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QUANTITATIVE DESCRIPTION OF THE SPINEL PHASE ($NiAl_2O_4$) LOCATED INTO Al_2O_3 MATRIX

The presented work focuses on the quantitative description of the spinel phase ($NiAl_2O_4$) located into Al_2O_3 matrix. Three series of samples were prepared. Series I, II and III containing following amount of nickel powder: 0.21% vol, 0.43% vol and 1.3% vol respectively. In order to obtain nickel aluminate spinel sintering was carried out in an oxidizing atmosphere (air). Based on the SEM observation and XRD analysis the presence of spinel phase was confirmed in all samples. Difference in volume fraction of the Ni in the compacts before sintering, resulted in the different content of the spinel phase in the final material. All tested composites were characterized by homogeneous distribution of $NiAl_2O_4$ in the whole volume of the material. The purpose of the study was also the use the stereological analysis to determine the shape parameters of new phase.

Keywords: nickel aluminate spinel $NiAl_2O_4$, SEM, stereological analysis

1. Introduction

Recently, it can be seen an increased demand for non-conventional materials with unique properties, which can be explained by a huge advance in the field of technology. Among these materials, great attention is paid to the composites with a ceramic matrix. Depending on the properties, these composites are used both as functional and construction materials.

The incorporation of plastic metallic particles into the ceramic matrix can improve the fracture toughness of ceramic material [1, 2]. Additionally, the metallic phase distributed in ceramic matrix can affect the characteristics relating to resistance to thermal shock and change the strength of the material [3].

The current state of knowledge indicates that the change of fracture toughness depends on many factors including the type of introduced metal, formation of new phases, their size, distribution, volume fraction, morphology [4-6]. In particular, a significant influence on a number of properties of composites have the newly created phases during the forming process. Examples of such phases are spinels. With presence of spinel we are dealing in case of Al_2O_3-Ni composite. This material can be obtained, inter alia, from Al_2O_3 through addition of nickel or nickel oxide. During the sintering of powder mixture new phase can appear depending on the applied sintering atmosphere. Under sintering in atmosphere with oxygen we can obtain spinel phase ($NiAl_2O_4$), which is involved in processes related to the fracture path deflection and change the fracture toughness of material [7].

Own previous research indicates that for the evaluation of the impact of the phase construction of composites on their properties it is needed a quantitative analysis of the size, shape and distribution of phases which are in composites [1,7,8]. In particular this concerns spinel phase, determine its volume fraction, size of spinel grains, their distribution and morphology parameters. The results presented in [8] for composites Al_2O_3/Ni with different volume fraction of Ni than in the previous study, revealed a complex morphology of the spinel phase. Therefore, the aim of this study was a quantitative analysis of the spinel in the Al_2O_3/Ni composite. The study was conducted on the three series of composites prepared from a mixture of Al_2O_3 and Ni with varying addition of the metallic phase.

2. Experimental

2.1. Materials

In the investigation α – alumina powder TM-DAR (Taimei, Japan) with an average grain size of 133 nm and density 3.96 g/cm^3, and nickel powder (Sigma Aldrich) of average particle size 8.5 μm and density 8.9 g/cm^3 were used. Fig. 1 shows the scanning electron microscopy image (secondary electrons mode) of Ni powder and its grain size distribution. Histogram of the size distribution of the equivalent diameter of nickel shows that powder is characterized by the lowest fraction of particles with a diameter of 11 to 12 microns. Based on the morphology of the Ni powder it was found that nickel was firmly agglomerated.

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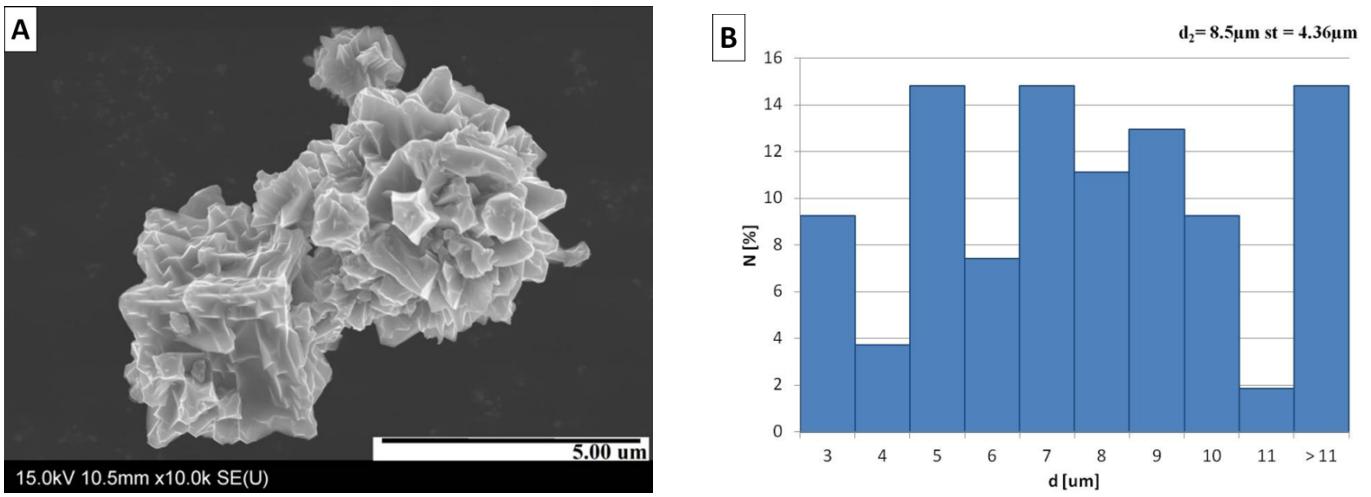

Fig. 1. A) Scanning electron microscopy image of nickel powder and B) distribution of the size of the powder particles (frequency N, diameter d_2)

2.2. Fabrication of the composites

The composites were fabricated by uniaxial pressing and sintering of Al_2O_3 and Ni powder mixture. Three series of samples were prepared, I, II and III, with following addition of nickel: I – 0.21% vol, II – 0.43% vol, III – 1.3% vol. Subsequently powder mixtures were pressed under a pressure of 50 MPa. Sintering process performed at temperature of 1400°C in air for 2 h. Application of air during sintering allows the formation of the spinel phase.

2.3. Characterizations methods

The microstructure of the composite was examined using Rigaku MiniFlex II X-ray diffractometer with Cu Kα radiation, λ = 1.54178 Å .

The density of the composites was determined by Archimedes method according to the PN-76/E-06307.

Microstructure observation of powders and cross sections of the sintered samples were made using scanning electron microscope Hitachi S-3500N and SU-70. In order to describe the microstructure of the composites quantitative analyses were carried out. The SEM images were first processed graphically and then subjected to quantitative analysis with the use of MicroMeter image analysis software [9,10]. The purpose of the study was to use stereological analysis to determine the volume fraction of spinel phase in the composites. Moreover, based on stereological analysis shapes parameters of voids present in the spinel phase there were defined coefficients describing: the elongation ($\alpha = d_{max}/d_2$), surface development ($R = p/\pi \cdot d_2$) and convexity ($W = p/p_c$) [10], where: d_{max} – maximum diameter of void projection in [µm], d_2 – diameter of circle of the same surface as the surface of the analyzed grain in [µm], p – perimeter of void in [µm], p_c – Cauchy perimeter in [µm].

3. Results and discussion

It has been found that composites after the process of sintering were characterized by the absence of cracks on the surface which may evidence of their good compactness. The obtained composites (Series I, II, III) had the intensive blue color after sintering, suggesting the presence of the spinel phase.

The density of sintered samples was about 96-98% of the theoretical density. Lower values of density is caused by the formation of spinel phase, which hinders compactness of material [11,12].

The results of X-ray phase analysis from the cross sections of composites confirmed the presence of two phases: Al_2O_3 and $NiAl_2O_4$ in all samples (Series I, Series II, Series III). Figure 2. presents an exemplary diffraction pattern.

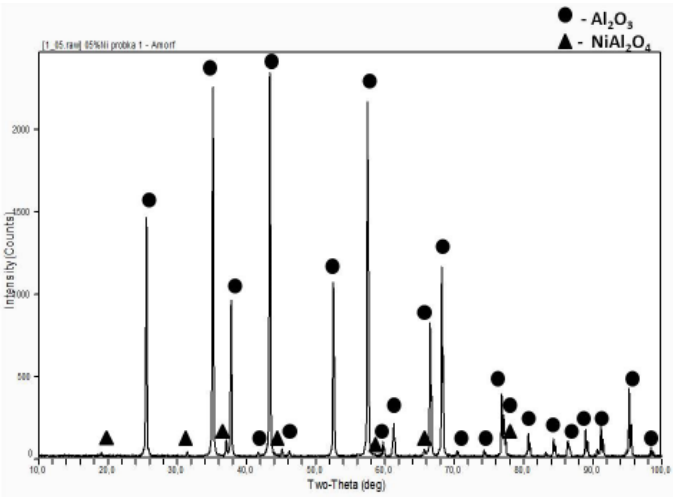

Fig. 2. X – ray phase analysis of composite sample (Series I)

Figures 3-5 were showed the exemplary SEM-images of the microstructure of composite samples with the histograms of the spinel size distribution. Size of spinel phase was determined

with regard to voids present in the middle part of spinel. SEM observation revealed the uniform distribution of the spinel phase in the whole volume of material. It was observed that the spinel phase takes two morphology forms. One is characterized by the void with oval shape in the middle and the other has an oval shape without void. These characteristic shapes of spinel are presented in Figures 3A and 4A. This type of spinel phase morphologies with void was observed earlier at works [8,11], and explained by difference in thermal expansion coefficients of Ni and $NiAl_2O_4$ [12,13]. The morphology of the spinel phase and the formation of voids was also the subject of the previous own research [8]. The estimated diffusion coefficients of Ni and Al_2O_3, suggested very intense diffusion of Ni in the direction of Al_2O_3 matrix, with together with highest thermal expansion coefficient of Ni may be responsible for formation of dense spinel structure with void inside [8].

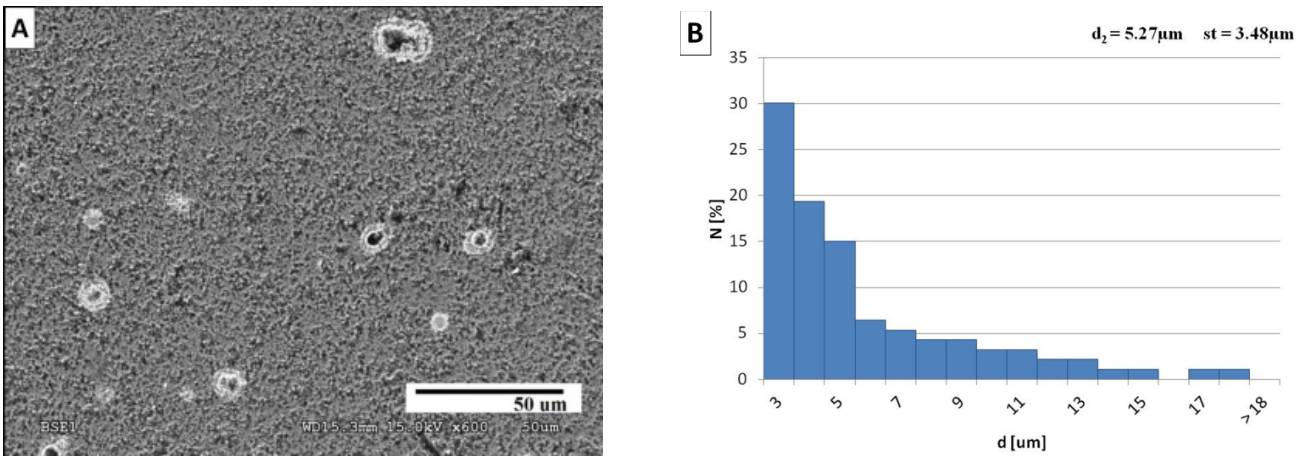

Fig. 3. Series I composite: A) scanning electron microscopy image of microstructure; B) distribution of size of the spinel phase particles (frequency N, diameter d_2)

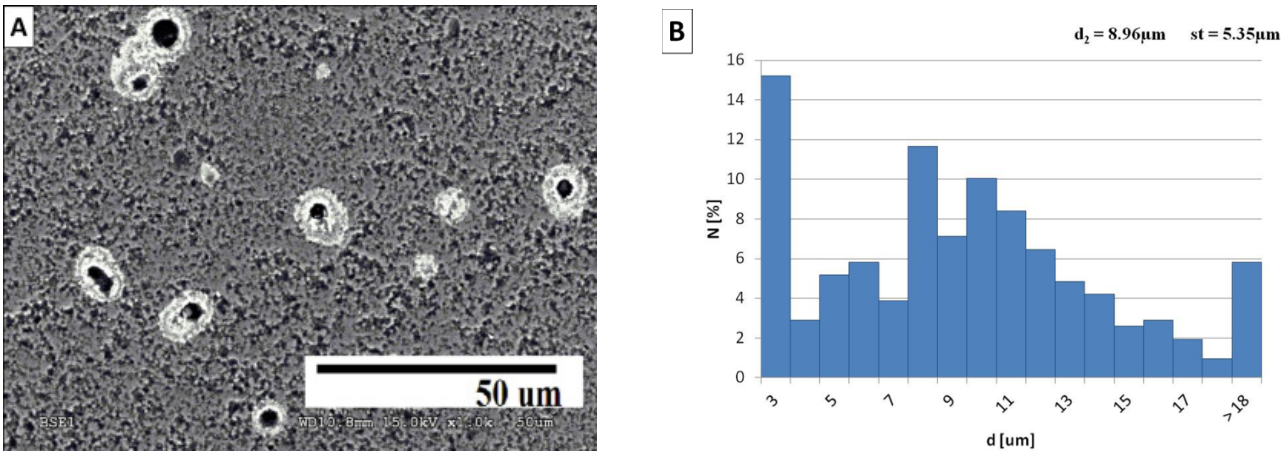

Fig. 4. Series II composite: A) scanning electron microscopy image of microstructure; B) distribution of Figure 5. Series III composite: A) scanning electron microscopy image of microstructure; B) distribution of size of the spinel phase particles (frequency N, diameter d_2)

Analysis of histograms showed that the Series I was characterized by 30% incidence of spinel phase particles with an average size 3÷4 µm (Fig. 3B). It was found that in the case of Series I, there are only few single particles of spinel phase with an average size higher than 13 microns, in contrast to the other two Series (Figs. 4B, 5B). It was observed that in the case of Series I and III, the particle size distribution of the spinel phase was a similar, whereas for Series II particle size distribution of $NiAl_2O_4$ was different. For this Series maximum of size of spinel phase particles was observed in the range 7÷11 µm.

The size and the volume fraction of the spinel phase were determined without taking account of voids present in this phase.

For all analysed composites Series the average particle size of spinel was 7.25 µm which is 1.25 µm less than the initial size of Ni powder particles (8.5 µm). The volume fraction of the spinel phase in composites increased compared with the initial nickel amount. For Series I it was 4 – fold increase of the $NiAl_2O_4$ volume fraction, for Series II 9 – fold and for Series III 5 – fold (Table 1). Previously, in the literature the 6 – fold increase of the spinel volume fraction was reported [12].

The observed changes of the spinel volume fraction compare with initial amount of Ni should be interpreted by considering the possible oxidation of the nickel particles. The intensive oxidation in air atmosphere of Ni particles can result in thick NiO layer around the Ni powder particles and in the volume increase of the formed spinel phase.

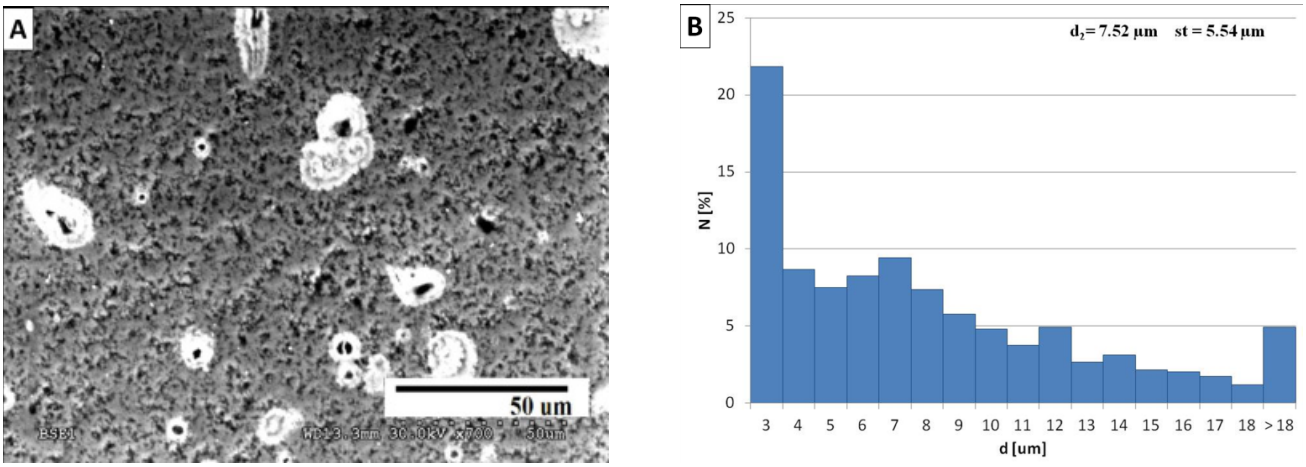

Fig. 5. Series III composite: A) scanning electron microscopy image of microstructure; B) distribution of size of the spinel phase particles (frequency N, diameter d_2)

The stereological analysis indicated that the voids in spinel areas in all Series had the similar – oval shape. This is evidenced by the values of shape parameters (the curvature of grain boundary, convexity) (Table 1). These values are close to one. The average size of voids inside the spinel areas was equal to 3.43 µm.

TABLE 1

Volume fraction of spinel phase and spinel voids and parameters describing shape coefficients of voids present in the spinel areas

Type of series		Series I (0.21% vol. Ni)	Series II (0.43% vol. Ni)	Series III (1.3% vol. Ni)
The volume of the spinel	[%]	1.00	4.00	7.00
The volume of voids in the spinel	[%]	0.05	1.50	1.00
Diameter d_2	[µm]	2.46 ±2.08	4.65 ±2.84	3.18 ±2.24
Voids elongation α	[-]	1.27	1.35	1.44
Curvature of grain boundary R	[-]	1.19	1.31	1.37
Convexity W	[-]	1.01	1.12	1.05

4. Conclusions

In the analyzed composites, the presence of two phases has been found: spinel phase ($NiAl_2O_4$) distributed in the Al_2O_3 matrix. SEM observations showed a homogeneous distribution of $NiAl_2O_4$. There was no delamination at the $Al_2O_3/NiAl_2O_4$ interface.

With the increase of the volume of nickel in the initial powder mixture, increase in the volume of the spinel phase was observed. This increase was: 4, 5 and even 9 times compared to the volume of nickel.

Stereological analysis confirmed that spinel is characterized by oval shape and average size of 7.25 µm. In some spinel particles voids were found, which determined average diameter was 3.43 µm.

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