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ABRASIVE WEAR OF CARBIDE — REINFORCED TZP COMPOSITES

ZUŻYCIE ŚCIERNE KOMPOZYTÓW NA OSNOWIE ZrO_2 WZMACNIANYCH WTRĄCENIAMI WĘGLIKÓW

Zirconia particulate composites containing hard carbide inclusions show very good abrasive wear resistance when compared to other ceramic systems. In the present paper abrasive wear susceptibilities of composites containing WC, SiC, TiC, (Ti, W) C, Cr_3C_2 and Cr_7C_3 are compared. A hot-pressing technique was used to manufacture the composites. In the dry sand abrasive test several of the composites reveal properties significantly better than the TZP matrix. Some factors influencing the wear properties of these materials are identified; these are the stress state of the material and the inclusion dispersion.

Kompozyty ziarniste na osnowie dwutlenku cyrkonu zawierające wtrącenia twardych cząstek węglikowych mają w porównaniu z innymi materiałami ceramicznymi bardzo dobrą odporność na zużycie ścierne. Prezentowany artykuł porównuje podatności na zużycie ścierne kompozytów zawierających wtrącenia węglików WC, SiC, TiC, (Ti, W) C, Cr_3C_2 i Cr_7C_3. Materiały te wytworzono stosując technikę prasowania na gorąco. Zidentyfikowano i omówiono niektóre z cech materiałów wpływające na podatność na ścieranie, m. in. dyspersję wtrąceń i stan naprężeń w materiale spowodowany różnicą we współczynnikach rozszerzalności cieplnej węglików i osnowy ZrO_2. Przedstawiono również jako materiał porównawczy wyniki testów podatności na ścieranie dla szeregu innych materiałów ceramicznych, cermetalicznych i metalicznych stosowanych jako materiały konstrukcyjne elementów maszyn i urządzeń.

1. Introduction

Over the past several years, a number of composite systems containing carbide inclusions in a zirconia matrix have been investigated. These materials show

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interesting mechanical properties. Compared to a TZP ceramic, they are harder, stiffer and have higher fracture toughness [1—8]. In addition, the measurements of wear resistance reveals that some of them have a very low wear susceptibility [4].

Oxygen-free manufacturing conditions, which are necessary to produce these composites, influence the properties of the zirconia matrix. They lead to some deoxidation of zirconia [4, 5], resulting in a decrease in the tetragonal-to-monoclinic phase transformability which is the dominant toughening mechanism in TZP materials [6]. The coefficient of thermal expansion (CTE) mismatch leads to the stresses in the composites under discussion. The lower coefficient of thermal expansion of the carbide additives induces tensile stresses in the matrix and compressive stresses in the carbides grains [2, 10]. It is expected that this stress state restrains the carbide grains to be pulled out during the wear test. It improves abrasive wear resistance of the whole system.

2. Experimental

An yttria stabilised zirconia solid solution containing 2.9 mole % Y_2O_3 and prepared by the coprecipitation-calcination technique [11], was used as the matrix material. Additives of 20 volume % WC, SiC, TiC, (Ti, W) C, Cr_3C_2 and Cr_7C_3, were mixed with the zirconia powder to produce a series of particulate composites. The commercially available WC, TiC and (Ti, W) C powders (Baildon, Poland) were applied. The SiC, Cr_3C_2 and Cr_7C_3 powders were obtained by the SHS technique [12]. The zirconia s.s. and carbide particle sizes, evaluated by specific surface area measurements (BET), are presented in table 1. Two different sizes of tungsten and silicon carbide particles were used in this study, and are marked as; coarse — C, fine — F.

TABLE 1

Particle size of the starting powders

Powder	ZrO_2 s.s.	WC–C	WC–F	SiC–C	SiC–F	TiC	(Ti, W) C	Cr_3C_2	Cr_7C_3
D_{BET} [nm]	15 ± 3	1600 ± 600	130 ± 50	1350 ± 500	160 ± 50	1200 ± 400	1600 ± 700	60 ± 25	60 ± 25

Composite powders were homogenised by rotation-vibration milling of zirconia and carbide powders in ethyl alcohol for 30 minutes. The composites were hot-pressed in a graphite die under argon atmosphere at 1300, 1400 and 1500°C for 30 minutes. By this method disc shaped samples 25 mm in diameter and 10 mm high were manufactured.

The bulk densities of the sintered bodies were measured by the Archimedes method and compared to the theoretical density of the composites estimated utilising data for the pure components.

The abrasive wear susceptibility of the resulting composites was measured using a test based on the ASTM Dry sand test. A schematic diagram of the test is provided in Fig. 1. Silicon carbide (SiC 60) was used as the abrasive powder (Fig. 2). Its grain size distribution is demonstrated in Fig. 3. This powder was introduced between the polished sample surface and a rubber wheel 50 mm in diameter and 15 mm wide, rotating at a speed of 1 revolution per second. A wheel load of 44 N was applied.

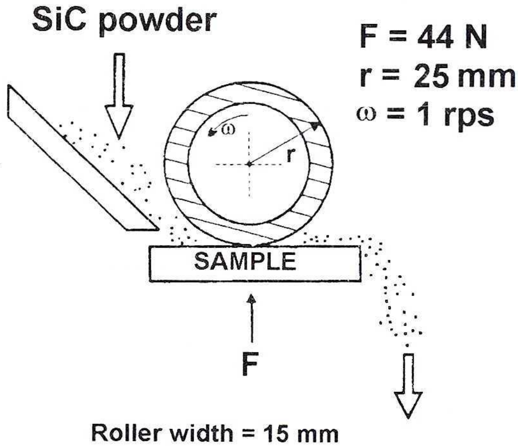

Fig. 1. Schematic drawing of the wear susceptibility tester

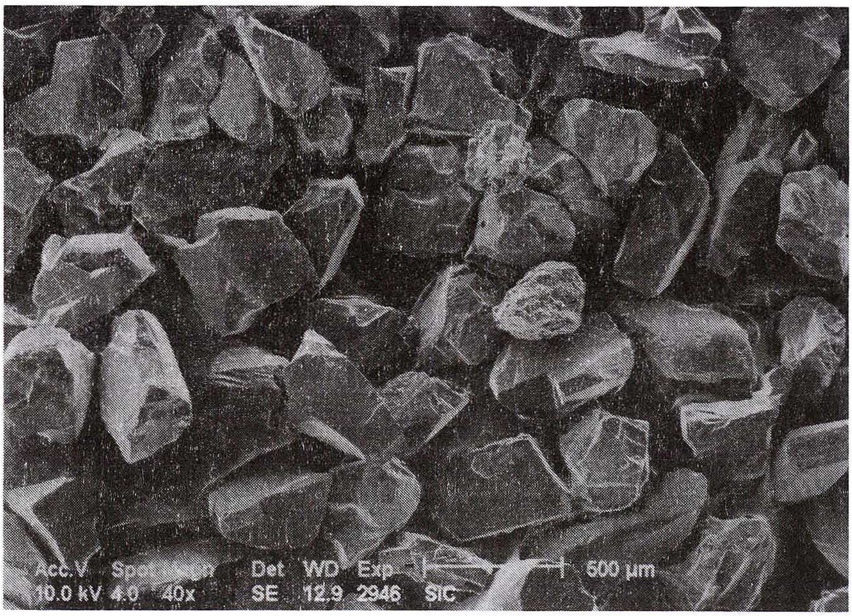

Fig. 2. SEM micrograph of the abrasive SiC grains

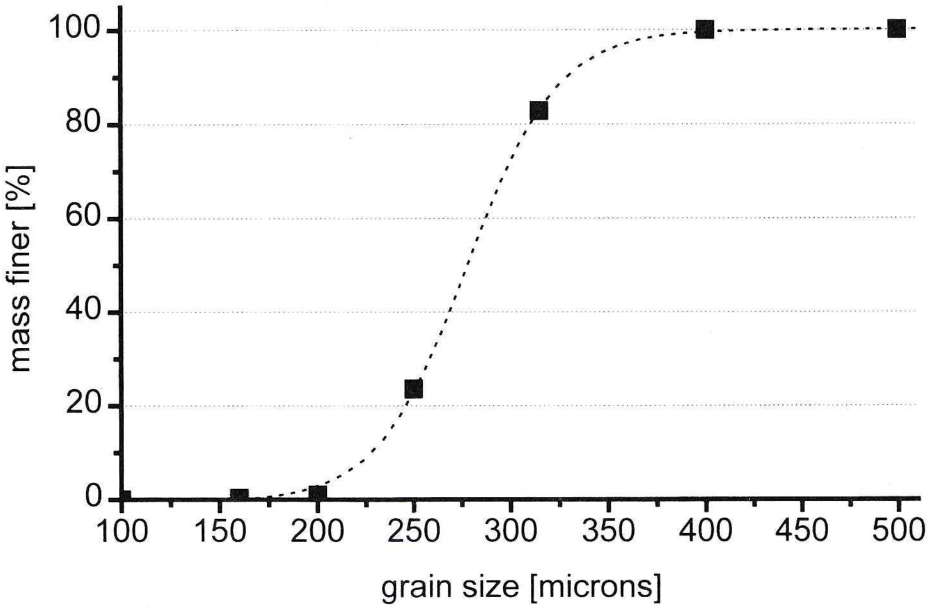

Fig. 3. Results of the sieve analysis for abrasive SiC grains

A test cycle of 5000 revolutions was used through out this work. Using the measured bulk densities of the samples, weight changes were converted into the volume of material removed during the test. This volume was utilised as a measure of the wear susceptibility of the materials. Three samples of each material were tested. Comparative results of the wear susceptibility measurements for a wide range of materials are collected at Fig. 7.

3. Results and discussion

Densities of the matrix and composite materials are presented in table 2. In all cases, densification exceeded 97% of the theoretical value. The highest densities were achieved in the TZP/WC system. The addition of finer carbide particles (WC–F, SiC–F) lead to the decreased composite density.

TABLE 2

Relative density of the matrix and composites

Density [%]/ /Temp.	TZP	WC–A	WC-B	SiC–A	SiC–B	TiC	(Ti, W) C	Cr_3C_2	Cr_7C_3
1300°C	99.2	—	—	—	—	97.0	97.3	—	—
1400°C	99.3	99.6	98.9	98.2	97.5	97.2	98.3	97.1	98.7
1500°C	99.5	99.4	99.1	—	—	97.4	98.4	—	—
±0.2 [%]									

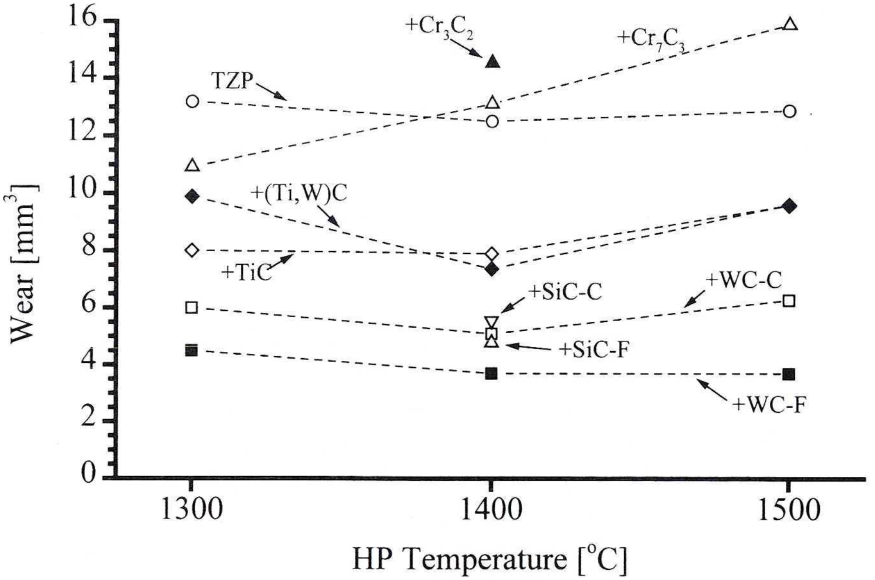

Fig. 4. Wear of the materials in applied tests

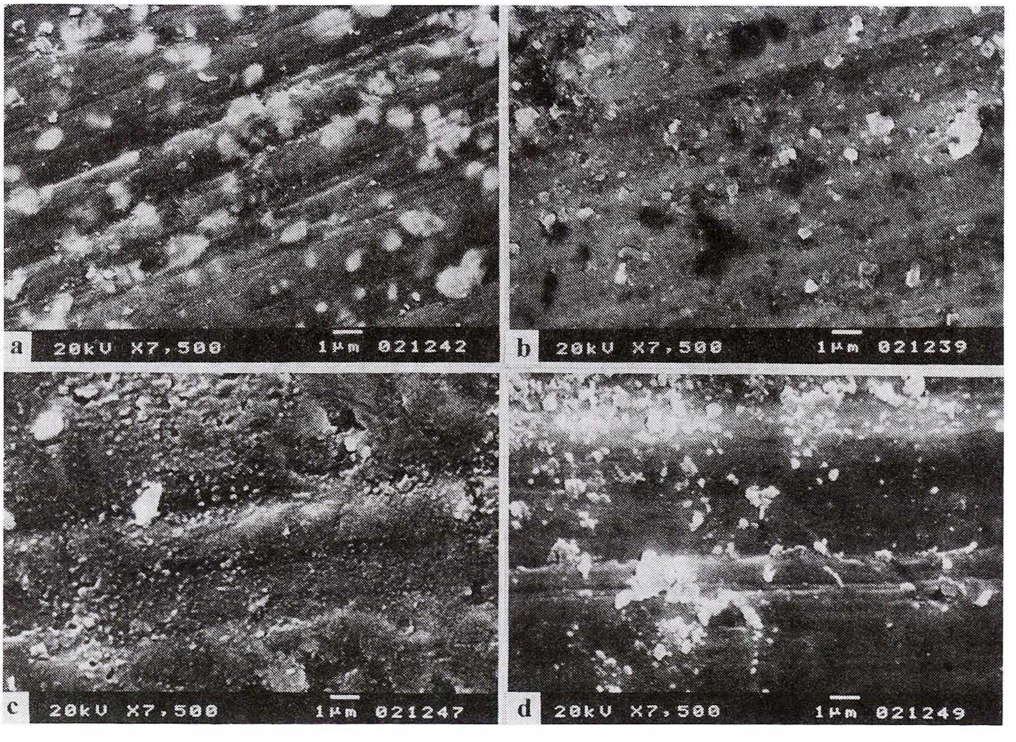

Fig. 5. SEM micrographs of the worn materials surface: a — TZP/WC-1 (1600 nm), b — TZP/(Ti, W)C (1350 nm), c — TZP/SiC (1600 nm), d — TZP/Cr_7C_3 (60 nm). All materials were hot-pressed at 1400°C

Figure 4 shows the wear test results for all tested materials. The lowest wear susceptibility (i. e. the highest wear resistance) occurs for the composites with WC and SiC additions. Reinforcement particles of smaller sizes in the TZP/WC and TZP/SiC composites — (WC–F, SiC–F) improve wear resistance to a greater extent than the coarser ones (WC–C, SiC–C).

SEM micrographs of the worn composite surfaces (Fig. 5) show that material is removed primarily by two mechanisms: ploughing of the TZP matrix by the SiC

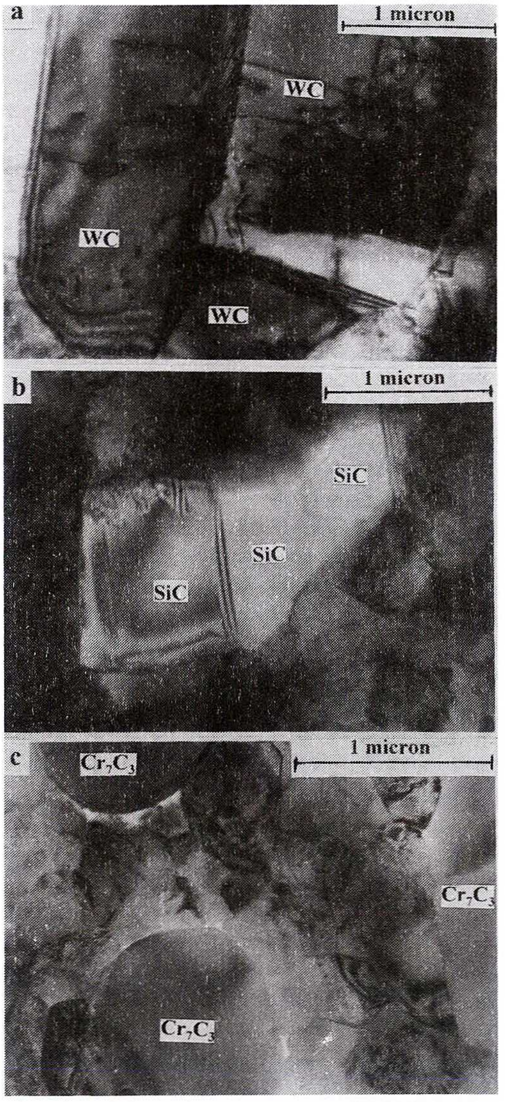

Fig. 6. TEM micrographs of the composites in the TZP mateix — 20 vol.% of indicated carbide systems. Unmarked grains are the zirconia ones. Phase identification was conducted with electron diffraction and EDS chemical analyses

abrasive grains (deep scratches visible on micrographs) and a pulling-out of the carbide inclusions from the matrix.

When the link between the carbide inclusions and the matrix is strong, the pulling-out mechanism consumes energy. The composites with finer carbide particles have larger surface of the interphase boundaries. Most probably more energy has to be consumed to pull out such fine particles from the matrix. Plausibly, this is the reason of the lower wear susceptibility of materials with fine carbide inclusions.

TABLE 3

Young's modulus (E), Poisson's ratios (ν), coefficients of thermal expansion (α) of the composites components used for calculations and estimated average values of the compressive stresses in the bodies containing 20 vol.% of the indicated carbides (σ_i)

Material	TZP	WC	SiC	TiC	(Ti, W) C	Cr_3C_2	Cr_7C_3
E [GPa]	210	730	480	430	500	400	400
ν	0.31	0.18	0.19	0.20	0.20	0.20	0.20
α [$\cdot 10^{-6}K^{-1}$]	11.0	5.2	4.95	8	8	10.3	10.0
σ_i [MPa]	—	1350	1270	625	620	200	135

TEM observations (Fig. 6) confirm that in all investigated systems the boundary between the matrix and carbide grains shows no cracks. In all of the composite systems investigated here there is a coefficient of thermal expansion mismatch between the matrix and the reinforcement phase. The TZP matrix has a largest CTE than any of the carbide phase which causes tensile stresses to build up in the matrix and compressive stresses to form in the inclusions and their vicinity during cool down from the hot-pressing temperature. Table 3 summarises the average values of these compressive stresses (σ_i), estimated by the Taya relations [9]:

$$\frac{\sigma_i}{E_m} = \frac{-2(1-f_i-f_v)\beta\alpha_1^*}{A} \tag{1}$$

$$A = (1-f_p)\left[\left\{1-\frac{f_i}{(1-f_p)}\right\}(2+\beta)(1+\nu_m)+\frac{3\beta f_i(1-\nu_m)}{1-f_p}\right], \tag{2}$$

$$\beta = \left(\frac{1+\nu_m}{1-2\nu_i}\right)\left(\frac{E_i}{E_m}\right), \tag{3}$$

$$\alpha_1^* = \int_{T_p}^{T_o}(\alpha_i-\alpha_m)\,\delta dT, \tag{4}$$

where T_o is room temperature, T_p is the temperature at which expansion mismatch stresses start to build up; f_i and f_p are the volume fraction of reinforcement particles and porosity, respectively; E_m, E_i, ν_m, ν_i are Young's moduli and Poisson's ratios of the matrix and reinforcement particles, respectively; α_m and α_i re the CTE's of the matrix and inclusions, respectively; δ is Kronecker's delta.

Temperature of 1200°C was assumed to be T_p [2]. Elastic data used in the calculations are collected in table 3, and were estimated using ultrasonic wave velocity propagation measurements [13].

The presented results seem to indicate that compressive forces exerted by the matrix on the inclusions influence strongly the wear susceptibility. The lowest wear is found in the systems with the largest estimated compressive stresses (TZP/WC, TZP/SiC). In the materials containing carbide inclusions with a CTE similar to the matrix, improvement in the wear behaviour is not observed.

TEM observations (Fig. 6) confirm indirectly the stress state in the composites. In the systems with a large CTE mismatch (TZP/WC, TZP/SiC), extinction contours are distinct in the carbide grains (Fig. 6 a and 6 b). These contours probably result from buckling of the thin foil, caused by the operating stresses [14]. It is worth noticing that this effect is less visible in the TZP/Cr_7C_3 material (Fig. 6 c). In this case, the CTE mismatch is much smaller than in others. It causes that comprehensive stress in the carbide grains has a relatively low value (table 3).

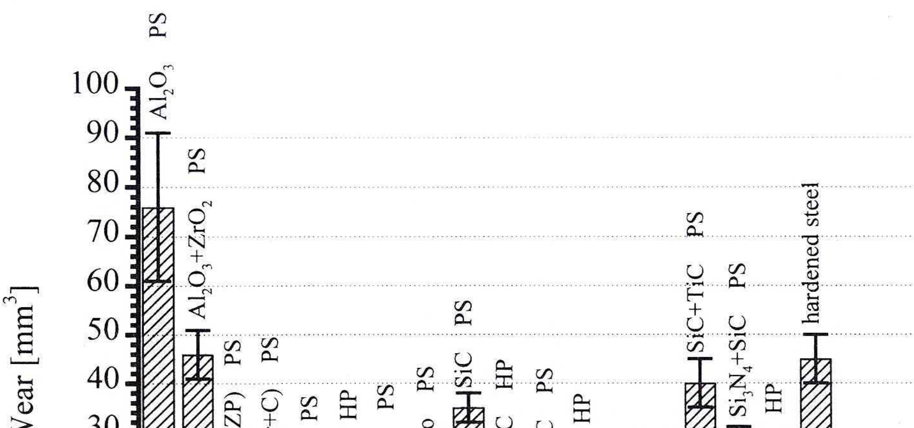

Fig. 7. Wear susceptibility of the selected materials. Intervals mark the range of wear for the different compositions and manufacturing conditions of the same kind of material (or the different suppliers for the commercially available materials). For instance: wear rate for alumina was measured for five different materials, from 95% to 99% of purity and density in the range from 3.80 to 3.98 g/cm^3. The measurement accuracy is 5% of the measured value. HP — hot-pressed materials, PS — pressureless sintering, Ar+C — heat treatment in the Ar atmosphere in a carbon bed

In order to locate the presented composites on the background of other materials, wear susceptibility of the vast range of different materials was measured. The test conditions were the same as those described in the presented paper. Commercial samples of Al_2O_3, yttria-stabilised ZrO_2 (Y-TZP), cemented carbides in the WC–Co system and hardened steels were used. All tested ceramic composite materials were made in our laboratory. Densities of all samples were not smaller than 98%. The results of the test are collected in figure 7. One can notice that widely used alumina has a relatively high wear susceptibility. Zirconia addition into the alumina matrix improves its properties — such a material has its wear susceptibility on the level of hardened steels. The lowest abrasive wear is shown by B_4C materials, yet their fabrication needs processing temperature higher than 2000°C.

Ceramic matrix composites, presented on Fig. 5, have better wear resistance than widely used ceramic and metallic materials. Composites on the SiC basis (SiC–B_4C or SiC–Si_3N_4) need expensive hot-pressing technique for fabrication of bodies of good properties. On this background composites basing on the TZP matrix show promising properties. It is important to notice that fully dense bodies can also be achieved by the pressureless sintering and their properties do not differ substantially from the hot-pressed ones.

4. Conclusions

Presented results seem to emphasise the role of compressive stresses exerted on carbide particles by the surrounding zirconia matrix in the wear susceptibility improvement. The stresses result from the CTE mismatch between the material components.

The TZP/carbide particulate composites show low wear susceptibility in comparison to other structural materials.

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