Polskie Towarzystwo Materiałów Kompozytowych
Polish Society of Composite Materials
Kompozyty 11: 3 (2011) 197-201
KOMPOZYTY
COMPOSITES

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Otrzymano (Received) 22.02.2011

FRACTURE TOUGHNESS OF Al_2O_3-Ni COMPOSITES WITH NICKEL ALUMINATE SPINEL PHASE $NiAl_2O_4$

The article presents the results of research on the modification of the properties of ceramic Al_2O_3 using particles of nickel. As starting materials, powders of Al_2O_3 and Ni were used, from which mixtures of Al_2O_3+x% vol. Ni (x = 0, 1, 3, 5) were prepared. They were subjected to sintering in an argon atmosphere at 1450°C for one hour. The physical properties of the composites such as: density, porosity, absorptivity and contractility were determined. Moreover, analyses of the received phase composites (from the surface and cross-section) have been made using the diffraction method, which showed $NiAl_2O_4$ spinel phase formation. Spinel is formed mainly at the border of Ni and Al_2O_3 grains. It was confirmed in the microstructure photographs taken using scanning and transmission electron microscopy methods. The mechanical properties have been investigated: hardness HV, nanohardness and fracture toughness (crack length measurement method with Vickers indentation). As the amount of nickel hardness HV decreased from 17.3 GPa to 100% Al_2O_3 to 13.2 GPa for Al_2O_3 + 5%vol. Ni, the nanohadrness values increased, which could have been caused by the presence of a spinel phase. The composites were characterized by higher resistance to brittle fracture than 100% Al_2O_3. This was due to blocking, deflecting and bridging cracks in nickel and by branching cracks by spinel particles.

Keywords: cermetals, Al_2O_3, fracture toughness, spinel phase

ODPORNOŚĆ NA PĘKANIE KOMPOZYTÓW Al_2O_3-Ni Z UDZIAŁEM FAZY SPINELOWEJ GLINIANU NIKLU $NiAl_2O_4$

W artykule przedstawione zostały wyniki badań nad modyfikacją właściwości ceramiki Al_2O_3 cząstkami niklu. Jako surowce wyjściowe wykorzystane zostały proszki Al_2O_3 i Ni, z których przygotowane zostały mieszaniny Al_2O_3+x% obj. Ni (x = 0, 1, 3, 5). Poddane zostały one spiekaniu w atmosferze argonu w temperaturze 1450°C przez jedną godzinę Oznaczone zostały właściwości fizyczne kompozytów, m.in: gęstość względna, porowatość, nasiąkliwość czy skurczliwość. Wykonane zostały także (metodą dyfrakcji) analizy fazowe otrzymanych kompozytów (z powierzchni oraz z przekroju), które wykazały powstanie fazy spinelowej $NiAl_2O_4$ głównie w warstwie powierzchniowej. Spinel ten wytworzył się głównie na granicy ziaren Al_2O_3 oraz Ni, co zostało potwierdzone na zdjęciach mikrostruktury wykonanych z użyciem skaningowego oraz transmisyjnego mikroskopu elektronowego. Zbadane zostały własności wytrzymałościowe: twardość HV_{30}, nanotwardość oraz odporność na kruche pękanie (metodą pomiaru długości pęknięć z odcisku Vickersa). Wraz ze wzrostem ilości niklu twardość *HV* obniża się z 17,3 GPa dla czystego Al_2O_3 do 13,2 GPa dla Al_2O_3+5% obj. Ni, natomiast wartość nanotwardości wzrosła, co mogło być spowodowane obecnością $NiAl_2O_4$. Kompozyty charakteryzowały się wyższą odpornością na kruche pękanie niż czyste Al_2O_3. Spowodowane było to blokowaniem, odchylaniem i mostkowaniem pęknięć na cząstkach niklu oraz rozgałęzianiem pęknięć przez obszary z obecnością spinelu.

Słowa kluczowe: cermetale, Al2O3, odporność na kruche pękanie, faza spinelowa

INTRODUCTION

Alumina ceramics is the one of the most widely used ceramic materials. This is mainly because of its availability and characteristics such as high hardness, abrasion resistance, stability in high temperature and chemical resistance [1, 2]. The factor which limits Al_2O_3 engineering applications is the low resistance of the material to fracture toughness.

Many research centers aim to improve these properties. They focus on the manufacture of composite materials based on Al_2O_3 ceramic matrix reinforced with particles, whiskers or fibers [3-5]. Extending the application of ceramic-metal composite is now becoming indispensable in many fields of science and technology. The Al_2O_3 + Ni composite is one of the most developed materials. Both literature data [6, 7] as well as the authors' own research [8, 9] indicate that depending on the sintering process of this material, it a new phase of spinel $NiAl_2O_4$ may be created. The spinel phase due to its hardness and brittleness can also be intensely involved in the fracture of composites.

The aim of this research was to obtain Al_2O_3-Ni composites with various contents of Ni and investigate the high stress intensity factor K_{IC} as well analyze the propagation of cracks in alumina-nickel composites.

EXPERIMENTAL METHODS

In the studies α-alumina powder α-Al_2O_3 (purity 99.99%) produced by the Taimei Co. Japan Ltd and Ni powder (purity 99.8%) produced by the Sigma-Aldrich were used. The average particle size of the Al_2O_3 powder was 0.21 microns while for the Ni powder it was 17.46 microns. The density was respectively: for nickel d = 8.9 g/cm^3, for alumina d = 3,89 g/cm^3.

With these materials the powder mixtures composition were made: α-Al_2O_3 + x% vol. Ni (x = 0, 1, 3, 5). They were subjected to homogenization in an ethanol medium in a ball mill for 1 hour. After drying at 60°C, the mass was crushed to obtain a homogeneous powder.

The powders were formed with the addition of a binder (PSA 5%) by uniaxial pressing at a pressure of 50 MPa, and then sintered in an argon atmosphere at 1450°C for one hour. The resulting shapes were cylinders with a diameter of 8mm and a height of 4mm. After the preparation of a sample (with diamond abrasive pastes) such characteristics as relative density, porosity, water soaking and others were measured with the use of the hydrostatic method.

Microstructure observations were made using a stereomicroscope - Olympus SZX10, a scanning electron microscope - HITACHI S-3500N and with transmission electron microscopy TM 1200. The computer program used in the stereological analysis of the obtained images was "MicroMeter" written by Tomasz Wejrzanowski [10].

Phase analysis of the samples was carried out by X-ray diffraction, measured by using a Philips PW 1830 diffractometer, operating in a θ÷2θ configuration (CuKa radiation = 1.5418 Å - monochromatic beam diffraction). Tests were performed on the surface and cross-sections of samples.

The hardness HV (with a load of 294 N) and critical fracture toughness factor K_{IC} were examined using a Future Tech FV-700E durometer, using a method based on crack length measurement from a Vickers diamond indentation. Only the central cracks were taken into account. For the calculation of the K_{IC} value the following equation was used [11]:

$$K_{IC} = 0,067 \cdot \left(\frac{E}{HV}\right)^{0,4} \cdot \left(\frac{c}{a}\right)^{-1,5} \cdot HV \cdot \sqrt{a}$$

where: $a = \frac{d}{2}$ (d-indentation diagonal), HV - Vickers hardness, E - Young's modulus, c - crack length.

Measurements of nanohardness were made with HYSITRON Triboindenter TI-900. Due to the difference in the distribution of phases, the measurements of the composites were made at the edges of the samples and in the middle.

RESULTS AND DISCUSSION

After the process of sintering, the obtained samples were characterized by the absence of cracks on the surface which may be evidence of their good compaction. The results of the study of the relative density (ρ_w), open porosity (P_o), soaking (N) and volume shrinkage (s_v) are presented in Table 1.

TABLE 1. **Relative density (ρ_w), soaking (N), open porosity (P_o) and shrinkage (s_v) of Al_2O_3+x%Ni composite depending on nickel content**

TABELA 1. **Zmiany gęstości względnej (ρ_w), nasiąkliwości (N), porowatości otwartej (P_o), skurczliwości (s_v) kompozytu Al_2O_3+x%Ni w zależności od zawartości niklu**

Ni [% vol.]	Ni [% wt.]	ρ_w [%]	P_o [%]	N [%]	s_v [%]
0	0	100	1.98	0.52	38.79
1	2.3	96.62	2.98	0.79	40.9
3	6.75	94.28	2.6	0.67	39.77
5	10.97	92.11	2.03	0.5	40.33

What can be concluded is that with an increasing content of metallic phase, the compaction of the sintered composites decreases as compared to 100% Al_2O_3. Their soaking and volume shrinkage remains at a similar level, though.

During the macroscopic observation, it was found that a characteristic feature of the samples with the addition of nickel was an intense blue color, suggesting the creation of a new phase. Although the sintering process was carried out under argon, the resulting composites have emerging nickel aluminate spinel precipitates in the outer zone of the sample (Fig. 1 - AREA I).

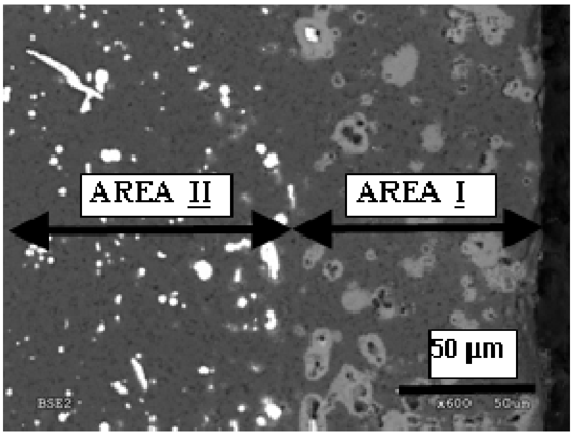

Fig. 1. SEM photo of cross-section of Al_2O_3+3% vol. Ni composite

Rys. 1. Zdjęcie z mikroskopu skaningowego przekroju poprzecznego kompozytu Al_2O_3+3% obj. Ni

The spinel phase occurs in the form of independent particles and as a layer surrounding the Ni particles. In addition to a layer at the edge, there are uniformly distributed nickel particles in the Al_2O_3 matrix in the entire volume (Fig. 1 - AREA II). The phase analysis tests of all the manufactured composites confirmed the move of nickel to spinel phase on the sample surface (Fig. 2A). In the case of longitudinal sections of the sample (Fig. 2B), most of the particles of nickel have not reacted and remained unbound in the form of small particles or agglomerates.

The distribution of phases evidenced by the fact that at the edge of the sample is a spinel phase and Al_2O_3, and in the middle of the sample Ni, Al_2O_3 and $NiAl_2O_4$ is related to the process of spinel formation and stabilization.

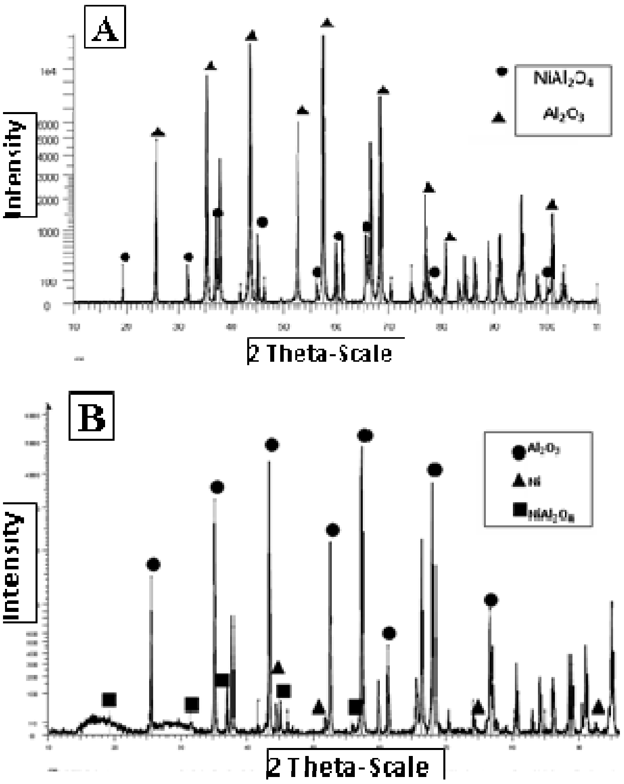

Fig. 2. Phase analysis of Al_2O_3+1% vol. Ni composite: A) made on sample surface (AREA I), B) made on cross-sectional sample (AREA II)

Rys. 2. Dyfraktogram kompozytu Al_2O_3+1% obj. Ni: A) wykonany dla powierzchni próbki (AREA I), B) wykonany dla przekroju poprzecznego próbki (AREA II)

The first factor that may control the formation of the spinel phase is the partial pressure of oxygen during the sintering process [12]. If there is a low pressure, the spinel which was created in the first sintering stage can reduce back to nickel. In the process of manufacturing the pressure was not measured. Another factor influencing the formation of the spinel phase is the contact of the sample with oxygen. Nickel can react with oxygen from the atmosphere or the Al_2O_3 to form spinel according to the reaction [12]:

$$Ni + Al_2O_3 + \frac{1}{2} O_2 \rightarrow NiAl_2O_4$$

Already during the preparation of powders while mixing, nickel powders can be oxidized to NiO and a spinel may have formed in the way described by the following reaction [13]:

$$Al_2O_3 + NiO \rightarrow NiAl_2O_4$$

In the solid state formation of the spinel, the so-called Wagner mechanism is in force [14].

The $NiAl_2O_4$ phase formed as a area surrounded by ceramics as presented in Figure 3.

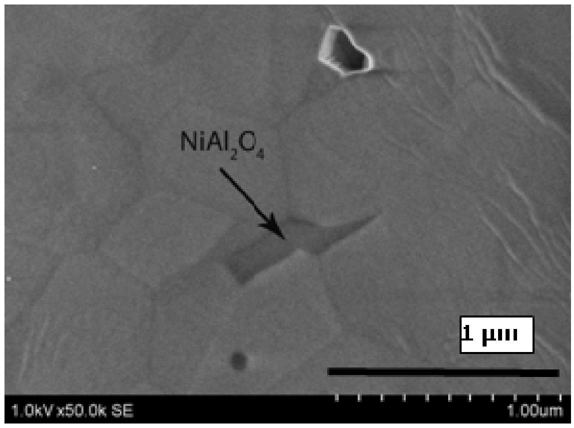

Fig. 3. Transmission electron microscope images of Al_2O_3+1% vol. Ni composite with spinel phase

Rys. 3. Mikrostruktura kompozytu Al_2O_3+1% obj. Ni z widoczną fazą spinelową obserwowaną z użyciem transmisyjnego mikroskopu elektronowego

For the Al_2O_3 +1% vol. Ni composite, stereological analysis was performed for particles of Ni and $NiAl_2O_4$. The results are presented in Table 2.

TABLE 2. **Selected stereological parameters for particles of Ni and spinel precipitates $NiAl_2O_4$**

TABELA 2. **Wybrane parametry stereologiczne dla cząstek Ni i wydzieleń spinelu $NiAl_2O_4$**

	NIKIEL	SPINEL
equivalent particle diameter d_2	3.69 µm	2.7 µm
min. projection of particle diameter d_{min}	3.1 µm	2.5 µm
max projection of particle diameter d_{max}	5.22 µm	4.51 µm
the average thickness of spinel phase g	-	1.35 µm
volume fraction of particles V_V	1%	5%
particle area A	13.52 µm^2	31.49 µm^2

Stereological analysis allowed us to confirm the thesis of M. Lieberthala [15], that the spinel particles have up to six times more volume, although they are smaller diameter particles than nickel.

Due to the heterogeneity of the phase generated, composites hardness HV_{30}, nanohardness and K_{IC} were made in two places: at the edge of the samples (Fig. 1 - AREA I) and in the middle (Fig. 1 - AREA II).

The presence of Ni particles decreases the hardness of the composite as shown in Table 3. Along with a rising the amount of nickel, the HV hardness decreases from 17.3 GPa for 100% Al_2O_3 to 13.2 GPa for Al_2O_3 + 5% vol. of Ni for measurements in the coastal part with the presence of spinel phase (AREA I). There is no significant difference in the hardness between AREA I and AREA II, which was verified by standard deviation.

The measurements of nanohardness in all the of produced samples were taken at a load of 10 mN. The averaged results are shown in Figure 4.

TABLE 3. **Hardness HV_{30} of Al_2O_3+x% Ni composites**
TABELA 3. **Twardość HV_{30} kompozytów Al_2O_3+x% Ni**

Nickel content [vol. %]	Vickers hardness HV_{30kG} [GPa]			
	AREA II		AREA I	
	HV_{30}	Standard deviation	HV_{30}	Standard deviation
0	17.02	1.41	17.33	0.99
1	13.91	0.82	14.6	0.73
3	13.17	0.84	13.57	0.62
5	12.02	0.53	13.24	0.55

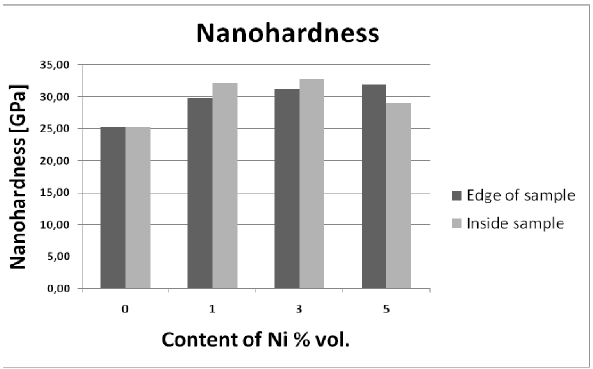

Fig. 4. Nanohardness Al_2O_3+x% Ni composites
Rys. 4. Nanotwardość kompozytów Al_2O_3+x% Ni

A summary of the average nanohardness values (averaged values for the edge and center of the sample) indicates that each of the three sets has a higher nanohardness as compared to Al_2O_3. With the increase of nickel content at the edge of the sample, nanohardness grows. This is a result of the growing proportion of hard-spinel phase with increasing nickel content in the material. The method of measuring the length of Vickers indentation cracks has been used to investigate the K_{IC} factor.

TABLE 4. **Fracture toughness (K_{IC}) of Al_2O_3+x% Ni composites**
TABELA 4. **Odporność na kruche pękanie (K_{IC}) kompozytów Al_2O_3+x% Ni**

Nickel content [vol. %]	Fracture toughness K_{IC} [MPa·m$^{1/2}$]			
	AREA II		AREA I	
	K_{IC}	Standard deviation	K_{IC}	Standard deviation
0	4.13	0.27	4.24	0.39
1	4.75	0.31	5.01	0.46
3	5.21	0.29	5.80	0.37
5	5.72	0.33	6.27	0.41

The fracture toughness of the studied composites increases with the increase of nickel content. This was due to several factors. Owing to the presence of plastic particles of Ni the cracks were deflected by a slowdown which prevented their further propagation (Fig. 5). Moreover, nickel particles cause crack relaxation via local plastic flow [16].

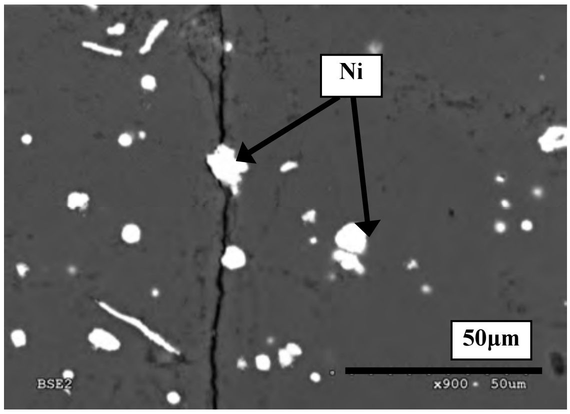

Fig. 5. Deflection of crack coming out of corners of Vickers indentation
Rys. 5. Ugięcie pęknięcia wychodzącego z naroża odcisku po wgłębniku Vickersa

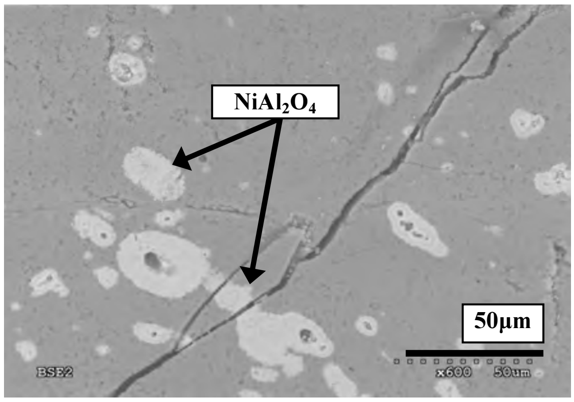

Fig. 6. Example crack propagation observed in spinel phase $NiAl_2O_4$ particle
Rys. 6. Przykładowa propagacja pęknięcia cząstki spinelu $NiAl_2O_4$

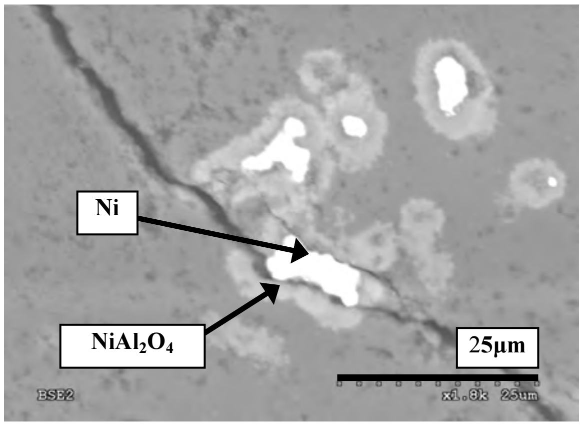

Fig. 7. Example crack propagation observed on Ni/$NiAl_2O_4$ particles border
Rys. 7. Przykładowa propagacja pęknięcia na granicy cząstki Ni/$NiAl_2O_4$

In the case of the spinel $NiAl_2O_4$particles most cracks had a transcrystallite character. A typical course of transcrystallite cracks of spinel particles is shown in Figure 6. Moreover the process of crack branching is observed.

In the case of a particle surrounded by a layer of nickel aluminate spinel phase cracking propagated along the boundary of two phases as shown in Figure 7.

CONCLUSION

In the present study composites of Al_2O_3-Ni with the presence of a nickel aluminate spinel phase were examined. The spinel phase distribution is not homogeneous. In the surface layer of the samples, the $NiAl_2O_4$ is located in the alumina matrix. In the central part of the samples, Ni particles in the alumina matrix as well as the Ni particles surrounded by the spinel layer have been identified. This structure has contributed to the strength properties of the composites, characterized by lower hardness and increased resistance to brittle fracture as compared to 100% Al_2O_3.

Acknowledgements

Authors would like to thank of Prof. M. Szafran and his group from the Department of Chemistry from the Warsaw University of Technology for help in preparing samples.

The results present in this paper have been funded within the KomCerMet Project (contract no. POIG.01.03.01-14-013/08-00 with the Polish Ministry of Science and Higher Education) financed by the Operational Program Innovative Economy 2007-2013.

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