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SINTERING AND PROPERTIES OF NbC_{1-x}-NbO₂ COMPOSITES

The paper presents results of research on sintering, polycrystals manufacture and determination of the characteristics of the obtained NbC_{1-x} - NbO₂ composites. For the manufacturing of composites powders synthesized from the elements in the solid phase reaction method in the laboratory of Department of Ceramics and Refractories WIMiC, AGH were used. As a result of grinding and drying, carbide powders have undergone a surface oxide passivation. In order to improve the granulation and moulding capacity of powders and to partially deoxidize them, a small amounts of Nowolak MR resin were introduced into powders, as a carbon precursor. The prepared granulates were used to manufacture composites with the pressureless sintering and hot pressing. Mechanical properties, thermal and chemical properties were investigated and compared with the results obtained for the single-phase niobium carbide polycrystals. It was found that the composites are characterized by: high hardness (HV~16 GPa; HK 12~14 GPa), higher than the polycrystals bending strength (~500 MPa) and fracture toughness (~5 MPa·m^{0.5}) and good thermal conductivity (12~15 W/m·deg). Oxidation resistance of the composites is the same as the single-phase materials.

Keywords: composites NbC_{1-x}-NbO₂, single-phase niobium carbide, mechanical, thermal and chemical properties

SPIEKANIE I WŁAŚCIWOŚCI KOMPOZYTÓW NbC_{1-x}-NbO₂

W pracy przedstawiono wyniki badań nad spiekaniem, wytwarzaniem polikryształów i określeniem właściwości uzyskanych kompozytów NbC_{1-x}-NbO₂. Do wytwarzania kompozytów użyto proszków syntezowanych w fazie stałej z pierwiastków w laboratorium Katedry Ceramiki i Materiałów Ogniotrwałych WIMiC, AGH. W wyniku mielenia i osuszania proszki węglowe uległy powierzchniowej pasywacji tlenkowej. W celu zgraniowania i poprawienia zdolności formierskich proszków oraz w celu częściowego odtlenienia proszków wprowadzono do nich niewielkie ilości żywicy Nowolak MR jako prekursora węgla. Z przygotowanych granulatów wytworzono kompozyty techniką spiekania swobodnego i prasowania na gorąco. Zbadano właściwości mechaniczne, cieplne i chemiczne, a następnie porównano je z wynikami uzyskanymi dla jednofazowych tworzyw z węglikiem niobu. Stwierdzono, że kompozyty charakteryzują się: wysoką twardością (HV~16 GPa; HK 12~14 GPa), wyższą od polikryształów jednofazowych wytrzymałością na zginanie (~500 MPa) i odpornością na kruche pękanie (~5 MPa·m^{0.5}) oraz dobrym przewodnictwem cieplnym (12~15 W/m·deg). Odporność na utlenianie kompozytów jest taka sama jak tworzyw jednofazowych.

Słowa kluczowe: kompozyty NbC_{1-x}-NbO₂, jednofazowy węgiel niobu, właściwości mechaniczne, cieplne i chemiczne

INTRODUCTION

Interstitial carbides, also called metal-like carbides, have a number of valuable and unusually associated properties, arising from the complex nature of the bonds, in which there are three components: covalent, ionic and metallic bonds [1-3]. Thus metal-like carbides exhibit characteristics typical of ceramic materials and metallic materials. Strong covalent - ion bonds causes metal-like carbides to have a high melting point, but also to be hard and brittle. Metallic component determines the good electricity and heat conductivity. Making full use of the properties of carbides becomes possible if they are present in the form of dense polycrystals, preferably single phase [2, 4, 5]. The development of technology for producing sintered carbides and the

conviction that metal-like carbides have poor sinterability, caused little interest in obtaining the single-phase polycrystals. In a few papers [2, 4-6] devoted to metal-like carbide sintering it was showed that the oxide contamination present in the powders should be reduced. It is believed that during sintering numerous gaseous products, detrimental to compaction, can be created. On the other hand, in papers [7, 8] relating to sintering of metal carbides from group 5 of the periodic system, it was shown that the presence of oxide contamination is not as bad as it follows from the theory. Niobium oxide (IV) is stable in the presence of carbide and free carbon [9], moreover that oxide can form liquid phases during sintering, activating densification.

Niobium oxide(IV) may remain in the microstructure of sinters, thereby forming a composite $\text{NbC}_{1-x}\text{-NbO}_2$. Effect of oxide phases on the physic-chemical properties of thus prepared composite has not been studied.

The aim of this work was to obtain $\text{NbC}_{1-x}\text{-NbO}_2$ composites and to determine their properties:

- mechanical: hardness, bending strength and fracture toughness,
- thermal: coefficient of linear expansion α and coefficient of thermal conductivity λ ,
- chemical: oxidation resistance.

PREPARATION OF $\text{NbC}_{1-x}\text{-NbO}_2$ COMPOSITES

Synthesis of NbC_{1-x} carbide powders

Preparation began with the synthesis of niobium carbide with assumed deviation from stoichiometry. Carbides were synthesized from the elements in the solid phase reaction technique. For this purpose, the substrates were prepared, which were the powders of metallic Nb (ABCR GmbH & Co.KG, No. AB201777) and phenol-formaldehyde resin "Nowolak MR" (ORGANIKA-SARZYNA). This resin leaves 50 mass % after pyrolysis in the form of amorphous, reactive carbon. Niobium carbide has a wide range of homogeneity, so the chemical composition of carbide is described by the NbC_{1-x} formula. Therefore, the substrates are prepared in a way allowing to obtain the synthesis of carbides with carbon deviation from stoichiometry, i.e. $\text{NbC}_{0.9}$ and $\text{NbC}_{0.8}$.

Metal and resin powders were wet homogenized in ethyl alcohol in a ball mill, WC-Co grinding medium. After evaporation of the alcohol prepared powder mixture was subjected to synthesis at $\sim 1200^\circ\text{C}$, 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 powders, in the last stage of preparation, were sieved through a sieve with size 0.056 mm. Sieving was to isolate the powders from mechanically strong grain agglomerates. Thus obtained NbC_{1-x} powders were characterized, with determination of the: 1) phase composition, using X-ray diffraction method, 2) quantitative phase composition (mass %) using Rietveld method, 3) specific surface area using BET method, 4) grain size distribution using DLS method, 5) morphology using SEM scanning electron microscopy, 6) concentration of oxygen and carbon using combustion method and gas analysis in LECO apparatus. Characteristics of both NbC_{1-x} powders are presented in Table 1.

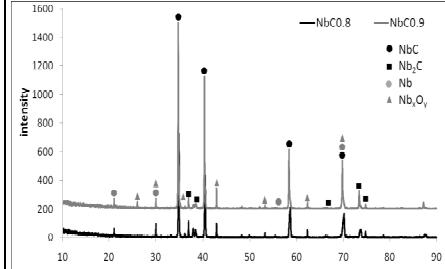
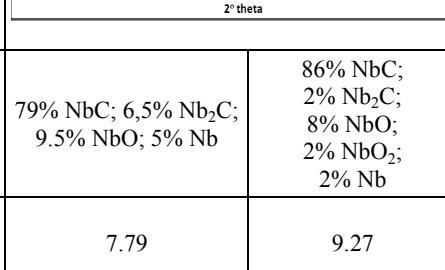
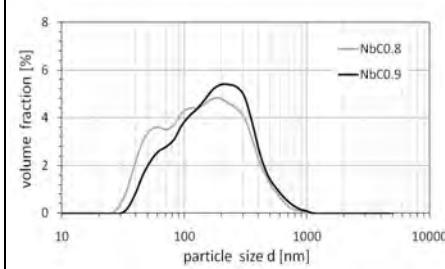
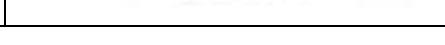
Preparation of raw samples

Quantitative analysis of the phase composition of powders (Rietveld method) revealed minor amounts of unreacted niobium, Nb_2C carbides and substantial amounts of niobium(II) and niobium(IV) oxides. According to the literature [1, 2] the presence of oxides is unfavorable from the viewpoint of sintering. During

sintering oxides may form volatile compounds, 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. Properly selected amount of carbon additive ensures that the sinters produced will be single-phase, according to the reaction



TABLE 1. Characteristic of niobium powders NbC_{1-x}
TABELA 1. Charakterystyka syntezowanych proszków NbC_{1-x}

	$\text{NbC}_{0.8}$	$\text{NbC}_{0.9}$
phase composition (XRD)		
Quantitative phase composition [mass %] (Rietveld method)	79% NbC; 6,5% Nb_2C ; 9,5% NbO ; 5% Nb	86% NbC; 2% Nb_2C ; 8% NbO ; 2% NbO_2 ; 2% Nb
carbon [mass %] (analyzer LECO)	7.79	9.27
calculated deviation from stoichiometry	$\text{NbC}_{0.88}$	$\text{NbC}_{0.91}$
Oxygen [mass %] (analyzer LECO)	2.36	2.36
S_{BET} [m^2/g] d_{BET} [nm]	4.16 m^2/g 185.4 nm	4.04 m^2/g 191 nm
Lattice parameter a [\AA]	$\text{NbC } a = 4.4532$	$\text{NbC } a = 4.4530$
Lattice parameter a according to [3][\AA]	$\text{NbC}_{0.78-0.85}$ $a = 4.4519-4.4618$	$\text{NbC}_{0.87-0.91}$ $a = 4.4649-4.4690$
Grain size distribution (DLS method)		

The calculations of 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 on the surface of the grains there are the most stable oxides of niobium i.e. niobium oxide(IV) and niobium oxide(V). Based on the quantitative phase composition of powders, determined using Rietveld method (Table 1), there was conducted a calculation of amount of carbon necessary to react with the free niobium into NbC carbide, saturate the octahedral gaps in Nb₂C carbides and reduce oxides present in the powders. Since the clear identification of the oxides layers passivating carbide grains is impossible, there was also calculated the amount of carbon necessary to react with oxygen in the form of carbon monoxide. Calculated according to the different approaches amounts of carbon, within the limits determined by the analytical methods, are significantly different from each other, so it was decided that the optimum carbon additive will be selected empirically. In Table 2 the calculated and introduced amounts of carbon additives are shown.

TABLE 2. Comparison of the calculated and the introduced carbon additives

TABELA 2. Porównanie obliczonych i wprowadzonych do proszków NbC_{1-x} dodatków węgla

carbides	carbon additive [mass %]			introduced carbon additive [mass %]
	by means of XRD	by means of LECO analyzer	by means of reaction C+1/2O ₂ =CO↑	
NbC _{0.8}	3.11±0.16	2.57±0.13	1.77±0.09	1.0; 1.5; 2.0; 2.5; 3.0
NbC _{0.9}	3.03±0.15	2.57±0.13	1.77±0.09	1.0; 1.5; 2.0; 2.5

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

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

Pressureless sintering

Green samples were pressureless sintered in the high-temperature dilatometer in argon atmosphere. The characteristics of the sintering process were carried out based on measurements of linear shrinkage (as measured along the diameter of the samples) of samples vs. temperature. Curves $\Delta d/d_0 = f(T)$ were recorded with a precision of 1 μm, while the increase in temperature to within 1°C. The temperature of the onset T₀ and of

the end T_S of the sintering were recognized on the basis of $\Delta d/d_0 = f(T)$ curves. It was assumed as the end of the sintering the appearance of the curves “plateau” or the occurrence of minor changes in the dimensions of the sample.

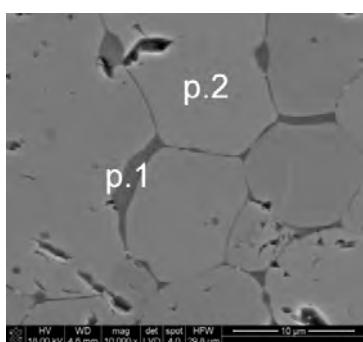
On the sintered bodies measurements of apparent density by the Archimedes method and phase composition using X-ray diffraction method were conducted. Samples of density greater than 90% T.D. were polished and the metallographic microstructure observation was performed under a scanning electron microscope (NovaNanoSEM 200 FEI Company). The density of the samples, the onset and end sintering temperatures T₀ and T_S, respectively and phase composition of the polycrystals are summarized in Table 3.

TABLE 3. Polycrystals densities, phase composition and determined temperatures T₀ and T_S i.e. onset and end of sintering, respectively

TABELA 3. Gęstości pozorne polikryształów, skład fazowy oraz temperatury początku T₀ i końca spiekania T_S w funkcji dodatku węgla

carbide	carbon additive [mass %]	phase composition (Rietveld method)	apparent density [kg/m ³]	relative density [%]	T ₀ [°C] onset of sintering temperature	T _S [°C] end of sintering temperature
NbC _{0.8}	1.0	98.1% NbC; 1.9% NbO ₂	7440	95.7	1250	1800
	1.5	100% NbC	7430	95.5	1200	1800
	2.0		7210	92.7	1150	1750
	2.5		7120	91.5		
	3.0		6870	88.2		
NbC _{0.9}	1.0	99.5% NbC; 0.5% NbO ₂	6870	88.3	1250	1800
	1.5	100% NbC	7340	94.3	1200	1800
	2.0		6990	89.9		
	2.5		7070	90.8	1150	1750

Basing on density measurements it was found that the optimal additive of carbon which ensures the highest density of sinters, in both carbides is close to 1.5 mass %. However, in the case of NbC_{0.8} powder high degree of sintering is achieved also when the additive of carbon is 1 and 2 mass %. The optimum additive of 1.5 mass % of carbon is smaller than the calculated on the basis of the analysis of oxygen content in powders made by LECO apparatus and calculated on the basis of the phase composition XRD (compare Table 2 to Table 3). Microstructure observation revealed that both samples of carbides sintered with additive of carbon 1 mass% are multiphase. The samples without conductive layers were tested using EDS analysis, in low vacuum (LVD) with acceleration voltages of 10 and 18 kV. Standardless corrections by holographic peak deconvolution and VIP Quant methods were performed. Results (Fig. 1) given as the mean values from several measurement points shown that at the grain boundaries and triple points a phase is present which elemental composition corresponds to niobium oxides.



a)

	mass % C	mass % O	mass % Nb
p.1	-	25.20	74.80
p.2	9.60	-	90.40

b)

Fig. 1. Microstructure (a) and quantitative EDS analysis (b) of $\text{NbC}_{0.8}$ polycrystal with 1% of carbon additive

Rys. 1. Mikrostruktura SEM (a) i ilościowa analiza EDS (b) w spieku $\text{NbC}_{0.8}$ z 1% dodatkiem węgla

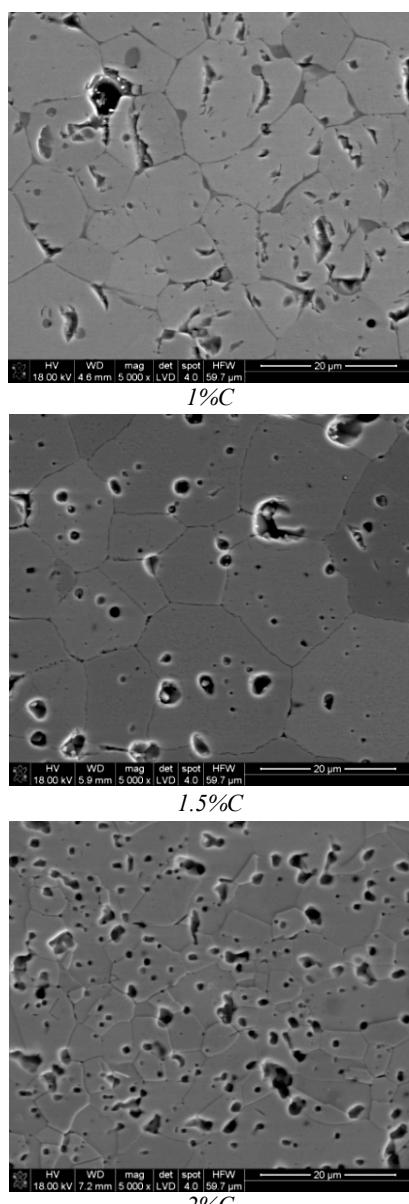


Fig. 2. SEM micrographs $\text{NbC}_{0.8}$ polycrystals with different carbon additive

Rys. 2. Mikrostruktury spieków $\text{NbC}_{0.8}$ aktywowanych różnym dodatkiem węgla

In the $\text{NbC}_{1-x}+1\%\text{C}$ samples, phases MeC_{1-x} and NbO_2 oxide were identified by X-ray diffraction method. The introduction of carbon in an amount greater than 1 mass %, i.e. 1.5 and 2 mass % does not change the density of polycrystals but significantly modifies the image of the microstructure. The microstructure of NbC_{1-x} sintered bodies activated with 1 mass % additive of carbon is characteristic of liquid phase sintering. The liquid phase is likely to be formed by niobium oxides, of which the most stable is niobium oxide(IV). According to the phase equilibria diagram of the $\text{Nb}-\text{C}-\text{O}$ system, niobium oxide(IV) is stable at high temperatures, even in the presence of carbon [9]. Oxide liquid phases have a positive effect on the sinterability of carbide and the resulting polycrystals are $\text{NbC}_{1-x}-\text{NbO}_2$ composites. Niobium carbide is the matrix of composites and inclusions are niobium oxide(IV). A slight increase in carbon additive causes more niobium oxide to be carbothermal reduced, the amount of the liquid phase is decreased, and the microstructure assumes the characteristics of a microstructure obtained during the solid-phase sintering (Fig. 2). Polycrystals prepared with greater than 1.5 mass % of carbon additive did not show the presence of oxides, they are single-phase.

Hot pressing

In order to test the oxides effect on the properties of the composite of $\text{NbC}_{1-x}-\text{NbO}_2$ it was decided to prepare samples adequate for testing by hot pressing technique. To both niobium carbide powders carbon was added in an amount of 1 mass %. Hot pressing was carried out at end of sintering temperatures T_s , which were determined basing on the dilatometric measurements (Table 3). If on the recorded shrinkage curve "plateau" was observed, process was stopped and the sample was kept at the final temperature for 0.5 hour. Samples characterization i.e. apparent density measurements by Archimedes method, XRD analysis of phase composition and microstructure observations (SEM) were performed. During the scanning electron microscope observations, analyses of the elemental composition (EDS) were carried out. The results are summarized in Table 4 and Figure 3.

TABLE 4. Conditions of hot pressing process, apparent and relative densities and phase composition of NbC_{1-x} polycrystals

TABELA 4. Warunki prasowania na gorąco, gęstości pozorne i względne oraz skład fazowy polikryształów NbC_{1-x}

carbide	atmosphere /sintering pressure	sintering temperature T_s [°C]	apparent density [kg/m³]	relative density [%]	phase composition XRD (Rietveld method) [mass %]
$\text{NbC}_{0.8}$	Argon flow; above	1600	7630	98.1	93% NbC 7% NbO_2
$\text{NbC}_{0.9}$	1200°C 25 MPa	1650	7370	94.8	97.5% NbC 2.5% NbO_2

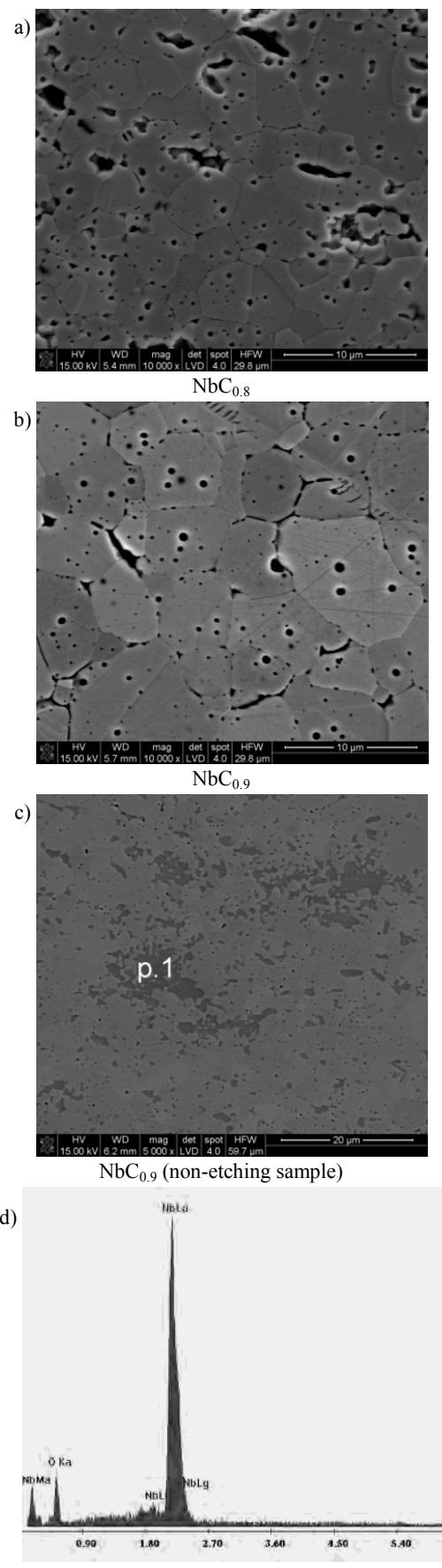


Fig. 3. SEM microstructure and EDS analysis of NbC_{1-x} sintered bodies (HP)

Rys. 3. Mikrostruktury SEM spieków NbC_{1-x} (HP) i punktowa analiza EDS spieku NbC_{0.9}

Results presented in Table 4 (phase compositions) and in Figure 3 (EDS analysis) show that the produced polycrystals are $\text{NbC}_{1-x}\text{-NbO}_2$ composites, in which the matrix is NbC_{1-x} and inclusions are niobium oxide(IV). The pictures of etched samples microstructure (Fig. 3a and 3b) show substantial porosity, which is formed by removing the oxide phases by molten alkali (75% KOH, 25% KNO₃, 480°C) used for chemical etching of the samples.

Mechanical, thermal and chemical properties of $\text{NbC}_{1-x}\text{-NbO}_2$ composites (HP)

Investigations of Vickers and Knoop hardness, fracture toughness (indentation fracture and single edge notched beam i.e. SNEB methods) and flexural strength (three-point bending test), thermal properties (thermal conductivity λ and the linear expansion coefficient α) and chemical properties (oxidation resistance) were performed on the produced hot pressed samples.

Hardness measurements were performed using a Future-Tech Corp. Model FV-700 hardness tester under a constant load of 9.81 N. The measurement results are collected in Figure 4.

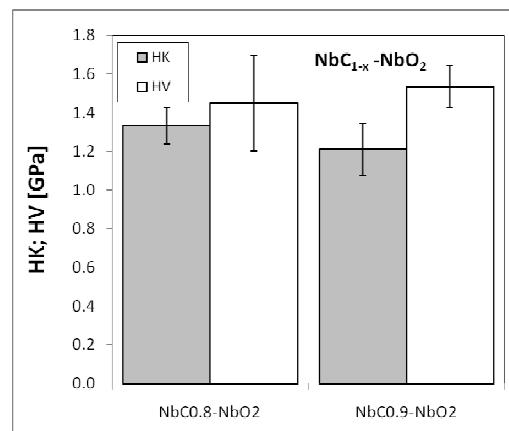
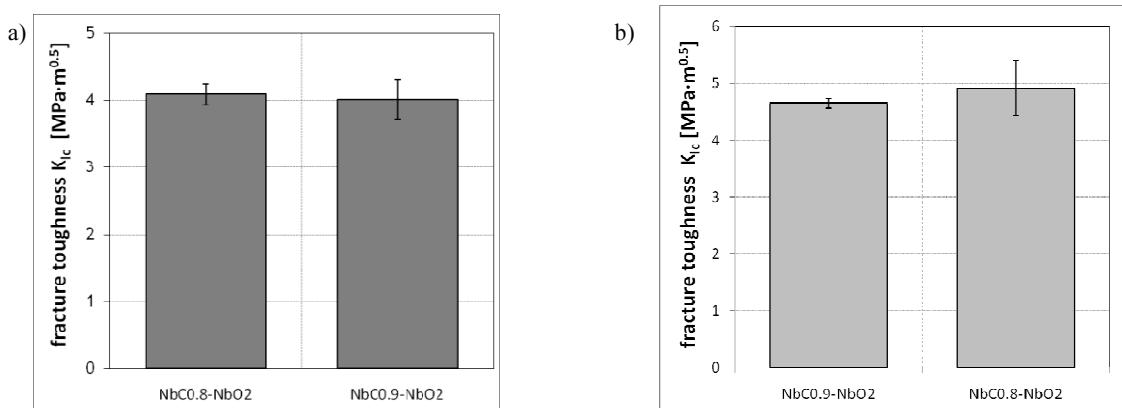
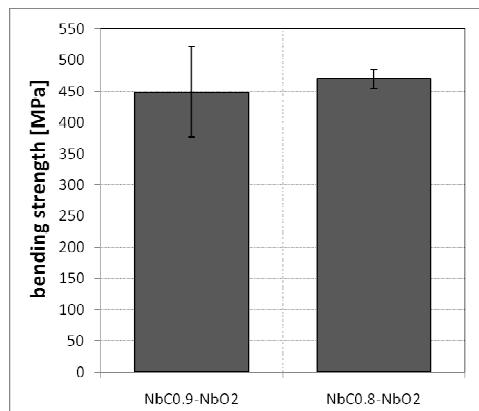
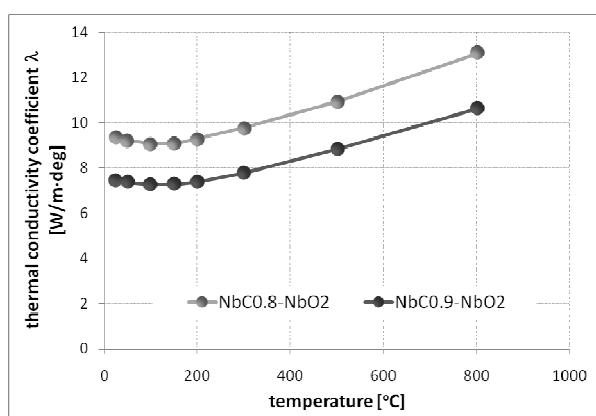


Fig. 4. Vickers hardness (HV_{1.0}) and Knoop hardness (HK_{1.0}) $\text{NbC}_{1-x}\text{-NbO}_2$ composites (load 9,81N)

Rys. 4. Twardość Vickersa i twardość Knoopa kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$

The value of the critical stress intensity factor K_{Ic} was determined using indentation fracture and single edge notched beam SNEB tests. Hardness measurements were carried out using the Future-Tech Corp. Model FV-700 hardness tester. The length of cracks emerging from the corners of the Vickers indentation were measured. The loads during the measurement were selected in such a way, that the measurement errors were reduced. The results are summarized in Figure 5a. The three-point bending notched beams (SNEB) test was performed on Zwick/Roel Z150 testing machine. The results are illustrated in Figure 5b. Bending strength was determined using three-point bending test in Zwick/Roel Z150 apparatus. Results are summarized in Figure 6.

Fig. 5. Fracture toughness $\text{NbC}_{1-x}\text{-NbO}_2$ composites: a) indentation method and, b) SNEB methodRys. 5. Wartości krytycznego współczynnika intensywności naprężen kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$: a) metoda wgłębnikowa, b) metoda SNEBFig. 6. Bending strength $\text{NbC}_{1-x}\text{-NbO}_2$ compositesRys. 6. Wytrzymałość na zginanie kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$ Fig. 7. Thermal conductivity coefficients λ vs. temperature $\text{NbC}_{1-x}\text{-NbO}_2$ compositesRys. 7. Wartości współczynników przewodzenia ciepła w funkcji temperatury kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$

The values of thermal conductivity λ were determined on the basis of the values of thermal diffusivity by LFA-Laser Flash Analysis. For this purpose, the measuring apparatus NETZSCH LFA 427 was used. The coefficient of linear expansion α has been determined in the range of 20–1000°C by means of NETZSCH DIL 402 C dilatometer. The value is determined by the slope of the $\Delta l/l_0 = f(T)$ regression lines. The results of mea-

surements of thermal conductivity λ are summarized in Figure 7 and the linear thermal expansion coefficient α are shown in Table 5.

Oxidation resistance measurements were performed by thermogravimetric analysis, which was conducted in a NETZSCH STA 449 F3 Jupiter® thermal analyzer, in air, in the temperature range of 20–1450°C. Figure 8 shows the graphs of thermogravimetric analysis of composites and single-phase NbC. Increase of sample mass was recorded, which is associated with the oxidation process.

TABLE 5. Values of linear expansion coefficients α of $\text{NbC}_{1-x}\text{-NbO}_2$ compositesTABELA 5. Wartości współczynników liniowej rozszerzalności cieplnej kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$

composite	value of linear expansion coefficient $\alpha \cdot 10^{-6}$ [1/deg.] 20–1000°C	values of linear expansion coefficient $\alpha \cdot 10^{-6}$ [1/deg.] carbide NbC, metallic niobium and niobium oxide (V) [1–3, 12]
NbC _{0.8} -NbO ₂	7.62	NbC: 6.6–6.65 Nb: 7.3 Nb_2O_5 : 5.3–5.9
NbC _{0.9} -NbO ₂	7.13	

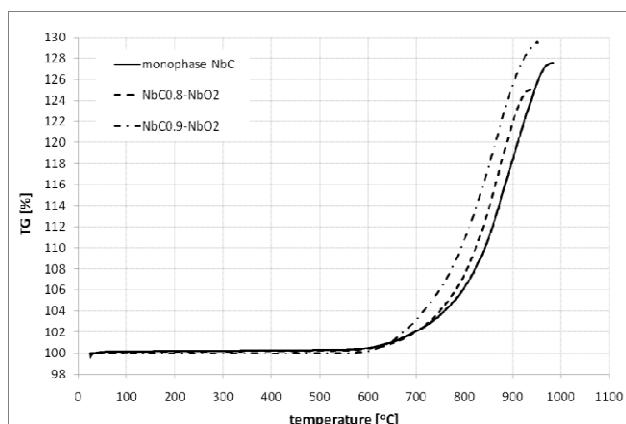
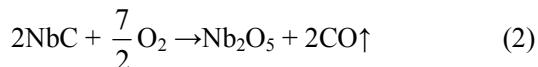
Fig. 8. Thermogravimetric curves of $\text{NbC}_{1-x}\text{-NbO}_2$ composites and monophase NbCRys. 8. Krzywe termograwimetryczne kompozytów $\text{NbC}_{1-x}\text{-NbO}_2$ oraz jednofazowego NbC

Table 6 shows the calculated efficiency of the oxidation process. For this purpose it was assumed that during the oxidation of composites, oxides with the highest degrees of oxidation of metal are formed, in this case, Nb₂O₅, according to reaction



This assumption was confirmed by analysis of the phase composition (XRD) of oxidation products (Table 6). According to the assumption and reaction (2) the maximum mass gain was calculated and referenced to mass increments read from thermogravimetric measurements.

TABLE 6. Efficiency of oxidation process NbC_{1-x}-NbO₂ composites

TABELA 6. Wydajność utleniania w kompozytach NbC_{1-x}-NbO₂

Composite	onset of oxidation temperature [°C]	maximal mass increase according to reaction (2) [%]	mass increase according to thermogravimetric curves [%]	efficiency of oxidation process [%]	phase composition of oxidation products (XRD)
NbC _{0.8} -NbO ₂	600-650	26.68	25.02	93.8	100% Nb ₂ O ₅
NbC _{0.9} -NbO ₂			26.55	99.5	

DISCUSSION OF THE RESULTS

The Vickers hardness of both composites is about 16 GPa, while the Knoop hardness vary between 12÷14 GPa. The hardness of single-phase polycrystalline NbC reaches 20 GPa [1-3, 6]. A relationship between the deviation from the stoichiometry of the carbide forming the matrix of composite and hardness was observed. The hardness is greater when the deviation from NbC_{1-x} stoichiometry is smaller. The fact of hardness decrease with increase in deviation from stoichiometry is theoretically justified. The greater deviation from stoichiometry, the greater the metallic component in the bond and the lower hardness. The presence of niobium oxide(IV) inclusions with a significantly lower hardness (4÷5 GPa) [11] than the matrix of the composite, i.e. niobium carbide may also affect the hardness.

K_{Ic} stress intensity factor determined by indentation fracture method is in the range of 3.5÷4.0 MPa·m^{0.5} [8, 9]. Fracture toughness determined with indentation fracture and SENB methods for NbC_{1-x}-NbO₂ composites is 4÷5 MPa·m^{0.5}. The observed increase in fracture toughness for carbide-oxide composites in compare to the single-phase materials can be explained by analyzing the path of the cracks. In single-phase materials crack runs through grains (Fig. 9a), while in composites it is deflected and kinked by the oxide inclusions (Fig. 9b).

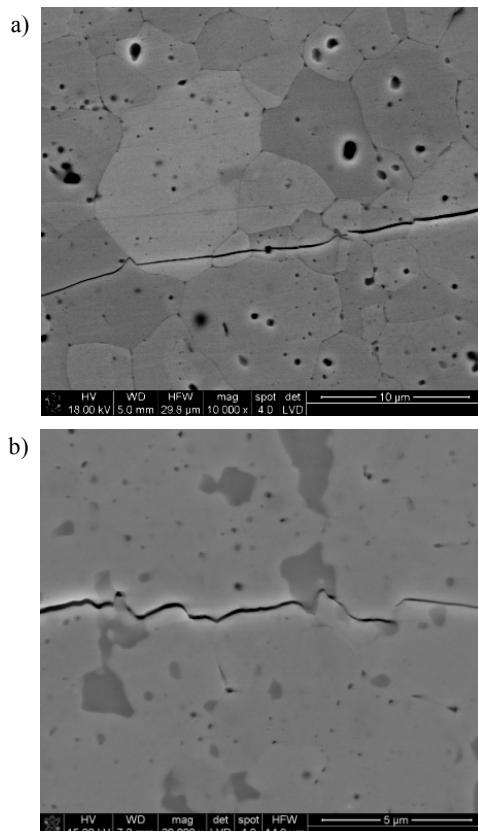


Fig. 9. Fracture path: a) single phase NbC sinter, b) NbC_{0.8}-NbO₂ composite

Rys. 9. Przebieg pęknienia: a) w jednofazowym spiekie NbC, b) w kompozycie NbC_{0.8}-NbO₂

The bending strength of ceramic materials depends primarily on the amount and size of stress concentrating defects, mainly pores. Obtained by hot pressing NbC_{1-x}-NbO₂ composites are non-porous materials. The calculated relative density of sinters (Table 4), compared to the theoretical density of NbC (7780 kg/m³), gives lower values. Taking into account the amount and density of oxide phases (4500 kg/m³), allows to calculate the degree of sintering of composites, which is close to 100%. Absence of pores, stress concentrating defects has a favourable effect on the high bending strength of both composites ~500 MPa. Single phase polycrystals exhibit lower flexural strength of about 200 MPa [8, 9].

Thermal conductivity of the analyzed composites increase with the increasing carbide matrix deviation from stoichiometry (greater metallic component in the bond of carbide matrix composites). Increase of the conductivity vs. temperature of the samples shown in Figure 7 is typical for the alloys or solid solutions. Arranging of the structure with increasing temperature in the case of interstitial carbides is probably responsible for increase of their thermal conductivity.

Both composites show high thermal expansion coefficient $\alpha \sim 7 \cdot 10^{-6}$ 1/deg and exceeds the typical values for carbide matrix and oxide phases [12]. This value is close to the value for the coefficient α of metallic niobium. It is believed that also in this case, the fraction of metallic component in the bond, which is getting stron-

ger with increasing deviation from the stoichiometry of the carbide matrix (Table 5), plays its significant role.

Oxidation resistance of composites does not differ from the single-phase materials (Fig. 8). Niobium oxides present in the matrix does not increase its oxidation resistance but more importantly, does not decrease it. Both in the case of single-phase and multi-phase sintered bodies active oxidation starts near the temperature of 600°C and at a temperature close to 1000°C the whole bulk of composites is oxidized.

CONCLUSIONS

- The use of small additives of carbon, which do not fully reduce oxide impurities, allows to prepare $\text{NbC}_{1-x}\text{-NbO}_2$ composites either by pressureless sintering or by pressure assisted sintering.
- Oxide contamination present in the niobium carbide powders can effectively activate sintering.
- Produced by hot pressing non-porous composites exhibit high flexural strength ~ 500 MPa, while the bending strength of single-phase materials is 300–350 Mpa.
- The presence of oxide inclusions raises the fracture toughness, by increasing the fracture energy by deflecting and kinking the fracture path.
- The presence of the oxide phase grains lowers the hardness of the composites with compare to the single-phase polycrystals.
- There was no effect observed of oxide inclusions on thermal expansion and oxidation resistance of $\text{NbC}_{1-x}\text{-NbO}_2$ composites.

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