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COMPOSITES THEORY AND PRACTICE

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ALUMINUM - CERAMIC COMPOSITE MATERIALS REINFORCED WITH NANOPARTICLES PREPARED VIA POWDER METALLURGY METHOD

The applied methods for preparation of the reference powders contains high-energy milling in planetary mills, resulting in a particles size reduction to the dispersion level. Such a reinforcing particle size allows one to obtain high wear resistance. Apart from size-reduction of the ceramic phase, mechanical coupling of hard ceramic and plastic metallic (matrix of the composite) particles takes place. Stable coupling between the ceramic and metallic particles was obtained by pressing and sintering in a high-temperature press. This method allows one to eliminate the problems occurring in classic casting technologies applied for the manufacturing of composites such as: low wettability of the particles by liquid metal or a heterogeneously distributed reinforcing phase. In addition, the applied modification of the composite composition with glassy carbon particles, contributed to the change in the wear mechanism of the composite and cooperating cast iron. Evaluation of the tribological properties was performed by friction and wear coefficient determination. SEM observations of the composite powder and of the composite allowed the authors to evaluate the influence of the powder preparation process parameters on the composite microstructure.

Keywords: high energy ball milling, sintering, nanocomposites, coefficient of friction, wear, powder technology

MATERIAŁY KOMPOZYTOWE ALUMINIUM-CERAMIKA UMACNIANE NANOCZĄSTKAMI OTRZYMYWANE METODĄ METALURGII PROSZKÓW

Przedstawiono rozwiązanie technologiczne umożliwiające wytworzenie drobnodyspersyjnych kompozytów na osnowie aluminium zbrojonych cząstkami ceramicznymi do zastosowań tribologicznych. W uzyskanych materiałach jako zbrojenie wykorzystano cząstki Al_2O_3 oraz SiC, każdorazowo o 20% udziale masowym. Zastosowane metody preparacji proszków referencyjnych polegające na wysokoenergetycznym mieleniu pozwoliły na rozdrobnienie ceramicznych cząstek do wielkości dyspersyjnej, umożliwiającej uzyskanie wysokiej odporności na ścieranie. Oprócz rozdrobnienia fazy ceramicznej, podczas mielenia następowało mechaniczne połączenie twardych cząstek ceramicznych z plastycznymi cząstkami metalicznymi stanowiącymi osnowę kompozytu. Następnie w wyniku prasowania i spiekania proszku uzyskano materiał kompozytowy. Metoda ta pozwala na eliminację problemów występujących w klasycznych technologiach odlewniczych, dotyczących głównie słabej zwilżalności cząstek ceramicznych przez ciekły metal oraz niejednorodności rozmieszczenia fazy zbrojącej. Dodatkowo zastosowana modyfikacja składu kompozytu cząstkami węgla szklistego przyczyniła się do zmiany mechanizmu zużycia pary trącej (kompozyt - żeliwo). Ocena właściwości tribologicznych kompozytu została dokonana na podstawie badań współczynnika tarcia i zużycia. Obserwacje mikroskopowe SEM proszku kompozytowego oraz kompozytu pozwoliły na ocenę wpływu parametrów procesu przygotowania proszku kompozytowego na mikrostrukturę kompozytu.

Słowa kluczowe: wysokoenergetyczne mielenie, prasowanie i spiekanie, nanokompozyty, współczynnik tarcia, zużycie, technologia otrzymywania

INTRODUCTION

The possibility of designing the phase composition and development of composite properties through the selection of the sort, form, size and fraction of the reinforcing phase has contributed to the application of this group of materials in various technical branches. For instance there are - among others - aluminum - and copper-matrix composites reinforced with ceramic particles. Al_2O_3 or SiC particles applied in the composites allowed the authors to obtain materials appropriate for frictional couplings, having advantageous mechanical properties, able to work at a significantly higher load, sliding velocity and temperature [1]. The ceramic particles applied in the composite contributed to the elevation of the friction coefficient as well as a decrease in the wear and stabilization of these properties during exploitation. The production technology of this group is based on a composite casting process, for example by introducing the particles into the melt by the mixing method. The production of materials with proper properties is difficult because of poor wettability of ceramics particles by liquid metal. This results in weaker bonding at the boundaries of components. It is a reason for the decrease in mechanical properties and changing of the wear mechanism for materials which work in friction conditions. The particles which were weakly connected with the matrix were taken out and then worked between the friction areas as a loose abrasive. Those effects lead to increased wear of the friction pair materials [2].

Furthermore in the classical methods of producing composite materials, especially gravity casting and blow-off during casting, led to the agglomeration and segregation of particles in the whole volume of the material. Innovative methods such as thixotropic casting, the *in-situ* method and bubbling of inert gas were used in order to eliminate the unfavorable effects of classical casting [3-5]. The biggest problem during the contact of liquid metal with ceramic particles is to avoid the formation of brittle phases (Al_4C_3) at the phase boundaries. It could happen if carbon particles are present in the liquid metal, and in the case of aluminum alloys, the formation of Al_4C_3 occurs [6, 7]. In order to reduce this unfavorable phenomenon in the present research, two-step technology was used in order to connect the components. The first step was the mechanical-chemical connection of brittle ceramic particles in ductile aluminum for the manufactured composite powders. In the second step, composites were produced from the powders by hot pressing and sintering technologies. These processes were utilized to obtain proper bonding between the matrix and reinforcement. High energy ball milling provides not only the production of powders but also fragmentation of particles to a dispersive or nanometic size. A lower particle size provides an increase in durability properties and an increase in the wear resistance [1, 2]. The results of the authors' own research presented in the paper [8] led to fragmentation of the reinforcement particles to a nanometric size in proper conditions of high energy ball milling for the reference powders.

According to preliminary assumptions on the total coverage of the metal particle surfaces by the fine ceramic particles, the size of the relevant particles and their mass fractions were considered. It has been anticipated that brittle ceramic particles would be reduced to a diameter below 1 μm due to the course of mechanical-chemical processing. Additionally, the reinforcement was shredded during ball milling to a size less than 1 μm. Reinforcing ceramic particles of SiC or Al_2O_3 and the addition of glassy carbon were used in the composite material. The glassy carbon addition was applied in order to improve the tribological properties, especially a decrease in the friction coefficient [9].

MATERIALS

Calculating the chemical composition allowing use of a wide potential of mechanical alloying was the preliminary step of the new technology. The ratio of the matrix particles volume to the reinforcement particles volume was set on the basis of the average particle diameters and their surface area (Fig. 1). Based on this ratio, the mass fraction of the components was specified. In the next step, the mass fraction of each type of particles was calculated. Taking into account the applied approximations and modification of the composition by glassy carbon, the final composition consisted of 73 mass.% Al, 20 mass.% Al_2O_3/SiC, 5 mass.% glassy carbon.

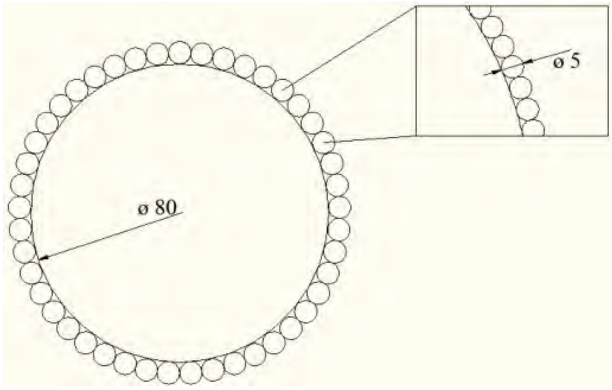

Fig. 1. Layer of ceramical particles with 5 μm diameter on surface of matrix particles with 80 μm diameter

Rys. 1. Warstwa cząstek ceramicznych o średnicy 5 μm na powierzchni cząstek osnowy o średnicy 80 μm

TABLE 1. **Selection of chemical composition**
TABELA 1. **Dobór składu chemicznego**

Particle	Average diameter [μm]	Number of particles	Density [g/cm^3]	Mass fraction [%]
Al	80	1	2.7	68÷71
Al_2O_3	5	1156	3.8	27
SiC	5	1156	3.2	23
C	24	6	1.1	5

Stearic acid (2 mass.%) was used to improve the milling and agglomeration conditions. Used as the matrix, the aluminum powder had a particles diameter between 45÷80 μm. A part of the screened particles of aluminum had a longitudinal dimension longer than 45 μm. The cause of this phenomenon was the penetration of elongated particles through the sieve. The applied screening was used for breaking agglomerates and particles whose size was substantially greater from established one.

There were three types of applied ceramic reinforcement:

1. alpha Al_2O_3 - Martoxid 70 (Al_2O_3 content over 99.8 mass.%, particles diameter d_{90} = 3 μm)
2. SiC - high purity and particle size 5÷10 μm

3. glassy carbon C - particle size 20÷80 μm. Modification of the composition by the comparatively low reactive glassy carbon was performed by employing much larger particles than than the Al_2O_3 and SiC ones. The possibility of breaking large brittle glassy carbon particles directly during ball milling was discovered during the preliminary trials.

In the first step of the technology, the composite powder was produced using the high energy ball milling process, performed in a planetary mill - Fritsch Pulverisette Premium Line 7. Alumina lining and alumina milling balls of 5 mm in diameter were used. The ceramic and metal particles were dried before milling for 24 hours at 70°C. The milling process was carried out in order to combine the hard ceramic particles with the ductile matrix particles, while reducing the size of the brittle ceramic particles. The formation of the composite powder was dependent especially on the milling parameters. They were selected experimentally taking into consideration several mechanical-chemical reactions occurring during the course of milling. The most important of them were the breaking energy of the particles, increase in the powders reactivity due to the formation of new surfaces and the temperature increase inside the mill bowl due to the collision and friction of the particles and milling media.

Too low values of milling energy led to component mixing without changing the particle size, however, too high values led to a temperature increase. This was the reason for an increased yield of alumina and the deposition of a metal layer on the mill bowl walls and on the surfaces of the milling balls (Fig. 2).

The best quality of resultant composite powder was obtained when the following milling parameters were applied:

1. rotation rate: 1000 rpm
2. milling time: 5 min
3. number of milling: 12
4. interval between each cycle: 30 min ball to powder weight ratio of: 4:1 New reactive surfaces of the aluminum powders particles formed during milling. This led to rapid oxidation if the composite powder was exposed to ambient atmosphere.

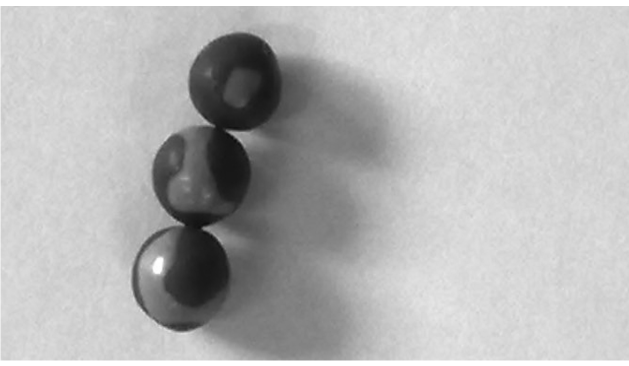

Fig. 2. Incorrect selection of grinding parameters - permanent deposition of Al (darker area) on surface of grinding media (lighter area)

Rys. 2. Niewłaściwy dobór parametrów mielenia – trwałe osadzenie Al (obszar ciemniejszy) na powierzchni mielników (obszar jaśniejszy)

In order to reduce this effect, a protective atmosphere was used. Milling in a nitrogen and argon atmosphere was performed. Because of the higher purity and lesser reactivity, argon was used in all the subsequent experiments. The milling chamber was opened after milling in the glove box, the powders were then placed in airtight boxes and were stored there until the hot-forming operation. Analysis of the size and distribution of the ceramic particles inside the aluminum matrix and quality assessment of the connection between the ceramic and aluminum phases were performed using a Scanning Electron Microscope, Hitachi S-3400N. A high value of fragmentation of the ceramic particles and mechanical bonding between the metallic and ceramic phases were found. For example, the diameter of aluminum oxide particles in the composite powder ranged from 0.2 to 2 μm, which indicates the high effectiveness of the performed processes (Fig. 3). In the case of such high fragmentation of reinforcement, the resultant composite particles could be considered as a material reinforced with nanoparticles. According to the survey [2], this was a reason for the increase in the mechanical properties of the bulk composite. In the case of reinforcement with SiC particles, similar results were obtained. Fragmentation of the ceramic particles up to a size under 1 μm and good connection with the matrix in the composite (Fig. 4) were achieved after the same milling.

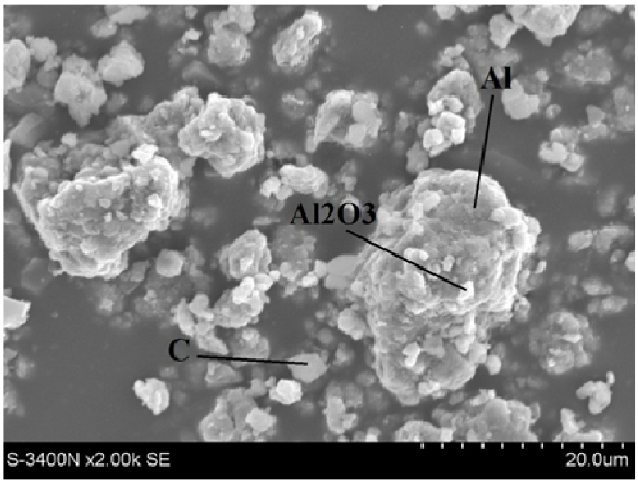

Fig. 3. Composite powder of Al–Al_2O_3+C, SEM

Rys. 3. Wygląd proszku kompozytowego Al–Al_2O_3+C, SEM

In both cases of composite powders, large surfaces on the aluminum particles non-oxidized and not coated by ceramics were visible. These effects determine the possibility of subsequent processes - pressing and sintering.

The last step of the technology consisted of pressing with simultaneous sintering in an induction, high-pressure Degussa press in order to obtain permanent matrix-ceramic connections. The best mechanical properties were achieved when two steps of heating were applied: holding at 480°C for 20 minutes followed by holding at 700°C for 15 minutes. The pressure of 15 MPa was applied. In this part of the experiments, permanent matrix-ceramic particles connection as well as uniform spatial distribution of the reinforcing phases were obtained as a result of correct selection of the process parameters (Figs. 5, 6).

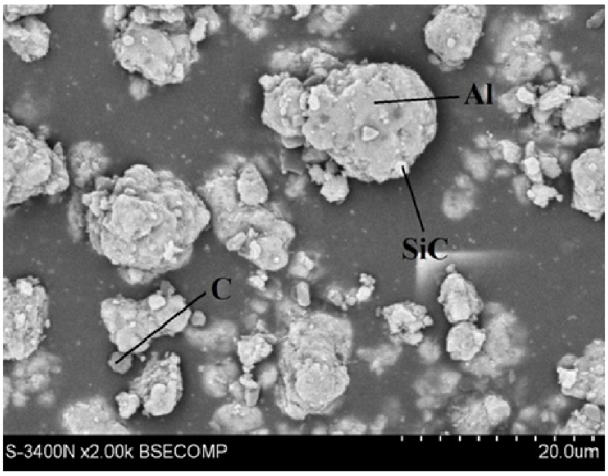

Fig. 4. Al-SiC+C composite powder, SEM

Rys. 4. Wygląd proszku kompozytowego Al-SiC+C, SEM

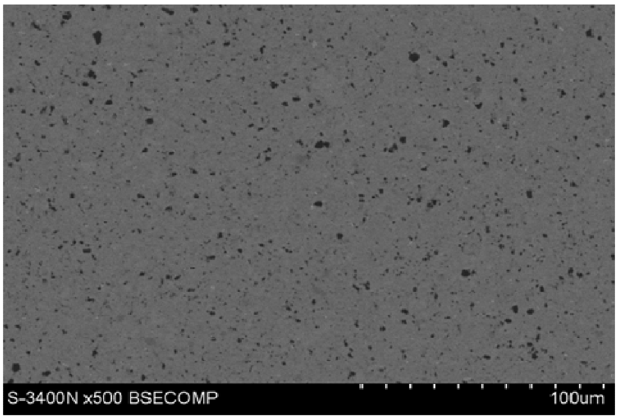

Fig. 5. Microstructure of Al-Al_2O_3+C composite,SEM

Rys. 5. Mikrostruktura kompozytu Al-Al_2O_3+C, SEM

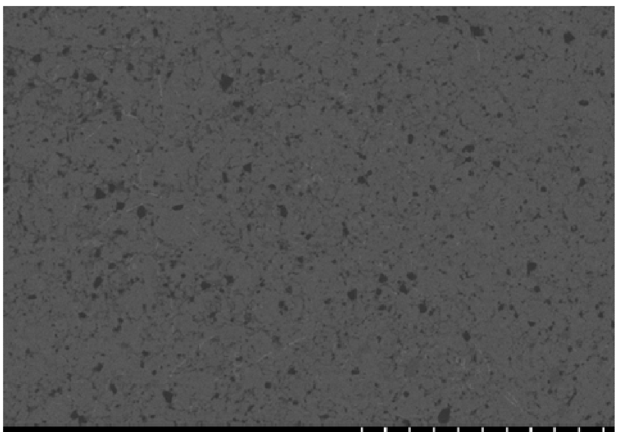

Fig. 6. Microstructure of Al-SiC+C composite, SEM

Rys. 6. Mikrostruktura kompozytu Al-SiC+C, SEM

Uniform distribution of the glassy carbon particles in the composite was observed by a Scanning Electron Microscope. The glassy carbon particles were reduced to a diameter under 2 μm as a result of the high-energy milling earlier described. However, microscopic studies revealed the tendency of glassy carbon particles to deposit at the boundaries of the matrix grains. This is evidence for the connection between the carbon and aluminum particles.

TRIBOLOGICAL MEASUREMENTS

Because the composites could be potentially used as friction materials, determination of the friction coefficient and wear rate were thus studied. The measurements were conducted in friction in air, cast iron (GJL300) as the pin, the produced composites as the disc, reciprocating movement of 0.05 m/min, with a load of 35 N and 50 N on a 50 m distance were used.

TABLE 2. **Results of tribological test**
TABELA 2. **Wyniki badań tribologicznych**

Composite	Friction coefficient	Wear [$m^3/m*10^{-12}$]	
		disc	pin
Al–Al_2O_3–C (load 35 N)	0.07÷0.17	119.70	7.69
Al–Al_2O_3+C (load 50 N)	0.03÷0.14	191.17	11.03
Al–SiC+C (load 35 N)	0.02÷0.10	21.33	6.41
Al–SiC+C (load 50 N)	0.02÷0.07	16.00	7.18

The results of these tests are shown in Table 2. The wide range of friction coefficient values is a result of the friction increase as an outcome of temporary unavailability of glassy carbon between the surfaces of the disc and the pin. Glassy carbon particles could serve as a lubricant. Silicon carbide exhibits slightly lower friction coefficient values. The mass losses analysis shows the strong influence of the reinforcing phase on the wear of the tested specimens. The composites with SiC particles exhibit a lower wear rate in comparison to those reinforced with Al_2O_3. The type of reinforcement influences the cast iron pin wear as well. Higher wear was noted for the aluminum oxide reinforcement. The reason for such a large difference in the mass losses could be caused by the various wear mechanisms (Fig. 7). In the composite reinforced with Al_2O_3 particles, the predominant wear mechanism is the abrasive action induced by cutting in micro areas (Fig. 7A). On the contrary, the abrasive action in the Al-SiC+C composite is not so pronounced. In these specimens, we can observe the plastic deformation effect and slight detachment, which can confirm wear by delamination. Moreover analysis of the chemical composition in the areas after friction shows dissimilarities in the qualitative analysis result.

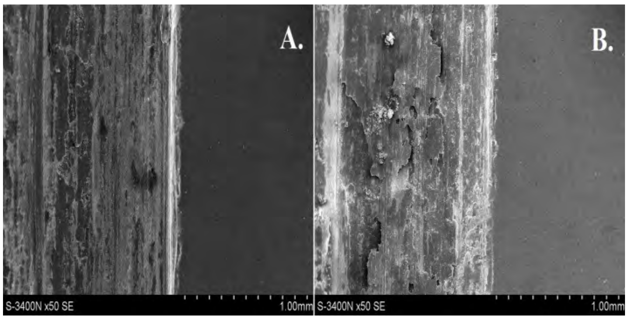

Fig. 7. Surfaces area after wear in Al-Al_2O_3+C (A.) and Al-SiC+C (B.) composite, SEM

Rys. 7. Powierzchnia śladu zużycia kompozytu Al-Al_2O_3+C (A.)/ Al-SiC+C (B.), SEM

In both materials, iron contamination derived from the counter specimen was found on the tested surfaces. A significant difference in the glassy carbon content was found in the areas after the friction tests. A much lower value of glassy carbon particles from the wear product was found in the composite reinforced with Al_2O_3 particles. A higher value of glassy carbon in the composites with SiC reinforcement in the friction areas could protect against wear since the carbon particles could act as a lubricant. This is a possible reason for the lower wear in the Al-SiC+C composite.

SUMMARY

The results of the performed research show an attempt to obtain composite materials reinforced with nanoparticles. Appropriate parameters of the high energy ball milling were used to produce composite powders with a specific phase composition, reinforced with nanoparticles. The resultant materials could be used in high loaded friction pairs, providing a low friction coefficient and high wear resistance. Description of the preliminary results of the performed research is the first step to further technological development, which allows the manufacturing of composites with nanoparticles reinforcement as a result of structure fragmentation in the high energy milling process.

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