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Polymer/filler derived NbC composite ceramics

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NbC containing ceramic composites were manufactured from poly(siloxane)/Nb/NbC filler mixtures by a high temperature reaction bonding process. During heating in an inert atmosphere the Si–O–C ceramic residue of the polymer reacted with the metallic Nb filler to form Nb_xSi_y, NbO and NbC. Samples with a high Nb/NbC ratio showed reduced porosity and increased hardness after pyrolysis at 1200°C. © *2003 Kluwer Academic Publishers*

1. Introduction

Transition metal carbides have a wide range of applications, e.g., as hard materials, cutting tools and wear-resistent coatings [1]. NbC shows excellent physico-chemical properties, which makes it an interesting candidate for high temperature wear-resistent applications: a high melting point (3600°C), a high hardness ($>$2000 kg/mm^2 at room temperature), a Young's modulus of 340 GPa and a coefficient of thermal expansion (CTE) of 6.7×10^{-6}/K from room temperature to 1000°C [2, 3]. While TiC, TaC and ZrC exhibit higher hardness in the low temperature range, NbC shows superior behaviour at temperatures above 500°C [4]. For the manufacture of oxide/carbide composites, hot isostatic pressing, as well as pressureless sintering of niobium oxide and niobium carbide powders has been applied [5, 6]. Pressureless sintering of Al_2O_3/NbC composites was carried out in the temperature range 1650–1750°C [7]. A density of 95% of the theoretical value and mechanical properties comparable to those of Al_2O_3/TiC ceramic composites have been achieved. The manufacturing temperature of NbC powder material is 1800°C, starting from a mixture of Nb_2O_5 and C [8]. The preparation of NbC composites, however, may be carried out at a significantly lower temperature when a reaction bonding process with a preceramic polymer is applied.

In the filler reaction bonding process a polymer/filler system is heated in inert (Ar) or reactive (N_2, NH_3, air) atmosphere above the decomposition temperature of the polymer. The gaseous and solid decomposition products can react with fillers to form carbide, oxide and nitride reaction products. In the case of reactive atmosphere processing, shrinkage of the polymer can be minimized, and near net shape manufacturing becomes possible. In addition, the rheological properties of the polymer can facilitate versatile shaping processes, e.g., injection molding, warm pressing and tape casting [9–14]. Recent work on poly(methylsiloxane)/Nb/Al_2O_3 derived ceramics showed the formation of a mullite/NbC composite ceramic, in which the filler Al_2O_3 reacted with the ceramic residue from polymer decomposition to form an interpenetrating mullite network [15]. Al_2O_3 particles were surrounded by the mullite phase and the metallic Nb filler formed a NbO_xC_y/NbC core shell structure. The material which was manufactured in inert argon atmosphere showed a flexural strength of 90 to 160 MPa and a Vicker's Hardness of up to 8 GPa [15].

The aim of the present work is to manufacture a polymer derived ceramic composite material using the polymer/filler route. NbC was used as an inert filler and elemental Nb filler reacted with the ceramic residue from polymer decomposition to form a Nb-C/Nb_xSi_y composite material.

2. Experimental procedure

Sample preparation was carried using Nb (Alfa, 99.8%, 40 μm) and NbC powder (Alfa, 99%, $<$10 μm) as fillers and commercial poly(methylsiloxane) (PMS, $[CH_3SiO_{1.5}]_n$, $n = 300 \ldots 350$, available as NH2100,

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Wacker Silicone AG, Germany) as following previous work [15]. The polymer/filler ratio was fixed at 60 vol% polymer and 40 vol% filler. The filler volume ratios were choosen to be Nb:NbC = 0:40, 10:30, 20:20 and 30:10. Rectangular specimens of 50 × 50 × 3 mm^3 were prepared by uniaxial pressing at 230°C for 45 min using a pressure of 2 MPa. Pyrolysis was carried out at 1200°C (Series A) and 1400°C (Series B), applying a heating rate of 5 K/min, a dwell time of 3 h and a cooling rate of 5 K/min in argon atmosphere. After pyrolysis the mechanical test bars were polished to a 7 μm SiC finish.

Density and porosity were measured by He pycnometry (Accupyc 330, Micromeritics, Duesseldorf) and Hg porosimetry (Porosimeter 2000, Carlo Erba Instruments). Phase composition and microstructural characterization were carried out by X-ray diffraction (XRD) analysis using monochromated Cu K_α radiation (Diffrac 500, Siemens AG, Mannheim), and scanning electron microscopy (SEM, Stereoscann MK II, Cambridge Instruments Cambridge, UK) equipped with a wavelength dispersive X-ray spectrometer (WDX, WDX-2A, Microspec Corporation, Fremont, CA, USA) and an energy dispersive X-ray spectrometer (EDX) with element mapping mode (Tracer Northern, Middleton, WI, USA). Flexural strength was measured by 4-point bending (20/40 mm, crosshead speed 0.1 mm/min). Vickers indentation with a load of 3 kN was carried out for hardness measurements and thermal expansion was measured using specimens of the size 3 mm × 3 mm × 10 mm in argon atmosphere with a heating rate of 5 K/min up to the maximum pyrolysis temperature of the samples (Dilatometer 6.225.3.03, Netzsch Gerätebau GmbH, Germany). For evaluation of the reactions between the polymer derived ceramic matrix and the Nb filler and the NbC filler, thermodynamic calculations were carried out using HSC Chemistry 4.1 thermodynamics and data package (Outokumpu Research Oy, Pori, Finland).

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the weight loss related to the total weight of PMS and the linear dimensional change as a function of the Nb filler content. In both series, weight loss decreased with increasing Nb content. In the B-series the weight loss at lower Nb content is significantly higher compared with the A-series. At the highest Nb loading (30 vol%) the weight loss of both, 1200°C (A) and 1400°C (B) pyrolyzed samples is comparable showing 9.1 and 9.6 wt%, respectively. The weight loss at 30 vol% Nb loading corresponds to the total weight loss of the filler-free poly(siloxane) at 1100°C [16]. The higher weight loss in the B-series at loadings of 40 vol% to 20 vol% NbC can not be explained only by the polymer decomposition. From thermodynamic calculations, reaction between the NbC filler and the ceramic residue (mainly SiO_2, SiC and C) are not likely to occur due to positive values of the Gibbs Free Energy in the investigated temperature range. Hence, it was assumed that an oxide layer at the surface (consisting of Nb_xO_y) of the NbC and Nb filler reacted with the ceramic residue from polymer decomposition. Two reactions seem likely to occur, see Fig. 2. Both reactions consume constituents of the polymer derived matrix, and the gaseous CO can be released from the residue. In addition carbothermal reduction of the constituents of the polymer derived ceramic matrix can occur and SiO gas and CO gas can release from the material, see Equations 1a and 1b.

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)} \tag{1a}$$

$$SiO_{(g)} + 2C \rightarrow SiC + CO_{(g)}. \tag{1b}$$

In the presence of Nb as reactive filler, however, reactions between the gaseous constituents and the metallic niobium are likely to occur, see Equations 1c and 1d.

$$8Nb + 3SiO_{(g)} \rightarrow Nb_5Si_3 + 3NbO \tag{1c}$$

$$2Nb + CO_{(g)} \rightarrow NbC + NbO. \tag{1d}$$

With increase of the niobium content a reduction of the weight loss related to the polymer was observed. The linear shrinkage covers a range from 6.7–8.7% in the A-series and shows a value between 8 and 9% in the B-series, corresponding to results observed in [17]. Total porosity is decreased with increasing the Nb content, and is generally higher in the B-series, Fig. 3.

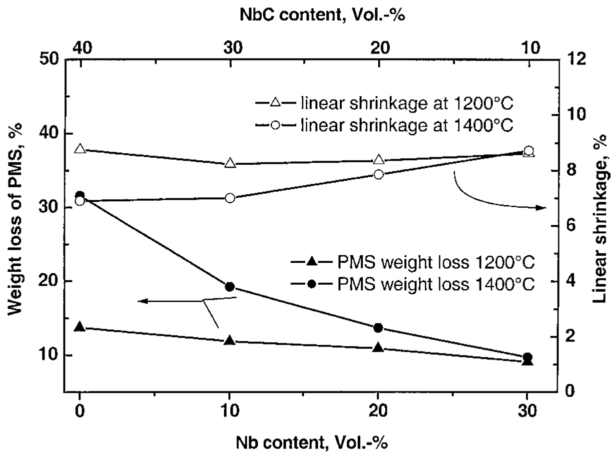

Figure 1 Weight loss and shrinkage of polymer derived NbC/Nb samples with different Nb/NbC ratios, pyrolyzed at 1200 and 1400°C.

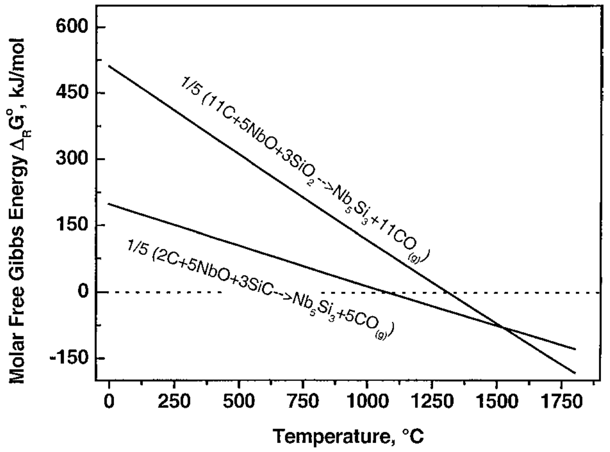

Figure 2 Gibbs Free Energy of reactions which could occur between 1200 and 1400°C.

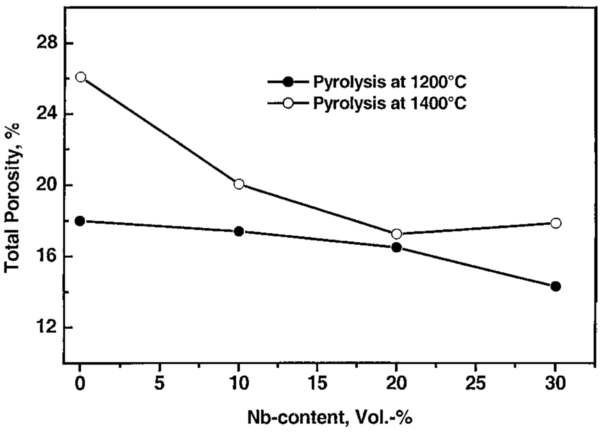

Figure 3 Total porosity of polymer derived NbC/Nb samples with different Nb/NbC ratios, pyrolyzed at 1200 and 1400°C.

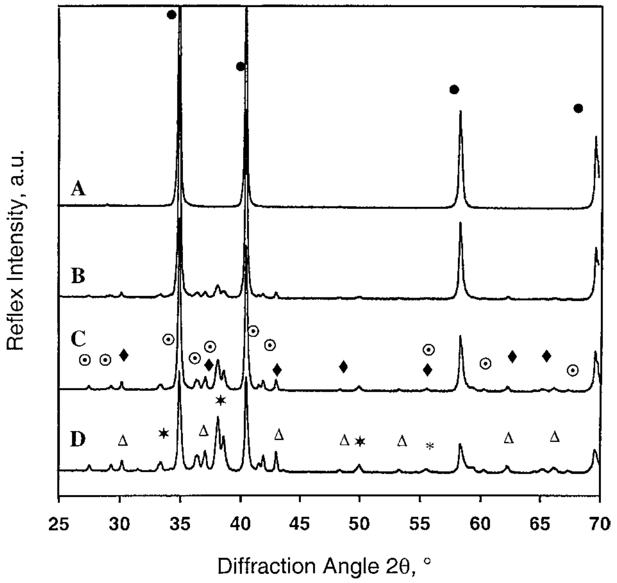

Figure 4 XRD patterns of samples with different Nb/NbC ratio pyrolyzed at 1200°C, A—40NbC, B—30NbC/10Nb, C—20NbC/20Nb, D—10NbC/30Nb; (∗), Nb; (•), NbC; (♦), Nb_3Si; (⊙), Nb_5Si_3; (Δ), NbO; (⋆), Nb_2C.

From this results the elemental niobium can be assumed to be a reactive filler.

Figs 4 and 5 show the XRD patterns of the ceramic composites as a function of the filler composition at 1200 and 1400°C, respectively. In the samples having only NbC fillers in the starting material (Sample A in A- and in B-series) NbC is the only phase identified by XRD. This suggests that no new phases were formed between the NbC filler and the polymer derived ceramic matrix. On adding Nb filler, in the B-series (1400°C), NbC, NbO and Nb_5Si_3 were identified. In the samples pyrolyzed at 1200°C unreacted Nb, Nb_2C and two intermetallics, Nb_3Si and Nb_5Si_3 were formed. NbC was found in all traces. However, NbC filler phase and NbC phase formed during pyrolysis from the reaction of Nb filler and free carbon from the ceramic residue, could not be differentiated by XRD. Formation via reaction (2c) is likely at 1200°C.

At 1400°C, Nb_2C and the Nb peaks completely disappeared (except in the 30Nb/10NbC sample, in which small amounts of unreacted Nb were detected) and the intensities of Nb_5Si_3 peaks increased.

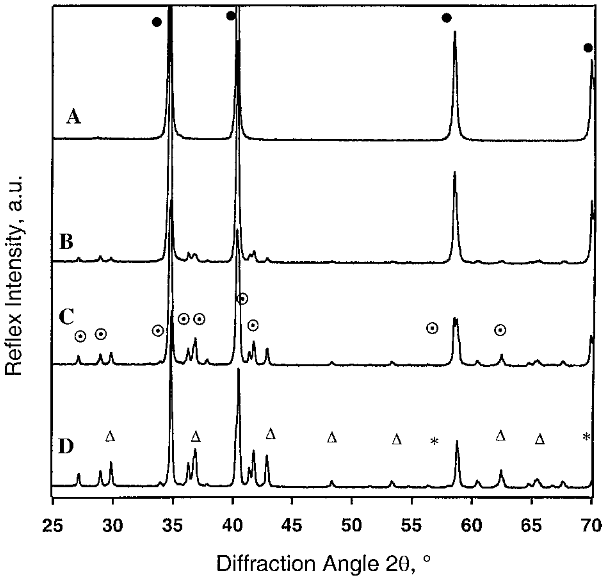

Figure 5 XRD patterns of samples with different Nb/NbC ratio pyrolyzed at 1400°C, A—40NbC, B—30NbC/10Nb, C—20NbC/20Nb, D—10NbC/30Nb; (∗), Nb; (•), NbC; (⊙), Nb_5Si_3; (Δ), NbO.

A typical SEM image and the elemental distribution of Si, O, C and Nb are shown in Fig. 6 for the sample with 30Nb/10NbC after pyrolysis at 1200°C and in Fig. 7 for the sample with the same composition, pyrolyzed at 1400°C. In the top image, Fig. 6, a small reaction rim can be observed around the large-light grey filler particle. A few Nb particles show dark spots inside the filler particle. The origin of the spots, however, is not yet clear. It was assumed that defects inside the Nb filler particle are preferred for carbon and oxygen diffusion and hence, the formation of low-carbon containing niobium compounds such as Nb_2C seem likely.

From elemental mapping, it can be concluded that this rim consists of Nb and Si while inside the Nb filler grain C and O were found. In Fig. 7 the reaction proceeded and delamination of the Nb/Si containing shell from the Nb/O/C containing core was observed. The intensity of the oxygen signal is significantly higher in comparison to the sample of the A-series. Summarizing the XRD, the SEM and element mapping investigations the following reaction sequences are likely to occur:

Reactions at ≤1200°C

$$5Nb + SiO_2 \rightarrow Nb_3Si + 2NbO \quad (2a)$$

$$11Nb + 3SiO_2 \rightarrow Nb_5Si_3 + 6NbO \quad (2b)$$

$$2Nb + C \rightarrow Nb_2C \quad (2c)$$

$$Nb + C \rightarrow NbC \quad (2d)$$

Reactions at ≤1400°C

$$8NbC + 3SiC \rightarrow Nb_5Si_3 + 3Nb \quad (3a)$$

$$Nb_2C + C \rightarrow 2NbC \quad (3b)$$

$$2Nb_3Si + SiC \rightarrow Nb_5Si_3 + NbC. \quad (3c)$$

The silicon carbide (SiC) in Equations 3a and c was formed as a reaction product during polymer-to-ceramic transformation in the temperature range from

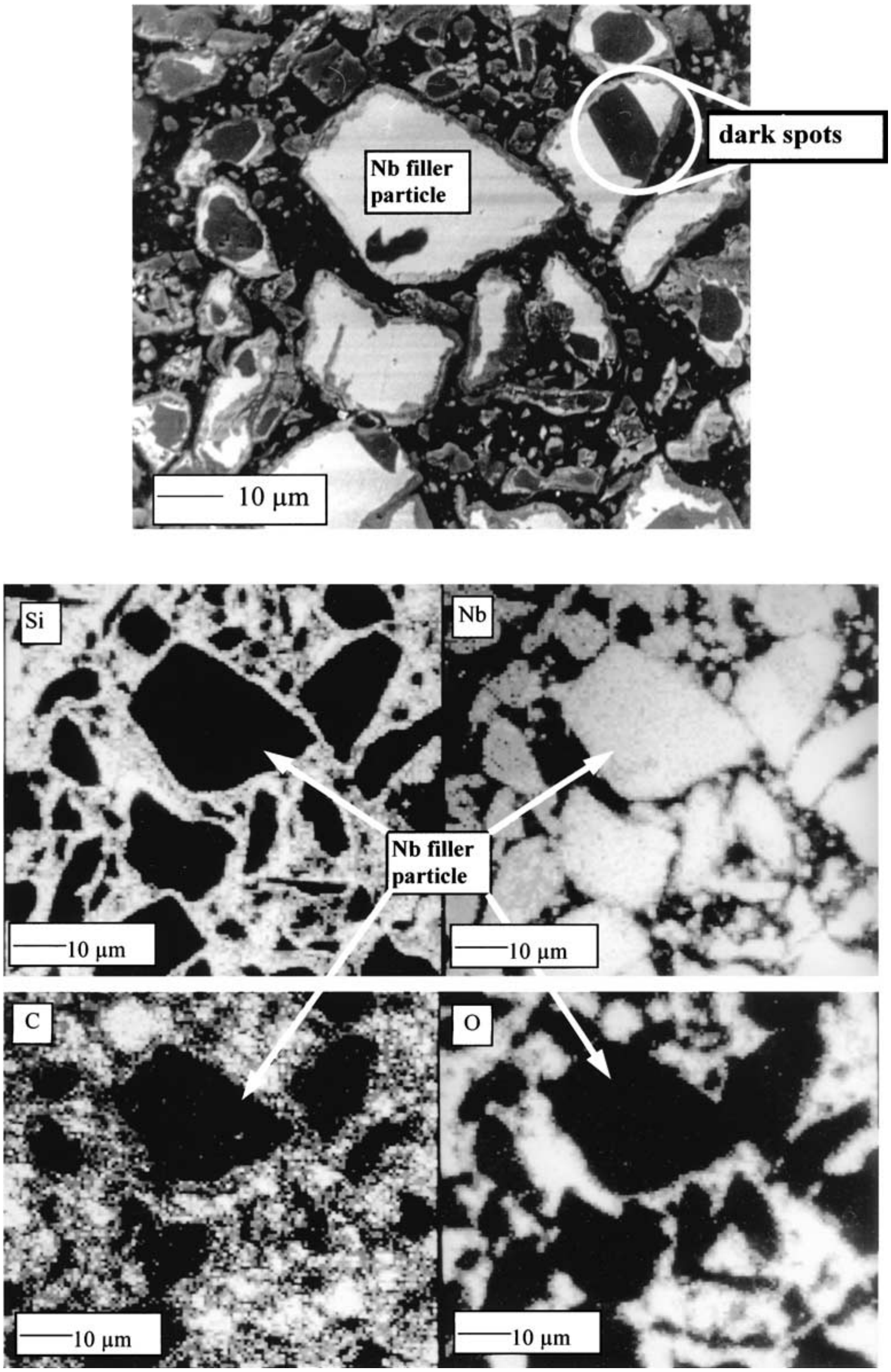

Figure 6 SEM photograph and element maping image of the 30Nb/10NbC sample pyrolyzed at 1200°.

1000–1400°C. It appears as nanocrystalline compound inside the polymer derived ceramic matrix [18–20].

Thermodynamic calculations have demonstrated a negative Gibbs Free Energy of reaction $\Delta_R G^o$ for reactions (1) to (4) in the applied temperature range. With respect to the ceramic residue of the methyl(polysioxane) with a composition of 0.75 SiO_2-0.25SiC-0.42C [11], the reaction process was summarized by connecting the reactions (2a)–(2d) and (3a)–(3c) the following overall reaction equation assuming a total conversion of the niobium filler reacted with the ceramic residue:

$$91Nb + 18SiO_2 + 6SiC + 9C \rightarrow 8Nb_5Si_3 + 36NbO + 15NbC. \qquad (4)$$

Fig. 8 shows the schematical drawing of the reaction processes and the phase formation according to

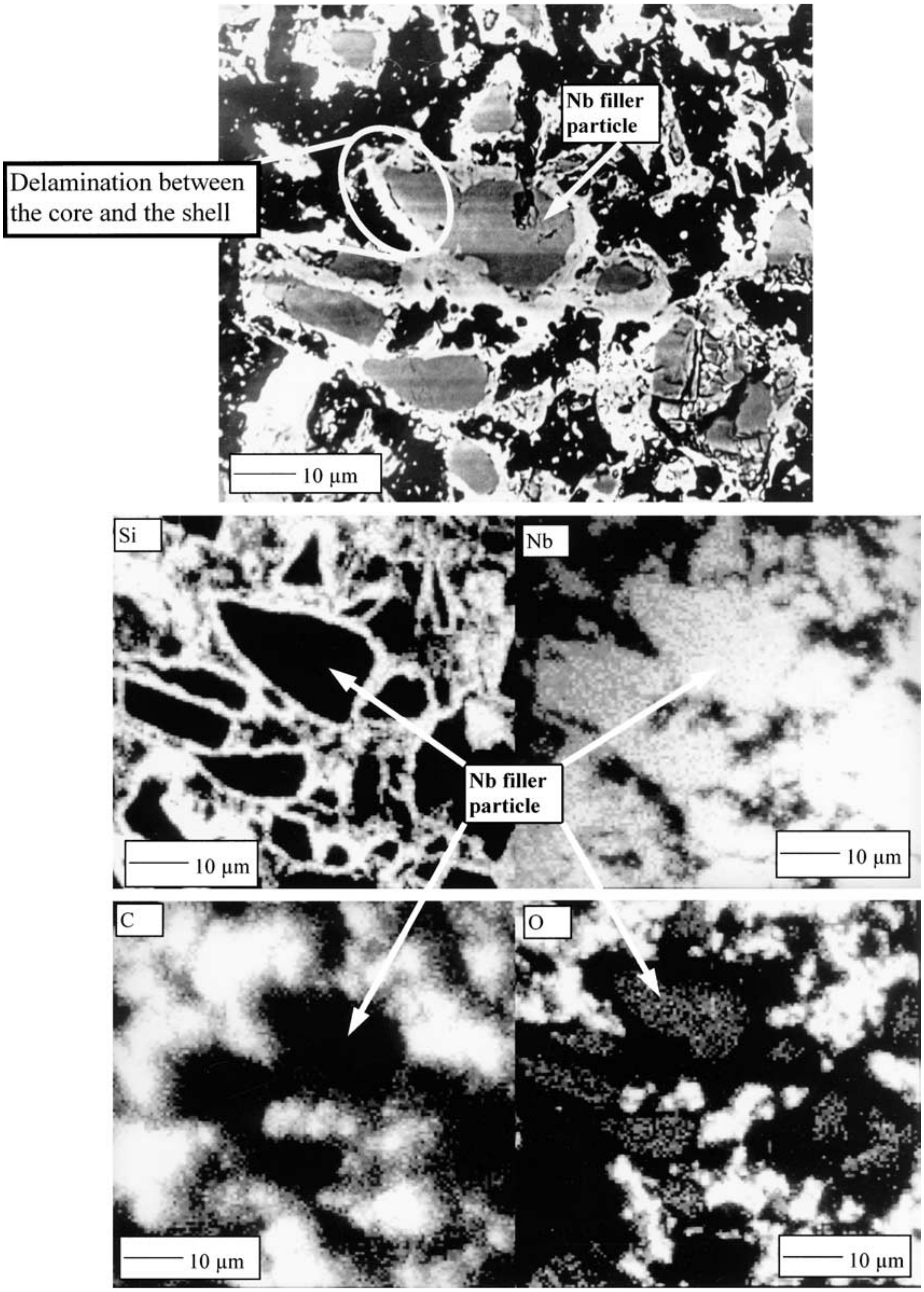

Figure 7 SEM photograph and element maping image of the 30Nb/10NbC sample pyrolyzed at 1400°C.

Equation 4 at 1200 and 1400°C. Taking into account, that the diffusion coefficient of Si in Nb ($D_{\mathrm{Si\,in\,Nb}} = 5.1 \times 10^{-9}$ cm^2 s^{-1}, 1100°C [21]) is smaller than the coefficients of O and C ($D_{\mathrm{O\,in\,Nb}} = 2.11 \times 10^{-7}$ cm^2 s^{-1} (at 1000°C) [22], $D_{\mathrm{C\,in\,Nb}} = 9.2 \times 10^{-9}$ cm^2 s^{-1} at 1000°C [23]), the formation of the *core-shell* structure is evident. The diffusion processes may be controlled by the shell layer thickness.

3.2. Properties

The flexural strengths of the A-series samples (pyrolysis at 1200°C) are higher than of the B-series, Fig. 9. This difference in mechanical strength may be caused by a set of various factors, e.g., porosity, grain size and phase distribution. Moreover, after reaction between the Nb filler and the matrix at 1400°C crack formation and debonding between the reaction shell and the

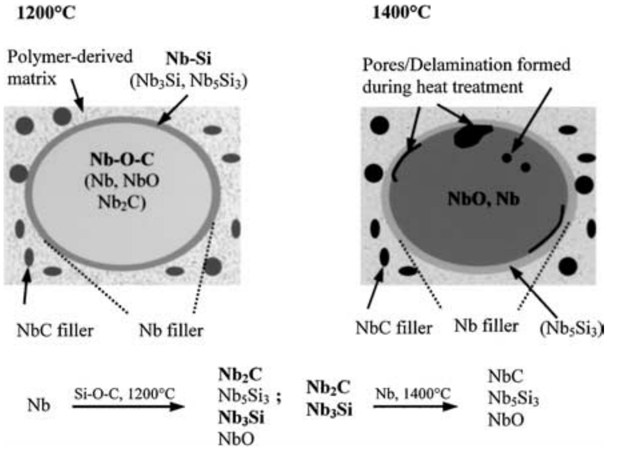

Figure 8 Schematic drawing of the Nb-filler/polymer derived ceramic matrix reaction process.

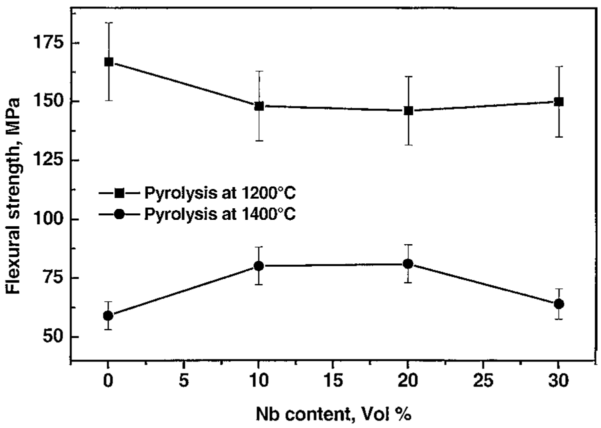

Figure 9 Flexural strength of the polymer derived samples with different Nb/NbC ratios, pyrolyzed at 1200 and 1400°C.

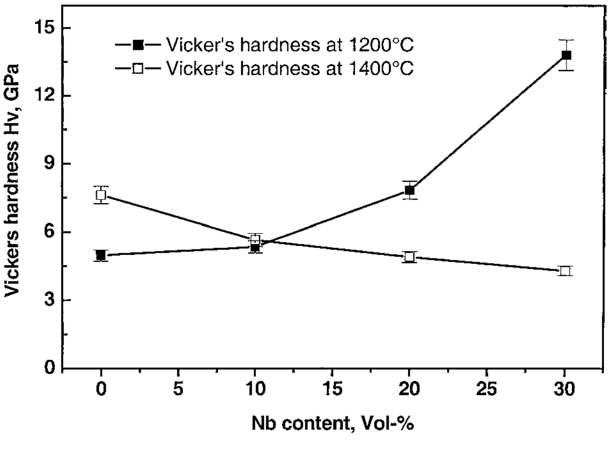

Figure 10 Vickers hardness of the polymer derived samples with different Nb/NbC ratio, pyrolyzed at 1200 and 1400°C.

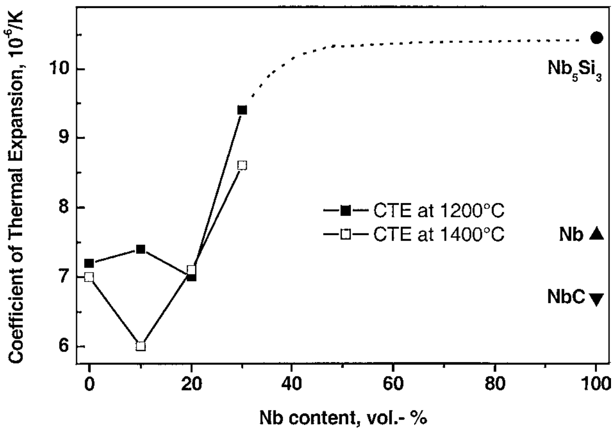

Figure 11 Coefficient of Thermal Expansion of the polymer derived samples with different Nb/NbC ratios, pyrolyzed at 1200 and 1400°C, For comparison: CTE of the pure substances, (●), Nb_5Si_3; (▲), Nb; (▼) NbC.

core formed with the Nb filler was found and additional porosity in the reacted filler grain occured, see Fig. 7 (top view). This may be caused by the thermal mismatch between the core and the shell of the reacted Nb filler.

The Vickers hardness is shown in Fig. 10. In the A-series an increase of the hardness is observed with increasing Nb content, while in the 1400°C pyrolyzed samples the hardness decreased with increasing Nb content. The highest value (~14 GPa) is found in the sample having 30 vol% Nb at a pyrolysis temperature of 1200°C. The increase in hardness with increasing Nb filler volume fraction may be due to the formation of the Nb_2C and NbC phases while at 1400°C the formation of by Nb_5Si_3 may lead to a decrease in hardness.

Fig. 11 shows the CTEs of both sample series as a function of filler composition. For comparison, the CTEs of the plain components found in literature are 7.3×10^{-6} K^{-1} for Nb [2], 6.7×10^{-6} K^{-1} NbC [2] and 10.45×10^{-6} K^{-1} for Nb_5Si_3 [24]. The CTE of the SiOC matrix phase at 1200°C is 4.95×10^{-6} K^{-1} [25]). The CTEs found in the sample Series A and B are a result of the phase composition of the composite material. The values of the CTEs of the composite material range between that of NbC and Nb_5Si_3 which indicate the CTE behaviour of a multi phase composite material. The phase composition can be controlled by the starting composition and the pyrolysis temperature.

4. Conclusions

Using metallic Nb and NbC fillers in a poly(methylsiloxane) matrix a NbC/NbO/Nb_5Si_3 composite material was formed during pyrolysis at 1200 and 1400°C. The reaction product shows a core shell structure in which a Nb_5Si_3 shell is formed at the interface between the metallic Nb filler particle and the SiOC matrix. Linear shrinkage is limited to less than 9%. The material showed a hardness of 14 GPa after pyrolysis at 1200°C.

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