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COMPOSITES THEORY AND PRACTICE

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CHARACTERIZATION OF ZIRCONIA COMPOSITES WITH NICKEL PARTICLES

The aim of this paper was to characterize the microstructure and selected properties of Ni-3YSZ composites. The composites were prepared from a powder mixture containing 90 vol.% ZrO_2 and 10 vol.% nickel powder. In the experiments the following powders were used: ZrO_2 powder stabilized by 3 mol% Y_2O_3 from TOSOH ZIRCONIA 3YSZ of an average particle size less than 100 nm and density 6.05 g/cm^3 and Ni powder from Sigma-Aldrich of an average particle size 1.5 µm and density 8.9 g/cm^3. The samples were formed by uniaxial pressing. Two series of samples were fabricated with different sintering temperatures: series I was sintered at 1400°C and series II was sintered at 1600°C. The sintering process was conducted in an argon atmosphere. The structure of the samples was examined by X-ray diffraction (XRD) after sintering. The microstructure of the composites was investigated by scanning electron microscopy (SEM). The chemical composition was examined by energy-dispersive X-ray spectroscopy (EDS). The selected physical properties of the prepared composites was measured by the Archimedes method. The hardness was measured using Vickers hardness testing. Based on the hardness measurements the K_{IC} values were determined. Uniaxial pressing and the sintering method enabled the manufacture of Ni-3YSZ composites. The microstructure observation revealed homogeneous distribution of the Ni particles in the ZrO_2 matrix in both series. The XRD patterns of the composites after sintering at 1400°C (series I) and 1600°C (series II) show that the composites consisted of three phases: t-ZrO_2, m-ZrO_2 and Ni. It was found that the temperature of 1400°C is not sufficient to obtain Ni-3YSZ composites with a high relative density.

Keywords: Ni-3YSZ system, ceramic-metal composites, uniaxial pressing

CHARAKTERYSTYKA KOMPOZYTÓW CYRKONOWYCH Z CZĄSTKAMI NIKLU

Celem pracy było określenie mikrostruktury i wybranych właściwości kompozytów Ni-3YSZ. Kompozyty wytwarzano z mieszaniny proszku zawierającej: 90% obj. ZrO_2 i 10% obj. proszku Ni. W eksperymencie zastosowano następujące proszki: proszek ZrO_2 stabilizowany 3% mol Y_2O_3, firmy TOSOH ZIRCONIA 3YSZ o średniej wielkości cząstek mniejszej niż 100 nm i gęstości 6,05 g/cm^3 oraz proszek Ni firmy Sigma-Aldrich o średnim rozmiarze cząstek 1,5 µm i gęstości 8,9 g/cm^3. Próbki zostały uformowane w wyniku prasowanie jednoosiowego. Przygotowano dwie serie próbek o różnych temperaturach spiekania: serię I spiekano w temperaturze 1400°C, a serię II spieczono w temperaturze 1600°C. Proces spiekania prowadzono w atmosferze ochronnej argonu. Za pomocą dyfrakcji rentgenowskiej (XRD) określono skład fazowy wytworzonych kompozytów. Mikrostrukturę kompozytów zbadano z wykorzystaniem skaningowej mikroskopii elektronowej (SEM). Skład chemiczny określono za pomocą spektrometru dyspersji energii promieniowania rentgenowskiego (EDS). Wybrane właściwości fizyczne przygotowanych kompozytów zostały zmierzone z użyciem metody Archimedesa. Twardości kompozytów określono metodą Vickersa. Na podstawie pomiarów twardości wyznaczono wartość odporności na kruche pękanie (K_{IC}). Metoda prasowania jednoosiowego pozwoliła na wytwarzanie kompozytów Ni-3YSZ. Obserwacje mikrostruktury ujawniły jednorodne rozmieszczenie cząstek Ni w osnowie ZrO_2 w obydwu seriach. Na podstawie analizy fazowej stwierdzono, że wytworzone kompozyty po procesie spiekania w 1400°C (seria I) oraz 1600°C (seria II) charakteryzowały się obecnością trzech faz: t-ZrO_2, m-ZrO_2 i Ni. Stwierdzono, iż temperatura 1400°C nie wystarcza do uzyskania kompozytów Ni-3YSZ o wysokiej gęstości względnej.

Słowa kluczowe: Ni-3YSZ, kompozyty ceramika-metal, prasowanie jednoosiowe

INTRODUCTION AND AIM OF STUDY

Yttria-stabilized zirconia ceramics (YTZP) are promising engineering materials due to their high flexural strength, high hardness, low thermal conductivity and biocompatibility [1]. However, because of their insufficient fracture toughness and high sensitivities to crack propagation, industrial application has been limited [2]. One of the methods of improving these properties of the ceramic is to fabricate ceramic-metal composites [3]. Ductile reinforcement can hinder crack propagation through mechanisms such as crack bridging or crack deflection [4]. In particular, zirconia-metal composites have been investigated in many systems such as ZrO_2-Nb [5, 6], ZrO_2-Ta [7], ZrO_2-stainless steel [8], ZrO_2-Pt [9], ZrO_2-Ni [10-12]. Due to the addition of the plastic phase the fracture toughness was improved. Moreover, improvement in toughness should

not lead to a decrease in the strength of the composite. Nowadays zirconia-nickel composites are attracting much attention because of their possible application in the production of solid oxide fuel cells [13, 14] due to the chemical and structural stability, electronic conductivity and catalytic activity of the composites. Another application of these composites could be thermal barrier coatings [15] or flow sensors [16]. Furthermore, this system is a good candidate to form a composite through the small mismatch between zirconia and nickel thermal coefficients and similar elastic moduli.

The main objective of the work is to investigate and compare the properties of the YTZP-10 vol.% Ni composite after sintering at two temperatures: above and below the melting point of nickel.

MATERIALS AND METHODS

In the investigation the following powders were used: a nickel powder (Sigma-Aldrich) with 99.99% purity and an average particle size of 3 μm and zircona stabilized by 3 mol% Y_2O_3 (3YSZ) powder with 99.99% purity and an average particle size of 100 nm. The particle sizes were measured by laser diffraction (Laser Particle Size Analyzer LA-960) conducted in a diluted well-dispersed suspension. The densities of Ni and ZrO_2 were 8.9 and 6.05 g/cm^3 respectively. Figure 1 shows the scanning electron microscopy (secondary electron) image of the ZrO_2 and Ni powders. The SEM observations revealed that the ZrO_2 particles show the tendency to create agglomerates (Fig. 1).

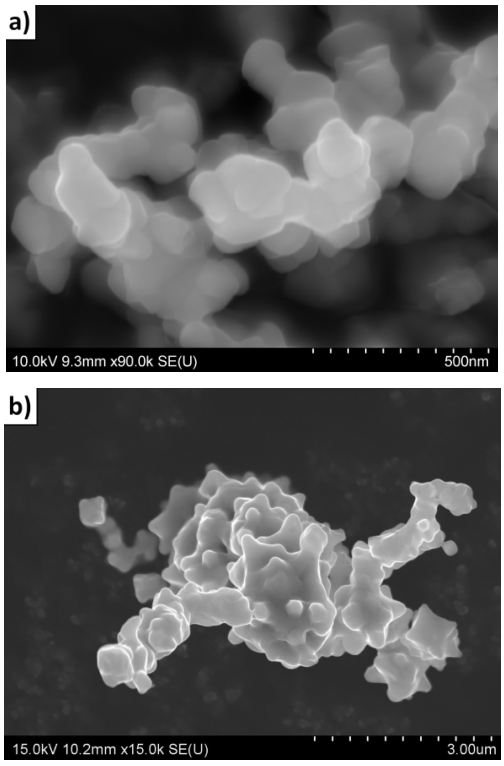

Fig. 1. Scanning electron micrographs of starting powders: a) ZrO_2 powder, b) Ni powder

Rys. 1. Zdjęcie SEM morfologii wyjściowych proszków: a) ZrO_2, b) Ni

The composites were prepared from powder mixtures containing 90 vol.% 3YSZ and 10 vol.% Ni powder. Two series of samples were prepared: Series I was sintered at 1400°C, and Series II was sintered at 1600°C. The powder mixtures were homogenized in ethanol in a planetary ball mill with a rotating speed of 300 rpm for 60 min. The next step was drying at 40°C for 48 hours. Subsequently, poly(vinyl alcohol) (PVA) was added to the powders as the binder and granulation was performed. Granulation of the powder with polyvinyl alcohol was carried out through sieves of 0.5 and 0.04 mm mesh widths. Then the samples were prepared by uniaxial pressing at a pressure of 160 MPa. The dimensions of the cylindrical samples were as follows: d = 20 mm, and h = 3 mm. The samples were sintered in argon atmosphere at the temperatures of 1400°C (series I) and 1600°C (series II). The dwell time was 2 hours. The heating and cooling rate was 5°C/min.

X-ray diffraction (XRD) was used to identify the phases present in the samples. Structural studies were carried out by means of a Rigaku MiniFlex II for 2θ values ranging from 20° to 80° with CuKα radiation and λ = 1.54178 Å. The analyses were conducted on sample cross-sections.

Certain selected physical properties of the obtained composites were measured by the Archimedes method according to Standard PN-76/E-06307. The mass of a dry test piece was determined by weighing, then its apparent mass when immersed in a liquid with which it was impregnated under vacuum, and then its mass in air while still soaked with the liquid. From these values its bulk density and apparent porosity were determined by calculation. Average values were calculated from measurements of 20 samples in each series. The relative densities of the composite bodies were calculated using the rule of mixtures. The values 6.05 g/cm^3 and 8.9 g/cm^3 as the theoretical densities of 3YSZ and Ni, respectively were used.

The microstructure of the samples was analyzed on a polished sample cross-section by a Nikon ECLIPSE LV150N optical microscope. The chemical composition was examined at points on a fracture of the sample by EDS (HITACHI SU-70).

The hardness of the composites was measured by the Vickers method on the polished sample surface under a load of 10 kG (98 N) with a 10-s holding time. Based on measurements of the length of cracks propagating from the corner of the hardness indentation, the fracture toughness of the material (K_{IC}) was determined. In this study, a Vickers hardness indenter was applied to propagate what are called median cracks on the surface. The K_{IC} values in this case can be estimated using the equation [17]:

$$K_{IC} = 0.067 \cdot \left(\frac{E}{H_V}\right)^{0.4} \cdot \left(\frac{c}{a}\right)^{-1.5} \cdot H_V \cdot \sqrt{a} \qquad (1)$$

where: E - Young's modulus; HV - Vickers hardness, c - crack length [μm], a - one half of the indent diagonal length [μm].

The bending strength of the composites was measured by the ball-on-ring (BOR) test [18-20]. The reported strengths represented the mean and standard deviation of at least 15 specimens. The values were computed using Kirstein and Woole's equation:

$$\sigma_{max} = \frac{3P(1-\upsilon)}{4\Pi t^2}\left[1 + 2ln\frac{a}{b} + \frac{(1-\upsilon)}{(1+\upsilon)}\left\{1 - \frac{b^2}{2a^2}\right\}\frac{a^2}{R^2}\right] \quad (2)$$

where: P is the load [N], υ - Poisson's ratio, t - disk thickness [m], a - radius of supporting ring [m], b - radius of ball (the region of uniform loading at the centre) [m], R - radius of sample [m]. For comparison, bending strength measurements for comparable homogeneous samples with monolithic zirconia were performed.

RESULTS AND DISCUSSION

Preliminary macroscopic observations of the composites from both series after the sintering process show that the sample surface was grey. Figure 2 presents photos of the prepared composite samples.

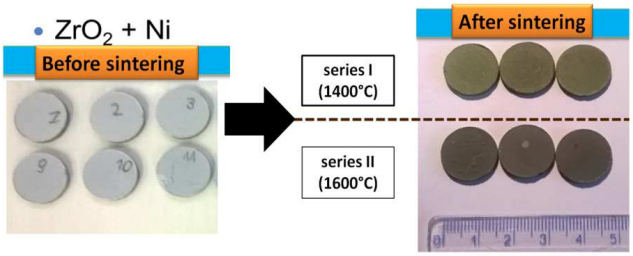

Fig. 2. Photograph of obtained composite samples

Rys. 2. Zdjęcie wytworzonych próbek

Figure 3 shows the X-ray diffractograms of the 3YSZ and composite samples sintered at different temperatures. The study indicates that the phase composition of the zirconia samples consists of tetragonal zirconia (t-ZrO_2). In the case of the composite samples, they consist of tetragonal zirconia (t-ZrO_2), nickel and a little monoclinic zirconia (m-ZrO_2). There is no reaction between the nickel and zirconia. The results show that the nickel has an effect on the phase transformation from t-ZrO_2 to m-ZrO_2. This indicates that the presence of ZrO_2/Ni interfaces could promote martensitic transformation in the composite system. A similar phenomenon was observed in [20] and [21].

Selected properties of the composite materials are presented in Table 1. It was found that in the case of Series I the relative density is significantly lower than in the case of series II. Moreover, the open porosity is about 12 times higher than in series II. These results confirm the fact that the sintering temperature of 1400°C was too low to obtain full densification of the composite material. It was observed that the linear shrinkage regarding sample height for series I (18.58%) is lower than series II (19.26%). It is in good agreement with the relative density values because the higher the density, the higher the sintering shrinkage.

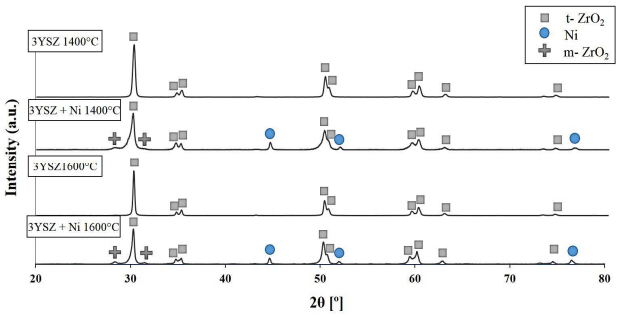

Fig. 3. Diffractograms of produced specimens

Rys. 3. Dyfraktogramy wytworzonych próbek

TABLE 1. **Selected properties of composite material: series I, series II**

TABELA 1. **Wybrane właściwości dla materiałów kompozytowych: seria I, seria II**

Property	Series I	Series II
Apparent density [g/cm^3]	4.21 ±0.04	5.88 ±0.02
Relative density [%]	66.44 ±0.89	92.80 ±0.75
Open porosity [%]	1.63 ±0.53	0.14 ±0.04
Linear shrinkage (sample height) [%]	18.58 ±0.24	19.26 ±0.35
Linear shrinkage (sample diameter) [%]	43.34 ±0.25	43.45 ±0.15

Table 2 lists the hardness values on the cross-section and the fracture toughness of the material (K_{IC}). It can be noticed that the samples sintered at 1400°C have a lower Vickers hardness than those samples which were sintered at 1600°C. A similar correlation was found in the case of the fracture toughness. This is due to the high porosity of the series I samples.

TABLE 2. **Vickers hardness values and fracture toughness of composites**

TABELA 2. **Twardość oraz odporność na kruche pękanie**

Mechanical properties		
	Vickers hardness	Fracture toughness
	[GPa]	[MPa·m$^{0.5}$]
Series I	6.32 ±0.45	8.26 ±0.85
Series II	7.84 ±0.39	9.67 ±0.47

The ball-on-ring test has been widely used to determine the biaxial strength of brittle materials [16-18]. The composite from series II shows a lower bending strength than the ceramic material obtained in the same conditions. In the case of zirconia samples the values of bending strength amounted to 705.73 ±71.75 MPa, while in the case of series I the authors failed to perform the measurements, however, in the case of series II this value was 459.81 ±10.61 MPa. It was observed that 3YSZ has a strength 1.5 times higher than the Ni-3YSZ composite. This difference between the values of bending strength may be result from, among others,

due to the fact that the metal particle size is bigger than the matrix grains. Microstructure observations of the composite sample cross-sections are shown in Figure 4. Homogeneous distribution of nickel particles in the zirconia matrix was revealed.

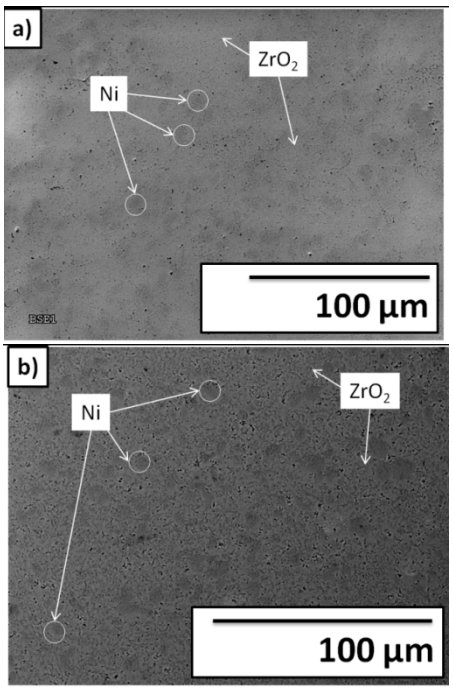

Fig. 4. SEM microstructure of ZrO_2-Ni composite: a) series I, b) series II

Rys. 4. Mikrostruktura kompozytu ZrO_2-Ni: a) seria I, b) seria II

Energy-dispersive X-ray spectroscopy analysis was carried out in selected areas on a fracture of both series after bending strength testing. The energy-dispersive X-ray spectroscopy was performed at three different locations in the composites. The investigation was conducted on the fracture, therefore the tested surface is not flat and the fact that incident radiation can bounce back from the surface and can arouse adjacent elements must be taken into account. In addition, it should be remembered that there may be a small amount of other phases on the surface on the fracture which are not visible under a microscope. Figure 5 shows the concentrations of nickel, zirconium, yttrium and oxygen from the fracture after sintering at 1400°C (Fig. 5a) and 1600°C (Fig. 5b) by using EDS investigation. The results of the concentration measurements of oxygen, nickel, yttrium and zirconium for the composites have been collected in Table 3. The observations have shown that the contents of elements at analyzed points 2 and 3 in both series, were noted as areas with a high content of zirconium. It was found that points 2 and 3 match the ceramic matrix. The EDS measurement showed that in both cases (sample series I and series II), point 1 corresponds to the nickel particles. From the EDS analysis, a transition of Ni into the ceramic matrix was revealed.

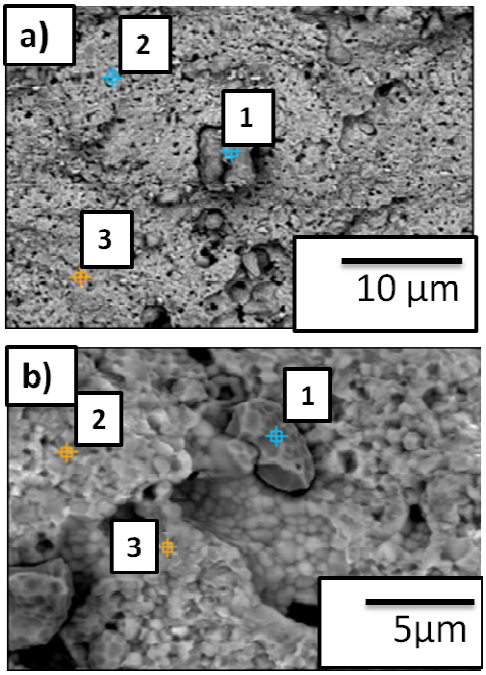

Fig. 5. Analysis of chemical composition at selected points on fracture of ZrO_2-Ni composite: a) series I, b) series II

Rys. 5. Analiza składu chemicznego wybranych punktów z przełomów kompozytu ZrO_2-Ni: a) seria I, b) seria II

TABLE 3. **Weight, atomic content of samples at selected points**
TABELA 3. **Zawartość masowa, atomowa próbek w różnych punktach**

ZrO_2-Ni composites								
Series I (Fig. 5a)								
	Weight %				**Atom %**			
	O	Ni	Y	Zr	O	Ni	Y	Zr
Point 1	0.6 ±0.1	96.7 ±0.4	0	2.7 ±0.2	2.4 ±0.2	95.9 ±0.4	0	1.7 ±0.1
Point 2	27.5 ±0.4	0	7 ±0.6	65.4 ±0.7	68.4 ±0.9	0	3.1 ±0.3	28.5 ±0.3
Point 3	4.6 ±0.5	0	11.2 ±1.3	84.2 ±1.7	21.5 ±2.	0	9.4 ±1.1	69.0 ±1.4
Series II (Fig. 5b)								
	Weight %				**Atom %**			
	O	Ni	Y	Zr	O	Ni	Y	Zr
Point 1	1.6 ±0.2	91.9 ±0.8	0.2 ±0.2	6.2 ±0.3	5.8 ±0.7	90.1 ±0.7	0.2 ±0.1	3.9 ±0.2
Point 2	34.3 ±0.5	1.0 ±0.1	5.1 ±0.2	59.7 ±0.4	74.6 ±1.1	0.6 ±0.1	2.0 ±0.1	22.8 ±0.2
Point 3	40.9 ±0.5	0.9 ±0.1	4.0 ±0.2	54.3 ±0.4	79.6 ±0.9	0.5 ±0.1	1.4 ±0.1	18.5 ±0.1

CONCLUSIONS

These studies provided evidence that:

- The uniaxial pressing and sintering method enabled the manufacture of Ni-3YSZ composites. The microstructure observation revealed homogeneous distribution of the Ni particles in the 3YSZ matrix in both series.
- The XRD patterns of the composites after sintering at 1400°C (series I) and 1600°C (series II) show that the composites consisted of three phases: t-ZrO_2, m-ZrO_2 and Ni. There was no reaction between nickel and zirconia. The results show that the nickel has an effect on the phase transformation from t-ZrO_2 to m-ZrO_2.
- It was found that the temperature of 1400°C is not sufficient to obtain Ni-3YSZ composites with a high relative density.
- The composites sintered at the lower temperature (1400°C) have lower mechanical properties than the composites sintered at the higher temperature (1600°C).

Acknowlegments

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