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Formation process of mixed silicon and tungsten carbide from copyrolysis of polysilane and metallic tungsten: Part I

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Copyrolysis of polysilane with metallic tungsten addition in the range of 0–12 at% W was performed. A significant decrease of the mass loss during the polysilane pyrolysis was observed. Also the specific surface area, gas evolution and occuring phase formation changed. The tungsten forms silicides and carbides depending on the applied pyrolysis temperature. The reactions are controlled by transport phenomena of carbon and tungsten. In the end of the process the silicon carbide (SiC) and tungsten carbide (WC) are stable. The obtained powders are sintered to porous ceramics with a significant pore gradient and a variation of the hardness in a micrometer range. © *1999 Kluwer Academic Publishers*

1. Introduction

Composite materials are regarded as promising materials for a number of applications. They possess the potential to improve high temperature strength, the toughness, to vary the electrical properties and to design the materials in a desired way.

The conventional route to produce ceramic composites is to mix different powders or powders with special components example, for whiskers, platelets or short fibers and then to sinter [1, 2]. In recent years new methods of production have been under development. Such new methods include simultanous plasma spraying of powders and short fibers [3], sol-gel methods which are suited to produce composites of alumina and titania [4], CVI processes to produce silicon carbide and titanium/silicon carbide composites [5, 6], polymer routes which can be used to obtain a number of composite ceramics by infiltration processes or by pyrolysis of polymer blends [7–9] and the active filler controlled pyrolysis (AFCOP) [10] or the directed metal oxidation process (DIMOX) [11].

This paper describes a route which uses a chlorine containing polysilane and additions of metallic tungsten. The high reactivity of the polymer enables the formation of carbon and silicon compounds of the added tungsten. The formation process will be described by results which are obtained from X-ray diffraction, IR-spectroscopy and ^{29}Si MAS-NMR-spectroscopy. The powder is characterized by density, specific surface area and chemical analysis. Furthermore first results of the sintering behaviour are given.

2. Experimental

The polysilane used was synthesized by the Institute of Inorganic Chemistry of the Freiberg University of Mining and Technology by a catalytically controlled homogenous redistribution of disilanes, as already published in [12]. The sample preparation includes the following steps:

- mixing of polysilane (average composition $SiC_{1.5}H_{3.6}Cl_{0.8}$) and tungsten powder (HC Starck, Berlin) in a mortar under a nitrogen atmosphere in a glove box, and variation of the amount of added tungsten: 2, 5, 6, 7, 8, 10, 12, 15, and 20 at% of the mixture
- pyrolysis of the mixed samples in an alumina tube furnace (Severn Furnace Ltd., UK) under argon with a 10 K/min heating rate, 1 hour dwell time, at temperatures of 600, 900, 1000, 1200, 1400, and 1500 °C
- higher temperatures were tested for pre-pyrolysed samples at 900 °C under argon for 1600, 1700 and 1800 °C in a furnace with carbon heater (KCE, Germany)
- mixing of pyrolysed powders with boron carbide (0.6%) and paraffine, pressing of the samples to 8 mm diameter cylinders and subsequent burn out of the paraffine at 700 °C under nitrogen
- sintering of pressed samples in the carbon heated furnace at 2050 °C, 1 h with 10 K/min heating rate

Chemical analysis was performed for oxygen and carbon by a combustion method and for nitrogen by gas extraction analysis. Chlorine was analysed by the Schöninger method [13]. Mass loss during pyrolysis of the polysilane-tungsten mixture was determined by mass measurement before and after pyrolysis. Density was measured by pycnometry in toluen. The specific surface area was analysed by the BET-method. X-ray diffraction was performed with CuK_α-radiation at IRIS HZG 4 for 2Θ 10–40 deg. The phase composition was calculated for selected samples by reflex fitting aided by a computer program. ^{29}Si MAS-NMR was performed with Bruker MSL 300. Electron Microprobe analysis was applied for silicon and tungsten analysis in powders and sintered samples. SEM and light microscopy was also used. Finally, the microhardness was determined by the Vickers method.

3. Raw materials

The composition of the used polysilane was: Si 40–50 wt % (11–15 at %), C 20–30 wt % (14–20 at %), Cl 15–20 wt % (4–6 at %), H 6–8 wt % (48–60 at %), O, N < 1 wt % (<1 at %). The polysilane was a brownish solid at room temperature and started to melt at about 150 °C. The tungsten powder was delivered by HC Starck (Germany). The particle diameter was 1–3 μm, the oxygen contamination amounted 0.1–0.2 wt %.

4. Conversion of the polysilane and tungsten in ceramic powders

The mass loss during pyrolysis was observed for different tungsten additions and after different pyrolysis temperatures. For comparison with pure polysilane the mass loss was calculated on the basis of the polysilane content. The loss of tungsten was obviously not significant in these experiments. Fig. 1 shows the detected mass loss depending on quantity of the tungsten addition. (The computer fitted full line represents the trend of the mass loss only qualitatively; i.e. the fictitious minimum about 6 wt % is not significant.) The samples were heated to 1400 °C at 10 K/min and soaked at this temperature for 1 h. A rather drastic drop of the mass loss was found in the range of 2–6 at % tungsten addition. Higher additions did not influence the mass loss behaviour significantly. The tungsten obviously reacts with cleaved or evaporated carbon and silicon compounds during pyrolysis as already proposed by Greil *et al.* [10]. The original 40% mass loss is decreased to about 20% by addition of tungsten powder; this is a fairly good value if one keeps in mind that almost 20 wt % chlorine is contained in the polysilane. That means that the original carbon and silicon content are used for the ceramic material formation. Further investigations will show which compounds are formed during the conversion process.

Fig. 2 shows the temperature dependence of the mass loss of samples with 8 at % tungsten addition between 600 and 1500 °C. The samples were heated up at 10 K/min and soaked for 1 h at the end temperature. A continuously increasing mass loss was found with increasing temperature as expected. After 600 °C the main part of the mass loss has already gone so that additional TG-measurements were performed. Fig. 3 shows the comparable parts of the polysilane related mass loss amounts depending on the temperature. The main mass loss occurs in the temperature range between 300 and 600 °C. At higher temperatures only a moderate mass loss was observed. A higher tungsten addition causes a concentration of the mass loss in a smaller temperature range of 400–600 °C. Because the mass loss is related to the crosslinking of the polymer it is obvious that the crosslinking starts at higher temperatures with the tungsten addition but goes much more efficiently after implementation of tungsten. This may be caused by a dilution effect on the polymer through the added tungsten at low temperatures and by a possible catalytic influence on the crosslinking at higher temperatures. Subsequently these groups can start a more efficient crosslinking at higher temperatures than at lower temperatures.

The mass loss is mainly related to the release of hydrogen chloride as already mentioned. The analysis of the chlorine content of the samples confirms this assumption. Fig. 4 shows the chlorine content depending on the pyrolysis temperature. 600 °C pyrolysis already

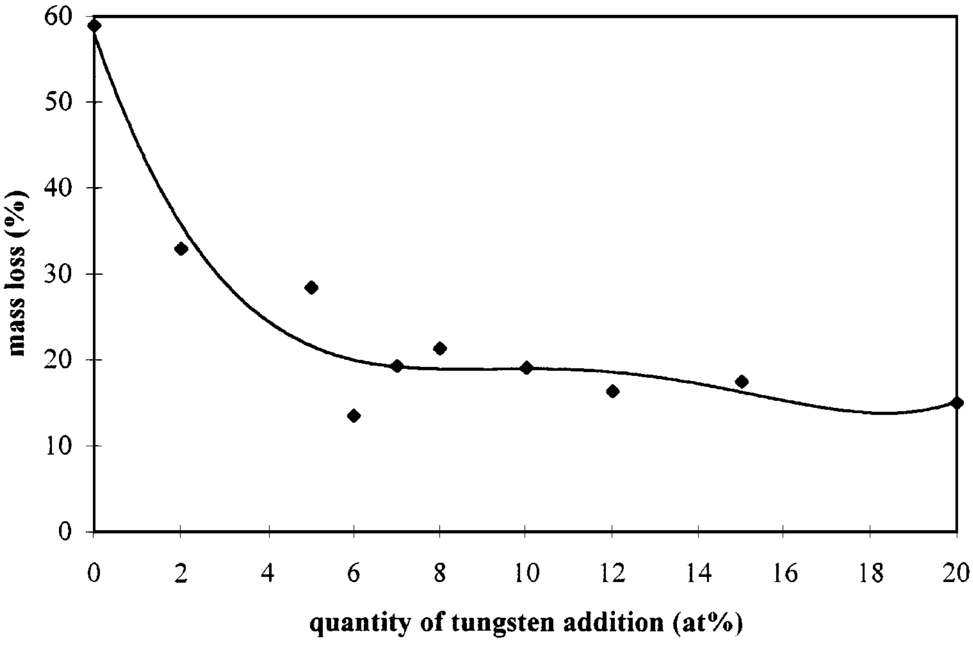

Figure 1 Mass loss of tungsten containing samples and pure polysilane samples depending on the tungsten addition.

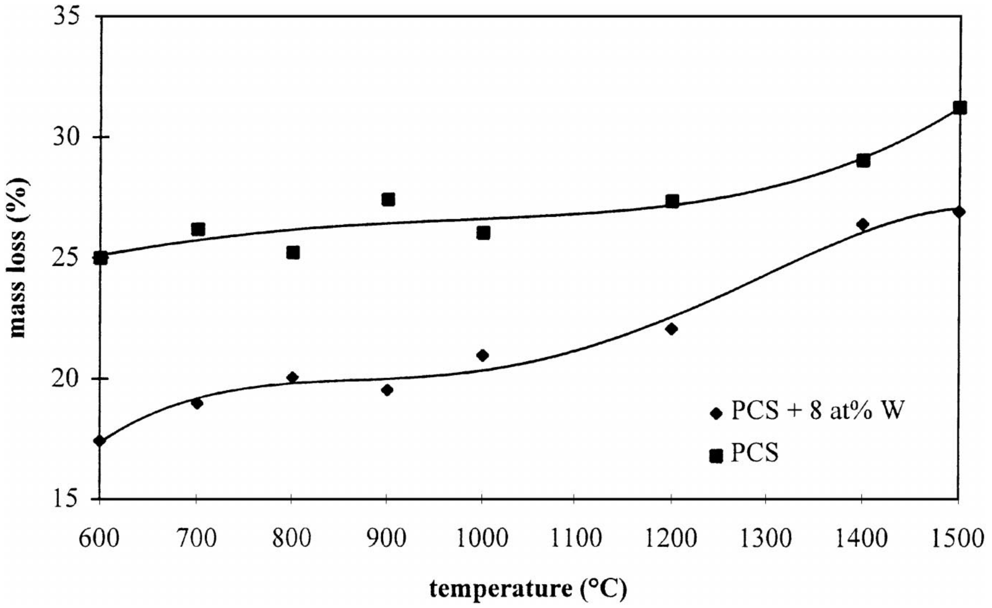

Figure 2 Mass loss of tungsten containing samples and pure polysilane samples depending on temperature.

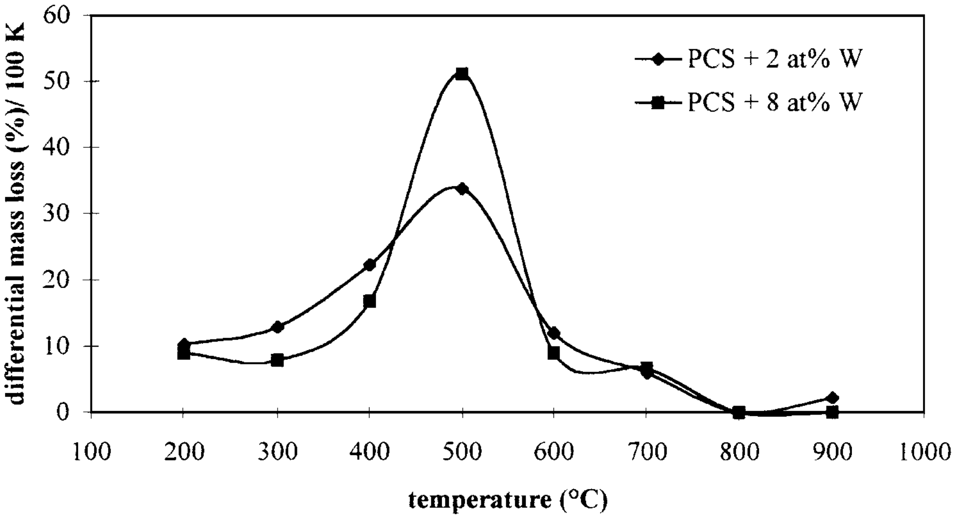

Figure 3 Partial mass loss with temperature.

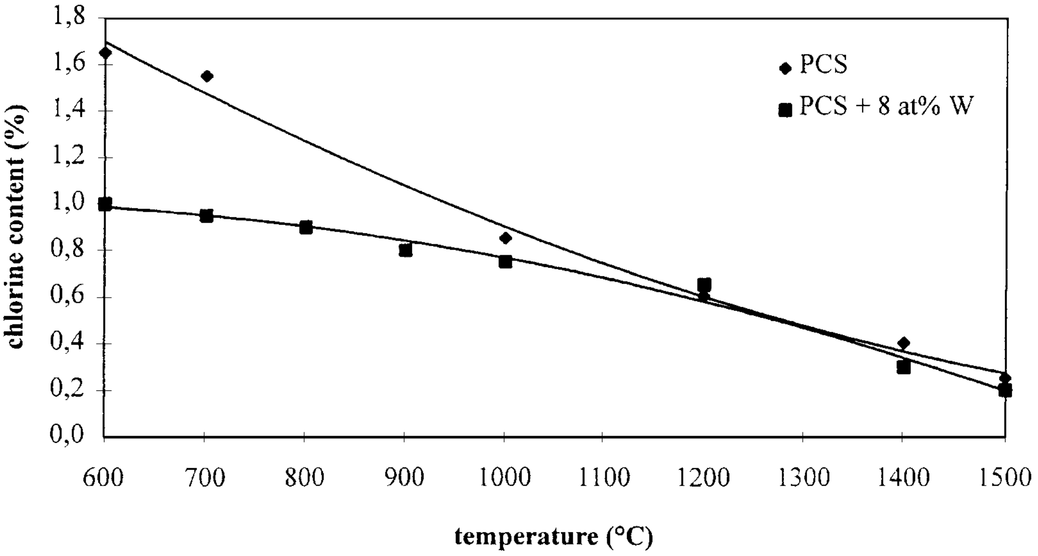

Figure 4 Chlorine content depending on temperature.

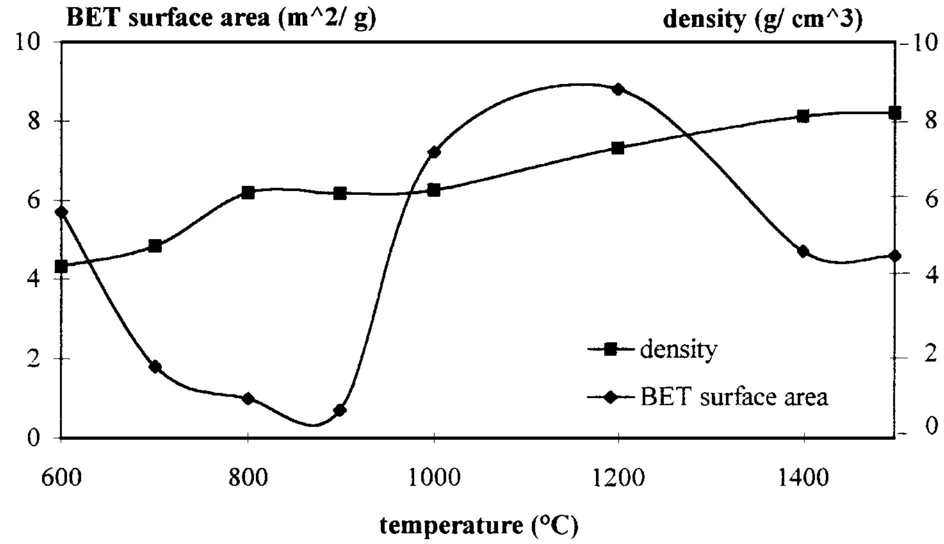

Figure 5 BET surface depending on temperature, density depending on temperature.

causes a loss of the majority of the original chlorine content. It drops from about 15 wt % to <2 wt % chlorine. The observed mass loss in the TG investigation is consequently related to the cleavage of chlorine and formation of hydrogen chloride. The further loss of chlorine is moderate as expected by the mass loss curves.

The specific surface area was measured for samples in the temperature range between 600 and 1500 °C. The temperature dependence is shown in Fig. 5. The specific surface area increased during the previous gas evaluation processes and the reaction of the tungsten powder with the polymer derived material. The first measured value of the sample which was pyrolysed at 600 °C is rather high due to the transformation of the polysilane into polycarbosilane as it was already discussed [14]. The silicon-chlorine bonds are cleaved up to this temperature and subsequently hydrogen chloride is formed. These processes cause a porous structure of the polycarbosilane material and a high specific surface area is created. The porous polycarbosilane particles change into a more compact amorphous silicon-carbon material at higher temperature as described in [14]. In this stage a decreasing specific surface area is observed. At temperature of more than 1000 °C the tungsten-silicon-carbon reactions start which causes an increase of the specific surface area again. After termination of the reactions the generally detectable drop of the specific surface area occurs. This is caused by the smoothening and coarsening of the single particles. The density of the material increased with higher temperature in certain steps as it is depicted in Fig. 5. The first step of density increase between 700 and 800 °C was related to the transformation from the silicon organic state to the inorganic state of the material [12]. The further increase was caused by the formation of crystalline phases of tungsten and silicon carbide which was completed at about 1400 °C.

5. Phase composition of the obtained powders

The results were confirmed by the X-ray investigations and the ^{29}Si MAS NMR spectroscopy. The ^{29}Si CP MAS-NMR-spectra of 600, 900 and 1200 °C samples show the SiC_4 coordination which obviously proves the existence of amorphous silicon carbide with regard to the chemical shift around −12 ppm (reference TMS) [10, 14]. The phase analysis of the X-ray patterns confirms that only metallic tungsten is present in the samples up to 1000 °C. Higher temperatures cause the formation of W_2C, W_5Si_3, WSi_2 and WC subsequently. At lower temperatures between 1000 and 1200 °C the formation of W_2C is preferred. Higher temperatures cause a transformation to WC also for the previously formed W_2C phase. This is not expected with regard to the thermodynamic data but may be caused by kinetic effects. It is properly caused by transport kinetics

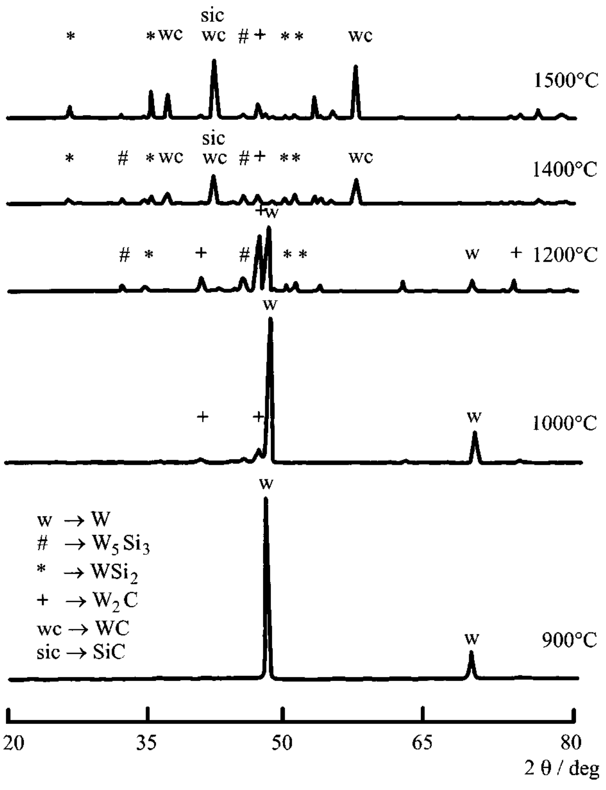

Figure 6 X-ray patterns depending on temperature.

of the carbon phase from the inorganic silicon-carbon network. For this reason also the formation of silicides is observed. The formation of fine dispersed silicon carbide and tungsten carbide powders is observed by pyrolysis of polysilane with tungsten powder. The particle size of the tungsten carbide is dominated by the original particle size of the tungsten powder. The silicon carbide particles have a nanocrystalline size. The formation of silicon carbide is obviously retarded by the tungsten addition. No significant SiC peak was observed in the X-ray pattern up to 1500 °C (Fig. 6). Compared to the results for tungsten free powders [14] this should be a result of the formation of tungsten carbides and tungsten silicides which disturb the crystallization processes in the material [15]. The amount of the tungsten addition also influences the formation of the crystalline phases. This behaviour could be applied to control the crystallization of the material and to produce simultaneously composites of designed properties with regard to electrical and mechanical behaviour. Another explanation for the missed SiC-peak should be also mentioned. The comparable intense WC peak is very close to the expected (111) peak of the β-SiC. The ratio of the intensities of SiC and WC due to the differences in the atomic numbers (1:16) and the overlap of the peaks are additional reasons which makes it difficult to detect the SiC phase in the X-ray pattern. Also this may cause a strong diminishing of the SiC-phase in the pattern.

6. Sintering

After mixing the obtained powders contain paraffin as a pressing aid and B_4C as a sintering aid. Samples were pressed uniaxially with 150 MPa and the paraffin was

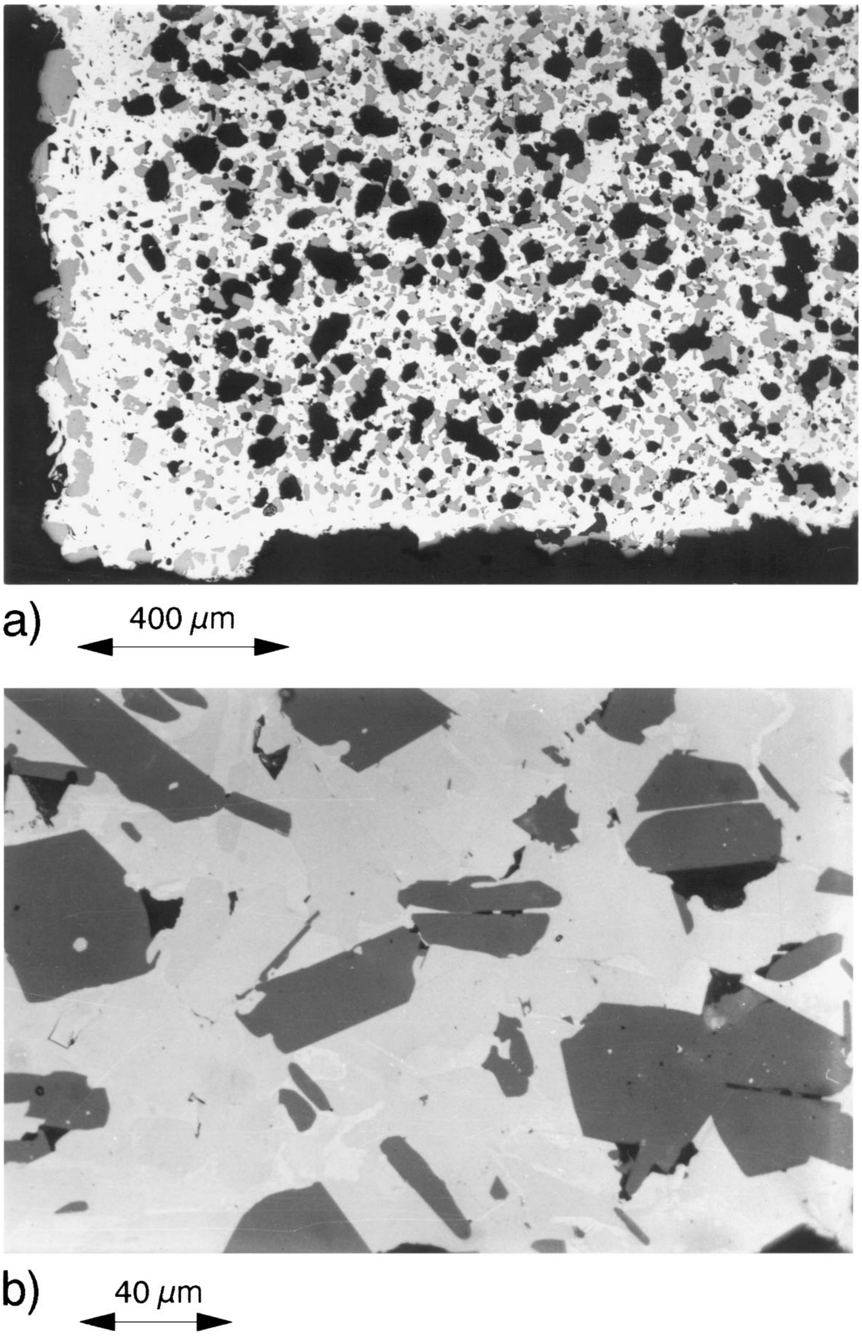

Figure 7 (a) Micrograph of sintered body (overview) and (b) micrograph of dense outer part of the sintered body of (a).

removed by heating to 500 °C under nitrogen. After pressureless sintering at 2050 °C the specimen reached 60% of theoretical density. The inner part was highly porous but the outer region became nearly dense as shown in Fig. 7a. Large areas of light and dark grey colour were observed by light microscopy. The composition of the different areas was analysed by electron microprobe. The dark areas are mainly composed of silicon and carbon whereas the light areas are composed of silicon, tungsten and carbon in different amount (Fig. 7b). The vickers hardness was measured and it was found that the dark areas show a hardness of 42–50 GPa and the light ones a HV of 17–23 GPa. These values confirm the existence of pure silicon carbide and mixed silicon tungsten and carbide or tungsten silicide particles in small dimensions. The areas of uniform colour which are observed by light microscopy does not correspond to single crystallites. The crystallite size which can be estimated from the X-ray patterns is only in the range of <100 nm whereas the area dimension of silicon carbide and mixed silicon carbide-tungsten carbide-tungsten silicide are observed in the range of 20 μm. The sintered products are gradually structured with regard to the porosity and may be used for applications with moderate strength demands, high hardness, high temperature resistance and low specific weight. It could be also useful to optimize the pore structure for filtration processes. Nevertheless an optimized sintering should produce higher densities which will improve the mechanical properties.

7. Conclusions

It is possible to produce intrinsic mixed powders of silicon carbide and tungsten carbide and silicide by pyrolysis of chlorine containing polysilane in presence of tungsten powder. The mass loss of the polysilane is reduced by the addition of tungsten which forms during the pyrolysis process of tungsten silicide and subsequently tungsten carbides of W_2C at lower temperatures around 1200 °C and WC around 1400 °C. The obtained powders can be sintered without pressure to produce structured ceramics of high porosity in the inner part and a dense surface. The ceramics consist of silicon carbide and tungsten carbide and small amounts of tungsten silicide. The samples show high hardness which shows inhomogeneities in the micron range.

References

1. M. W. BARSOUM and T. EL-RAGLY, *J. Amer. Ceram. Soc.* **79** (1996) 1953.
2. S. IIO, H. YOKOI, M. WATANABE and Y. MATSUTO, *ibid.* **74** (1991) 296.
3. R. DITTRICH, E. MÜLLER, M. BRUNE and H.-D. STEFFENS, *cfi/Berichte* **74** (1997) 291.
4. V. RAMAN, O. P. BAHL and U. DHAWAN, *J. Mater. Sci.* **30** (1995) 2686.
5. M. F. GONON, G. FANTOZZI, M MURAT and J. P. DISSON, *J. Eur. Ceram. Soc.* **15** (1995) 185.
6. S. MASAKI, K. MORIYA, T. YAMAMURA, M. SHIBUYA and H. OHNABE, *Ceram. Trans.* **58** (1995), edited by A. G. Evans and R. Naslain, Amer. Ceram. Soc., p. 187.
7. J. LÜCKE, M. KEUTHEN and G. ZIEGLER, *ibid.* **51** (1995), edited by H. Hausner, G. L. Messing and S.-ichi Hirano, Amer. Ceram. Soc., p. 205.
8. C. E. BORSA and R. J. BROOK, *ibid.* **51** (1995), edited by H. Hausner, G. L. Messing and S.-ichi Hirano, Amer. Ceram. Soc., p. 653.
9. O. FUNAYAMA, H. MOROZUMI, M. IKADA and T. ISODA, *J. Ceram. Soc. Jap. Int. Ed.* **103** (1995) 413.
10. P. GREIL, *J. Amer. Ceram. Soc.* **78**(4) (1995) 835.
11. M. S. NEWKIRK, A. W. URQUHART, H. R. ZWICKER and W. BREVAL, *J. Mater. Res.* **1** (1986) 812.
12. H.-P. MARTIN, E. MÜLLER, R. RICHTER, G. ROEWER and E. BRENDLER, *J. Mater. Sci.* **32** (1997) 1381.
13. W. SCHÖNINGER, *Z. Analyt. Chemie* **28** (1961) 181.
14. H.-P. MARTIN, E. MÜLLER and E. BRENDLER, *J. Mater. Sci.* **31** (1996) 4363.
15. H.-P. MARTIN, PhD, TU Bergakademie Freiberg, Faculty of Engineering Science, 1994.

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