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The effects of mechanical properties and sintering duration on the wear behaviour of silicon nitride

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Abstract. The effects of hot pressing parameters and mechanical properties on wear of silicon nitride ceramics were analyzed. The weakest microstructure constituent was the brittle crystal boundary phase that broke and chipped off during the wear tests. The volume loss of separate ceramic materials during the wear tests depended mainly in inverse proportion to the hardness of the ceramics. Both microcutting and microcracking mechanisms played a part in the wearing of Si_3N_4 ceramics. Based on these experimental results the volume loss and also the wear resistance of the ceramics under study can be described by the model $V \sim H_V^{-1}$.

1. Introduction

Si_3N_4 based ceramics proves to be one of the advanced materials. An important position of silicon nitride in the industry is given by its properties, especially by its hardness and wear resistance, room and high-temperature strength (up to 1400°C) and by its resistance to corrosion and creep [1]. Si_3N_4 has been successfully used as wear resistant material in a wide variety of engineering applications involving contact with metallic surfaces such as drawing dies, roller bearings, cutting tools, and automotive or aerospace engine parts. The friction coefficient of 0.17 in a couple with Si_3N_4 and 0.15 with a bearing steel were achieved, using a hydrocarbon binder resulted in 0.13 and/or 0.11. Abrasive wear is the most common mechanism of ceramic material removal. Two basic mechanisms of surface damage are applied during the abrasive wear of ceramics: microcutting and microcracking [2-4].

The mechanisms of microcutting can be described according to a model that comes from Rabinowitz´s conception of abrasive wear mechanism description [5]. In this model the abrasive particle in the cone shape makes grooves on the surface of the solid body. The removed material volume V can be described by equation (1):

$$V = \frac{F.l}{\pi.tg\alpha.H_V} \tag{1}$$

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where F is the force necessary to get the abrasive particle into the abraded material, l is the length of a groove on the surface if the cone moves during relative motion in parallel with the worn material surface, H_V is the hardness of ceramics, and α is the angle of the cone which participates in the grooving of the surface. It follows from equation (1) that the removed material volume is dependent only on one material property, hardness H_V.

If we consider the mechanism of microcracking, the abrasive particle creates a crack in the plane of the load axis after the overrun of the specific limit value of the load. Cracks spread to the sample surface, where they can develop into a fracture [3, 6]. The volume of wear V can be expressed by means of equation (2).

$$V = \frac{F^{9/8}}{K_{IC}^{1/2}.H_V^{5/8}}.\left(\frac{E}{H_V}\right)^{4/5}.l \tag{2}$$

In this equation (2) l is length of path of abrasive particle, F is load on the abrasive particle, K_{IC} is fracture toughness of the ceramics, H_V is the hardness of the ceramics and E is the modulus of elasticity of the worn ceramic material. According to equation (2) the removed material, volume V, is dependent on three material properties: the modulus of elasticity E, the fracture toughness K_{IC} and hardness H_V.

According to some works [5,7] the ratio of K_{IC}/H_V values appears as the main characteristic determining dominant wear mechanisms of brittle materials during abrasive wear. This parameter defines the dominant wear mechanism at the point of contact. The mechanism of microcutting is dominant at a high value of this rate and simultaneously at a high value of fracture toughness, i.e. wear volume will be depended on hardness ($V \sim 1/H_V$). Brittle fractures dominant at a low value of the rate K_{IC}/H_V, i.e. wear will increase with decreasing fracture toughness ($V \sim K_{IC}/H_V$). This influences the growth of wear intensity. According to equations (1) the intensity of microcutting decreases with the hardness of ceramics, and according to equation (2) the intensity of microcracking decreases with fracture toughness of the worn surface. This can lead to a transition from plastic microcutting to brittle microcracking during abrasive wear [2]. Besides the mechanical properties of ceramics, the character of the structure like grain size and β-Si_3N_4 phase ratio plays an important role in determining how the ceramics will react to specific states of stress which arise under specific conditions of wear [3, 8].

2. Materials and experiments

The wear resistance test specimens were prepared from powdered silicon nitride, hot-pressed with sintering additives of yttrium oxide and aluminum oxide. The amounts of sintering additives Y_2O_3 and Al_2O_3 were different in separate specimens, but the proportion of Y_2O_3 and Al_2O_3 was the same for all the prepared specimens. The Y_2O_3 and Al_2O_3 powders were added in concentrations that could set creating $Y_3Al_5O_{12}$ phase (YAG - yttrium aluminium garnet) in ceramic materials. This phase contributed to the sintering ability of the ceramics [8]. The designations and compositions of the studied materials are given in table 1.

Table 1. Chemical composition of ceramic samples.

Ceramic sample	Concentration (wt.%)		
	Si_3N_4	Y_2O_3	Al_2O_3
5 % YAG	bulk	7.75	2.14
10 % YAG	bulk	10.34	4.30

Initial powder compositions were wet mixed in alcohol. After drying and sieving, the powder was compacted in steel dies. The final densification was accomplished using hot pressing techniques in a nitrogen atmosphere with the purity of 99.99 % and an overpressure of 75 kPa. All samples were hot

pressed at a temperature of 1680 °C and a pressure of 34 MPa. Three various sintering times 5, 15 and 30 min were applied.

Densities of the hot pressed ceramics were measured by the Archimedes's method. Hardness and fracture toughness were determined by means of Vickers indentation method with a testing load of 98 N. The fracture toughness was also determined by means of Vickers indentation. This method is based on the measurement of crack lengths that rise from the indentation corners. The more brittle the tested material is, the longer are initiated cracks. The wear resistance was evaluated by means of grinding the sample using a pin on disk method. Test samples with diameters of 8.4 mm and a height of 10 mm were placed in contact with corundum grinding paper with a graininess of 120 μm. The grinding trajectory was 125 m and the pressure was 1.5 MPa. Sliding speed max. 0.5 $m.s^{-1}$, radial movement 1.5 mm/ot, dry friction. For experiments was used the equipment for abrasive wear testing (figure 1). The wear resistance was determined based on the volume loss of the samples relative to the grinding trajectory according to equation (3):

$$V_{V/s} = \frac{\Delta m}{\rho . l} \tag{3}$$

where $V_{V/s}$ is volume loss of the samples, Δm is weight loss of the samples, ρ is density of the sample and l is grinding path of the sample.

The microstructures of the hot pressed ceramics were observed using a scanning electron microscope. In order to identify the microstructure created, the hot pressed specimens were subjected to XRD analysis.

Figure 1. The test equipment.

3. Results

The effects of densification, mechanical properties and the microstructure on the wear resistance of the prepared ceramics samples were evaluated.

3.1 Densification and microstructure

Average values from measured densities in particular ceramic samples are included in table 2. The densities of the ceramic samples were influenced by the amount of additives (Y_2O_3 and Al_2O_3) and by the sintering time. They increased with increasing the concentration of additives and sintering time from 3.21 to 3.27 $g.cm^{-3}$. These values corresponded to the relative density from 97.2 to 98.5 %, which indicate good densification of samples. The smallest density, 3.21 $g.cm^{-3}$, was measured in the 5 % YAG sample with the smallest concentration of the additives, sintered for 5 min. The highest value of 3.27 $g.cm^{-3}$ was achieved in the 10 % YAG sample sintered for 5 and 15 min.

Table 2. Density of ceramic samples.

Ceramic sample	Density ($g.cm^{-3}$)		
	5 min	15 min	30 min
5 % YAG	3.21	3.24	3.25
10 % YAG	3.27	3.27	3.26

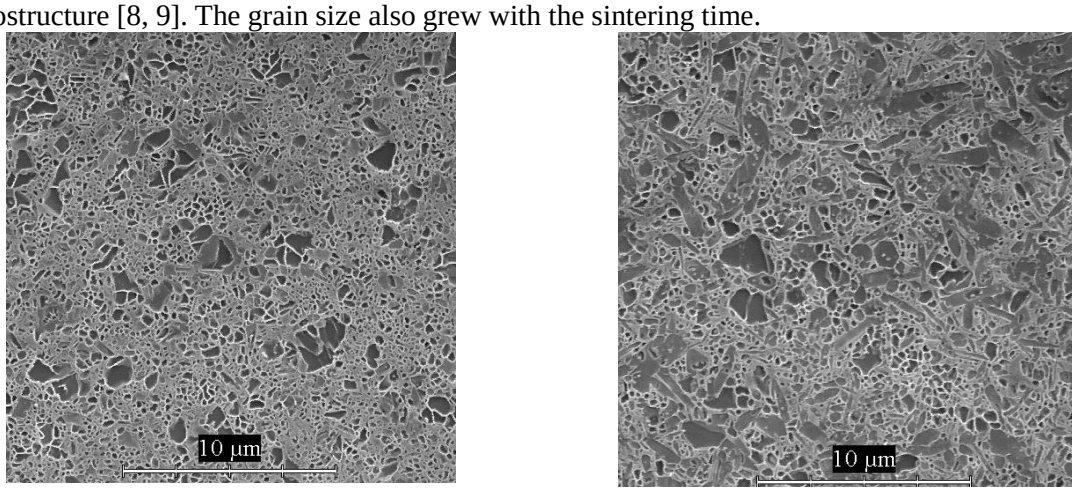
Each of the samples with different compositions and pressing time were analyzed. The phase composition of samples was identified by the XRD method (Tab. 3). Only two phases were found in all specimens α-Si_3N_4 and β-Si_3N_4 phases. Phases with a concentration below 5 % couldn't be identified using the XRD method.

Table 3. β-Si_3N_4 phase ratio of ceramic samples.

Ceramic sample	β-Si_3N_4 phase ratio (wt.%)		
	5 min	15 min	30 min
5 % YAG	45	58	75
10 % YAG	43	62	100

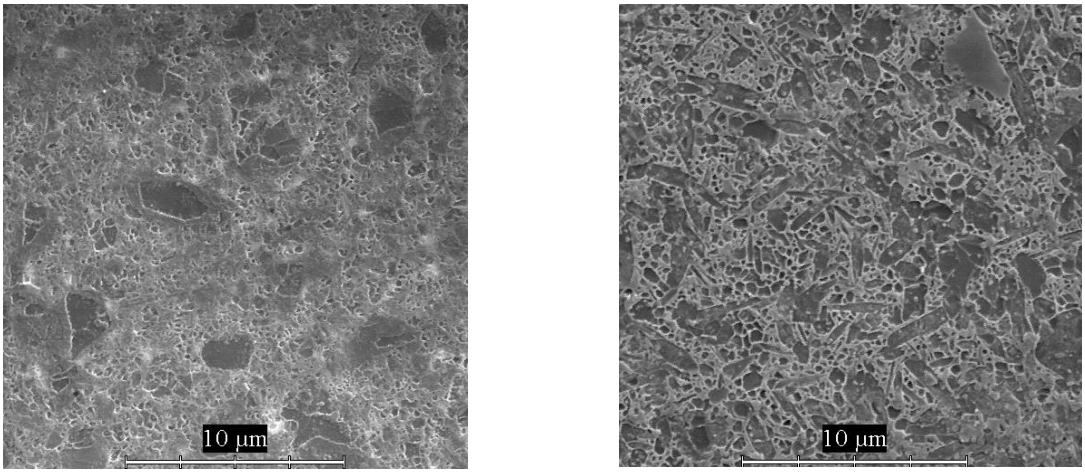
During hot-pressing, the initial α-Si_3N_4 powder was transformed to β-Si_3N_4 phase, which can be seen from table 3. The transformation stage increases with both the additive concentrations and the sintering time. The portion of β-Si_3N_4 phase from 43 to 45 % was measured by XRD at a shorter sintering time of 5 min for all prepared compositions. There were small differences between separate compositions, but these were within the measurement error, which was 5 %. The complete 100 % transformation of α-Si_3N_4 powder into β-Si_3N_4 phase was achieved only in the 10 % YAG samples with the highest concentration of additives and sintered for 30 min.

The study of the microstructure confirmed the effect of the composition on the formed phases. The microstructure consisted of α- Si_3N_4 and β-Si_3N_4 phase, figure 2 and 3. The amount of overextended β-Si_3N_4 grain increased with both the additive content and at the sintering time and reached the full β-Si_3N_4 microstructure at the highest additive content and longest time, which can be seen in figure 2a) (ceramic sample 10 % YAG sintered for 30 min). This can be explained by the increase in the transformation velocity at higher additive contents and longer times. With the increase of the additive amount, both the grain size and the ratio of a binding phase at the grain boundary increased. This crystal boundary phase is relatively brittle and can by indicated as the weakest component of the microstructure [8, 9]. The grain size also grew with the sintering time.



(a) (b)

Figure 2. Microstructure of ceramics sample with 10% YAG sintered for a) 5 min b) 30 min.



(a) (b)

Figure 3. Microstructure of ceramics sample with 5% YAG sintered for a) 5 min b) 30 min.

The effect of the additional concentration and sintering time on the wear of ceramic samples can be seen in figure 4. From this figure it can be seen that the volume change during the wear test decreased with the increasing of the additions and with sintering time. The highest wear resistance was achieved in the 10 % YAG sample, which was pressed for only 5 min, and the least wear resistance was with the 5 % YAG specimen with the smallest additional content, pressed for the longest time of 30 min.

3.2 Effects of sintering parameters and mechanical properties on wear

In work [10] was found the highest hardness at each prepared composition was always achieved at shorter sintering times of 5 min. When prolonging the time to 30 mins, the hardness slightly decreased, which can be explained by the increasing of grain size and increasing of β-Si_3N_4 phase amount with sintering time that was described above. Thus the hardness decreased with increasing of grain size and also by increasing of the β-Si_3N_4 phase amount what could be explained by lower hardness of prismatic β-Si_3N_4 crystals in comparison to narrow α-Si_3N_4 crystals [11].

The effects of the measured mechanical properties on the wear properties of the ceramic samples were studied in detail and are presented in the figures 5, 6 and 7.

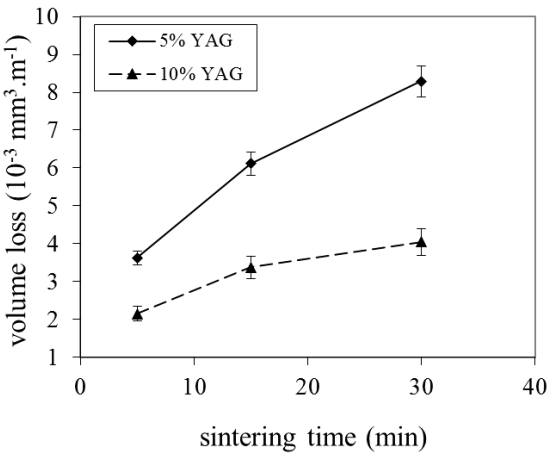


Figure 4. Effect of pressing time and additive concentration on wear of ceramics.

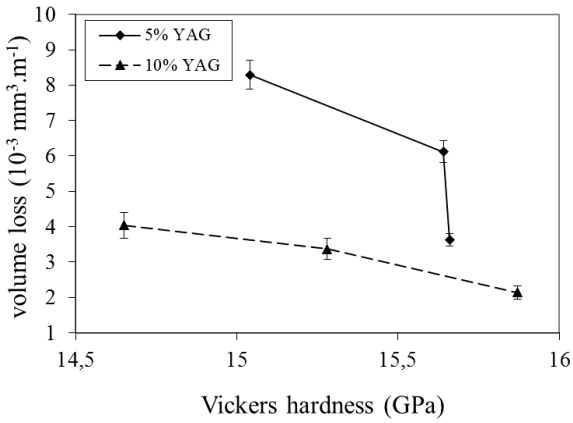


Figure 5. Effect of hardness on wear of ceramics.

Hardness had a positive effect on wear resistance (figure 5). Higher hardness resulted in less wear. As the highest hardness was measured in the higher concentration of additives (ceramics 10 % YAG), these samples had the smallest volume losses. The highest volume losses were measured in the 5 % YAG samples with the least additives that was pressed for 5 min. The results in figure 5 correspond well with model ($V \sim H_V^{-1}$), where the volume losses V during the wear tests vary inversely in proportion to the hardness H_V of the ceramics.

A very interesting development was noted when the effect of fracture toughness on wear was measured (figure 6). All compositions showed the same progress. At first wear increased up to the maximum value. After reaching the maximum value wear decreased slightly. This can be explained by the relationship between the β-Si_3N_4 phase and grain size, but the differences between the separate samples within each composition were relatively small. The effect of grain size was dominant. The highest grain size was always in the sample with a middle value of fracture toughness. That means the wear behaviour can't be described only by the effect of fracture toughness on wear.

Wear behaviour may be better described by the model which reflects the effect of ratio fracture toughness / hardness on wear rate. This can be seen in figure 7. These relations fit very well for each separate composition. The higher the value of the calculated ratio of fracture toughness to hardness is, the higher the wear rate is. The highest wear rate was noticed in the 5 % YAG specimen that contained the smallest concentration of additives that was pressed for 30 min. The ratio of fracture toughness to hardness accurately describes the relationship between the decrease of wear resistance in spite of the transformation progress α-Si_3N_4 phase to the β-Si_3N_4 phase, and the increase in the rate of wear in spite of grain growth.

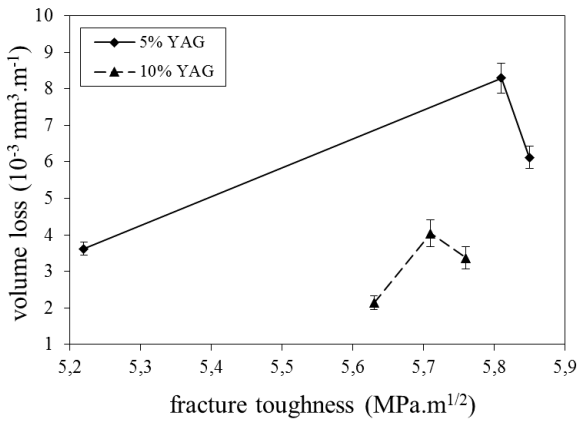


Figure 6. Effect of fracture toughness on wear of ceramics.

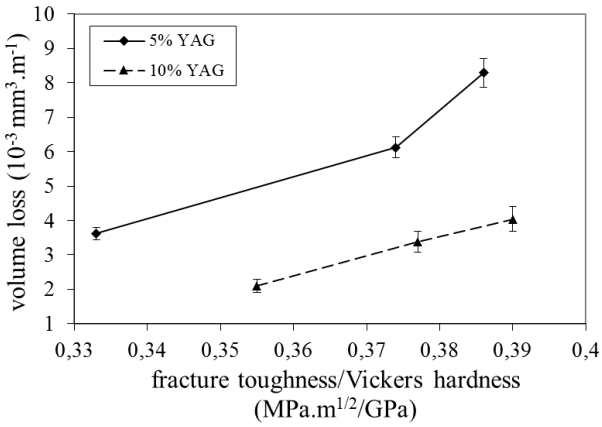
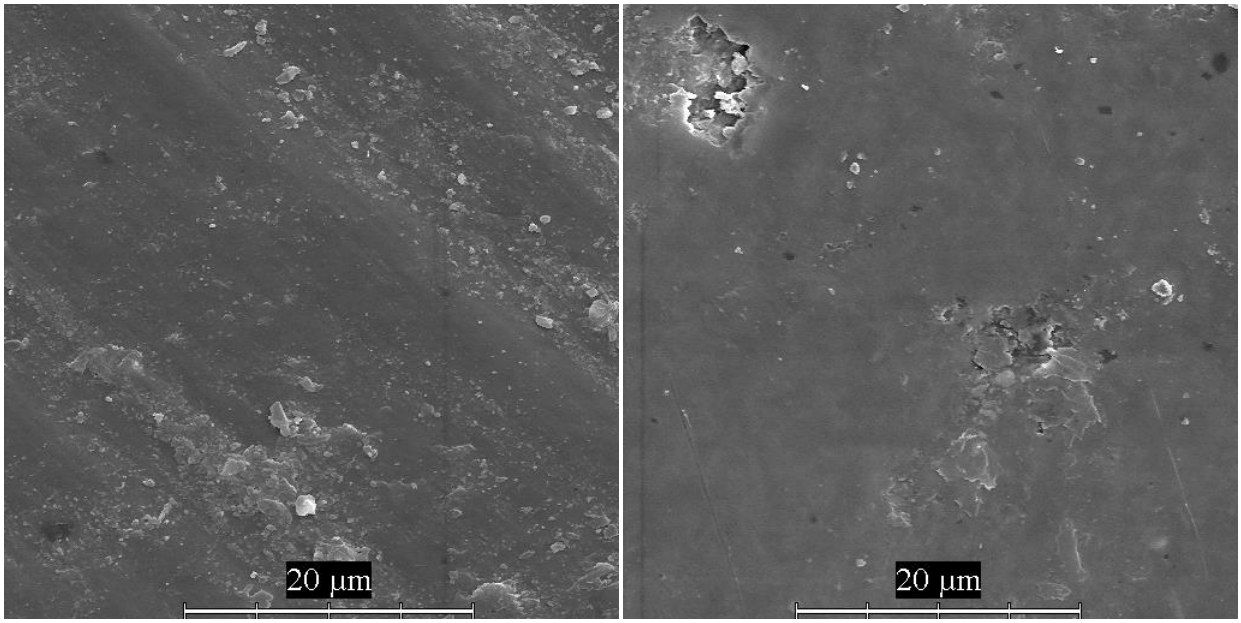


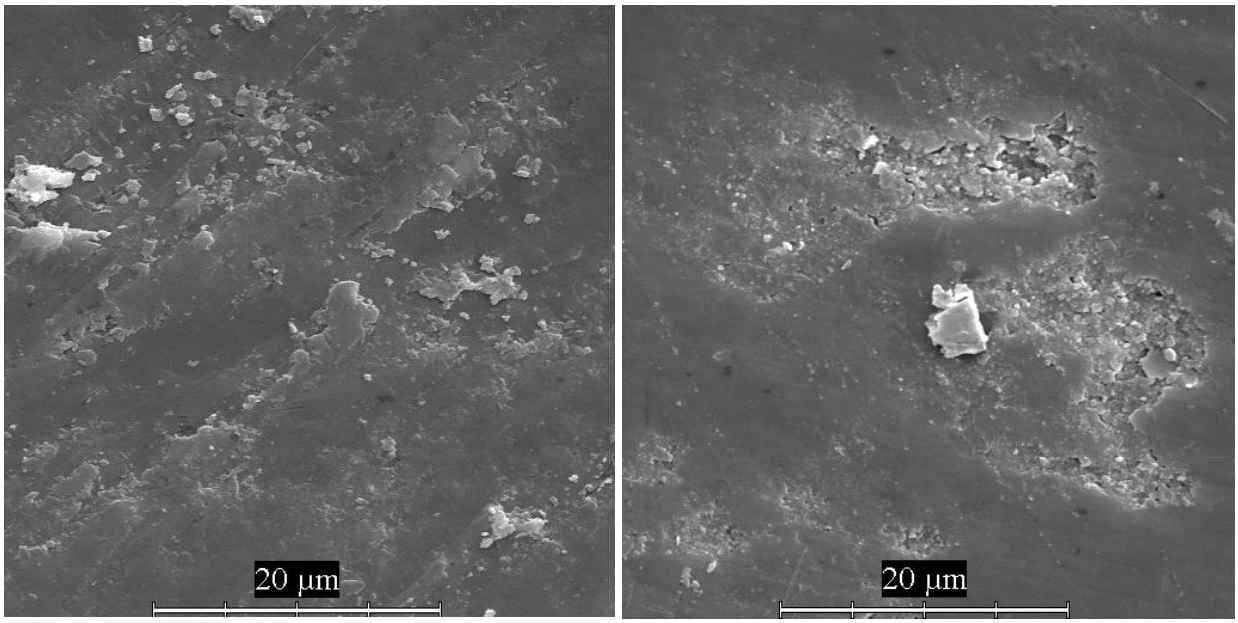
Figure 7. Effect of ratio fracture toughness / Vickers hardness on wear of ceramics.

The ceramic surfaces after the wear tests confirmed the effect of additive concentration and sintering time on the wear resistance of specimens that were described above. The specimens which were pressed for a longer time showed greater damage than the specimens pressed for a shorter time. The specimens with higher contents of additives showed less damage than the specimen with smaller additive concentrations. These specimens have higher portions of binding phases, which is present on the grain boundary. The binding phase has a positive effect on the densification, which generally improves the mechanical properties of the ceramic materials. On the other hand, the binding phase is the weakest component of the microstructure. This brittle crystal boundary phase broke and chipped off during the wear tests, which can be seen in figure 8 and 9. Prolongation of pressing time is connected to grain growth, which caused less wear resistance, thus the larger volumes of the surface were extracted.



(a) (b)

Figure 8. Surface of ceramic sample with 10% YAG after wear test sintered for a) 5 min b)30 min.



(a) (b)

Figure 9. Surface of ceramic sample with 5% YAG after wear test sintered for a) 5 min b)30 min.

Consistent with the theoretical background, the volume loss depends on hardness ($V \sim H_V^{-1}$) when the dominant mechanism of wear is microcutting. If the dominate mechanism is microcracking, the volume loss depends on the ratio hardness / fracture toughness ($V \sim K_{IC}/H_V$). All ceramic surfaces were damaged by microcutting and also by microcracking. This can be clearly seen from the observed surface after the wear tests (figures 8, 9). Several scratches and also damaged areas are visible. These areas are characteristic with dropped out material and many microcracks. These characteristic

scratches and pits with microcracks were presented on all specimens. Thus both mechanisms caused some wear on all specimens. However the extent of ceramic surface damage increased with pressing time.

Both models could be used to interpret the experimental data during the wearing process of Si_3N_4 ceramic with alumina abrasive. In our case, the experimental data corresponded better with the model, which assumes that microcutting as the dominant mechanism. Since there were only very small changes in the fracture toughness of separate specimens, the effect of ceramic hardness can be consider as dominant. Thus the volume loss during wear can be described by the first model ($V \sim H_V^{-1}$).

4. Conclusions

This paper concentrated on the analysis of the wear mechanism of Si_3N_4 based ceramics fabricated by hot pressing. The effect of preparation parameters chosen, such as chemical composition, sintering conditions in the microstructure, mechanical properties and wear resistance, was evaluated. It was found that wear resistance of hot pressed silicon nitride ceramics depends on the amount of a binder as well as on pressing time. Changes in wear resistance are associated with changes in material structure occuring on compacting the material of concern. The direct proportion between wear resistance and hardness and fracture toughness of ceramics has been demonstrated. Wear was mostly influenced by the hardness of ceramic materials. The specimen with the highest hardness achieved the highest wear resistance. Wear resistance of ceramics decreased with the grain growth and with the transformation progress of narrow α-Si_3N_4 phase to prismatic β-Si_3N_4 phase.

The weakest microstructure constituent was the brittle crystal boundary phase that broke and chipped off during the wear tests. Two damage mechanisms were taken into consideration on ceramic surfaces during the wear of Si_3N_4 ceramic pin samples with alumina grinding disks. Specimen surfaces were damaged by microcutting and also by microcracking mechanisms. The volume loss V of separate ceramic materials during the wear tests depended mainly inversely in proportion to the hardness H_V of the ceramics. Based on these experimental results the volume loss and also the wear resistance of the studied ceramics can be described by model $V \sim H_V^{-1}$.

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