Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

14: 2 (2014) 106-110

COMPOSITES THEORY AND PRACTICE

Justyna Zygmuntowicz*, Aleksandra Miazga, Katarzyna Konopka

Warsaw University of Technology, Faculty of Materials Science and Engineering, ul. Wołoska 141, 02-507 Warsaw, Poland
**Corresponding author. E-mail: zygmuntowicz.j@gmail.com*

Received (Otrzymano) 19.03.2014

MORPHOLOGY OF NICKEL ALUMINATE SPINEL ($NiAl_2O_4$) FORMED IN THE Al_2O_3-Ni COMPOSITE SYSTEM SINTERED IN AIR

The aim of this paper was to characterize the microstructure, especially the morphology of $NiAl_2O_4$ spinel phase in Al_2O_3-Ni composite system. The composites were prepared from the powder mixture contains: 90 vol. % of Al_2O_3 and 10 vol. % of nickel powder. Two series of samples were prepared: Series I with addition of nickel powder of average particle size 8.5 µm and Series II with addition of nickel powder of average particle size 1.5 µm. The presence of the spinel phase in composites was confirmed by both X-ray phase analysis and SEM observations. All tested samples were characterized by homogeneous distribution of $NiAl_2O_4$ phase in the whole volume of the material. The spinel has on oval shape with characteristic void inside. Two areas of spinel phase were identificated. The inner part is compact and consisted of large grains of spinel. In contrast, the outer part is porous and consisted of smaller grains of spinel. In aim to describe the spinel morphology the stereological analysis was done. Results showed that there is no evident influence of Ni initial grain powder size on the spinel formation and morphology. Formation of the spinel retarded the densification of the composites of Al_2O_3-Ni system.

Keywords: $NiAl_2O_4$ spinel phase, SEM, X-ray phase analysis, stereological analysis

MORFOLOGIA SPINELU ($NiAl_2O_4$) W KOMPOZYTACH Z UKŁADU Al_2O_3-Ni SPIEKANYCH W POWIETRZU

Celem niniejszej pracy była charakterystyka mikrostruktury, w szczególności morfologii fazy spinelowej $NiAl_2O_4$ w kompozytach z układu Al_2O_3-Ni. Wykonano dwie serie próbek różniących się między sobą średnią wielkością wyjściowo zastosowanych cząstek proszku niklu. Do przygotowania Serii I wykorzystano nikiel o średniej wielkości cząstek 8,5 µm, natomiast w II Serii użyto cząstek o średniej wielkości 1,5 µm. Na podstawie obserwacji SEM stwierdzono obecność fazy spinelowej w każdej z badanych serii, potwierdziły to również wyniki rentgenowskiej analizy fazowej badanych kompozytów. Wszystkie badane spieki cechowały się jednorodnym rozmieszczeniem fazy $NiAl_2O_4$ w całej objętości kompozytu. Faza spinelowa posiada owalny kształt z pustką w środku. Wyróżnić można dwa obszary. Wewnętrzny obszar spinelu jest zwarty i składa się z dużych ziaren spinelu. Przeciwnie, zewnętrzny obszar jest porowaty i złożony z drobniejszych ziaren spinelu. Do opisu morfologii spinelu została użyta analiza stereologiczna. Na podstawie tej analizy stwierdzono, że rozmiar użytego proszku Ni nie wpływa na formowanie i morfologię wytworzonego spinelu. Ponadto stwierdzono, że obecność fazy spinelowej utrudnia zagęszczenie kompozytu.

Słowa kluczowe: faza spinelowa $NiAl_2O_4$, SEM, analiza stereologiczna, rentgenowska analiza

INTRODUCTION

The intensive development of techniques and technologies in recent years, lead to the increasing requirements for the ceramic composites. These materials should be characterized by respective mechanical properties such as high hardness, high fracture toughness and various functional features.

In order to improve mechanical properties of ceramic composites evenly dispersed second phase such as metal or ceramic are introduced to a ceramic matrix. The incorporation of the ductile metal particles could enhance the facture toughness with respect to a ceramic matrix.

In some ceramic-metal composites systems, during the processing the new phase can appeared, including spinels. In the case of Al_2O_3-Ni system the $NiAl_2O_4$ spinel can occurred. These composites are characterized by high fracture toughness [1]. Furthermore, the microstructural stability at high temperature for ceramics is essential for high temperature applications [2]. As reported by references alumina matrix composite with $NiAl_2O_4$ spinel phase has been used as a dehydrogenation of n-hexanol, CO reduction by propane, a catalyst for the decomposition of methane and preparation of polymethylbenzenes [3]. This type of composites with the spinel phase have been intensively investigated at the Department of Materials Science and Engineering, Warsaw University of Technology [1, 4-8]. These composites are testing due to the analyze of spinel phase

formation as well as its influence on hardness and crack propagation. Especially, the correlation of process parameters on the spinel formation, its morphology and properties of composites has not been understood yet. Because of that, the microstructure of the of alumina matrix composite with $NiAl_2O_4$ spinel phase was characterized in the presented work. Moreover, two initial Ni-powders with different size of powder were used. The special attention was concentrated on description of the $NiAl_2O_4$ spinel phase morphology. To obtain in composites the spinel phase the sintering of green bodies was carried out in air. Scanning electron microscopy observation (SEM) as well as the quantitative analysis of spinel by using stereological methods were performed.

MATERIALS AND METHODS

In the experiment, the following powders were used: α-Al_2O_3 TM-DAR Company (Japan) (with an average particle size of 133 ±30 nm and a density of 3.96 g/cm^3 [9]), and two types of nickel powders produced by Sigma Aldrich differ in average particle size. The powders were characterized by an average particle size 8.5 μm (mark further as A) and 1.5 μm (mark further as B) respectively. In Figure 1 SEM images of the starting powders are presented.

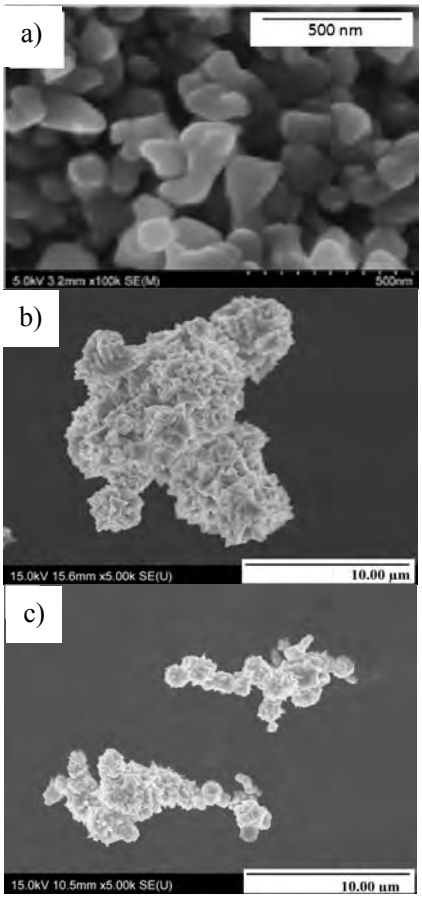

Fig. 1. SEM images of morphology of starting powders: a) α-Al_2O_3 powder, b) the nickel powder A, c) the nickel powder B

Rys. 1. Wyjściowe proszki: a) proszek α-Al_2O_3, b) proszek niklu A, c) proszek niklu B

The composites were prepared from the powder mixture contains: 89.6 vol. % of Al_2O_3 and 10.4 vol.% of nickel powder. Two series of samples were prepared: Series I with addition of nickel powder A and Series II with addition of nickel powder B. Schematic of fabrication of Al_2O_3-$NiAl_2O_4$ composites is shown in Figure 2.

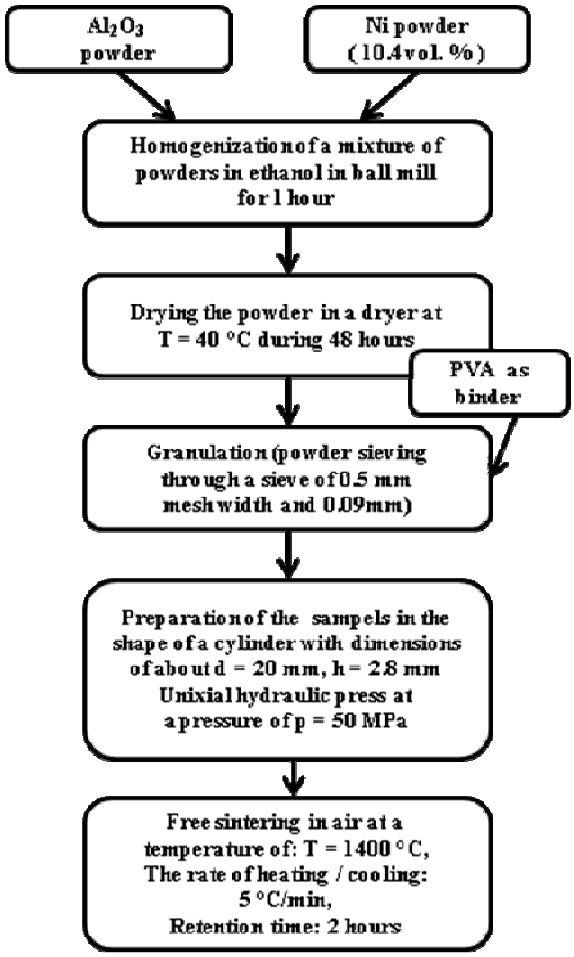

Fig. 2. Schema of the fabrication of Al_2O_3-$NiAl_2O_4$ composites

Rys. 2. Schemat wytwarzania kompozytów Al_2O_3 z fazą $NiAl_2O_4$

X-ray phase analysis was performed by a Rigaku MiniFlex X-ray diffractometer II. Two analyses were done at the surface and at the cross section of samples (Fig. 3).

The density and open porosity of the composites were determined by Archimedes method according to the PN-76/E-06307. Microstructure observation of the longitudinal sections of samples (Fig. 3) were made using a high resolution scanning electron microscope Hitachi S-3500N. The longitudinal section were prepared by cutting the samples along the axial direction with diamond saw. The polished longitudinal section were prepared by grinding and polishing with diamond paste 1 μm and 0.05 μm.

Quantitative description of the microstructure of the composites was made on the basis of SEM images of randomly selected areas on the longitudinal section using computer image analysis equipped into the program Micrometer [10]. Average values of shape

parameters are used for quantitative description of pores elongation ($\alpha = d_{max}/d_2$), curvature of grain boundary ($R = p/(\pi \cdot d_2)$) and convexity ($W = p/p_C$) [11].

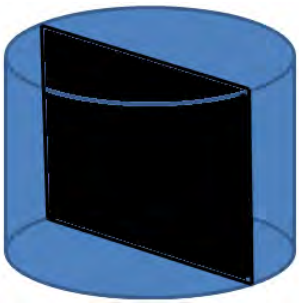

Fig. 3. Schema of sample for XRD and SEM tests with analyzed longitudinal section

Rys. 3. Schemat próbki do badań XRD i SEM z zaznaczonym badanym przekrojem

RESULTS AND DISCUSSION

According to the literature, spinel phases as $NiAl_2O_4$ formation depends on the atmosphere of sintering [12]. The possible phase composition in Al_2O_3-Ni system can be as follows: Al_2O_3-Ni, Al_2O_3-Ni, $NiAl_2O_4$, Al_2O_3-NiO, $Al_2O_3 + NiAl_2O_4 + NiO + Ni$ and Al_2O_3-$NiAl_2O_4$. Spinel $NiAl_2O_4$ is formed in composites during sintering in an air atmosphere with a high oxygen partial pressure. There was the reaction of Ni or Al from the Al_2O_3 or oxygen from the gas phase according to the equation [13, 14]:

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

The obtained composites (Series I and Series II) had the intensive blue color after sintering, suggesting the presence of the spinel phase. The results of X-ray phase from the surfaces and the longitudinal sections of composites confirmed the presence of two phases $NiAl_2O_4$ and Al_2O_3. Figure 4 presents an exemplary diffraction pattern.

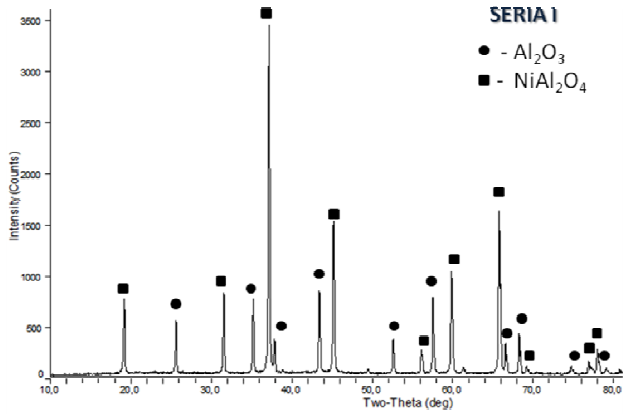

Fig. 4. X-ray phase analysis from the central part of composite sample (longitudinal section), phase Al_2O_3 and $NiAl_2O_4$

Rys. 4. Przykładowy wynik rentgenowskiej analizy fazowej z centralnej części kompozytu

It was found that the resulting diffraction patterns for both Series I and Series II differ from each other slightly in peaks offset. These shifts may be related to the texture of produced spinels, where the crystallographic cell parameters are slightly different from those of the literature data.

The SEM observation of microstructure showed homogeneous structure in the volume of each sample. Figure 5 presents an example of the microstructure of composite samples. In both series, it was observed that the spinel phase is characterized by an oval shape.

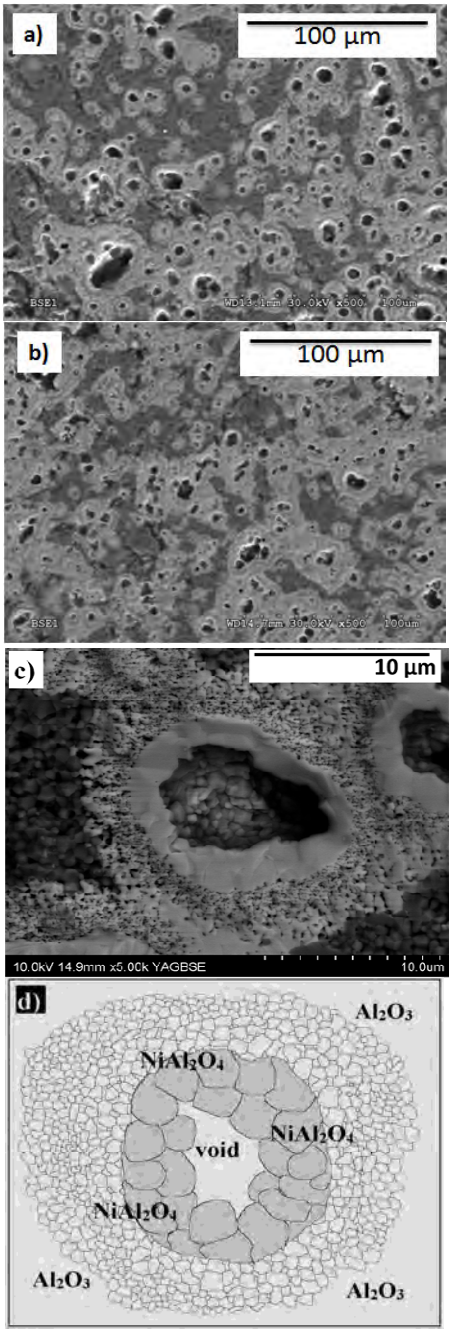

Fig. 5. SEM images of microstructure Al_2O_3–$NiAl_2O_4$ composite: a) Series I, b) Series II, c) Scanning Electron Micrograph of the $NiAl_2O_4$ spinel phase, d) Schema of the $NiAl_2O_4$ spinel phase morphology

Rys. 5. Obraz SEM mikrostruktury kompozytu Al_2O_3–$NiAl_2O_4$: a) seria I, b) seria II oraz c) obraz SEM mikrostruktury fazy spinelowej $NiAl_2O_4$, d) schemat powstawania morfologii spinelowej $NiAl_2O_4$

Moreover, the $NiAl_2O_4$ present in these Series (I and II) has characteristic voids. The shape of spinel area is similar to a "doughnut" [4]. This form of the spinel phase may result from the difference in the values of the thermal expansion coefficient [4, 13]. According to work [13] assuming that each Ni particle reacts to form one $NiAl_2O_4$ spinel particle, the size of the spinel phase is about 6-fold increase in volume. As a consequence of a volume expansion accompanied by the spinel formation, the particles are pushed out as the reaction is taken place and the large voids existed (Fig. 5c, d) [2]. Moreover, the high values of spinel volume in composites were noticed.

The volume fraction of the spinel phase at composites was determined by stereological method. Series I had the higher value of the volume fraction (61.6%) of the $NiAl_2O_4$ spinel phase than Series II (54.8%). Stereological analysis of the voids existing inside the spinel area are presented in Table 1. It was found that the voids in both series of composites had the same shape parameters whose values are close to unity. This means that the voids in the both series have similar shape-sphere. For the Series I the diameter (d_2) of void is a slightly larger than for Series II. However, there is no evident correlation between the initial size of Ni powders, and volume contribution of spinel and size of voids inside them.

TABLE 1. **Parameters describing shape coefficients of voids present in the spinel areas**
TABELA 1. **Parametry określające współczynniki kształtu pustek występujących w obszarach spinelu**

Type of series	Initial size of powder $d_{2\,Ni}$ [μm]	$d_{2\,void}$ [μm]	$\alpha = d_{max}/d_2$	$R = p/(\pi \cdot d_2)$	$W = p/p_C$
Series I	8.5 ± 0.51	5.65 ± 0.57	1.33	1.15	1.08
Series II	1.5 ± 0.44	4.29 ± 0.24	1.33	1.16	1.07

Additionally, the study of spinel morphology showed that spinel is consisted of two areas (Fig. 5). The inner part of spinel area around the voids is compact. Its width is equal to 1.45 ±0.16 μm. In contrast, the edges of the spinel phase structure were more porous and less compact. This region of spinel has a width equal to 2.98 ±0.12 μm. The grains of spinel in inner part are bigger than in outer part. This means according to the literature [15] that, during the process of formation one equivalent of $NiAl_2O_4$ on the Ni-side or NiO-side of the original interface, two equivalents of $NiAl_2O_4$ are formed on the Al_2O_3-side. On the basis of the Arrhenius relationship and on the data from work [16, 17], the diffusion coefficients were calculated. In the case of nickel particles the diffusion coefficient was equal to $3.55 \cdot 10^{-11}$ cm^2/s and for the alumina $8.31 \cdot 10^{-17}$ cm^2/s. The estimated values of diffusion coefficients were confirmed the idea that the intense diffusion of Ni in the direction of Al_2O_3, was resulted in a compact structure.

All samples were characterized by similar values of apparent density (3.35÷3.43 g/cm^3). Nonetheless, these values are close to each other, and the difference between them is within the limits of type I error. Both composites are highly porous. Open porosity for Series I samples is equal to 12.62 ±0.58, for Series II 16.42 ±0.03. This results confirmed the fact that the spinel formation in composites retard the process of densification [18, 19].

SUMMARY AND CONCLUSIONS

Sintering in the air compacted mixture of Ni and Al_2O_3 powders leads to homogeneous distribution of the $NiAl_2O_4$ spinel phase in ceramic matrix. In both obtained composites with different initial size of Ni powders the morphology of spinel and its size is similar.

The quantitative description of spinel phase was an useful tool to describe the morphology. The spinel has on oval shape with characteristic voids. Two areas of spinel phase are selected. The inner part is compact and has a smaller width. In contrast, the outer part is porous, consisted of smaller grains of spinel and makes larger area.

Formation of the spinel retarded the densification of the composites of Al_2O_3-Ni system. There is no evident influence of Ni initial grain powder size on the spinel formation and morphology. The slightly higher value of volume fraction of $NiAl_2O_4$ was noticed.

Acknowledgements

This work was supported by the Faculty of Material Science and Engineering Warsaw University of Technology. The authors thank for the support of this work to Professor M. Szafran and his group of science research from Department of Chemistry, Laboratory of Advanced Ceramics at Warsaw University of Technology.

REFERENCES

[1] Konopka K., Miazga A., Właszczuk J., Fracture toughness of Al_2O_3-Ni composites with nickel aluminate spinel phase $NiAl_2O_4$, Composites 2011, 11, 3, 197-201.

[2] Tuam W.H., Lin M.C., Tzing W.H., The coarsening behavior of duplex $Al_2O_3/NiAl_2O_4$ composites, Materials Chemistry and Physic 1997, 48, 156-159.

[3] Dhak D., Pramanik P., Particle size comparison of soft-chemically prepared nickel and copper aluminate spinels, International Symposium of Research Students on Materials Science and Engineering, December 20-22, Chennai, India 2004.

[4] Konopka K., Lityńska-Dobrzyńska L., Dutkiewicz J., SEM and TEM of $NiAl_2O_4$ spinel phase distribution in alumina matrix, Archives of Metallurgy and Materials 2013, 58, 2, 501-504.

[5] Konopka K., Kuczyński P., Miazga A., Riegert D., Wpływ atmosfery spiekania na mikrostrukturę i właściwości kom-

pozytów Al_2O_3-Ni, Materiały Ceramiczne 2012, 64, 1, 89-93.

[6] Gizowska M., Miazga A., Konopka K., Szafran M., The influence of sintering temperature on properties of Al_2O_3-Ni composites, Composites 2012, 12, 1, 33-38.

[7] Miazga A., Konopka K., Gizowska M., Szafran M., Alumina matrix ceramic-nickel composites formed by gelcasting method, Composites 2012, 12, 2, 138-141.

[8] Miazga A., Konopka K., Gizowska M., Szafran M., Preparation of Al_2O_3-Ni cement composites by aqueous gelcasting, Powder Metallurgy and Metal Ceramics 2014, 52, 9-10, 567-571.

[9] http://www.taimei-chem.co.jp/product/english/01.html

[10] Michalski J., Wejrzanowski T., Pielaszek R., Konopka K., Łojkowski W., Kurzydłowski K.J., Application of image analysis for characterization of powders, Materials Science Poland 2005, 23, 1, 79-86.

[11] Wejrzanowski T., Computer Assisted Quantitative Description of the Functionally Graded Materials, Master's Thesis, Warsaw University of Technology, Warsaw 2000.

[12] Tuan W.H., Lin M.C., Reaction sintering of $Al_2O_3/NiAl_2O_4$ composites, Journal of Materials Science Letters 1996, 15, 735-737.

[13] Lieberthal M., Kaplan W.D., Processing and properties of Al_2O_3 nanocomposites reinforced with sub-micron Ni and $NiAl_2O_4$, Materials Science and Engineering 2001, 302, 83--91.

[14] Sun X., Yeomans J., Optimization of a ductile-particle-toughened ceramic, Journal of the American Ceramic Society 1996, 79, 10, 2705-2717.

[15] Bolt P.H., Lobner S.F., Geus J.W., Habraken F.H.P.M., Interfacial reaction of NiO with Al_2O_3 $(11\bar{2}0)$ and polycrystalline α-Al_2O_3, Applied Surface Science 1995, 89, 339-349.

[16] Mrowec S., Teoria dyfuzji w stanie stałym: wybrane zagadnienia, Państwowe Wydawnictwo Naukowe, Warszawa 1989.

[17] Schmalzried H., Reakcje w stanie stałym, Państwowe Wydawnictwo Naukowe, Warszawa 1978.

[18] Tuan W.H., Lin M.C., Wu H.H., Preparation of Al_2O_3/Ni composites by pressureless sintering in H_2, Ceramics International 1995, 21, 221-225.

[19] Konopka K., Nickel aluminate spinel ($NiAl_2O_4$) in Al_2O_3-Ni composites, Inżynieria Materiałowa 2010, 3(175), 457-459.

