. During this stage, the surface is highly elastically deformed.

elastic deformation creates a tensile stress on the surface that produces cracks when a threshold is passed. Then, the cracks are produced and the grains are allowed to deform plastically driven by the water pressure according to the slip planes that have been released (Fig. 11). This plastic deformation occurs at the same time as the surface is still highly elastically deformed. The surface (plastically deformed) fits the new geometry of the bulk material (elastically deformed). Later, the pressure from the collapsing bubbles ends and the bulk material tends to return to its original geometry but it is not totally allowed by the new surface plastically deformed. Consequently, the result is a surface that has suffered a local plastic deformation, creating the pit and creating a region with some residual stresses. The residual stress is created because the plastically deformed surface fits the elastically deformed bulk, and when the pressure of the collapsing bubble disappears, the bulk tends to go to the original state, but the new surface does not match that geometry and creates a residual stress state, with compressive and tensile regions within the pit and its surroundings. This residual stress discussion is further supported by the zirconia results discussed in the next section.

4.2. Discussion about phase transformation delay

As demonstrated in Section 3, there is a transformation delay of tetragonal zirconia to monoclinic after cavitation exposure. When the surface of partially stabilized zirconia is exposed to cavitation, the eroded surface suffers some spontaneous transformation in the following weeks when stored at room temperature. This happens in the absence of ambient moisture since some samples have been stored with a protective grease layer and they have developed the same spontaneous transformation. Then, according to the literature the mechanism to drive the phase transformation is stress. In this case, as no forces are applied, it is the residual stress from the pseudoplastic deformation pits.

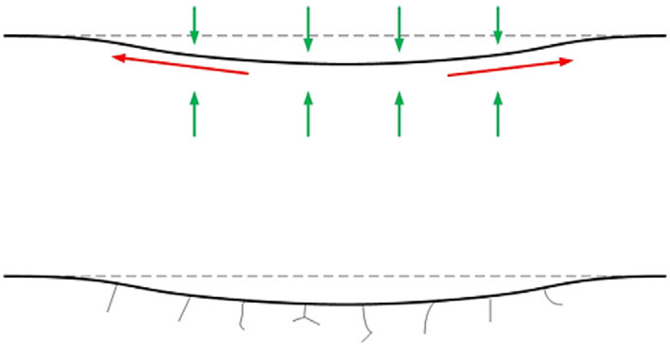

Fig. 10. The water pressure deforms elastically the surface and creates cracks.

As the phase transformation is driven by the residual stress, other surface states were considered as an attempt to emulate the surface state resulted from cavitation erosion. The surface is subjected to various mechanical processes in order to create such a residual stress state. These were: polishing with polycrystalline diamond suspension of 6 μm size; distribution of microindentations; and lapping. The idea of these experiments is to create a residual stress state that may drive a phase transformation with a similar delay as the one that occurs in cavitation erosion in order to understand the mechanism of the delay. Although these experiments have helped to understand the phase transformation delay, no delay is observed in other experiments apart from cavitation erosion. This is discussed below.

It is known that abrasive wear creates a region around the groove of plastic deformation due to the plowing mechanism; this region creates a residual stress state. In the work by Deville et al. [13] the ageing of a scratch from polishing on the zirconia surface is monitored at 140 °C, in steam at 3 bar. The stress related to the scratch accelerates the phase transformation in that work. In the same way, the scratches created by polishing and by lapping are monitored but no transformation is detected when stored at room temperature. Although it is probable that the stress created during the abrasive wear is high enough to induce transformation to monoclinic phase in the surroundings of the scratch, the residual stress state associated with this

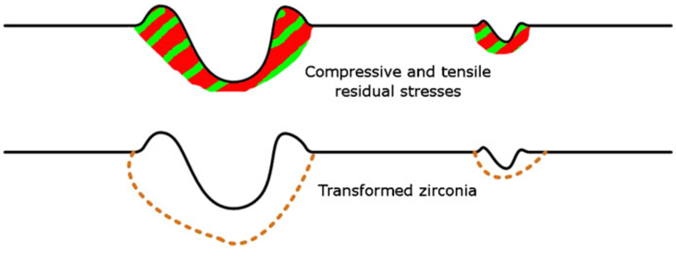

Fig. 12. Explanation of the lack of further phase transformation in an abrasive scratch. The transformed zirconia is created during the abrasion as it is known.

scratch is unable to transform further tetragonal zirconia into monoclinic. This is represented in Fig. 12. Around the scratch, due to the plastic deformation, there are regions with compressive and tensile residual stresses. However, these residual stresses are unable to induce further transformation when stored at room temperature within the first months. It is also expected that due to the stresses during the abrasion, there is transformed zirconia in the surroundings of the scratch.

A similar situation to the abrasion scratches happens within the indentation. It is known that the indentation produces plastic deformation around and that there is a residual stress state around the indentation due to the plastic deformation. During the indentation, it is expected that some tetragonal zirconia transforms into monoclinic due to the stress applied by the indenter. But the residual stress associated with the indentation is unable to induce further transformation when the sample is stored at room temperature. An explanation of this is shown in Fig. 13; some transformed zirconia is expected to be created due to the stresses induced by the applied force of the indenter. The residual stresses that are created in the region of the indentation due to the plastic deformation are unable to induce further phase transformation.

In the three experiments, polishing, lapping and indentation, the residual stress associated to the plastic deformation is located close to the mentioned characteristics. The regions between these characteristics do not develop any phase transformation, as the surface remains unchanged. For this reason, it is concluded that the residual stress created by these characteristics is not widely spread enough along the surface, and it is localized in the region where phase transformation has already been made by the applied forces rather than the residual stresses. Conversely, the residual stress state created by pseudoplastic cavitation pits is well spread all along the surface; the cavitation erosion creates a surface that has a slight plastic deformation and their associated residual stresses. The applied forces in the impact are not able to induce a complete phase transformation of the grains affected by the pseudoplastic deformation pits and the residual stress. Then, with the time, the residual stress spontaneously induces phase transformation in adjacent grains that remain as metastable tetragonal zirconia.

Fig. 14 shows a representation of this state; the surface is cracked and deformed. This plastic deformation of the grains creates a residual stress that is compressive or tensile depending on the direction and on the location. This residual stress is large enough to spontaneously create phase transformation. As there is an increase of volume in the phase transformation from tetragonal to monoclinic, when a grain is transformed to monoclinic, a new residual stress state in the surroundings is generated that may induce further phase transformation. There is a chain reaction effect.

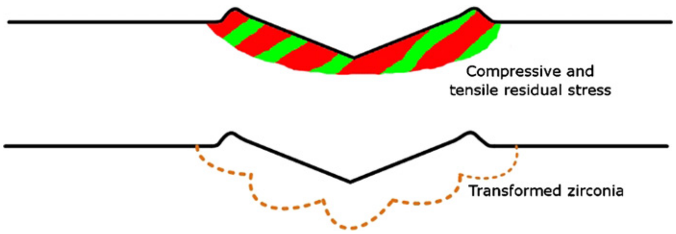

Fig. 13. Explanation of the lack of further phase transformation in an indentation. The transformed zirconia is created during the indentation as it is known.

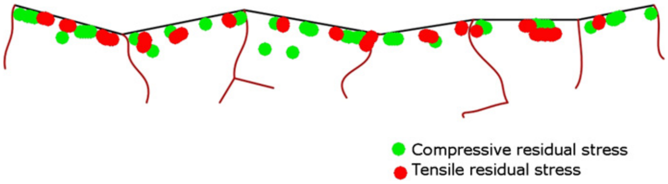

Fig. 14. Explanation of the residual stress state in zirconia due to cavitation erosion.

Subcritical crack propagation is the behaviour where the cracks do not respond instantaneously to the applied stress. In ceramics cracks may slowly grow under an applied stress well below of the stress needed to propagate a crack normally. This phenomenon is present for both silicon nitride or partially stabilized tetragonal zirconia [15]. This characteristic may have some influence on the phase transformation delay of partially stabilized zirconia. It is possible that the subcritical crack propagation plays a role to change the residual stress state during the ageing process of the surface. However, it is clear that this role is secondary, and that the main reason for such large topographic changes on the surface is the phase transformation of surface grains. The evidence for this hypothesis is that, although silicon nitride suffers subcritical crack propagation, no sample of silicon nitride has shown any topographic change on the eroded surface when stored at room temperature. Consequently, the subcritical crack propagation is not the main mechanism for the topographic changes on the surface of zirconia.

The surface changes of the partially stabilized zirconia are progressive and they take around 2 months. They have been monitored with different materials, and this behaviour is present within all materials considered. There is a transformation rate that might be the subject of future investigations. Igawa et al. [16] studied the phase transformation rate for metastable tetragonal zirconia powder at high temperature. The powder was composed by grains of different sizes and it was assumed that the whole grain transform instantly from tetragonal to monoclinic phase. In the present study, there are several questions that are not answered. These questions are related to the way that transformation occurs. For example it is not clear if a whole grain of tetragonal zirconia transforms instantly to a whole grain of monoclinic, or there is a transition plane that moves along the grain. This plane might move with the transformation of planes of atoms that change from tetragonal to monoclinic. Also, another factor that may influence transformation kinetic is the role of some kind of diffusion of atoms inside the lattice. How a crystal of tetragonal transforms into monoclinic phase is something that is out of the scope of this research. However, it might explain the delay of the transformation. It is clear that the main cause to induce further transformation after the cavitation exposure has ended is the residual stress but it is unknown why this happens with a delay.

Finally, clear phase transformation delay is presented in zirconia, ''I'', ''J'', ''K'' and ''M''. Zirconia ''K'' is YTZP, that is partially stabilized tetragonal zirconia with yttria. Zirconia ''I'' is MgPSZ, that is a partially stabilized tetragonal zirconia with magnesia. The composition of zirconia ''M'' is unknown. The transformation of phase, apparently from Fig. 5, is less intense in zirconia ''K'' than in the others. Zirconia ''K'' has a higher percentage of yttria than the other YTZP, for this reason, the percentage of partially stabilized zirconia could be smaller and this could explain the less amount of transformation on its surface. When the proportion of oxide is higher than the amount necessary to achieve partially stabilized tetragonal zirconia, a cubic crystal structure that is stable appears, called stabilized zirconia [17]. It is concluded that the phase transformation delay is linked to the existence of partially stabilized tetragonal phase regardless of the oxide that is used to retain the tetragonal phase at low temperature.

5. Conclusions

Pseudoplastic deformation pits from cavitation erosion are larger in silicon nitride than in zirconia, although silicon nitride is harder than zirconia. Also, the number of pseudoplastic deformation pits in silicon nitride is much higher than in zirconia for the same cavitation exposure time.

A theory to explain this unexpected behaviour is developed according to the established knowledge. The fracture toughness of zirconia is higher than that of silicon nitride. The pseudoplastic deformation pits are formed when the stress induced by the impact of the collapsing bubble is high enough to create cracks on the surface. In the case that cracks are not created, the surface returns elastically to its original geometry. As the fracture toughness is higher in zirconia, the creation of pits are more unlikely and when they are created, they are smaller than in silicon nitride. This explanation is supported by the results but no direct evidence has been achieved due to the small size of the cracks and the limitations of the laboratory equipment.

Partially stabilized zirconia presents a delay in the phase transformation after being exposed to cavitation erosion regardless of the oxide used to stabilize it. Several commercial zirconias, stabilized with magnesia or yttria, present the phase delay when their surface is ''activated'' by cavitation exposure. This ''activation'' of the surface happens with cavitation exposure but does not happen with polishing, lapping or indentations. The cavitation damage produces a surface state that is characteristic and different to others due to the appearance of a light pseudoplastic deformation widely and uniformly spread on the surface.

References

[1] W.J. Tomlinson, S.J. Matthews, Cavitation erosion of structural ceramics, Ceramics International 20 (1994) 201–209.

[2] U. Litzow, K.-H.Z. Gahr, J. Schneider, Cavitation erosion of advanced ceramics in water, International Journal of Materials Research: Zeitschrift fuer Metallkunde 97 (2006) 1372–1377.

[3] D. Niebuhr, Cavitation erosion behavior of ceramics in aqueous solutions, Wear 263 (2007) 295–300.

[4] W.J. Tomlinson, N. Kalitsounakis, G. Vekinis, Cavitation erosion of aluminas, Ceramics International 25 (1999) 331–338.

[5] B. Karunamurthy, M. Hadfield, C. Vieillard, G. Morales, Cavitation erosion in silicon nitride: experimental investigations on the mechanism of material degradation, Tribology International 43 (2010) 2251–2257.

[6] B. Karunamurthy, M. Hadfield, C. Vieillard, G.E. Morales-Espejel, Z. Khan, Cavitation and rolling wear in silicon nitride, Ceramics International 36 (2010) 1373–1381.

[7] G. García-Atance Fatjó, M. Hadfield, C. Vieillard, J. Sekulic, Early stage cavitation erosion within ceramics—an experimental investigation, Ceramics International 35 (2009) 3301–3312.

[8] G. García-Atance Fatjó, A. Torres Pérez, M. Hadfield, Experimental study and analytical model of the cavitation ring region with small diameter ultrasonic horn, Ultrasonics Sonochemistry 18 (2011) 73–79.

[9] C.-J. Ho, H.-C. Liu, W.-H. Tuan, Effect of abrasive grinding on the strength of Y-TZP, Journal of the European Ceramic Society 29 (2009) 2665–2669.

[10] S. Wada, K. Yokoyama, Differences in the tetragonal to monoclinic phase transformation rate in hot water of 3 mol% Y_2O_3–ZrO_2 ceramics under different surface conditions, Journal of Ceramic Society of Japan 107 (1999) 92–95.

[11] T. Kosmac, C. Oblak, P. Jevnikar, N. Funduk, L. Marion, The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic, Dental Materials 15 (1999) 426–433.

[12] D.J. Green, An Introduction to the Mechanical Properties of Ceramics, Cambridge University Press, Cambridge, 1998.

[13] S. Deville, J. Chevalier, L. Gremillard, Influence of surface finish and residual stresses on the ageing sensitivity of biomedical grade zirconia, Biomaterials 27 (2006) 2186–2192.

[14] J. Li, L. Zhang, Q. Shen, T. Hashida, Degradation of yttria stabilized zirconia at 370 K under a low applied stress, Materials Science and Engineering A 297 (2001) 26–30.

[15] J.B. Wachtman, Mechanical Properties of Ceramics, Wiley, New York/Chichester, 1996.

[16] N. Igawa, T. Nagasaki, Y. Ishii, K. Noda, H. Ohno, Y. Morii, J.A. Fernandez-Baca, Phase-transformation study of metastable tetragonal zirconia powder, Journal of Materials Science 33 (1998) 4747–4758.

[17] D.W. Richerson, Modern Ceramic Engineering: Properties Processing and Use in Design, Dekker, New York, 1982.