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COMPOSITES

Piotr Putyra*, Paweł Figiel, Marcin Podsiadło, Piotr Klimczyk

Institute of Advanced Manufacturing Technology, ul. Wrocławska 37a, 30-011 Krakow, Poland
** Corresponding author. E-mail: Piotr.Putyra@ios.krakow.pl*

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ALUMINA COMPOSITES WITH SOLID LUBRICANT PARTICIPATIONS, SINTERED BY SPS-METHOD

The paper presents the sintering results of Al_2O_3-Ti(C,N) ceramics with the additions of solid lubricant materials. Al_2O_3-Ti(C,N) based ceramics with solid lubricating substances were sintered by the SPS-method. In the phase known as lubricants, the following materials were used: MoS_2, WS_2, $CaSO_4$, $SrSO_4$ and MoO_3 and CaO. The Al_2O_3-Ti(C,N) ceramics were also prepared with the addition of TiB_2. The SPS-sintered materials were characterized by values of relative density from 93 to 99%. In the case of the addition of 10 and 30% TiB_2, the relative density, Young's modulus and hardness HV1 were close or equal to the values of the base material. For other additions, the Young's modulus ranged from 74 to 83% and hardness from 62 to 76% of the Young's modulus and hardness value for the base material. Regardless of the additive or its volume, the fraction of the friction coefficient was 49 to 86% of the friction coefficient value for the base material. Taking into account the value of the friction coefficient and the physical and mechanical properties, the most promising material is a ceramic with the addition of TiB_2 or MoO_3 with CaO.

Keywords: **alumina, SPS sintering, hardness, density, Young Modulus, friction coefficient**

CERAMIKA Al_2O_3-Ti(C,N) Z DODATKAMI STAŁYCH SUBSTANCJI SMARUJĄCYCH, SPIEKANA METODĄ SPS

Przedstawiono wyniki badań dotyczących spiekania ceramiki o osnowie Al_2O_3Ti(C,N) z dodatkami faz poślizgowych. Scharakteryzowano właściwości mechaniczne i tribologiczne wytworzonych materiałów. Spośród faz określanych jako poślizgowe do badań wykorzystano następujące materiały: MoS_2, WS_2, $CaSO_4$, $SrSO_4$ oraz MoO_3 i CaO. Biorąc pod uwagę niski współczynnik tarcia ceramiki o osnowie TiB_2, wytworzono również ceramikę Al_2O_3Ti(C,N) z dodatkiem wysokotopliwej fazy TiB_2. Materiały spiekane metodą SPS odznaczały się wartościami gęstości względnej od 93 do 99%. W przypadku materiałów z dodatkiem 10 i 30% TiB_2 wartości gęstości względnej, modułu Younga oraz twardości HV1 były zbliżone bądź równe wartościom materiału bazowego. Dla pozostałych dodatków moduł Younga wynosił od 74% do 83%, a twardość od 62 do 76% wartości modułu i twardości materiału Al_2O_3-Ti(C,N). Niezależnie od rodzaju dodatku i jego udziału objętościowego obniżono współczynnik tarcia od 49 do 86% wartości współczynnika tarcia materiału bazowego. Najniższą wartość współczynnika tarcia zmierzono dla materiału po spiekaniu SPS z dodatkiem WS_2. Materiał ten jednak odznaczał się względnie niskim modułem Younga oraz twardością. Biorąc pod uwagę wartość współczynnika tarcia oraz właściwości fizyczne i mechaniczne, najbardziej obiecującym materiałem jest ceramika z dodatkiem TiB_2 oraz MoO_3 i CaO.

Słowa kluczowe: **ceramika Al_2O_3, spiekanie SPS, twardość, gęstość, moduł Younga, współczynnik tarcia**

INTRODUCTION

Carrying out the machining process without the use of liquid cooling lubricants results in a reduction in investment and production costs. A reduction in friction and the elimination of fluids from the production process can be achieved by coating the tool surface or by adding lubricating substances resistant to the action of high temperatures, to the structure of the tool solid. In the case of sliding materials, it is not sufficient that the material have a layered crystal structure. The prerequisite is the existence in such a structure of weak bonds between the layers [1, 2].

Another well-known and commonly used lubricating agent is molybdenum disulphide, which, like graphite, has a layered structure and is characterised by a low coefficient of friction. The low coefficient of friction of MoS_2 is maintained up to 200°C [3]. In the case of a WS_2 based sliding phase, decomposition occurs at a little higher a temperature (approx. 450°C), whilst complete oxidation does not occur even when the temperature is raised to 600°C. The MoS_2 lubricant layers can also be produced with the use of chemical or mechanical methods as described in papers [4, 5].

In the case of high-speed machining, solid sliding agents should be characterised by a low friction coefficient and resistance to oxidation at temperatures exceeding 800°C. In such a case, the layers are composed of high- and low-temperature phases, which, as a result of the reaction to temperature and friction, become more temperature stable phases. In accordance with this mechanism, phases can be formed which are characterised by good tribological properties at high temperatures, for example: $PbMoO_2$ and $ZnWO_4$ (MoS_2 + $PbO \rightarrow PbMoO_4$; WS_2+$ZnO \rightarrow ZnWO_4$) [6]. On the basis of the mechanical and tribological studies results presented in [7], it may be stated that the content of sliding agents in tool ceramics should not exceed 10%.

Among those materials characterised by a higher temperature resistance than graphite or MoS_2, worthy of mention are: $CaSO_4$, $BaSO_4$ and $SrSO_4$. As stated in other works [7, 8], sulphate-based sliding phases are characterised by a lower friction coefficient, even at temperatures of around 600°C. The high temperature resistance and good tribological properties of $SrSO_4$ layers are confirmed by the results presented in paper [9]. $PbMoO_4$, $ZnMoO_4$ and $ZnWO_4$ layers have similar properties (friction coefficient, wear resistance, high-temperature wear resistance). At low temperatures, sulphate-based sliding layers and those containing MoO_4^{2-} or WO_4^{2-} ions are characterised by a higher friction coefficient and are rapidly damaged. This is confirmed by the results of the tribological studies presented in paper [7]. A promising material for use in tool ceramics as a solid lubricating agent is $BaCrO_4$. This phase is characterised by a low and constant friction coefficient over a wide temperature range, up to approximately 800°C. $ZrO_2(Y_2O_3)$-$BaCrO_4$ ceramics produced by SPS (Spark Plasma sintering) are characterised by a higher resistance to abrasive wear, in comparison to $ZrO_2(Y_2O_3)$-base ceramics [10].

EXPERIMENTAL

Materials and procedure

The Al_2O_3-Ti(C,N) ceramics with the addition of various lubricating substances were subjected to investigation. The base material was composed of the following powders: Al_2O_3 (A16SG, ALCOA) with the addition of ZrO_2 (FLUKA) and with the addition of 25 vol.% Ti(C,N) (H.C. STARCK). The average sizes of the Al_2O_3; ZrO_2 and Ti(C,N) particles were smaller than 1 μm.

Al_2O_3-Ti(C,N) base ceramics with the addition of solid lubricating substances were sintered by the SPS method.

To the base material were added:

1. 10 vol.% $CaSO_4$ (POCH)
2. 10 vol.% $SrSO_4$ (POCH)
3. 10 vol.% WS_2 (WP-801, AEE, 1÷5 μm)
4. 10 vol.% MoS_2 (Mo-801, AEE, 1÷5 μm)
5. 10 vol.% TiB_2 (HC STARCK, 2.5÷3.5 μm)
6. 30 vol.% TiB_2 (HC STARCK, 2.5÷3.5 μm)
7. 10 vol.% MoO_3 (POCH) + CaO (POCH)

The materials for SPS sintering were pressed in a graphite die with a pressure of 35 MPa and in vacuum conditions. The maximum pressure was obtained after 10 minutes. Vacuum and pressure time (10 minutes) are needed to vent the mixture in the graphite die. The sintering process was operated in a nitrogen atmosphere.

The sintering parameters for Al_2O_3-Ti(C,N) base ceramics with additives were determined with respect to the melting point of the solid lubricant materials. The sintering parameters are presented in Table 1. The shrinkage of those materials during the sintering process is shown as graphs in Figures 1-3.

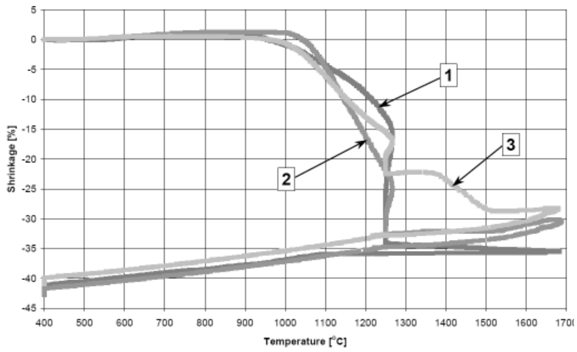

Fig. 1. Shrinkage of materials sintered by SPS-method: 1 - Al_2O_3-Ti(C,N); 2 - Al_2O_3-Ti(C,N)+10%TiB_2; 3 - Al_2O_3-Ti(C,N) + 30%TiB_2

Rys. 1. Zmiana objętości materiałów w trakcie procesu spiekania: 1 - Al_2O_3-Ti(C,N); 2 - Al_2O_3-Ti(C,N)+10%TiB_2; 3 - Al_2O_3-Ti(C,N) + 30%TiB_2

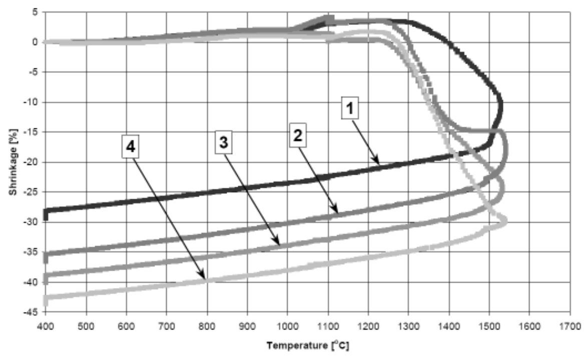

Fig. 2. Shrinkage of materials sintered by SPS-method: 1 - Al_2O_3 -Ti(C,N); 2 - Al_2O_3-Ti(C,N)+MoS_2; 3 - Al_2O_3 -Ti(C,N)+WS_2; 4 - Al_2O_3-Ti(C,N)+MoO_3+CaO

Rys. 2. Zmiana objętości materiałów w trakcie procesu spiekania: 1 - Al_2O_3-Ti(C,N); 2 - Al_2O_3-Ti(C,N)+MoS_2; 3 - Al_2O_3-Ti(C,N) + WS_2; 4 - Al_2O_3-Ti(C,N)+MoO_3+CaO

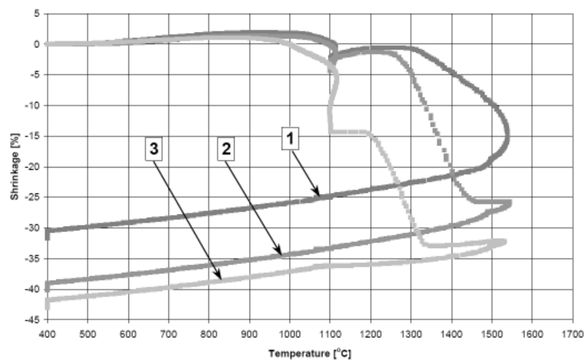

Fig. 3. Shrinkage of materials sintered by SPS-method: 1 - Al_2O_3-Ti(C,N); 2 - Al_2O_3-Ti(C,N)+$CaSO_4$; 3 - Al_2O_3-Ti(C,N) + $SrSO_4$

Rys. 3. Zmiana objętości materiałów w trakcie procesu spiekania: 1 - Al_2O_3-Ti(C,N); 2 - Al_2O_3-Ti(C,N)+$CaSO_4$; 3 - Al_2O_3-Ti(C,N) + $SrSO_4$

TABLE 1. **Sintering parameters of Al_2O_3-Ti(C,N) base ceramic with additives (T_t - melting point; P_{max} - max. pressure; T_{Pmax} - temperature at max. pressure; T_s - sintering temperature; t_s - sintering time; P_{Ts} - pressure at sintering temperature)**

TABELA 1. **Parametry procesu spiekania ceramiki Al_2O_3-Ti(C,N) z dodatkami (T_t - temperatura topnienia; P_{max} - ciśnienie maksymalne; T_{Pmax} - temperatura przy ciśnieniu maksymalnym; T_s - temperatura spiekania; t_s - czas spiekania; P_{Ts} - ciśnienie przy temperaturze spiekania)**

Additives	T_t °C	P_{max} MPa	T_{Pmax} °C	T_s/t_s °C/s	P_{Ts} MPa
$CaSO_4$	1450	35	1100	1500 60	10
$SrSO_4$	1605	35	1500	1500 60	35
WS_2	1250	35	1000	1500 60	10
MoS_2	1185	35	1000	1500 60	10
TiB_2	2996	35	1650	1650 60	35
MoO_3 CaO	795 2580	35	1000	1500 60	10

Methodology

After sintering, the materials were subjected to a study of their physical and mechanical properties. The apparent density ρ_p, was measured using the hydrostatic method. Young's modulus measurements of the sintered samples were also taken, using the ultrasonic method of measuring the transition speed of transverse and longitudinal waves, using a Panametrics Epoch III flaw detector. The hardness was determined by the Vickers method at a load of 9807 mN using a digital hardness tester (Future Tech. Corp. FM-7) The tribological studies were performed using a UMT-T2 universal testing machine. Analysis of the tribological properties of the individual materials was performed at a temperature of 22°C and the friction radius was in the range of 3 to 5 mm. The force of the counter-sample on the tested material was 10 N, the speed of the sample was 0.100 m/s and the friction road was 100 m. The physical, mechanical and tribological investigations were performed on the samples with a ground and polished surface.

Results of investigations

The results of the measurements of density, Young's modulus and Vickers hardness are contained in Table 2. The results of the measurements of the friction coefficient for Al_2O_3-Ti(C,N) base ceramics with solid lubricant participation are contained in Table 3.

The SPS sintered materials were characterized by the values of relative density from 93 to 99%. In the case of the TiB_2 addition, the relative density, Young's modulus and hardness *HV*1 were close or equal to the values of the base material. For the other additives, the Young modulus ranged from 74 to 83% and hardness from 62 to 76% of the value for the base material, Al_2O_3-Ti(C,N).

TABLE 2. **Properties of Al_2O_3-Ti(C,N) base ceramic with additives, sintered by SPS-method (T_s - sintering temperature; ρ_w - relative density; E - Young modulus; HV - Vickers hardness)**

TABELA 2. **Właściwości ceramiki bazowej Al_2O_3-Ti(C,N) z dodatkami, spiekanej metodą SPS (T_s - temperatura spiekania; ρ_w - gęstość względna; E - Moduł Younga; HV - twardość Vickersa)**

Materials	T_s °C	ρ_w %	E GPa	HV	
				HV1	σ
Al_2O_3-Ti(C,N)	1650	97.9	401	2042	56
Al_2O_3-Ti(C,N) 35MPa - 1000°C	1500	84	231	842	22
Al_2O_3-Ti(C,N) 35MPa - 1100°C	1500	86	292	1106	20
Al_2O_3-Ti(C,N) +$CaSO_4$	1500	96.7	333	1338	80
Al_2O_3-Ti(C,N) +$SrSO_4$	1500	95.8	297	1260	14
Al_2O_3-Ti(C,N) +WS_2	1500	91.8	297	1308	51
Al_2O_3-Ti(C,N) +MoS_2	1500	96.8	301	1346	30
Al_2O_3-Ti(C,N) +10%TiB_2	1650	97.7	392	1996	55
Al_2O_3-Ti(C,N) +30%TiB_2	1650	96.6	402	2106	54
Al_2O_3-Ti(C,N) +MoO_3+CaO	1500	96.7	325	1570	56

Table 2 presents the measurement results of relative density, the Young modulus and hardness which were recorded for the base material Al_2O_3-Ti(C,N) after sintering by the SPS-method with parameters similar for materials with solid lubricant additives. The base material sintered at reduced parameters was marked by the lowest relative density, Young's Modulus and hardness.

The materials with low melting phases exhibited better sinterability than the base material, by increasing the presence of diffusion in the liquid phase, as evidenced by the curves shown in Figures 2 and 3.

Application of the SPS method made it possible to lower the temperature of sintering of the base ceramics Al_2O_3-Ti(C,N) and significantly shorten the time of this process. The materials after sintering by SPS had a modified surface layer with a high content of graphite, which must be removed by grinding.

Based on the results of the tribological investigations, it was found that the additives induce a lower friction coefficient. The values of this coefficient for materials with solid lubricant additives after SPS sintering ranged from 49 to 86% of the coefficient for the base materials. The lowest value of the friction coefficient (0.25) was measured for the material with the WS_2 phase. A low friction coefficient was also observed for the materials with 10% TiB_2 and 30% TiB_2, and with the addition of MoO_3 and CaO, which were characterized by the best mechanical properties.

TABLE 3. **Tribological results of Al_2O_3-Ti(C,N) base ceramic with additives, sintered by SPS method**

TABELA 3. **Wyniki badań tribologicznych ceramiki bazowej Al_2O_3-Ti(C,N) z dodatkami, spiekanej metodą SPS**

Materials	Friction radius	Friction coefficient	
	mm	COF	σ-COF
Al_2O_3-Ti(C,N)	3	0,51	0,06
Al_2O_3-Ti(C,N)+$CaSO_4$	3	0,37	0,04
	4	0,42	0,05
Al_2O_3-Ti(C,N)+$SrSO_4$	3	0,38	0,05
	4	0,30	0,06
Al_2O_3-Ti(C,N)+WS_2	3	0,25	0,03
	4	0,29	0,04
Al_2O_3-Ti(C,N)+MoS_2	3	0,44	0,07
	4	0,40	0,09
Al_2O_3-Ti(C,N)+10%TiB_2	3	0,33	0,06
	4	0,35	0,04
Al_2O_3-Ti(C,N)+30%TiB_2	4	0,35	0,05
	5	0,39	0,08
Al_2O_3-Ti(C,N)+MoO_3+CaO	3	0,31	0,05
	4	0,32	0,05

CONCLUSIONS

Presented in this study are the results of the mechanical and tribological studies of Al_2O_3-Ti(C,N) base ceramics with additives to reduce friction resistance. Irrespective of the type of additive, it was possible to reduce the friction coefficient to between 49 and 86% of the base material coefficient.

The lowest friction coefficient was measured for the material after SPS sintering with WS_2, but this material was characterized by a relatively low Young's Modulus and hardness.

Taking into account the value of the friction coefficient and the physical and mechanical properties, the most promising material is a ceramic with the addition of TiB_2 or MoO_3 with CaO.

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