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THE ABRASIVE WEAR SUSCEPTIBILITY OF INNOVATIVE ATZ TYPE COMPOSITES PRODUCED BY SINTERING MIX OF ZIRCONIA POWDERS WITH DIFFERENT CHEMICAL COMPOSITION

Composites based on tetragonal zirconia polycrystals modified with corundum inclusions ATZ (*alumina toughened zirconia*), are one of the basic and more commonly used ceramic structural materials. They are used especially willingly as parts of devices and machinery working in both dry and wet wear conditions in the presence of hard abrasive particles intensifying wear processes. The mechanical properties of such composites, strength and fracture toughness mainly, strongly depend on their chemical and phase compositions as well as microstructure. The aim of the present work was to investigate an innovative type of ATZ material composed of a mixture of two ZrO_2 powders with different chemical composition and a small addition (2.3 vol.%) of nanometric corundum powder. The proper composite materials additionally contained 10 or 20 vol.% commercially available corundum particles. Tests were carried out on the mentioned materials for abrasive wear susceptibility according to the ASTM Dry Sand Test and ASTM Miller Test, using silicon carbide particles as the abrasive medium. As a reference materials, typical TZP (*tetragonal zirconia polycrystals*) material prepared using commercial powder and ZTA (*zirconia toughened alumina*) material containing 5 vol.% zirconia dispersed in an alumina matrix were used. The obtained results allowed the usability of the individual composite materials to be verified under various operating conditions.

Keywords: **zirconia, alumina, composites, zirconia toughened alumina, abrasive wear susceptibility**

PODATNOŚĆ NA ZUŻYCIE ABRAZYJNE KOMPOZYTÓW TYPU ATZ OTRZYMANYCH W PROCESIE SPIEKANIA MIESZANINY PROSZKÓW DWUTLENKU CYRKONU O RÓŻNYM SKŁADZIE CHEMICZNYM

Kompozyty na osnowie tetragonalnego dwutlenku cyrkonu, modyfikowane wtrąceniami korundowymi (*alumina toughened zirconia*, ATZ), są jednym z podstawowych i częściej stosowanych ceramicznych tworzyw konstrukcyjnych. Szczególnie chętnie są stosowane jako elementy maszyn i urządzeń pracujące w warunkach tarcia suchego lub w obecności wody, często w obecności twardych cząstek intensyfikujących procesy zużycia. Właściwości mechaniczne tego typu kompozytów, głównie wytrzymałość i odporność na kruche pękanie, silnie zależą od ich składu chemicznego, fazowego i mikrostruktury. Celem niniejszej pracy było zbadanie innowacyjnego typu kompozytów ATZ, w którym jako osnowę zastosowano mieszaninę dwóch proszków ZrO_2 o różnym składzie chemicznym z niewielkim (2,3% obj.) dodatkiem nanometrycznego proszku korundu. Właściwe materiały kompozytowe zawierały ponadto komercyjnie dostępne ziarna korundu w ilości 10 lub 20 % obj. Wykonano dla tych materiałów testy podatności na zużycie ścierne luźnym ścierniwem węglika krzemu według norm ASTM - Dry Sand Test i Miller Test. Jako materiałów odniesienia użyto typowego materiału TZP (*tetragonal zirconia polycrystals*) uzyskanego z komercyjnego proszku oraz materiału typu ZTA (*zirconia toughened alumina*). Otrzymane wyniki pozwoliły zweryfikować użyteczność poszczególnych typów kompozytu w różnych warunkach pracy.

Słowa kluczowe: **dwutlenek cyrkonu, tlenek glinu, kompozyty, dwutlenek cyrkonu wzmocniony tlenkiem glinu, podatność na zużycie ścierne**

INTRODUCTION

Composites in the alumina/zirconia system because of their very good properties and relatively non expensive technology are currently the basic structural ceramic materials. Different types of these composites such as ZTA (*zirconia toughened alumina*) or ATZ (*alumina toughened zirconia*) are manufactured in huge volumes all over the world. They are widely used, for example, as elements of machines, devices and technological lines, cutting tools or anti-ball guards - a good example of which are applications of this type of materials in the automotive industry [1-3]. The very good mechanical properties of composites in combination with low chemical reactivity allow their use in extreme conditions, including power engineering, e.g. as elements of ball valves used in ash removal installations. The good biocompatibility of both oxides allows the use of composites as elements of knee or hip joint prostheses, as well as in dental prosthetics [4]. Another field of applications of ATZ composites (i.e. energetics) is connected with utilizing their thermal properties [5]. These materials are usually obtained according to the traditional scheme for producing composite materials: single-phase powders - usually of a submicron average grain size - are mixed mechanically, the product is formed, then naturally sintered or by supporting this process with pressure [6, 7]. The mechanical properties of this type of materials strongly depend on both their chemical and phase composition as well as on the microstructure [8-10]. The critical stress intensity coefficient, which is a measure of the resistance to brittle fracture, reaches in this type of materials a value exceeding 10 $MPam^{0.5}$, while the bending strength exceeds even 1.5 GPa.

For individual applications, not only mechanical properties are decisive. So-called useful properties like wear susceptibility measured under specific, individual conditions are also important.

The aim of the research presented in this paper was to determine abrasive wear susceptibility of an innovative type of ATZ material under dry and wet conditions and to compare it with commonly used TZP and ZTA materials.

EXPERIMENTAL PROCEDURE

The starting zirconia powders for composite preparation were obtained by the precipitation/calcination method detail described in [11]. Two zirconia powders were prepared. The first was powder of pure nanometric ZrO_2 and the second one was a solid solution of 4 mol.% Y_2O_3 in ZrO_2. The final composition of the base material was supplemented with an addition of 2.3 vol.% nanometric alumina powder (TM-DAR, Taimicron). This material is designated in the whole paper as BC. Based on the BC material, two composites were prepared with additions of 10 or 20 vol.% submicrometric corundum grains (Nabalox, 713-10, Nabaltec). These materials were designated as BC1 and BC2, respectively. Samples from all the powder mixtures were first uniaxially pressed and then re-pressed isostatically under 200 MPa, then sintered at 1450°C for 2 h. Under the same conditions, samples of commercial zirconia powder containing 3 mol% yttrium oxide (TZ-3Y Tosoh) were compacted and sintered. This material was used as the reference one (its designation in the paper is TZP). Another reference material was a zirconia toughened alumina type one (ZTA) prepared by mixing of 95 vol.% alumina powder (TM-DAR, Taimicron) and 5 vol.% zirconia powder (TZ-3Y Tosoh). The conditions of mixing, compaction and sintering was the same as in the case of the BC-series materials. This material was designated as AZ5.

The apparent densities of the sintered samples were determined by the Archimedes method. Hydrostatic weighing was performed at 21°C. The theoretical densities were calculated based on the phase composition determined by means of the X-ray diffraction method (Empyrean, Panalytical, diffractometer) supported by Rietveld analysis to determine the quantitative contents of the individual phases. The relative densities were calculated using both values: apparent and theoretical.

The wear susceptibility of the sintered bodies was determined by ASTM standards - Dry Sand Test [12] measurements in dry conditions and the Miller Test [13] for measurements in slurry. In both kinds of tests, silicon carbide grains SiC 60 (mean grain size of about 300 micrometers) were used. The results of the Dry Sand Test are presented as a mean value of the material volume removed during the test after 2000 rotations of a rubber wheel. Three tests were performed for each tested material type. The Miller Test results are also presented as a mean value of the material volume removed during the test. Each individual test lasted 2 hours. Three tests were also performed for each tested material type. Such a presentation of the results gave the possibility of simple comparison between the wear susceptibility of the tested materials.

Micrographs of the worn surfaces were obtained with a scanning microscope Nova Nano SEM 200 (FEI Company).

RESULTS AND DISCUSSION

The characteristics of the phase composition and densification level of the investigated samples are collected in Tables 1 and 2. The investigated materials were densified on a level typical for structural materials used for common applications (> 98% relative density). The phase composition measurements revealed that only the BC and BC1 materials contain small amounts of a monoclinic zirconia phase. This small amount of monoclinic zirconia phase present in the BC material is responsible for its very good behavior during fracture. This material is very resistant to slow crack propagation and is relatively tougher than typical Y-TZP material [11]. The incorporation of corundum grains leads to a decrease in the monoclinic zirconia content even to zero in the case of the BC2 material.

TABLE 1. **Phase compositions of sintered materials**
TABELA 1. **Skład fazowy spieków**

Material	Phase content [mass %]		
	Tetragonal ZrO_2	Monoclinic ZrO_2	Corundum Al_2O_3
BC	93.8	5.0	1.2
BC1	87.2	3.1	9.7
BC2	81.1	0	18.9
TZP	100	0	0
AZ5	7.5	0	92.5

Level of uncertainty of measurement ±0.2 mass %

TABLE 2. **Densification of sintered materials**
TABELA 2. **Zagęszczenie spieków**

Material	Apparent density [g/cm^3]	Theoretical density [g/cm^3]	Relative density [%]
BC	5.988	6.010	99.63
BC1	5.684	5.810	98.20
BC2	5.579	5.610	99.46
TZP	6.022	6.100	98.72
AZ5	4.069	4.096	99.35

Confidence interval level ±0.1 g/cm^3 or 0.05%

The results of all the performed tests of abrasive wear susceptibility are collected in Table 3. One can notice that the test environment strongly influenced the material behavior (when compared to other tested materials). The susceptibility to abrasive wear under dry conditions is strongly dependent on the corundum phase content in the tested material. Actually, the BC1, BC2 and AZ5 composites were much less susceptible (more resistant) than the TZP and BC materials with a dominant zirconia content. It confirmed the previous observations [14] that composites in the ZrO_2/Al_2O_3 system could be more resistant to abrasive wear than monophase materials. The most probable reason is the presence of a strong interphase (corundum/zirconia) boundary and residual stresses caused by mismatch of the coefficients of thermal expansion [15]. These additional factors not present in the pure zirconia materials strongly influenced the interphase cohesion and limited grain removal. As a result, we observed a low volume of loss during the test.

The tests in the wet environment (in slurry) revealed that the dominant role in the destruction of the materials with the high corundum content was played by the influence of water on the grain boundaries. It was observed in previous investigations on the degradation of alumina materials in water [16, 17]. The combination of intensive local mechanical load and water action lead to fast destruction of the corundum/corundum grain boundaries. We observed this process as a very high susceptibility to abrasive wear in the case of the AZ5 composite. In case of the BC materials which are practically fully composed of zirconia phases, relatively high abrasive wear susceptibility is most probably caused by the very high tendency to phase transformation (tetragonal to monoclinic) in the presence of water [18]. The typical TZP monophase material showed the lowest tendency to degradation in such conditions. However, the BC2 and BC1 composites were relatively highly resistant because of the presence of a distinct amount of corundum/zirconia interphase boundaries.

TABLE 3. **Summarized results of abrasive wear susceptibility tests**
TABELA 3. **Podsumowanie wyników testów podatności na zużycie ścierne**

Material	Volume loss during Dry Sand Test [mm^3]	Volume loss during Miller Test [mm^3]
BC	6.2 ±0.5	15.3 ±1.4
BC1	4.2 ±1.0	13.7 ±5.9
BC2	4.1 ±0.3	11.8 ±2.2
TZP	5.2 ±0.8	10.5 ±1.4
AZ5	4.3 ±1.1	20.4 ±2.5

The SEM micrographs of the worn surfaces of the investigated materials displayed in Figures 1 and 2 give some additional information about the wear mechanisms of the individual materials. During the Dry Sand Test, relatively high load (49 N according to the ASTM standard) on the abrasive grains caused the effect of sample surface ploughing (all micrographs in Fig. 1). This is connected with the abrasive wear mechanism action during the test. The coarse abrasive grains were pressed into the rubber wheel and consequently were pulled through the sample surface. As an effect, some scratches on the sample surfaces could be detected. These scratches are visible in the figures as lines parallel to the direction of abrasive medium movement. The width of the mentioned scratches correlates with the total volume loss of individual samples. The widest scratches were observed for the BC and TZP materials, the most susceptible to abrasion wear in this test. The scratches observed in the BC1 and BC2 cases were distinct. In the case of the relatively resistant AZ5 material, the scratches were not so wide and the mechanism of mass loss was different. Some distinct holes of a few microns in size were formed on the surface.

During the Miller Test (Fig. 2), the effective load acting on the sample surface is lower than in the Dry Sand Test (a larger sample surface area was subjected to abrasion). Distinct scratches could be observed only in the case of the TPZ and BC materials. These materials are composed practically only of zirconia. In the materials with a distinct corundum content (AZ5, BC1 and BC2) scratches were practically not detectable. On the surfaces of the samples of the materials with the highest susceptibility to abrasive wear in a wet environment (AZ5, BC and BC1) holes were distinctly visible. The higher the wear susceptibility, the higher the number of holes (AZ5, BC and BC1, respectively).

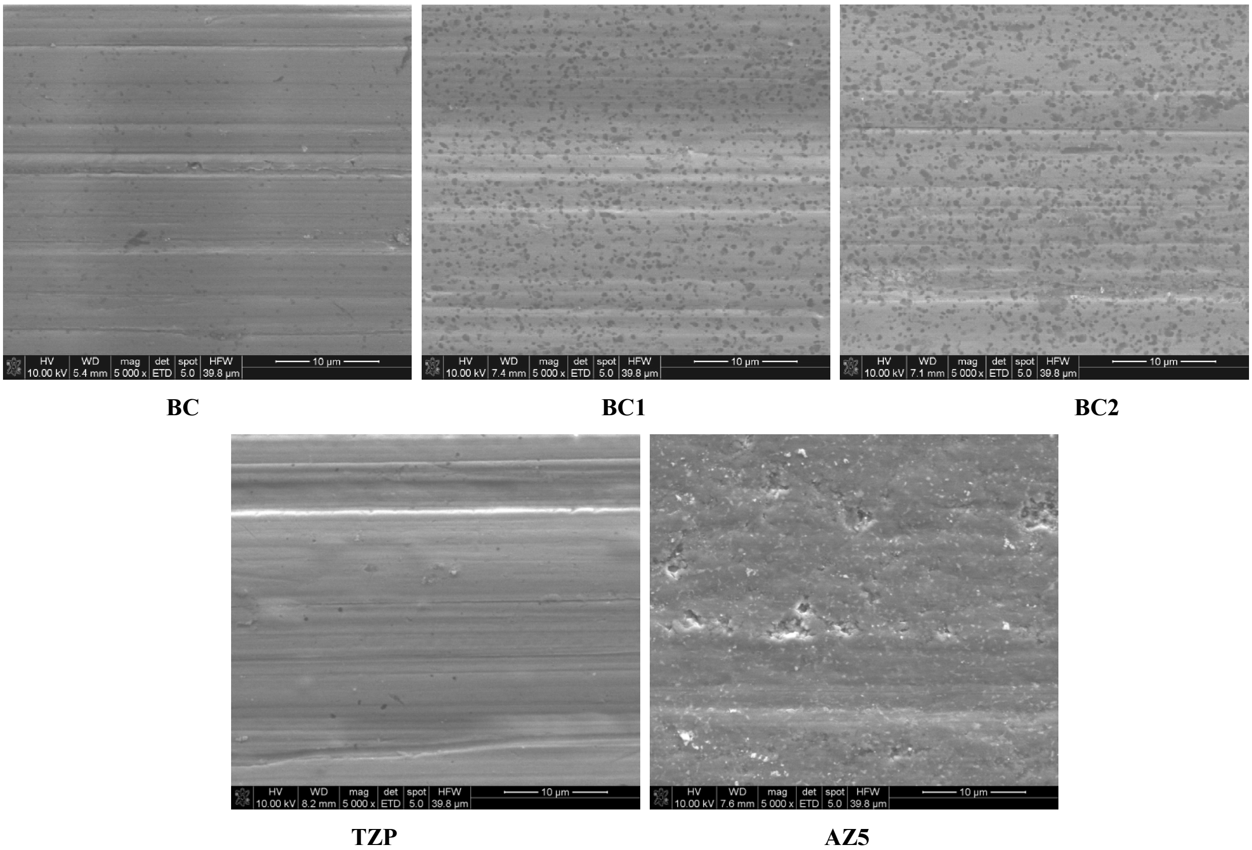

Fig. 1. SEM micrographs of worn surfaces after Dry Sand Test
Rys. 1. Obrazy SEM powierzchni po teście Dry Sand

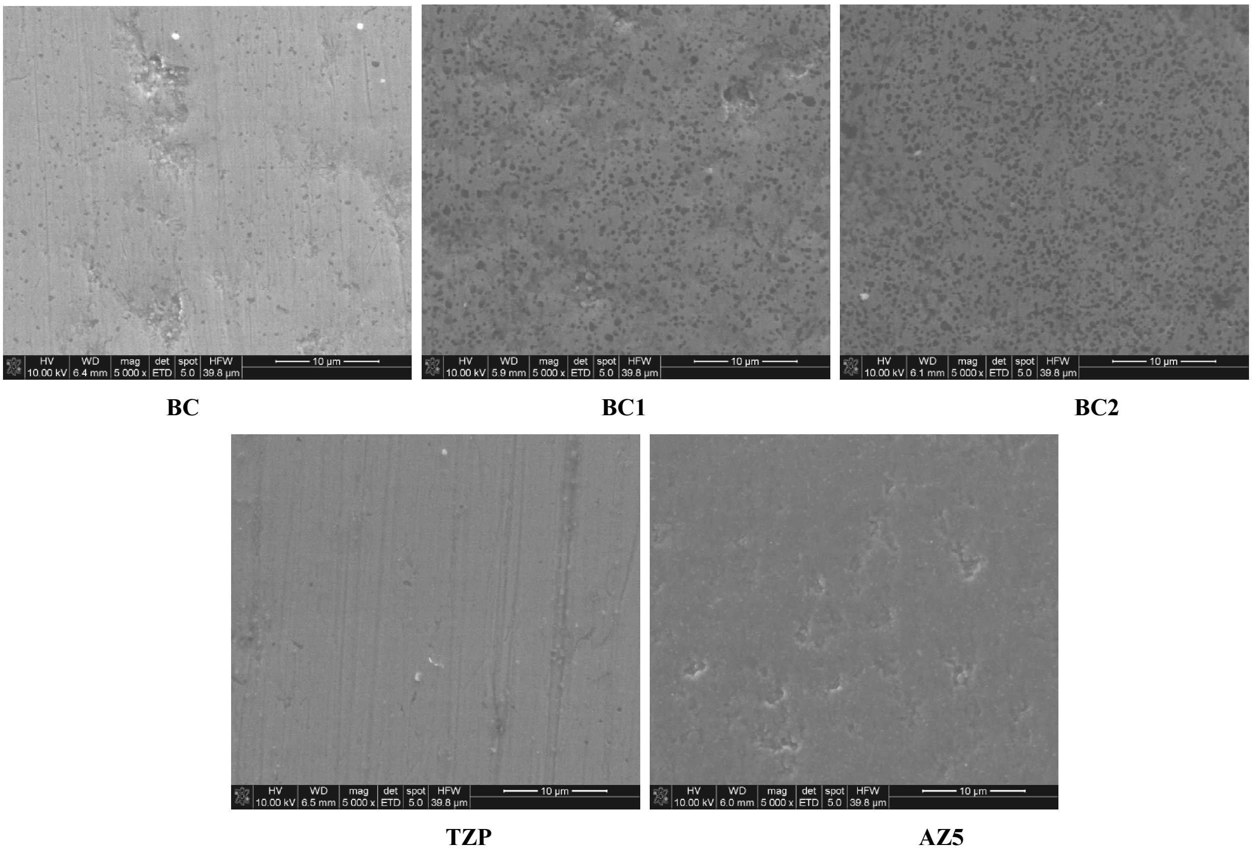

Fig. 2. SEM micrographs of worn surfaces after Miller Test
Rys. 2. Obrazy SEM powierzchni po teście Millera

The AZ5 material, which was one of the most resistant in the dry conditions test, exhibited the worst resistance in the Miller Test. This confirmed that the grain boundaries in alumina materials (corundum/corundum) are relatively weaker than the zirconia/zirconia and zirconia/corundum ones. Furthermore, the results of the Miller Test for the BC material were not satisfying. The relatively high abrasive wear susceptibility could be explained by the presence of some amount of monoclinic phase and the strong tendency in this material to transform the tetragonal phase into a monoclinic phase one, which is additionally supported in a water environment [4]. The TZP and BC2 material exhibited the best properties measured in the Miller test. TZP is fully tetragonal polycrystalline zirconia and BC2 is the composite with the highest content of corundum. Due to this fact, the BC2 material also has a highly developed interphase (zirconia/corundum) grain boundaries area. Most probably this is a factor which decreases its abrasive wear susceptibility in a wet environment.

SUMMARY

The performed tests allowed us to compare the abrasive wear susceptibility of novel types of zirconia/corundum composites showing very good fracture toughness (in the range of 8÷9 $MPam^{0.5}$ [11]) and slow crack resistance (see [11]) when compared to well-known materials like TZP and ZTA. Tests were performed for two different environments of work - in dry and wet conditions. It was stated that the novel BC material containing a small amount of corundum was not resistant to abrasive wear, most probably due to the content of a monoclinic zirconia phase, which was profitable to limit crack propagation in the macro-scale but did not act efficiently when the damage was only local like during the abrasive wear tests.

Incorporating a distinct amount of corundum grains into the BC material improved its properties. The abrasive wear susceptibility of the BC1 and BC2 composite was much lower for both dry and wet conditions. This fact could be explained when one takes into account the synergic action of a few factors. The first is that the BC1 and BC2 materials have a significant content of interphase (alumina/zirconia) grain boundaries. As was reported previously, such boundaries were stronger than the alumina/alumina grain boundaries present in the monophasic alumina material [15]. It influenced the possibility of removing whole grains during the abrasive tests. It was especially visible during the Miller Test because pure alumina material is not resistant to abrasion in the presence of water [16]. Another profitable factor is the presence of residual stresses caused by mismatch of the coefficients of thermal expansion. The distribution of these stresses limited effective action of the stresses applied during the wear tests. Particularly in the Dry Sand Test, the corundum phase volume, harder than the zirconia one, dominantly influenced the wear susceptibility. This was unlike what happened during the Miller Test when the presence of water intensively degraded the alumina/alumina grain boundaries. Therefore, the materials with the mixed alumina/zirconia composition were more resistant to degradation.

The tests showed that among the investigated materials under dry conditions the BC2 and BC1 composites have the lowest abrasive wear susceptibility, and the AZ5 material which was a commonly used ZTA type material also has a very similar test result. Under wet conditions the ZTA material was the worst one. Under wet conditions the TZP material has the lowest abrasive wear susceptibility. The values measured for BC2 and BC1 were very close to that measured for TZP.

It is worth noting that the BC2 and BC1 materials seemed to be more universal they showed a low level of abrasion wear susceptibility in both the tested work environments. In conclusion, parts made of the BC2 or BC1 composite may not be sensitive to changes in the working environment.

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