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COMPOSITES THEORY AND PRACTICE

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SINTERING, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF $NbC_{0.8}$-Nb_xO_y COMPOSITES AND SINGLE-PHASE NbC POLYCRYSTALS

The study presents the results of investigations of the influence of niobium oxides and the addition of carbon on the pressureless sintering of niobium carbide powder and the properties of the obtained sinters. For this purpose, niobium carbide of a specific deviation from stoichiometry was synthesized ($NbC_{0.8}$). After the crushing process, all the characteristics of the powder were determined and the powder was found to contain niobium oxides in the quantity of a few percentage of the weight. Next, samples were prepared without any additives and with additives of 1 and 2% of carbon weight. The samples were pressureless sintered at the following temperatures: 1900, 2000 and 2100°C in argon flow by heating them at the final temperature for 1 hour, then their apparent density was measured. A qualitative and quantitative analysis of the microstructure was performed on metallographic micro-sections and the phase composition of the sinters was determined. It was found that the presence of niobium oxides in the NbC powders has an advantageous influence on the sintering process. Single-phase polycrystals can be prepared by the addition of carbon. Some mechanical properties were additionally determined from the sinters including: hardness and fracture toughness and next, an attempt was made to correlate them with the image of the microstructure of the composites and single-phase polycrystals.

Keywords: **metal-like carbides, NbC_{1-x}-Nb_xO_y composites, pressureless sintering, qualitative and quantitative analysis of the microstructure, hardness, fracture toughness**

SPIEKANIE, ANALIZA MIKROSTRUKTURY ORAZ WŁAŚCIWOŚCI MECHANICZNE KOMPOZYTÓW $NbC_{0.8}$-Nb_xO_y I POLIKRYSZTAŁÓW JEDNOFAZOWYCH NbC

W pracy przedstawiono wyniki badań nad wpływem tlenków niobu na spiekalność węglika niobu. W tym celu zsyntezowano węglik niobu o określonym odstępstwie od stechiometrii ($NbC_{0.8}$). Po procesie rozdrabniania dokonano pełnej charakterystyki proszku i stwierdzono, że w proszku obecne są tlenki niobu w ilości kilku % mas. Następnie przygotowano próbki bez jakichkolwiek dodatków oraz z dodatkiem 1 i 2% mas. węgla. Próbki spiekano swobodnie w temperaturze: 1900, 2000 i 2100°C, w przepływie argonu, wygrzewając je w temperaturze końcowej przez 1 godzinę. Wykonano pomiary gęstości pozornej spieków, na zgładach metalograficznych przeprowadzono jakościową i ilościową analizę mikrostruktury, a także określono skład fazowy spieków. Stwierdzono, że obecność w proszku NbC tlenków niobu wpływa korzystnie na proces spiekania. Wprowadzenie dodatku węgla ujednorodnia skład fazowy spieków, nie pogarszając ich gęstości. Przeprowadzono badania właściwości mechanicznych, takich jak: twardość i odporność na kruche pękanie, a następnie podjęto próbę skorelowania ich z obrazem mikrostruktury kompozytów i jednofazowych polikryształów.

Słowa kluczowe: **węgliki metalopodobne, kompozyty NbC_{1-x}-Nb_xO_y, spiekanie bezciśnieniowe, jakościowa i ilościowa analiza mikrostruktury, twardość, odporność na kruche pękanie**

INTRODUCTION

Carbides are divided into three groups of compounds: diamond-like, metal-like and salt-like carbides [1-3]. Both diamond-like carbides are of industrial importance, i.e. silicon carbide and boron carbide as well as some metal-like carbides, mostly tungsten carbide and titanium carbide. Polycrystals are produced from both metal-like carbides on a broad scale, in which the carbide grains are bound using metallic phases, such as cobalt or nickel. These materials are called cemented carbides and they have a broad range of applications due to their good mechanical properties, i.e. high hardness, high bending strength and high fracture toughness [4-6], which result from the combination of typical characteristics of ceramic and metallic materials. The mechanical properties of sintered carbides greatly deteriorate at elevated or high temperatures mostly due to the presence of the metallic binding phase. This problem does not exist in the case of single-phase polycrystals. There are, however, difficulties in the formation of single-phase polycrystals from diamond-like and metal-like carbides. The main reasons why it is difficult to produce single-phase carbide sinters using the pressureless sintering technique include low diffusion coefficient values, high melting points which reach 4000°C and translate into high sintering temperatures [2, 7-9]. For metal-like carbides, the lack of interest in the production of single-phase sinters also results from the ability to obtain cemented carbides. One of the reasons for difficult sintering also includes the presence of passivation oxide layers on carbide grains, which become decomposed at sintering temperatures, leading to the production of numerous gaseous products, thus preventing the formation of dense sinters [2, 7-9]. Studies [10-13] on the other hand have presented results of research showing that as regards niobium carbides, the presence of passivation oxide layers may be a factor which activates NbC sintering. NbC_{1-x}-Nb_xO_y composites with good physicochemical properties are obtained [10, 13]. Moreover, studies can be found in which carbide sintering is activated by the addition of carbon [7-9], whose tasks involve partial or complete reduction of passivation oxide layers.

As shown by research, an appropriately selected carbon additive makes it possible to produce dense single-phase sinters with isometric grains, which are characterized by good mechanical, thermal and chemical properties [9, 14, 15].

A qualitative and quantitative analysis of the microstructure is helpful in investigating the influence of niobium oxides and the additive of carbon on niobium carbide sintering; the results of this analysis are presented in this study.

PREPARATION

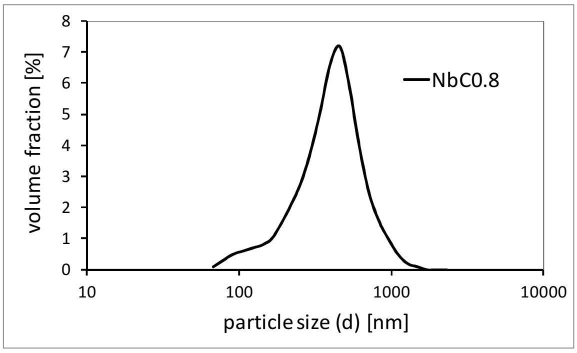
Synthesis of $NbC_{0.8}$ carbide powder

Niobium carbide with assumed deviation from stoichiometry $NbC_{0.8}$ was synthesized from the elements in the solid phase reaction technique. The substrates were the powders:

1. metallic niobium (ABCR GmbH & Co.KG, No. AB201777),
2. phenol-formaldehyde resin Nowolak MR (Organika - Sarzyna). This resin leaves 50 mass % after pyrolysis in the form of amorphous, reactive carbon.

The metal and resin powders were wet homogenized in ethyl alcohol in a ball mill, WC-Co grinding mediums. After evaporation of the alcohol, the prepared powder mixture was subjected to synthesis at ~ 1200°C, for one hour, under argon flow. Then the obtained product was crushed in an Abbich mortar and ground in a rotary-vibratory mill for 4 hours, in ethanol with WC-Co balls. The resulting powder, in the last stage of preparation, was sieved through a sieve of the size of 0.056 mm. Sieving was to isolate the powders from mechanically strong grain agglomerates. The thus obtained NbC_{1-x} powders were characterized, with determination of the: 1) phase composition, using the X-ray diffraction method and quantitative phase composition (mass %) using the Rietveld method, 2) specific surface area using the BET method, 3) grain size distribution using the DLS method, 4) morphology using SEM scanning electron microscopy, 5) concentration of oxygen and carbon using the combustion method and gas analysis in a LECO apparatus. The characteristics of the $NbC_{0.8}$ powder are presented in Table 1.

TABLE 1. **Characteristics of niobium powder $NbC_{0.8}$**
TABELA 1. **Charakterystyka syntezowanego proszku $NbC_{0.8}$**

	$NbC_{0.8}$
Quantitative phase composition [mass %] (Rietveld method)	79.5% NbC; 13.4% Nb_2C; 2.9% NbO; 4.3% NbO_2
Carbon [mass %] (analyser LECO)	10.84
Calculated deviation from stoichiometry	$NbC_{0.92}$
Oxygen [mass %] (analyser LECO)	7.12
S_{BET} [m^2/g] d_{BET} [nm]	11.65 m^2/g 65.6 nm
Lattice parameter $\boldsymbol{a}$ [Å]	NbC $\boldsymbol{a}$ = 4.4616
Lattice parameter $\boldsymbol{a}$ according to [3][Å]	$NbC_{0.78-0.85}$ a = 4.4519-4.4618
Grain size distribution (DLS method)	

Preparation of raw samples

Quantitative analysis of the phase composition (Table 1) of the powder revealed minor amounts of unreacted niobium, Nb_2C carbides and substantial amounts of niobium(II) and niobium(IV) oxides. According to the literature [2, 7-9] the presence of oxides is unfavourable from the viewpoint of sintering. During sintering oxides volatile compounds may form, hindering densification. Oxide layers passivating carbide grains can be reduced using carbon, which is preferably introduced into the powder in the form of a solution of Nowolak MR resin. A properly selected amount of carbon additive ensures that the produced sinters will be single-phase, according to the reaction (1):

$$Nb_xO_y + (x+y)C \rightarrow xNbC + yCO\uparrow \qquad (1)$$

The calculations of the amount of carbon necessary to reduce the oxide impurities was based on the chemical analysis conducted by the combustion method and gas analysis using the LECO apparatus (Table 1). It is assumed that the most stable oxides of niobium are on the surface of the grains. Based on the quantitative phase composition of the powders determined using the Rietveld method (Table 1), a calculation, was conducted of the amount of carbon necessary to react with the free niobium into NbC carbide, saturate the octahedral gaps in Nb_2C carbides and reduce oxides present in the powders. Since clear identification of the oxides layers passivating carbide grains is impossible, the amount of carbon necessary to react with oxygen in the form of carbon monoxide was also calculated. The amounts of carbon calculated according to the different approaches, within the limits determined by the analytical methods, are significantly different from each other, so it was decided that the optimum carbon additive would be selected empirically. In this way it was decided add to powder of two different carbon additives 1.0 and 2.0 mass %.

Carbon was introduced by wet mixing of the Nowolak MR resin powder with the carbide powder in ethanol, in the ball mill, for 12 h. Then the alcohol was evaporated from the slurry and the resulting mixture sieved through a perlon sieve to granulate them.

The thus prepared granules were used for moulding raw samples by the uniaxial two-sided pressing technique, p = 150 MPa, in a matrix made of zirconium oxide. The raw samples had the dimensions: diameter ~13 mm and a height of 2 to 5 mm. The raw samples were then additionally compacted by cold isostatic pressing under 250 MPa. The measured green density of the raw samples was 55÷60% T. D. of single-phase NbC.

Pressureless sintering

The green samples were pressureless sintered in a high-temperature reactor Thermal-Technology in argon flow. The sintering process was carried out vs. sintering temperature: 1900, 2000 and 2100°C. The apparent density of the sinters was measured by the Archimedes method and phase composition analyzed using X-ray diffractometry. The density of the samples and quantitative phase composition (Rietveld method) of the polycrystals are summarized in Table 2.

TABLE 2. **Apparent and relative densities of $NbC_{0.8}$ polycrystals**

TABELA 2. **Gęstości pozorne i względne polikryształów $NbC_{0.8}$**

Carbide	Temperature of sintering [°C]	Carbon additive [mass %]	Quantitative phase composition [mass %]	Apparent density [kg/m³]	Relative density [%]
$NbC_{0.8}$	1900	0.0	96.4% NbC; 3.6% Nb_xO_y	7450	95.8
		1.0	98.2% NbC; 1.8% Nb_xO_y	7410	95.2
		2.0	100% NbC	7210	92.7
	2000	0.0	97.8% NbC; 2.2% Nb_xO_y	7390	95.0
		1.0	100% NbC	7480	96.2
		2.0	100% NbC	7370	94.7
	2100	0.0	95.4% NbC; 4.6% Nb_xO_y	7260	93.3
		1.0	100% NbC	7350	94.5
		2.0	100% NbC	7390	95.0

QUALITATIVE AND QUANTITATIVE ANALYSIS OF POLYCRYSTAL MICROSTRUCTURE

Metallographic microstructure observation of the sinters was performed under a scanning electron microscope (NovaNanoSEM 200; FEICompany). Samples of a density greater than 90% T.D. of NbC were polished. To see the grain boundaries, the microsections were subjected to chemical etching in melted alkaline salts (25% KNO_3+75% KOH; 480°C). Images of the composite microstructures as a function of sintering temperatures and the additives are presented in Figure 1. Large light grey grains are, as shown by the EDS analysis presented in Figure 2, niobium carbide grains, while fine darker grains which occur mostly at the grain boundaries, at triple points and locked inside the NbC grains, are most likely to be niobium oxides. The microsections shown in Figure 1 were subjected to chemical etching, which may lead to the erroneous conclusion that the materials are porous as the majority of niobium oxides were etched under the influence of the melted alkaline salts.

The quantitative analysis of the microstructure of the tested composites was conducted using Aphelion software, which is dedicated for such tasks. Multi-shade images of the material (microsection surfaces) microstructure performed using a scanning microscope (with 256 possible shades of grey), saved as graphic files, were processed (filtering and binarization; Fig. 3) which were aimed at obtaining binary images (0 is assigned to black and 1 is assigned to white), presenting the selected elements of the input images (e.g. grain boundaries) [16]. The use of appropriate image transformations (logical, arithmetic and morphological) made it possible to obtain separate binary images presenting:

- grains of the matrix phase of the composite,
- particles of the oxide phase situated on the boundaries of the matrix grains,
- particles of the oxide phase situated inside the matrix grains.

In this way, it was possible to perform an independent quantitative analysis of individual elements of the microstructure of the tested composites.

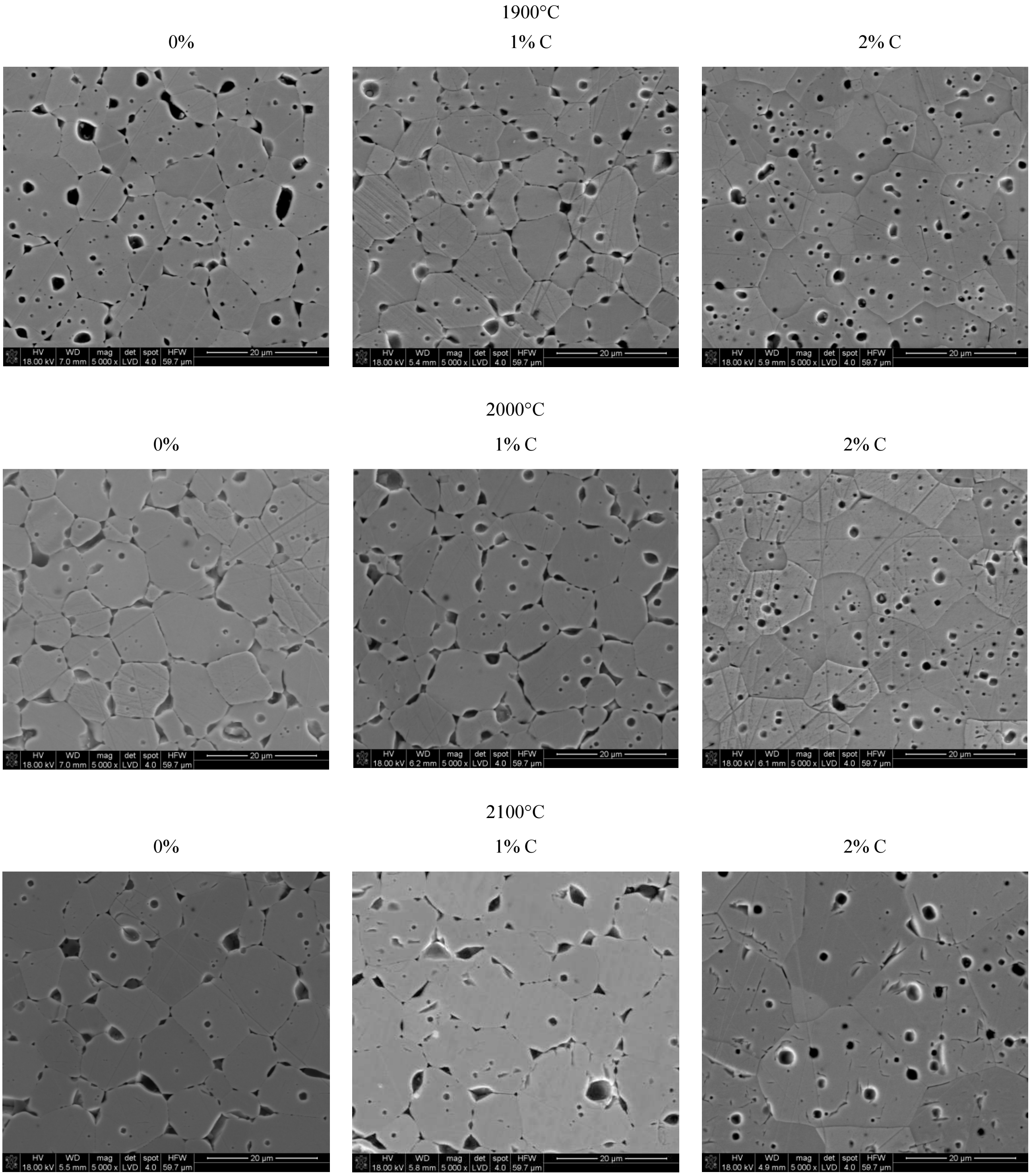


Fig. 1. SEM micrographs of $NbC_{0.8}$-Nb_xO_y composites and $NbC_{0.8}$ single-phase polycrystals vs. sintering temperature and carbon additive

Rys. 1. Mikrofotografie SEM kompozytów $NbC_{0.8}$-Nb_xO_y i jednofazowych polikryształów $NbC_{0.8}$ w funkcji temperatury spiekania i dodatku węgla

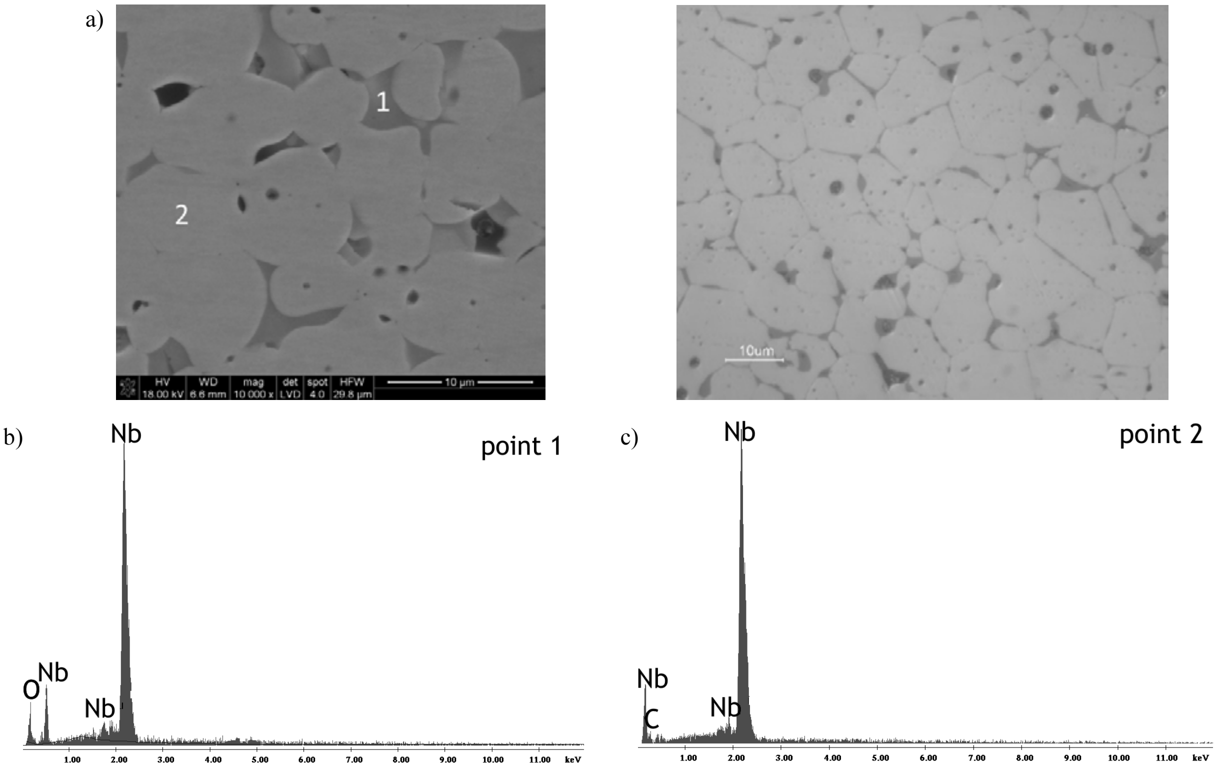


Fig. 2. SEM and optical microscope micrographs (a) of unetched microsection of $NbC_{0.8}$-Nb_xO_y composite and EDS point analyses (b and c). Sintering temperature 1900°C

Rys. 2. Mikrofotografia SEM nietrawionej próbki kompozytu $NbC_{0.8}$-Nb_xO_y (a) oraz punktowa analiza chemiczna EDS (b i c). Temperatura spiekania 1900°C

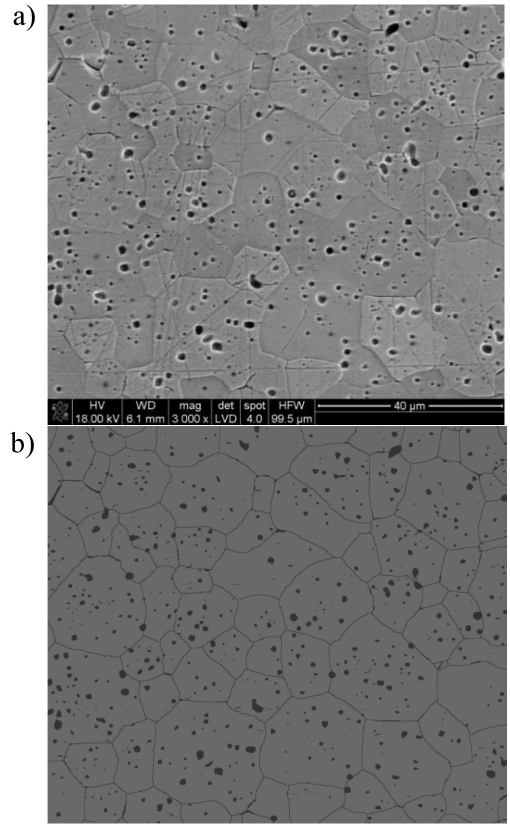


Fig. 3. Example of SEM micrograph (a) of NbC sinter (T_S = 2000°C; 2.0% mass of carbon additive) and binary image (b)

Rys. 3. Przykładowa mikrofotografia SEM (a) spieku $NbC_{0.8}$ (T_S = = 2000°C; 2,0% mas. dodatku węgla) i odpowiedni obraz binarny (b)

The following stereological parameters were selected to characterize the microstructure of the composites [17]:

- volume of the oxide phase per unit volume V_V,
- equivalent diameter d_2 of the NbC grains,
- mean diameter D of the NbC grains,
- surface area of the grain boundaries per unit volume S_V.

The volume fraction of the dispersed (oxide) phase was determined using the planimetric method by measurements of the total surface area of all objects representing oxide phase particles on the binary images. The stereological relation was used in the calculations:

$$V_V = A_A = \frac{A_S}{A_i}, \qquad (2)$$

where: A_A - surface fraction, A_s - total surface area of objects representing oxide phase particles, A_i - surface area of the binary image.

The size of the cross sections of the composite matrix grains as seen in the images were characterized using their equivalent diameter d_2, which was calculated from the following relationship:

$$\bar{d}_2 = \left(\frac{4A}{\pi}\right)^{0.5}, \qquad (3)$$

where A - surface area of an object presenting grain in a binary image.

Mean diameter *D*, which characterized the size of the grains in three dimensions, was determined using the Saltykov method of diameter reversal. The *D* value was calculated on the basis of the following relationship:

$$D = 1.5788 \cdot \left(E\left(d_2^{-1}\right)\right)^{-1} \qquad (4)$$

where $E(d_2^{-1})$ - the arithmetic mean of equivalent diameter reversal for all the measured matrix grains.

Relative surface S_V is the surface area of the boundaries of a given type in a unit volume of the material. The relative surface was determined by the secant method using the stereological relationship:

$$S_V = 2P_L \qquad (5)$$

where: P_L - the number of points intersecting the boundaries of a given type per unit length of a secant line running in a binary image.

TABLE 3. **Results of quantitative analysis of microstructure of $NbC_{0.8}$-Nb_xO_y composites**

TABELA 3. **Wyniki ilościowej analizy mikrostruktury kompozytów $NbC_{0.8}$-Nb_xO_y**

Sintering temperature [°C]	**1900**			**2000**			**2100**		
Carbon additive [% mas.]	0.0	1.0	2.0	0.0	1.0	2.0	0.0	1.0	2.0
$V_v(Nb_xO_y)$ [%]	4.73	3.51	3.9	4.10	4.53	3.88	4.49	4.32	2.84
$V_v(Nb_xO_y)_{IG}$/ $V_v(Nb_xO_y)$ [%]	22.28	24.21	61.01	12.74	14.16	79.85	13.51	13.92	62.64
d_{2max}(NbC) [μm]	20.2	15.5	23.9	19.3	18.8	24.2	19.3	20.9	50.2
$\bar{d}_2$ (NbC) [μm]	8.6 ±1.9	7.5 ±1.6	8.7 ±1.9	8.0 ±0.4	7.5 ±0.4	11.2 ±0.6	8.6 ±1.8	9.6 ±2.0	18.6 ±1.5
D(NbC) [μm]	10.4 ±2.3	9.9 ±2.2	10.7 ±2.3	10.7 ±0.6	9.7 ±0.5	14.3 ±0.7	11.5 ±2.4	11.7 ±2.5	23.6 ±1.9
S_v [m^{-1}]	0.272	0.318	0.259	0.305	0.315	0.206	0.268	0.241	0.121

Description of Table 3:

$V_V(Nb_xO_y)$ - volume of oxide phase per unit volume of composite: $V_V(Nb_xO_y) = V_V(Nb_xO_y)_{IG} + V_V(Nb_xO_y)_{OGB}$

$V_V(Nb_xO_y)_{IG}$ - volume of oxide phase occurring inside NbC grains per unit volume of composite

$V_V(Nb_xO_y)_{OGB}$ - volume of oxide phase occurring on grain boundaries per unit volume of composite

$V_V(Nb_xO_y)_{IG}/V_v(Nb_xO_y)$ - fraction of volume of oxide phase occurring inside NbC grains in total volume of oxide phase in composite

d_{2max}(NbC) - maximum equivalent diameter of NbC phase (it is a measure of size of largest grain observed on microsection)

(NbC) - average equivalent diameter of NbC grains

D(NbC) - average diameter of NbC grains

S_V(NbC) - surface area of grain boundaries of NbC phase per unit volume of composite

The parameters describing the microstructure in the quantitative manner are collected in Table 3. Figure 4 presents the results of calculations of mean diameter D of the grains; next, in Figure 5, the results of the calculations of the surface area of the NbC grain boundaries per unit volume of composite are shown, while Figure 6 presents the results of calculations of the volume of the oxide phase per unit volume of the composite. All the parameters are provided as a function of the sintering temperature and the quantity of carbon.

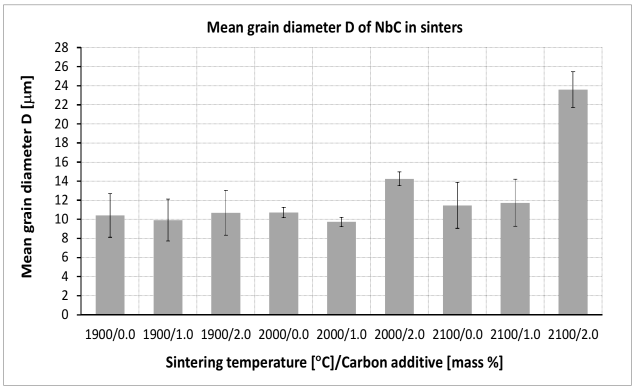


Fig. 4. Measurement results of mean diameter of NbC grains as function of sintering temperature and carbon additive

Rys. 4. Wyniki pomiarów średniej średnicy ziaren NbC w spiekach w funkcji temperatury spiekania i dodatku węgla

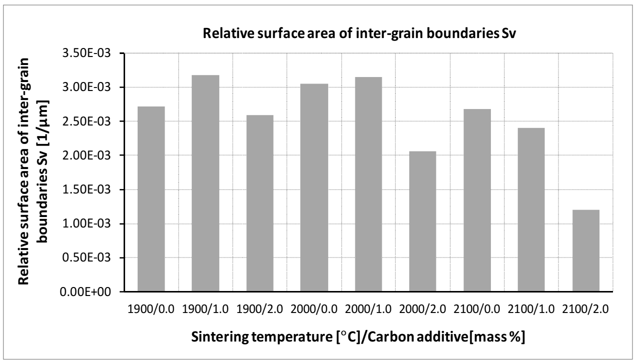


Fig. 5. Measurement results of surface area of grain boundaries of NbC phase per unit volume of composite as function of sintering temperature and carbon additive

Rys. 5. Wyniki pomiarów powierzchni względnej granic międzyziarnowych fazy NbC w spiekach w funkcji temperatury spiekania i dodatku węgla

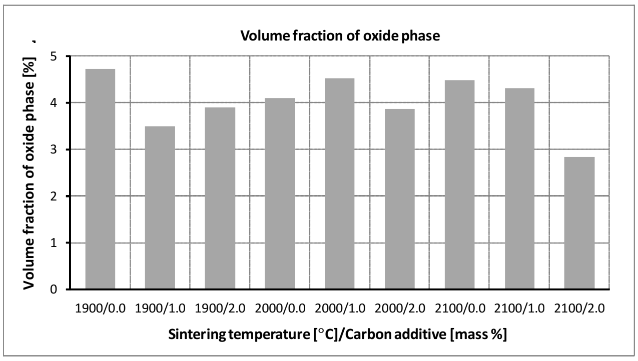


Fig. 6. Measurement results of oxide phase volume per unit volume of $NbC_{0.8}$-Nb_xO_y composite as function of sintering temperature and carbon additive

Rys. 6. Wyniki pomiarów udziału objętościowego fazy tlenkowej w kompozytach $NbC_{0.8}$-Nb_xO_y w funkcji temperatury spiekania i dodatku węgla

MEASUREMENTS OF MECHANICAL PROPERTIES

An attempt was also made to correlate the results of the quantitative analysis of the microstructure with the basic measurements of the mechanical properties of the composites, i.e. Vickers and Knoop hardness and fracture toughness. The hardness measurements were performed in accordance with the Vickers and Knoop methods, a standard load of 1 kg was used, which corresponds to the force of 9.81 N. The measurements of fracture toughness were performed using the indentation method. For this purpose, using the Vickers pyramid, prints were made under a load of 3 kg and next, the length of the cracks coming from the corners of the print were measured and on the basis of the calculated value of the $0.25 < l/a < 2.50$ ratio (where: l - the average length of cracks; a - the average half of the diagonal of the cavity), the fracture toughness value was calculated using the Niihara formula [18]. The results are given in Table 4.

TABLE 4. **Results of Vickers and Knoop hardness and fracture toughness measurements of $NbC_{0.8}$-Nb_xO_y composites**

TABELA 4. **Wyniki pomiarów twardości Vickersa i Knoopa oraz odporności na kruche pękanie kompozytów $NbC_{0.8}$-Nb_xO_y**

Carbide	Temperature of sintering [°C]	Carbon additive [mass %]	Hardness		Fracture toughness [MPa $m^{0.5}$]
			$HV_{1.0}$ [GPa]	$HK_{1.0}$ [GPa]	
$NbC_{0.8}$	1900	0.0	15.50 ±1.34	12.18 ±0.32	3.65 ±0.14
		1.0	15.85 ±1.48	12.97 ±0.43	3.77 ±0.16
		2.0	16.29 ±0.65	12.57 ±0.29	3.43 ±0.24
	2000	0.0	15.01 ±0.88	12.59 ±0.43	4.36 ±0.21
		1.0	15.08 ±0.54	12.47 ±0.52	4.36 ±0.14
		2.0	15.57 ±1.65	11.77 ±0.75	4.02 ±0.27
	2100	0.0	15.42 ±0.58	11.85 ±0.22	4.53 ±0.26
		1.0	16.00 ±0.80	12.14 ±0.44	4.56 ±0.30
		2.0	16.05 ±0.55	11.75 ±0.48	4.08 ±0.18

DISCUSSION OF RESULTS

On the basis of the density measurements presented in Table 2, it can be concluded that polycrystals with a high degree of sintering (93÷95%) can already be obtained at the lowest sintering temperature, which is 1900°C. The relative density does not present the actual porosity since the density of niobium carbide was adopted as the theoretical density, which is 7780 kg/m^3. The number and type of oxide phases was not taken into account in the density calculations, due to significant difficulties in defining them precisely. Polycrystals sintered at 2000°C show the highest density, 95÷96% of the theoretical NbC density. The density measurements prove that niobium oxides present in the niobium carbide powder effectively activate niobium carbide sintering. In accordance with the literature data and the research presented in studies [10, 13, 19], niobium oxides are stable in the presence of carbide up to their melting temperatures. The lower the degree of niobium oxidation is, the higher the melting temperatures of niobium oxides is, i.e. NbO (II) - 1940°C; NbO_2 (IV) - 1915°C and Nb_2O_5 (V) - 1512°C [19]. Therefore, it is very likely that liquid phases are formed during the sintering process, which activates densification and, as a result, this leads to the formation of dense sinters. The carbon additive does not have a significant influence on the polycrystal density, but it does influence their phase composition and the appearance of the microstructure in a significant manner. The sintering investigation of the commercial NbC powder (ABCR; cat. no AB200820) without any sintering additives and with a 0.25÷0.35% weight percent of oxide impurities was performed. Unfortunately, despite sintering at the high temperature of 2100°C, full densification of the samples was not achieved (78% of T.D. of NbC). The facts mentioned above have shown that the presence of niobium oxides in the synthesized NbC powder have a good influence on its sinterability. The sinters made of powder without the carbon additive are multi-phase ones (Table 2). Niobium carbide is the dominant phase - 95÷98%. Niobium oxides were identified in the polycrystals in the amount of 2÷5%, with deviation from stoichiometry which is difficult to determine unambiguously. Therefore, it can be said that these materials are $NbC_{0.8}$ - Nb_xO_y composites in which niobium carbide is the matrix and niobium oxides are inclusions (Figures 1 and 2). As regards carbide and oxide composites, no significant influence of the temperatures on their phase composition was observed. Both of the aforementioned phases can be identified at each of the sintering temperatures. These results are yet another confirmation of the stability of niobium oxides at high sintering temperatures ~2000°C in the presence of niobium carbide.

The carbon additive, in accordance with the assumption, wholly or partially reduces oxide phases and therefore their presence is not found in the phase composition of the polycrystals, although they can be noticed in the microstructure (Fig. 2). However, the number of oxide phases is probably so low that they are below the detection level of the XRD method. 100% niobium carbide is identified for the polycrystals sintered with the 2.0% carbon additive at sintering temperatures of 1900, 2000 and 2100°C, as well as for the polycrystals sintered with the 1.0% carbon additive at sintering temperatures of 2000 and 2100°C. The influence of the temperature on the thermal decomposition of oxide phases can be noticed - the higher the temperature, the stronger their decomposition (Table 2).

The presence of oxide phases which activate the sintering process is also confirmed in the microstructure images of the composite microstructure and single-phase sinters. Images of the microstructures presented collectively in Figure 1 show ovoid NbC grains and oxide phases at the grain boundaries, at triple points and inside the grains. Oxide phases can be seen particularly well at each of the sintering temperatures for composites formed of powder with no carbon additive. The SEM microphotographs presented in Figure 1 can give an erroneous impression of porosity as the oxide phases are etched under the influence of the melted alkaline salts. An unetched, practically pore-free microsection is presented in Figure 2a, which also presents the results of chemical analysis in micro-areas (EDS analyses), allowing for the identification of individual phases in the composites (Figs. 2b and 2c).

An analysis of the microstructure showed that an increase in the amount of carbon added and an increase in the sintering temperature activate the growth of NbC grains. These observations are confirmed by quantitative analysis of the microstructure and accurate measurements of mean diameter *D*(NbC) (Fig. 4), equivalent mean diameter d_2(NbC) and maximum grain diameter $d_{2\max}$(NbC) (Table 3) and measurements of the surface area of the grain boundaries of the NbC phase per unit volume of composite (Fig. 5). The higher the additive of carbon i.e. 2 mass % and the higher the sintering temperature (2000 and 2100°C) are, the stronger the growth of grains is, which is confirmed by the growing values of average grain diameter D(NbC) and equivalent grain d_2 and average maximum grain diameter $d_{2\max}$(NbC). The surface area connected with the growth of the grain boundaries as a function of carbon additive and sintering temperature decreases, which is shown in the data presented in Figure 5 and Table 3. One should notice the fact that strong growth of NbC grains occurs after exceeding 1% of the carbon added, i.e. when the majority of sintering oxide phases is reduced and when the sintering temperature is higher than 2000°C. Moreover, according to the data presented in Table 3 and in Figure 4, in the case of composites made from powder without the carbon additive, it does not occur, regardless of the sintering temperature. Thus, it can be supposed that the presence of oxide phases, even in a small amount, effectively inhibits the growth of NbC grains. In addition, the SEM photographs presented in Figure 1 show that an increase in the amount of carbon added, regardless of the sintering temperature, makes the grain boundaries straight while some of the oxide phases are closed within the growing grains (Fig. 1). These observations are confirmed by calculations of the volume fraction of the oxide phase inside the NbC grains in the total volume of the oxide phase in NbC sinters collected in Table 3 and presented in Figure 7.

The volume of oxide phases on the grain boundaries per unit volume of composite decreases as opposed to the volume of oxide phases inside the grains per unit volume. The total volume of oxide phases $V_V(Nb_xO_y)$ per unit volume of composite strongly decreases when the amount of carbon additive is 2% and sintering temperature is 2100°C (Fig. 6 and Table 3). These calculations confirm the effective role of carbon as a reducing agent for niobium oxides and, at the same time, an additive which activates the sintering and leads to the creation of single-phase NbC sinters. The combination of density measurements with the qualitative and quantitative analysis of the microstructure, analysis of the phase composition and measurements of basic mechanical properties suggests that the optimal sintering temperature is 2000°C. At this temperature, which constitutes approx. 0.5 of the NbC melting temperature, fine-grained NbC_{1-x}-Nb_xO_y composites can be obtained and also single-phase fine-grained polycrystals owing to the introduction of carbon in the amount of 1÷2 mass %.

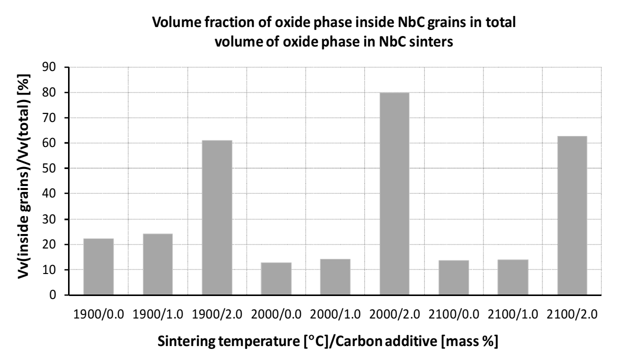


Fig. 7. Volume fraction of oxide phase inside NbC grains in total volume of oxide phase in NbC sinters

Rys. 7. Udział objętości fazy tlenkowej rozmieszczonej wewnątrz ziaren NbC w całkowitej objętości fazy tlenkowej w spiekach NbC

An attempt was also made to combine the changes in the microstructure with the basic mechanical properties of sinters, i.e. hardness and fracture toughness. An increase in Vickers hardness and a decrease in fracture toughness were observed for all the sintering temperatures as a function of carbon additive (Table 4). An increase in hardness is caused by a decrease in the volume fraction of oxide phases, which are even more reduced if the carbon additive is higher and at higher sintering temperatures (Fig. 6; Table 3), and which are characterized by much lower hardness [20] (4÷5 GPa) as compared to the composite matrix, NbC. For hardness measurements using the Knoop method, no relationship is observed between the hardness and structure of the polycrystals, which can be connected with the features of the measurement method itself. The decrease in volume fraction of the oxide phases as well as locking them within growing grains when the carbon additive is higher, in the case of sintering temperatures of 2000 and 2100ºC, is the reason why the value of the fracture toughness decreases. The presence of oxide phases, as shown in studies [10, 13], has an advantageous influence on increasing the effective cracking energy mostly due to the deviations and involvement of cracks near the oxide phase grains. In the $NbC_{0.8}$-Nb_xO_y composites, cracking at the grain boundaries is also observed which effectively increases the value of fracture toughness.

CONCLUSIONS

The qualitative and quantitative assessment of the microstructure, together with measurements of the density, mechanical properties and analysis of the phase composition of polycrystals made of NbC powder synthesised under laboratory conditions, in which considerable amounts of niobium oxides are identified, lead to the conclusions that:

- Niobium oxides present in the powder effectively activate the sintering of $NbC_{0.8}$-Nb_xO_y and composites and NbC polycrystals.
- Without any additives, it is possible to create $NbC_{0.8}$-$Nb_xO_{y,}$ composites at each of the selected sintering temperatures.
- The carbon additive, which is considered to be a reducing agent for oxide impurities at sintering temperatures of 2000 and 2100°C, allows for creating single-phase NbC polycrystals.
- The carbon additive (2 mass %) greatly reduces niobium oxides and activates the growth of NbC grains, which is confirmed by the results of quantitative analysis of the microstructure.
- Among the three sintering temperatures, i.e. 1900, 2000 and 2100°C, 2000°C is considered to be the optimal temperature as the composites and single-phase polycrystals produced at this temperature are characterised by the highest density, fine-grained microstructure and good mechanical properties.

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REFERENCES

[1] Pierson H.D., Handbook of Refractory Carbides and Nitrides, Ed. Notes Publication, New Jersey 1996.

[2] Stobierski L., Carbide Ceramics, AGH, Krakow 2005 (in Polish).

[3] Kosolapova T.Y., Carbides: Properties, Production, and Applications., Plenum Press, New York 1971.

[4] Brookes K.J.A., Half a century of hardmetals, Metal Powder Report 1995, 50, 12, 22-28.

[5] Upadhyaya G.S., Materials science of cemented carbides - an overview, Materials and Design 2001, 22, 483-489.

[6] Gibas T., Spieki ceramiczne i cermetale, WNT, Warszawa 1961.

[7] Gubernat A., Sintering of metal-like carbides., Ceramic Materials 2007, 3, 111-117 (in Polish).

[8] Gubernat A., Stobierski L., Metal-like carbides. Part I. Sinterablity investigations, Ceramic Materials 2009, 2, 113--118 (in Polish).

[9] Gubernat A., Synthesis, sintering and properties of single-phase carbides, Ceramika/Ceramics 114, PTCer, Krakow 2013 (in Polish).

[10] Mucha J., Gubernat A., Stobierski L., Sintering and properties of NbC_{1-x}-NbO_2 composites, Composites Theory and Practice 2013, 13(3), 185-192.

[11] Gubernat A., Pressureless sintering of single-phase tantalum carbide and niobium carbide, J. Eur. Cer. Soc. 2013, 33, 2391-2398.

[12] Gubernat A., Zych Ł., The isothermal sintering of the single-phase non-stoichiometric niobium carbide (NbC_{1-x}) and tantalum carbide (TaC_{1-x}), J. Eur. Cer. Soc., 34, 2014, 2885--2894.

[13] Mucha J., Niobium carbide - niobium oxide composites, Master's Thesis, AGH, Krakow 2014 (in Polish).

[14] Gubernat A., Stobierski L., Goryczka P., Metal-like carbides. Part II. Investigations of mechanical and chemical properties, Ceramic Materials 2009, 2, 119-124 (in Polish).

[15] Mucha J., Investigations on properties of single-phase carbides polycrystals, Engineering Thesis, AGH, Krakow 2013 (in Polish).

[16] Wojnar L., Majorek M., Komputerowa analiza obrazu, Fotobit Design, Kraków 1994.

[17] Ryś J., Stereologia materiałów, Fotobit Design, Kraków 1995.

[18] Niihara, K.A., fracture mechanics analysis of indentation-induced Palmqvist crack in ceramics, J. Mater. Sci. Lett. 1983, 2, 221-223.

[19] ACerS-NIST Phase Equilibria Diagrams CD-ROM Database Version 3.1, 2007.

[20] Huijbregts W.M.M., Brabers M.J., Oxidation of niobium and of niobium coated with aluminium in steam-air mixtures, Proceedings S.E.R.A.I. Journee Internationales d'étude sur l'óxydation des metaux, Bruxelles 1965.