

# Reaction bonded niobium carbide ceramics from polymer-filler mixtures

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Manufacturing of novel reaction bonded Niobium Carbide (NbC) containing ceramic composites derived from polymer/filler mixtures was investigated. Poly(methylsiloxane) filled with 40 vol.% of a mixture of metallic Niobium (Nb) (reactive filler) and alumina powder (inert filler) was pyrolysed in inert atmosphere up to 1450°C. During pyrolysis metallic niobium reacted with carbon from the decomposition products of the preceramic polymer binder to form microcrystalline composites of NbC, Al<sub>2</sub>O<sub>3</sub> and a silicon oxycarbide glass. Microstructure formation of specimens prepared with different niobium to alumina ratio in the starting mixture was experimentally examined and compared to thermodynamic phase equilibria calculations. Materials of high NbC content exhibit high hardness and wear resistance. © 2000 Kluwer Academic Publishers

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## 1. Introduction

Transition metal carbides have widespread applications because of unique physical properties such as high melting points, hardness, electrical conductivity and superconductivity [1]. Transition metal carbides have been used as catalysts in chemistry as well as wear resistant coatings on machining tools as well as reinforcing dispersoids in ceramic matrix composite materials in mechanical engineering. Alumina containing up to 40 wt.% of TiC particles was developed as a cutting tool material which exhibits significantly higher fracture toughness, hardness and thermal conductivity compared to single phase alumina ceramics [2–4]. Hot isostatic pressing as well as pressureless sintering of oxide-carbide powder mixtures was used to fabricate simple shaped components for tooling applications [3, 5]. Pressureless sintering of alumina-niobium carbide composites was examined to provide fundamental information on the microstructure-property relationships [6].

Niobium carbide (NbC) has many excellent physico-chemical properties such as a high melting point (3600°C), hardness (Vickers hardness >2000 kg/mm<sup>2</sup>), Youngs modulus (340 GPa) and a thermal expansion coefficient ( $6.7 \times 10^{-6}/\text{K}$  from room temperature to

1000°C) compatible to alumina ( $6\text{--}9 \times 10^{-6}/\text{K}$ ). In contrast to other carbides such as TiC, TaC or ZrC, which exhibit a higher hardness at room temperature, NbC maintains a higher hardness at temperatures above 500°C. Five solid single-phase regions exist in the niobium-carbon system: a solid solution of carbon in niobium (bcc), Nb<sub>2</sub>C (hcp), NbC (fcc), -Nb<sub>4</sub>C<sub>3-x</sub>, and -NbC<sub>1-x</sub> [7]. The compositional range of Nb<sub>2</sub>C is very limited at low temperatures, whereas NbC varies from NbC<sub>0.70</sub> to NbC<sub>0.99</sub>. Industrial production of NbC makes use of Nb<sub>2</sub>O<sub>5</sub>/C mixtures and heating temperatures above 1800°C [8]. Moreover, 72% of the main known world niobium reserves are concentrated in the high-grade ore deposites in Brazil [9].

Reaction bonding of a metallic filler powder by a preceramic polymer binder is a novel approach to obtain composite ceramics of variable composition and high dimensional stability during processing [10]. The preceramic polymer, which can be a poly(silane), -(carbosi)lone), -(silazane) or -(siloxane), offers versatile shaping techniques to form components of complex geometry by pressureless casting, injection molding, extrusion, etc. During pyrolysis in an inert atmosphere (Ar, N<sub>2</sub>) the polymer decomposes to an amorphous

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ceramic residue and carbon bearing solid (C) and gaseous decomposition products (hydrocarbons  $C_xH_y$ ) which may react with the metallic filler to form new carbide phases. A variety of possible reactive fillers including Ti, Zr,  $CrSi_2$ ,  $MoSi_2$ , etc. were investigated with the polymer binder phase derived from poly(siloxanes) containing methyl, phenyl, vinyl and hydrogen as the major functional groups bonded to silicon in the polymer structure [10, 11]. Recent work on poly(siloxane)-Mo filler derived  $Mo_2C$ -SiOC ceramics showed that composite materials with an extremely low residual porosity of less than 3% could be obtained [12]. The mechanical properties are dominated by the formation of a three-dimensionally interconnected network of the carbide reaction phase.

In the present work the formation of reaction bonded niobium carbide ceramics derived from poly(methylsiloxane)-Nb mixtures was studied. The microstructure transformations were investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM). While Nb is a reactive filler in this system,  $Al_2O_3$  is an inert filler which may be used to control microstructure formation e.g. the carbide network connectivity. Strength and hardness were measured for various filler compositions. Thermodynamic phase equilibria calculations were carried out in order to explain possible phase reactions dominating the polymer-ceramic transformation in this novel reaction bonding process.

## 2. Experimental procedure

A commercial poly(methylsiloxane)  $CH_3SiO_{1.5}$  with an average molecular mass of 22 000 g/mol was used as the preceramic binder precursor (NH 2100, Chemische Werke Nuenchritz, Nuenchritz, Germany). The polymer is a powder at room temperature with a melting temperature of 50°C. The total carbon content attains 13.2 wt.% and the polymer contains approximately 4 wt% of Si-OH groups. Due to the release of water upon polycondensation of [Si-OH] groups curing has to be done under pressure at 230°C.

Niobium (Nb) powder (Chempur, Karlsruhe, Germany) with a mean particle size of 22  $\mu m$  and a purity of 99.9 wt.% was combined with  $\alpha$ - $Al_2O_3$  (CT 2000 SG, Alcoa, Ludwigshafen, Germany). The mean particle size of  $Al_2O_3$  was 0.8–1.0  $\mu m$  and the purity >99.8 wt.%. Polymer and filler powder (40 vol.%) were mixed with a solvent (acetone) and homogenized by intensive mechanical stirring (Ultratorax) and ultrasonic mixing. After removing the solvent (rotavapor) the solid powder mixtures were dried at 45°C for 12 h and then milled and sieved (100  $\mu m$ ) to obtain a feedstock powder. The Nb/ $Al_2O_3$ -ratio was varied from 40/0, 30/10, 20/20, to 10/30 (by vol.%), respectively, maintaining a total filler content of 40 vol.% in the polymer/filler feedstock.

Rectangular specimens of 50 × 50 × 3 mm<sup>3</sup> were prepared by uniaxial pressing of approximately 14 g of the feedstock powder in a laminate press at 230°C for 45 min with a pressure of 2 MPa. During warm pressing the poly(methylsiloxane) curing via polycondensation of Si-OH groups takes place resulting in an unmeltable thermoset. Aluminium acetylacetonate ( $AlO_6C_{15}H_{21}$ )

was added as a curing catalyst (0.1 wt.%). Specimen bars for mechanical testing (the specimens were pyrolyzed in Ar in an electrically heated closed tube furnace. A typical heating cycle involved heating up to 500°C at 5°C/min, holding this temperature for 4 h, a second ramp at 1–2°C/min up to the final temperature of 1400°C/1450°C with 4 h or 6 h dwell time, and a final cooling ramp with 5°C/min.

Densities of the cured and of the pyrolyzed (reaction bonded) products were measured by helium pycnometry (Accupyc 330, Micromeritics, Duesseldorf, Germany). Phase composition of crystalline constituents was examined by X-ray analysis using monochromated  $CuK_{\alpha}$ -radiation (Diffrac 500, Siemens, Mannheim, Germany). Microstructure of the pyrolyzed material was analyzed by SEM (Stereoscan MK II, Cambridge Instr., Cambridge, GB) equipped with EDAX for element mapping. Rectangular bars (50 × 4 × 3 mm<sup>3</sup>) were used for flexural strength measurements (4 point bending 20/40 mm, crosshead speed 0.1 mm/min). Hardness was measured by Vickers indents using a load of 3 kN.

## 3. Results and discussion

### 3.1. Reaction bonding

Fig. 1 shows the weight change and dimensional change during the reaction bonding process as a function of the filler composition (e.g. Nb to  $Al_2O_3$ ). With increasing Nb (and decreasing  $Al_2O_3$ ) content linear shrinkage is reduced from 6.7% (10/30) to 4.8% (40/0) whereas total weight loss simultaneously increased from 0.3 up to 3.1 wt.%, respectively. X-ray analysis shows the formation of NbC in a multiphase composition with additional amounts of  $SiO_2$ ,  $Al_6Si_2O_{13}$  (mullite),  $Al_2O_3$  and NbO. Fig. 2 gives the X-ray spectrum of the specimen containing 10/30 of Nb/ $Al_2O_3$  in the starting mixture, pyrolyzed at 1400°C for 6 hours. Depending on the Nb/ $Al_2O_3$ -ratio the phase composition significantly changes as shown in Fig. 3. While the peak intensities for residual  $Al_2O_3$  (012) and  $Al_6Si_2O_{13}$  (210) (formed by reaction of  $Al_2O_3$  and  $SiO_2$  from the polymer derived residue) decrease with increasing Nb content, the fraction of NbO (011) exhibits a pronounced increase.

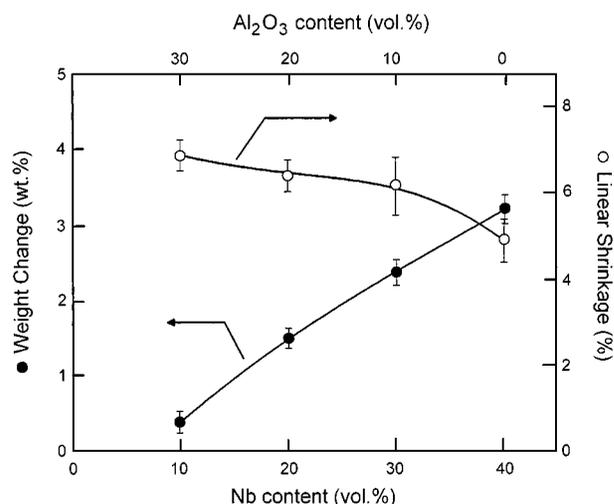


Figure 1 Weight change and shrinkage during pyrolysis at 1450°C as a function of filler composition.

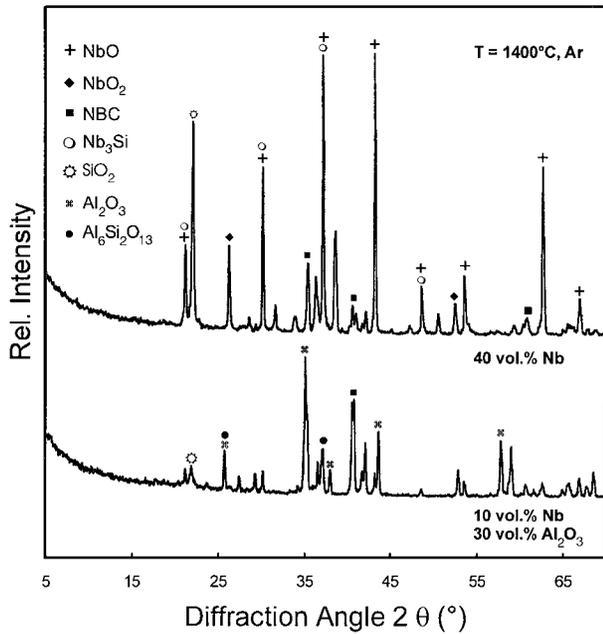


Figure 2 X-ray diagrams of specimens containing 10/30 a) and 40/0 b) of Nb/Al<sub>2</sub>O<sub>3</sub> pyrolyzed at 1400°C for 6 h.

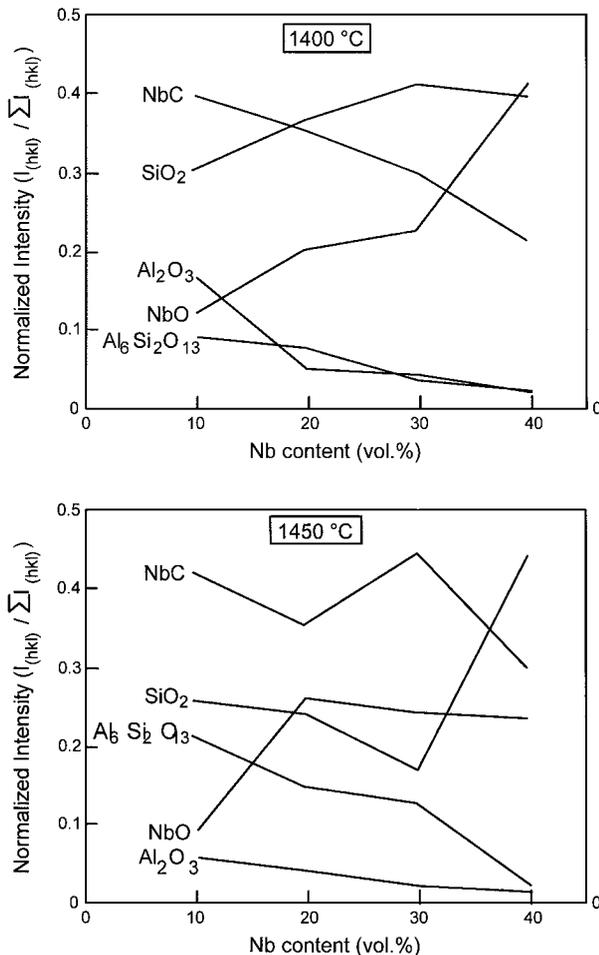


Figure 3 Normalized X-ray intensities ( $I_{(hkl)}/\sum I_{(hkl)}$ ) of the pyrolyzed specimens as a function of filler composition: (111)NbC, (101)SiO<sub>2</sub>, (012)Al<sub>2</sub>O<sub>3</sub>, (210)Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>, (011)NbO.

Simultaneously the intensity of NbC (111) is reduced suggesting that excessive Nb (with respect to the C content available from the polysiloxane) reacts with oxygen from the polymer derived SiO<sub>x</sub>C<sub>y</sub> phase according to



and



The composition of the polymer derived SiO<sub>x</sub>C<sub>y</sub> ceramic residue determined by thermobarometric analysis of filler free poly(methylsiloxane) [13] is SiO<sub>1.47</sub>C<sub>0.73</sub> which corresponds to a molar composition of 1SiO<sub>2</sub>, 0.36SiC and 0.6C, respectively. The amount of free carbon associated to the ceramic residue attains 8.7 wt.%. Thus, for the given polymer/filler ratio (e.g. 60 vol.% poly(methylsiloxane) and 40 vol.% filler) a tentative amount of carbon  $m_C^{\text{SiOC}}$  available for carburization reactions can be calculated and compared to the total consumption of carbon when all of the Nb would react to NbC,  $m_C^{\text{NbC}}$ ,

$$m_C^{\text{SiOC}} = \left( \frac{0.6M_C(\rho V)_{\text{SiOC}}}{M_{\text{SiO}_2} + 0.6M_C + 0.36M_{\text{SiC}}} \right) \left( \sum_i \rho_i V_i \right)^{-1} \\ = 0.12 \left( \sum_i \rho_i V_i \right) \quad (3)$$

$$m_C^{\text{NbC}} = 0.1139(\rho V)_{\text{NbC}} \left( \sum_i \rho_i V_i \right) \quad (4)$$

$\rho_i$  are the densities (SiOC: 2300 kg/m<sup>3</sup>; Nb: 8400 kg/m<sup>3</sup>; NbC: 7800 kg/m<sup>3</sup>; Al<sub>2</sub>O<sub>3</sub>: 3980 kg/m<sup>3</sup>) and  $V_i$  the volume fractions (SiOC = 0.6; Nb = 0.1–0.4; Al<sub>2</sub>O<sub>3</sub> = 0.3–0) in the starting green compact. As may be seen from Fig. 4 the carbon content from the polymer fraction is supposed to be sufficient for complete carburization up to approximately 20 vol.% of Nb filler powder whereas higher Nb contents may only partly be carburized. The corresponding boundary concentration for the case of carbon deficient NbC<sub>0.8</sub> solid solution shows a slightly higher Nb fraction to be completely carburized.

Thermodynamic phase equilibria calculations in the system Nb-Al-Si-O-C were carried out to estimate phase reactions during the reaction bonding process.

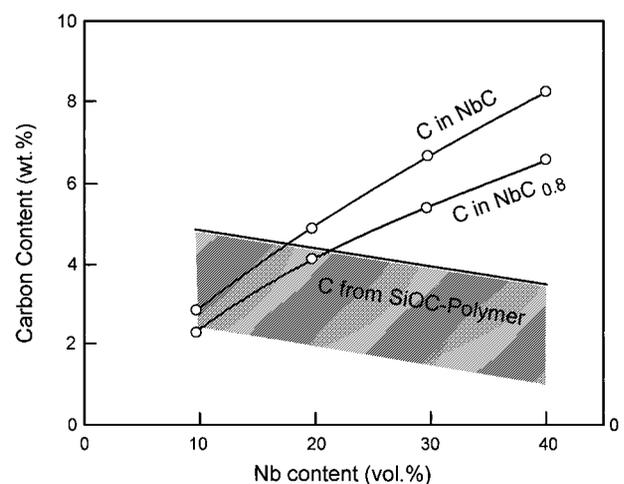
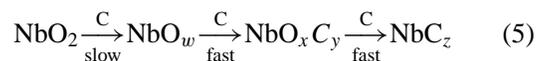


Figure 4 Calculated carbon content necessary for carburization of Nb and carbon content available from the SiOC-Polymer.

Though the calculations are based on equilibria conditions, the results may allow to a first approximation the prediction of phase reactions which should occur with increasing temperature and time. The program EQUITHERM (VCH Verlag, Weinheim, Germany) is based on the minimization of Gibbs free energy for a set of product phases at a given temperature and starting composition. For the thermodynamic calculations NbC, Nb<sub>5</sub>Si<sub>3</sub>, NbO, Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> (reaction product phases) and Nb, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiC, C (educt phases) were taken into account. Due to the lack of thermodynamic data for the pyrolysis product of the polymer binder phase a mixture of 1 mol SiO<sub>2</sub> + 0.36 mol SiC + 0.6 mol C was assumed to approximate the Si-O-C composition. Even though thermodynamic equilibria conditions may not be attained, thermodynamic phase stability calculations provide to a first approximation trends of phase reactions which can be expected to occur during pyrolysis of the polymer/filler mixtures. Fig. 5 shows the phase stability diagram of the polymer/filler mixtures at a pyrolysis temperature of 1400°C as a function of the Nb content. NbC is formed up to a maximum of approximately 33 wt.% at 10/30 (Nb/Al<sub>2</sub>O<sub>3</sub>). While the fractions of initial Al<sub>2</sub>O<sub>3</sub> and the reaction product Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> diminish NbO becomes stable at higher Nb contents.

In contrast to the calculations which predict the formation of significant amounts of Nb<sub>5</sub>Si<sub>3</sub> to be formed and some residual Nb the experimental analyses always reveal the presence of extended amounts of NbO but no metallic or intermetallic phases. Only for the case of NbO as a starting constituent of the polymer/filler mixture, Fig. 5 (right), significant fractions of NbO remain in equilibria with the reaction product NbC. Analysis of carburization reaction mechanisms of niobium oxides with various metal oxidation number from +5 (Nb<sub>2</sub>O<sub>5</sub>) to +2 (NbO) revealed that NbC was formed only from

niobium oxides with metal oxidation number not lower than +4 [8]. When NbO was carburized in a CH<sub>4</sub>/H<sub>2</sub> atmosphere XPS measurements provided evidence of the formation of a reactive intermediate oxycarbide phase which finally transformed to the niobium carbide suggesting the following reaction sequence



where  $2 < w < 1$  and  $1 > z > 0.7$ . Supposing NbO<sub>w</sub> has been formed by oxidation of the starting Nb powder, the formation reaction of NbC may have taken place according to above mentioned reaction (5). From the displacement of the Nd<sub>3d5/2</sub> photopeak to lower binding energies when the carbon content in NbC<sub>z</sub> was varied from  $z = 0.744$  to 0.94 [14] a progressive carbon enrichment in the oxycarbide NbO<sub>x</sub>C<sub>y</sub> was postulated to occur during carburization reaction [8].

### 3.2. Microstructure

Fig. 6 shows a SEM micrograph of the pyrolyzed microstructure of the specimen containing 40 vol.% of Nb in the starting mixture. A residual porosity is present in the SiOC matrix phase with an average pore size of less than 1 μm. The bright filler particles are embedded in the dark matrix of fine grained polymer derived SiOC. NbC of whisker like morphology is formed on the surface of large particles which exhibit a high fraction of oxygen in the center. From XRD analysis NbO was found to occur as a major constituent in the specimens with increasing Nb content in the starting mixture.

Depending on the Nb/Al<sub>2</sub>O<sub>3</sub> ratio of the filler the reaction bonding process may be classified into an oxide bonding and a carbide bonding process. Fig. 7 shows a

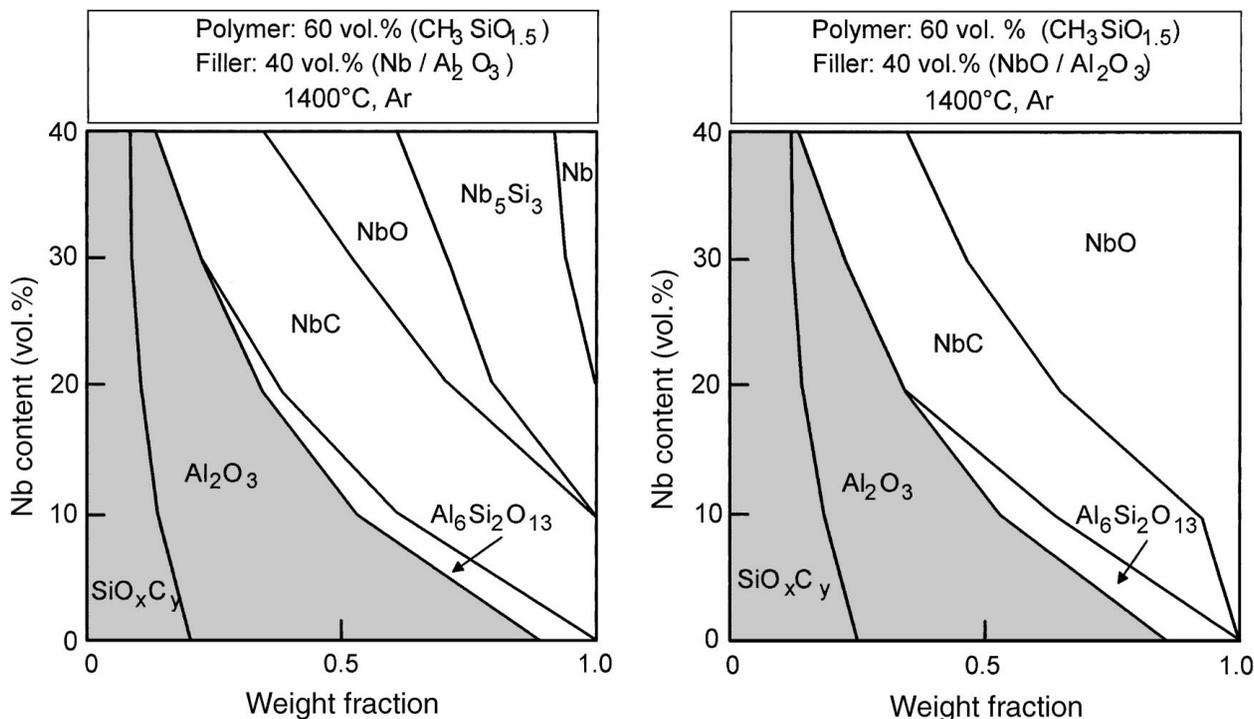


Figure 5 Phase stability diagrams calculated for the initial specimen compositions containing Nb (left) and NbO (right) as the filler component.

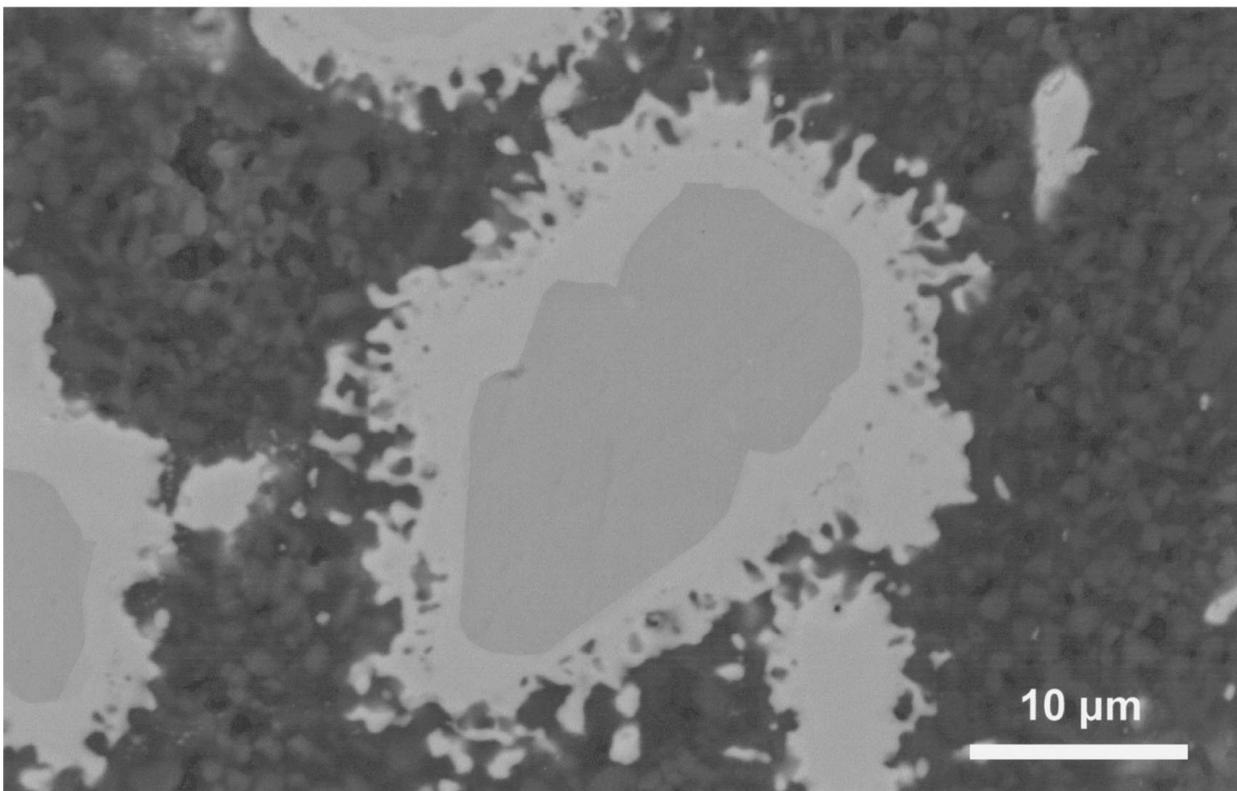
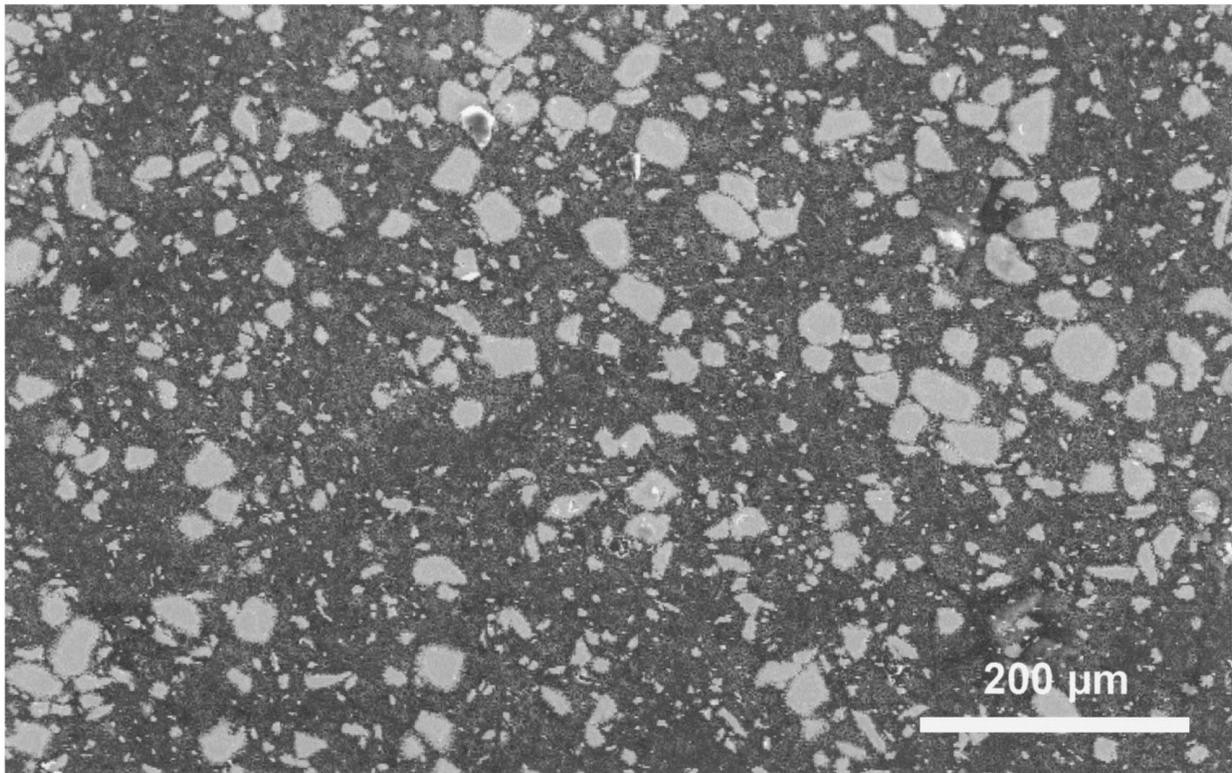


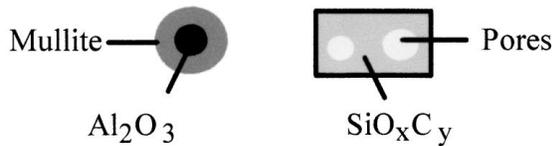
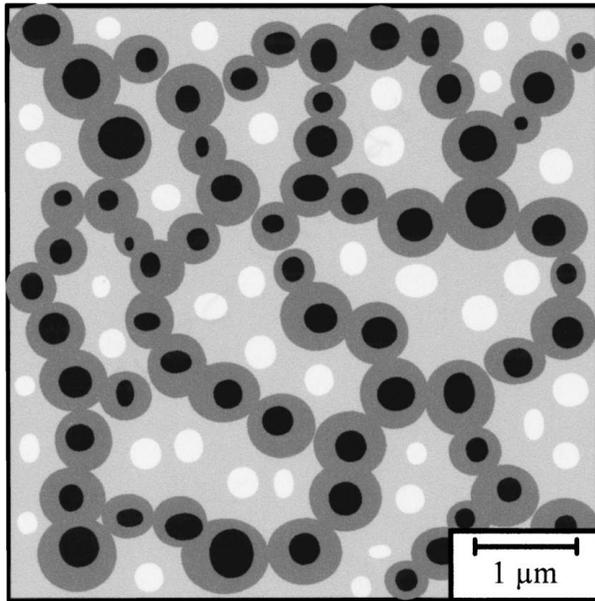
Figure 6 SEM micrograph of the microstructure of specimen (40 vol.% Nb/0 vol.%  $\text{Al}_2\text{O}_3$ ) pyrolyzed at  $1400^\circ\text{C}$ .

schematic model of the two alternative reaction bonded microstructures. Formation of  $\text{Al}_6\text{Si}_2\text{O}_{13}$  at  $1400^\circ\text{C}$  is supposed to be associated with the formation of a liquid phase in  $\text{Al}_2\text{O}_3$  rich compositions which may give rise to pronounced sintering as indicated by a linear shrinkage of up to 7%. In contrast, formation of niobium carbide as the reaction bonding phase is dominated by a solid-solid or solid-gas reaction (Equation 5), respec-

tively. Due to the large particle size of the initial Nb powder of  $22\ \mu\text{m}$  isolated filler particles in the polymer derived matrix may not be able to form a three-dimensionally interconnected network.

For the reaction kinetics of the oxide carburization two models [15], the *Nucleation Model* and the *Shrinking Core Model*, were discussed [8]. From the particular microstructure of the filler particles which is

Filler:  $\text{Al}_2\text{O}_3$



Filler: Nb

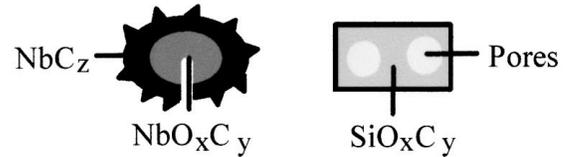
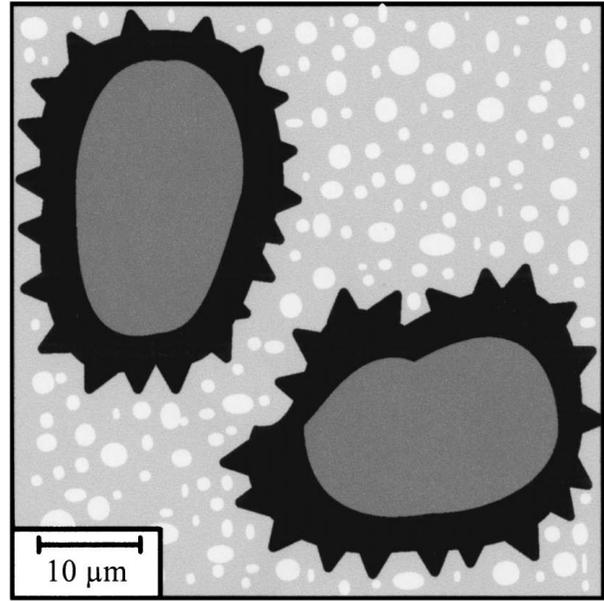


Figure 7 Schematic model of reaction bonded microstructure formation in the system containing  $\text{Al}_2\text{O}_3$  (left) and Nb (right) in the starting mixture.

characterized by fiber like reaction product morphology extending into the matrix, Fig. 6, kinetics of the carburization reaction of the oxide (oxycarbide) particles is supposed to follow the nucleation model as it has been found for the niobium oxide carburization reaction [8]. The extent of reaction  $\alpha$  follows a first order nucleation controlled reaction [16]

$$\frac{d\alpha}{dT} = \frac{d^2}{\beta} (1 - \alpha) k_0 \exp\left(-\frac{E}{RT}\right) \quad (6)$$

where  $d$  is the particle diameter,  $\beta$  is the heating rate ( $dT/dt$ ) and  $k_0$  and  $E$  are the pre-exponential factor and the activation energy of the dominating transport mechanism. Equation 6 shows that the reaction rate can be significantly accelerated by using filler with a smaller particle size  $d$ . While metallic Nb powder is limited to a medium particle size due to its pronounced reactivity with oxygen niobium oxide powder can easily be processed into small particle size. Thus, fine grained niobium oxide powder may be used instead of metallic niobium to achieve complete carburization at lower temperatures.

### 3.3. Mechanical properties

The mechanical properties of the multiphase reaction products depend on the phase content e.g. polymer derived SiOC matrix phase, alumina, mullite, niobium oxycarbide and niobium carbide. Porosity and residual stresses due to differences in thermal dilatation during cooling from pyrolysis temperature between the various phases may further exert a strong influence on the me-

chanical behavior. Fig. 8 shows the variation of strength and hardness as a function of the filler composition. The strength exhibits a maximum of 150 MPa at 20 vol.% Nb and 20 vol.%  $\text{Al}_2\text{O}_3$  in the starting mixture. The low maximum strength may be associated with large particle size of Nb (average  $22 \mu\text{m}$ ). At higher volume fractions clusters of the large Nb particles are likely to occur due to insufficient dispersion of the heavy Nb particles in the polymer powder mixture. These clusters and pores may act as large defects for failure initiation under load. As a consequence, an increase of strength can be expected when a reactive filler powder of significantly smaller particle size will be used for the reaction bonding process. Taking niobium oxides ( $\rho(\text{NbO}) = 7300 \text{ kg/m}^3$ ,  $(\text{NbO}_2) = 4900 \text{ kg/m}^3$ ,  $(\text{Nb}_2\text{O}_5) = 4600 \text{ kg/m}^3$ ) instead of niobium ( $\rho(\text{Nb}) = 8570 \text{ kg/m}^3$ ) may further help to achieve a more homogeneous

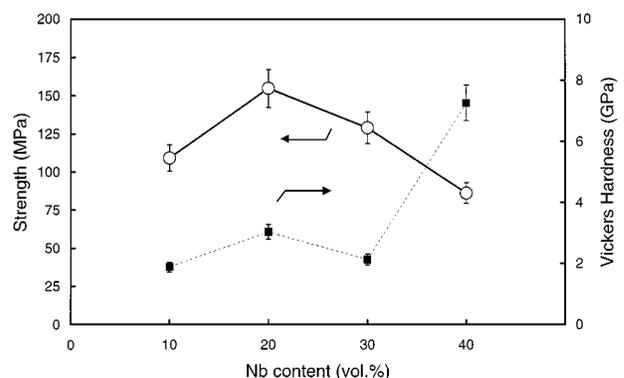


Figure 8 Bending strength and Vickers hardness as a function of filler composition in the specimens pyrolyzed at  $1400^\circ\text{C}$ .

dispersion of the filler in the polymer matrix ( $=1000\text{--}1200\text{ kg/m}^3$ ) due to a much smaller difference of specific mass so that cluster formation at higher volume fractions will be reduced.

Hardness at low Nb contents is in the range of 2 GPa only which indicates the porous  $\text{SiO}_x\text{C}_y$  matrix to dominate the deformation behavior.  $\text{Al}_2\text{O}_3$  which has a hardness of 23 GPa does not increase the matrix hardness because of its small particle size ( $<1\ \mu\text{m}$ ). A significantly higher hardness of 7.5 GPa is observed at the highest Nb content of 40 vol.%. Compared to 20 GPa of single phase NbC, however, the lower hardness suggests that the niobium carbide phase does not form large single phase areas in the reaction bonded microstructure. The niobium oxycarbide intermediate, which is supposed to form when niobium oxide is carburized, may have a significantly lower hardness compared to the carbide phase.

#### 4. Conclusions

Using metallic niobium powder and alumina dispersed in a poly(methylsiloxane) preceramic a reaction bonded oxycarbide composite material was produced at  $1400^\circ\text{C}$ . X-ray analysis suggested that the initial niobium has been oxidized to a niobium oxide intermediate. During pyrolysis of the polymer carbon from the gaseous hydrocarbon species ( $\text{CH}_4$ ) will react with the niobium oxide intermediate to form niobium (oxy)carbide. Thus, niobium oxide of significantly smaller particle size than metallic niobium may be used as starting filler material. Due to a smaller particle size further improvement of strength can be expected. An increase of the fraction of niobium carbide may be achieved by use of a polymer with higher carbon content e.g. polymer containing phenyl instead of methyl functional groups. A higher fraction of niobium carbide of smaller particle size is supposed to lead to improved mechanical properties in the reaction bonded materials.

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