JOURNAL OF MATERIALS SCIENCE **34** (1999) 2671–2678

# Formation process of mixed silicon and titanium carbide from copyrolysis of polysilane and metallic titanium: Part II

H.-P. MARTIN, E. MÜLLER
*Institute of Ceramic Materials, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany*

In part I we reported a copyrolysis of polysilane with metallic tungsten [1]. Now copyrolysis of chlorine containing polysilane with metallic titanium addition in the range of 0–10 at % Ti 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 changes. The titanium forms preferently carbides and temporary silicides depending on the applied pyrolysis temperature. The reactions are controlled by transport phenomena of carbon and titanium. In the end of the process silicon carbide (SiC) and titanium carbide ($TiC_x$) are stable.

## 1. Introduction

Ceramic composite materials are regarded to as promising materials for a number of applications. A survey on various technologies for producing ceramic composites was already given in part I of this paper [1].

Here we describe a route which uses a chlorine containing polysilane and additions of metallic titanium. The inclusion of TiC into SiC materials may improve the high temperature strength, the toughness and vary the electrical properties. The route applied here was already used for the production of tungsten carbide/silicon carbide composite powders [1]. The high reactivity of the polymer enables the formation of carbon and silicon compounds of the added fine grained titanium. 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.

## 2. Experimental

The used polysilane was synthesized by the Institute of Inorganic Chemistry of the Freiberg University of Mining and Technology by a catalytically controlled homogenous redistribution of disilanes, what was already published in [2]. The sample preparation was carried out in an analogous way like the formerly described preparation of the tungsten containing system [1]. Therefore, it should be repeated only shortly here:

- mixing of polysilane and titanium powder (HC Starck, Berlin, mean particle diameter $d < 63\,\mu$m; and Johnson Matthey, Alfa Products, $d < 2\,\mu$m) in a mortar under nitrogen atmosphere in a glove box, variation of the added titanium: 2, 5, 8 or 10 at % of the mixture.
- pyrolysis of the mixed samples in an alumina tube furnace (Seven Furnace Ltd., UK) under argon with 10 K/min heating rate, 1 h dwell time, temperature of 600, 700, 800, 1000, 1200, and 1400 °C.

To determine the chemical composition of the products, the mass loss during the pyrolysis and the structure development (XRD, NMR, SEM) the same methods and equipments were used as described in part I [1].

## 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 starts to melt at about 150 °C. The titanium powder was delivered by HC Starck and Johnson Matthey Alfa Products. The particle diameter was $<63\,\mu$m, the oxygen contamination amounted 0.4 wt % and $<2\,\mu$m, O = 2 wt %, respectively.

## 4. Conversion of the polysilane and titanium in ceramic powders

The mass loss during pyrolysis was observed for different titanium 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 titanium was obviously not significant in these experiments similar to the former described experiments with tungsten [1]. Fig. 1 shows the detected ceramic yield for samples with different

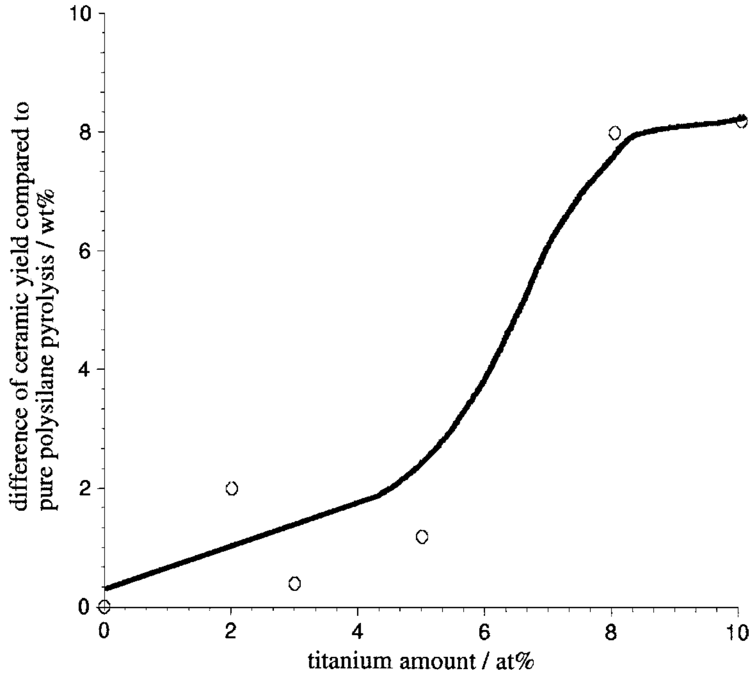


*Figure 1* Ceramic yield difference after pyrolysis of polysilane depending on titanium addition.

titanium additions (2, 3.5, 5, 8, 10 at %) and for a titanium free sample. The samples were heated to 1000 °C. The effect up to 5 at % Ti is not significant but a higher titanium amount shifts the ceramic yield to a higher value. Additions >8 at % Ti do not influence the ceramic yield significantly. The titanium obviously reacts with cleaved or evaporated carbon and silicon compounds during pyrolysis. The original 40% mass loss is decreased to about 30%, which is related to the polysilane amount, by addition of titanium powder. The decrease of the mass loss is distributed over the whole pyrolysis period. This was observed by thermogravimetry. This differential mass loss was lower in the case of a titanium addition. That means that the original carbon and silicon content are used for the ceramic material formation. The further investigations will show which compounds are formed during the conversion process. But the formation of the titanium compounds are not the real reason for the decrease of the mass loss in the low temperature range because the chemical formation of detected titanium compounds occurs only at high temperatures as it will be shown later in this paper.

Fig. 2 shows the temperature dependence of the mass loss of samples with 8 at % titanium addition up to 900 °C which are derived from thermogravimetric results. The samples were heated up with 10 K/min. The

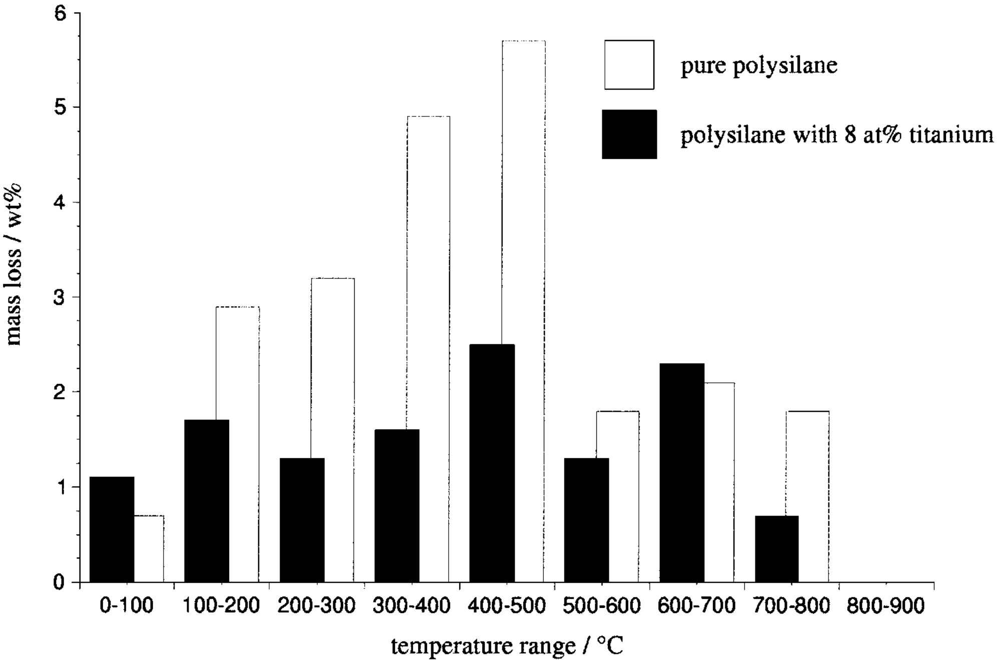


*Figure 2* Differential mass loss of polysilane and polysilane with titanium, total mass loss of these samples: polysilane 23.6 wt %, polysilane with titanium 12.5 wt % (only polysilane regarded).

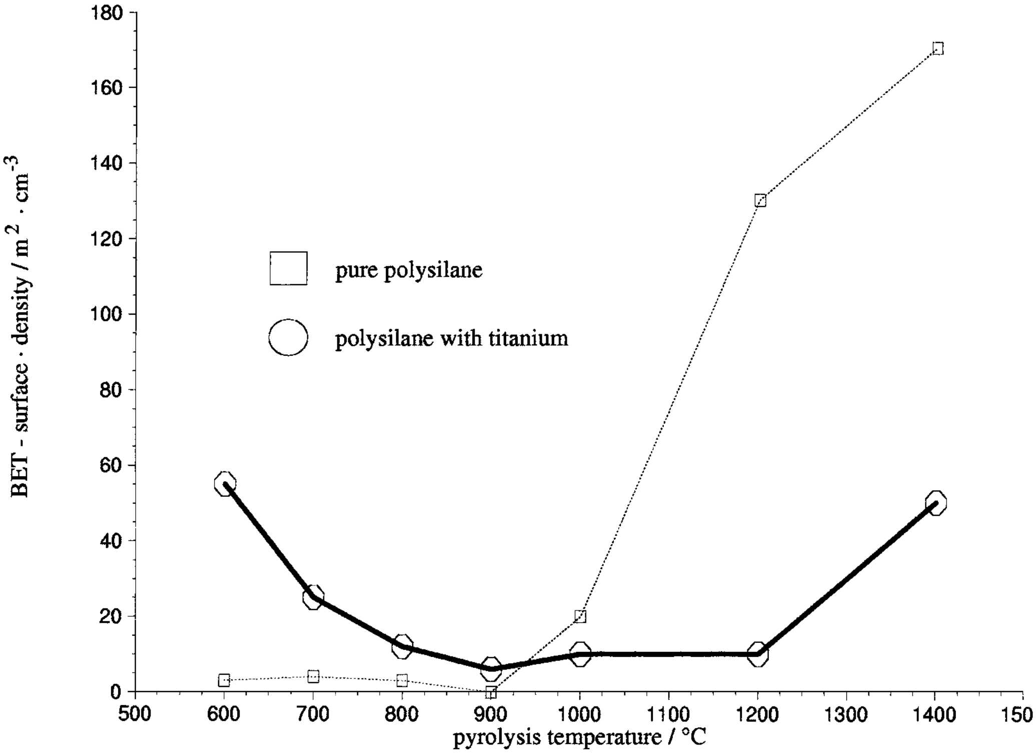


*Figure 3* Specific surface area of pyrolyzed polysilane and polysilane with 8 at % titanium addition after pyrolysis depending on temperature, comparable by multiplying with powder density.

mass loss of the titanium added sample is lower over the temperature range as it was already mentioned. This shows the efficient reduction of the mass loss by the titanium which may promote the crosslinking of the polymer molecules by catalytic effects and enables also diffusion of carbon and silicon into the titanium metal. Also a dilution effect which can influence the pyrolysis at low temperatures may be regarded. In opposite to the former described tungsten additions the titanium effects the mass loss also in the critical range between 400 and 500 °C where the mass loss is rather high. The observed mass loss in the TG investigation is related to the cleavage of chlorine and formation of hydrogen chloride as it was mentioned in [1].

The powder properties determine the processing success. So the specific surface area, the density and the powder morphology were examined. The specific surface area was measured for samples of the temperature range between 600 and 1500 °C. The temperature dependence of the pyrolyzed polysilane and pyrolyzed titanium added polysilane is shown in Fig. 3. The specific surface area of different materials was made comparable by multiplying the data with the density of the samples. The specific surface area increases during the previous gas evolution processes and the reaction of the titanium powder with the polymer derived material. But the total area is decreased with respect to the no titanium containing samples. This effect is obviously caused by the moderate mass loss and conversion of the polysilane as it is expected from the results of the mass loss investigations. Especially the specific surface area of the titanium containing sample after 600 °C pyrolysis is rather high compared to the pure polysilane and the earlier discussed tungsten containing sample [1]. The conversion of the polysilane into polycarbosilane which is associated with structural transformations and the cleavage of hydrogen chloride and other species is obviously promoted. 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 [3]. In this stage a decreasing specific surface area is observed. At temperature of more than 1200 °C the titanium-silicon-carbon reactions become significant which causes an increase of the specific surface area again. This effect starts at higher temperatures than those observed with tungsten addition. It is obvious that especially the titanium carbide and the silicon carbide formation increase the specific surface area. The formation of silicides only cause a slight increase of the surface of the powder particles.

The density of the material is increasing with higher temperature almost continuously (Fig. 4). The increase is related to the transformation from the silicon organic state to the inorganic state of the material [1]. The further increase is caused by the formation of crystalline phases of titanium silicides, titanium carbide and silicon carbide what is completed at about 1400 °C.

## 5. Structural conversion and phase composition of the obtained powders

IR spectra of the pyrolyzed samples were recorded to estimate the structural change in dependence on the pyrolysis temperature. Fig. 5 shows the ratio between the intensity of the Si-$CH_3$ vibration and the Si-C vibrations which include all vibrations of Si-C in the carbosilane

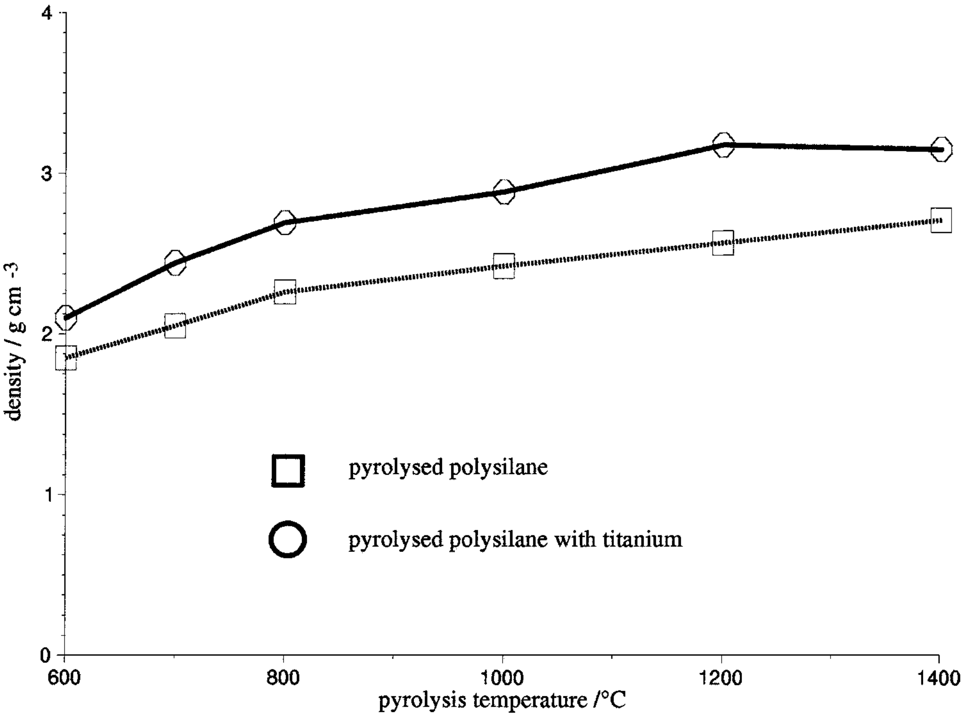


*Figure 4* Density of pyrolyzed polysilane and polysilane with 8 at % titanium addition after pyrolysis depending on temperature.

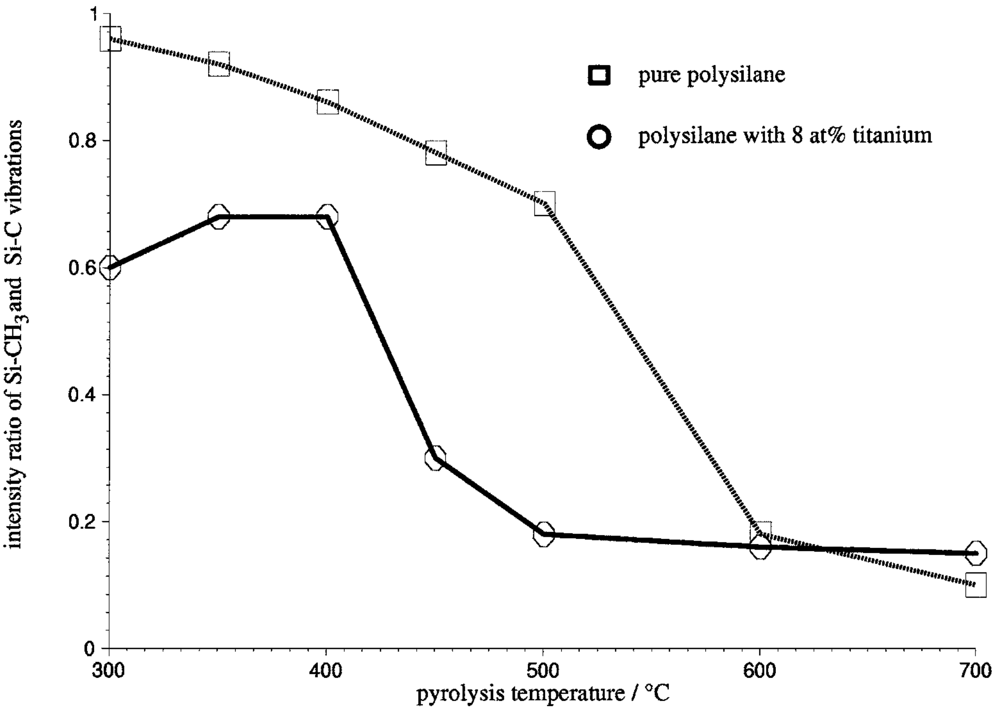


*Figure 5* Intensity ratio of IR-bands at 1250 cm$^{-1}$ (Si-CH$_3$) and 800 cm$^{-1}$ (Si-C) depending on temperature.

or silicon carbide lattice. A decrease of the ratio indicates the progress of the crosslinking and the formation of a Si-C network. As it is depicted in Fig. 5 the cross-linking and formation of the Si-C network starts at lower temperatures and in a more efficient way by addition of titanium metal to the polysilane. This behavior confirms the lower mass loss found by the already described TG investigation. The reason for this observed influence of the titanium addition may be of catalytical nature. The polysilane and polycarbosilane crosslinking is obviously completed at 500 °C whereas it is completed at temperatures >600 °C if no titanium is added.

The IR results are confirmed by 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 (reference TMS) [4] (Fig. 6). After 600 °C pyrolysis temperature the silicon atoms are embedded in a polycarbosilane structure which is characterized by silicon atoms surrounded by carbon atoms which are bonded to hydrogen atoms. The chemical shift of the $^{29}$Si peak is centered around 0 ppm. A weak signal is also found

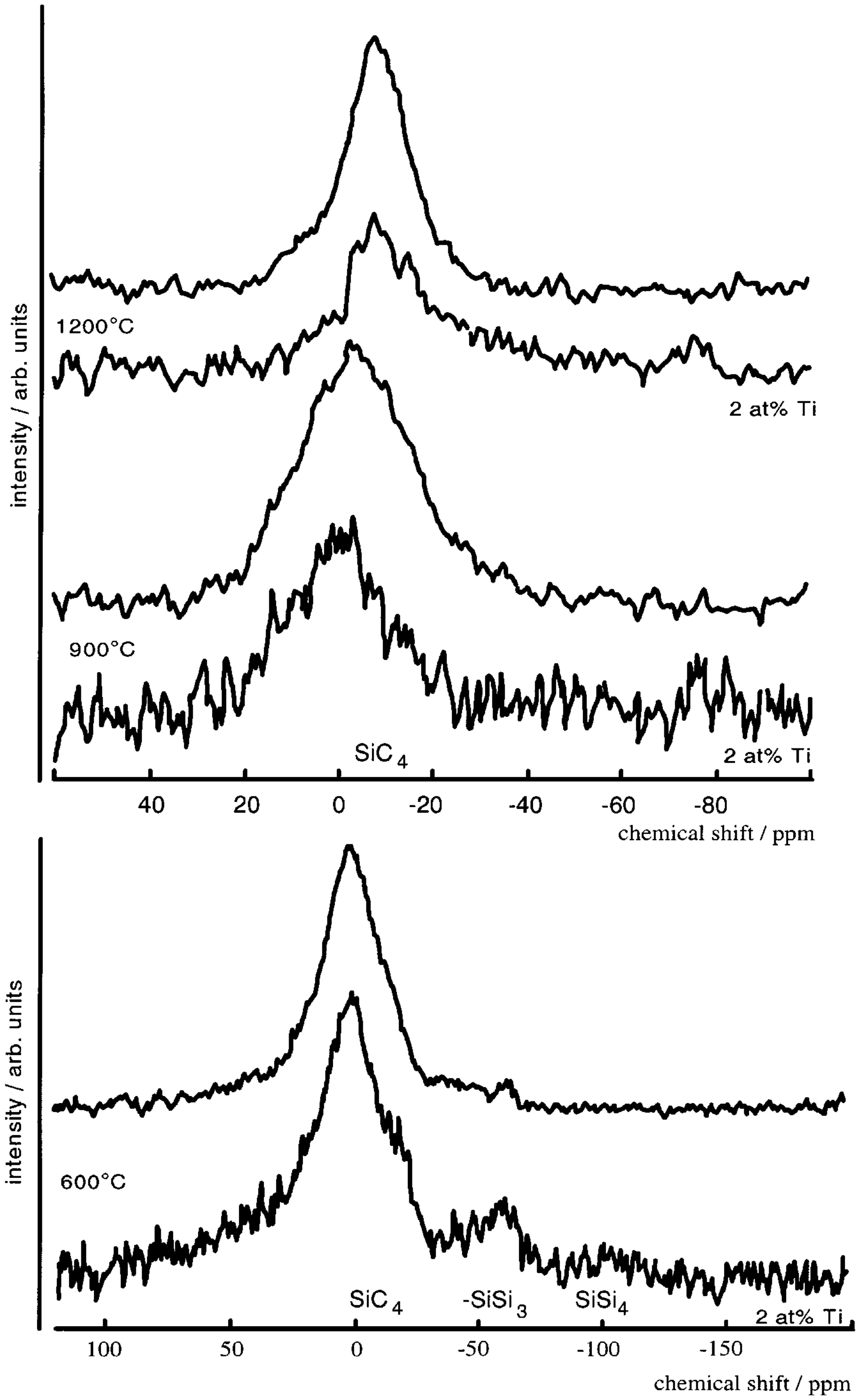


*Figure 6* $^{29}$Si CP MAS NMR spectra of 2 at % titanium added polysilane and pure polysilane after pyrolysis depending on temperature.

around −60 ppm chemical shift which refers to polysilane remains [2]. An increase of the pyrolysis temperature up to 900 °C does not shift the peak significantly as it is observed for silicon carbide structures [2]. This proofs that the structure is stable over a wide temperature range as one can expect from a well cross-linked silicon-carbon network. The silicon carbide structure formation is delayed compared to the titanium free pyrolyzed samples. This is probably caused by the disturbing effect of the formation of titanium silicides and titanium carbide what demonstrates the influence of the metallic addition in the conversion process. Especially the titanium containing sample shows a strongly disturbed $SiC_4$ signal what is obviously caused by the rearrangements which are described later in this paper. In opposite to the titanium containing sample the pure polysilane shows a stronger $SiC_4$ signal.

The phase analysis of the X-ray patterns (Fig. 7) confirms that only metallic titanium is present in the samples up to 600 °C. Higher temperatures between 700 and 1000 °C cause the formation of $Ti_5Si_3$ and TiSi. These two compounds are the dominating ones after 1000 °C pyrolysis. A reformation occurs with further temperature rise to 1200 °C. The existing titanium silicides form titanium carbide and $TiSi_2$. Finally titanium carbide is observed as the only crystalline phase. But also silicon carbide is expected which is probably covered by the titanium carbide peak. The SiC can be distinct after higher pyrolysis temperature (>1800 °C) when the crystallization of the SiC component is completed so

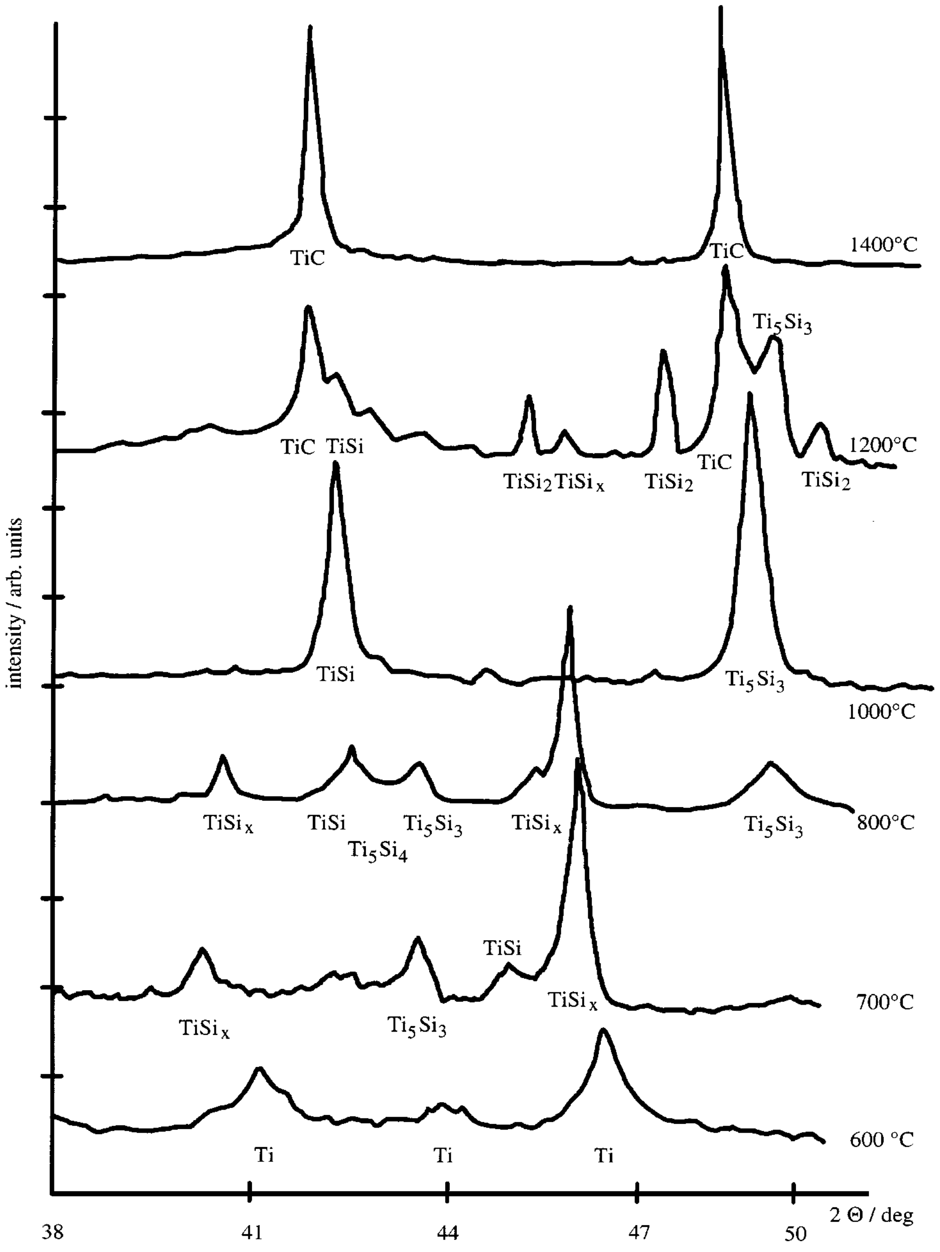


*Figure 7* X-ray diffraction patterns of polysilane with 8 at % titanium addition after pyrolysis depending on temperature (1 h soaked).

that the X-ray peak intensity of the SiC becomes remarkable.

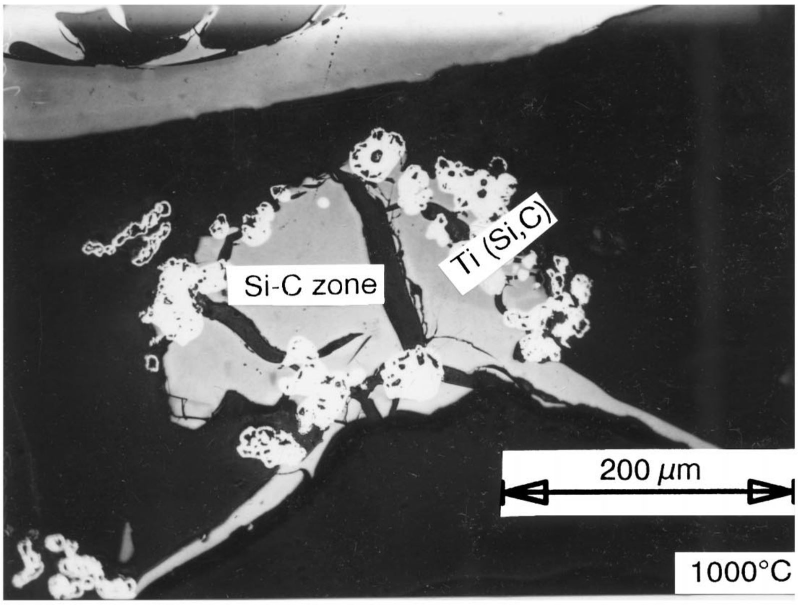
The images of light microscopy complete the interpretation of the proposed conversion process. Fig. 8 demonstrates samples after pyrolysis at 1000 and 1200 °C which are embedded in epoxy resin and polished. A coarse titanium powder (HC Starck, $<63\,\mu$m) was applied to enable a observation by light microscope. Naturally, we expect slower reactions of the titanium and the polymer precursor due to the larger grains. But the principle reaction should occur at least on the grain surface. The sample after 1000 °C is characterized by distinguished titanium grains which are close to the polycarbosilane particles. A reaction zone can be recognized which probably refer to the detected titanium silicides. The higher temperature causes a complete incorporation of the titanium in the polycarbosilane particles. The titanium rich zones are distinguished by the light color. They should associated to the titanium carbide and to titanium silicide as it was also proved by electron microprobe analysis.

Investigations were performed to characterize the amount of titanium carbide and silicon carbide in the samples with relation to the titanium additions. Table I gives a comparison of the calculated and measured data which are in rather good agreement. The higher amount of $TiC_x$ which are found by XRD may be caused by the instoichiometric composition of the titanium carbide.

As generally known the carbon content of the titanium carbide can range from $TiC_{1.0}$ to $TiC_{0.2}$. Therefore the lattice parameter was regarded to conclude for the carbon content in dependence on the titanium addition

TABLE I TiC amount depending on the titanium addition calculated and detected by X-ray peak intensity of the (111) TiC peak

| Titanium amount (at %) | Calculated TiC fraction (at %) | Detected TiC fraction (at %) |
|---|---|---|
| 2 | 5 | 7 |
| 5 | 16 | 16 |
| 8 | 27 | 35 |



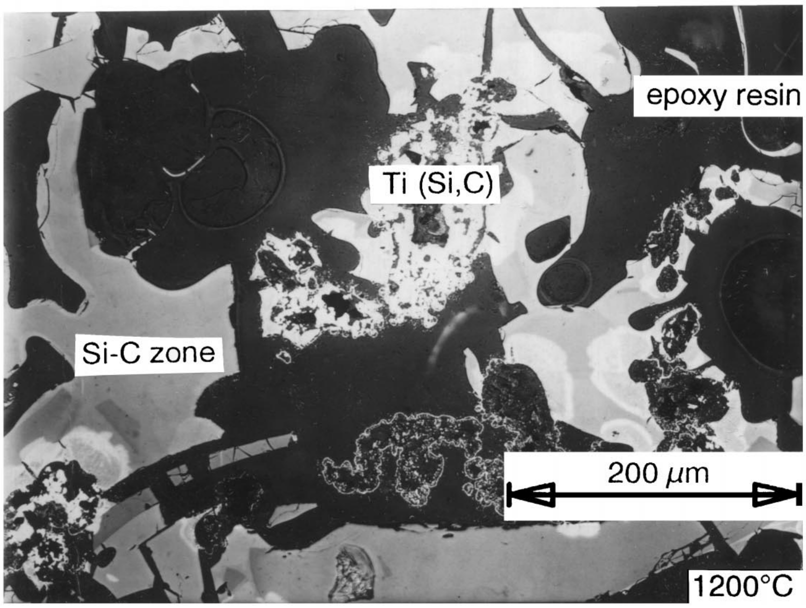


*Figure 8* Light micrographs of pyrolyzed polysilane with 8 at % titanium after 1000 and 1200 °C (1 h).

and the pyrolysis temperature. Table II gives the results for $x$ referring to $TiC_x$. Additionally the influence of the titanium amount on the crystallite size of the titanium carbide and the silicon carbide was examined. The results are shown in Fig. 7. The formation of titanium carbide during the pyrolysis of polysilane with included titanium powder occurs after formation of titanium silicides. The diffusion rate of silicon and carbon determines the formation process of the compounds. High amounts of titanium result in a high number of small titanium carbide crystals. Therefore the diffusion paths of the carbon from the Si-C network into the titanium domaines become shorter and the thermodynamical prefered formation of titanium carbide is more efficient. So the silicon carbide crystallites are larger whereas the titanium carbide crystallites are smaller in the mentioned case.

TABLE II Composition of the $TiC_x$ derived from the lattice parameter with regard to [16] depending on titanium amount after pyrolysis at 1400 °C and depending on pyrolysis temperature on samples with 8 at % Ti addition

| Titanium amount (at %) | $a_0$ (nm) | $x$ |
|---|---|---|
| 2 | 0.428 | 0.30 |
| 5 | 0.429 | 0.45 |
| 8 | 0.430 | 0.55 |
| Pyrolysis temperature | | |
| 1200 °C | 0.4298 | 0.53 |
| 1400 °C | 0.4306 | 0.56 |
| 1900 °C | 0.4289 | 0.43 |

## 6. Conclusions

It is possible to produce intrinsic mixed powders of silicon carbide and titanium carbide and silicide by pyrolysis of chlorine containing polysilane in presence of

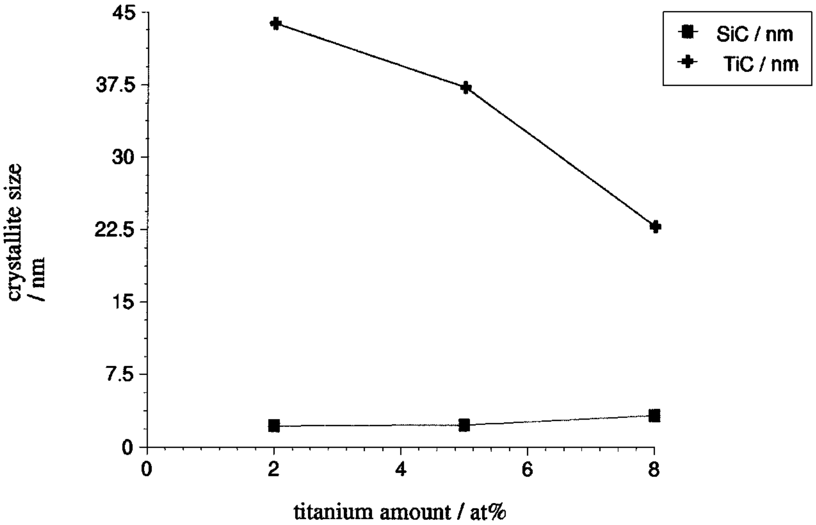


*Figure 9* Mean crystallite size of the SiC and TiC components after pyrolysis at 1400 °C (1 h) depending on titanium addition, calculated from peak broadening of the (111) X-ray peak.

titanium powder. The reactivity of the polysilane enables a early formation of titanium compounds. The mass loss of the polysilane is significantly reduced by the addition of $>5$ at % titanium which promotes the cross-linking of the polysilane and the later formed polycarbosilane by a catalytic effect and forms in a first step titanium silicides at temperatures $>1000$ °C and subsequently at temperatures $>1200$ °C titanium carbide of $TiC_x$ composition. The crystalline structure of the products can be controlled by the titanium amount. Higher titanium additions lead to larger SiC crystallites and smaller $TiC_x$ crystallites with higher carbon content e.g., increasing $x$-value.

## Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft (Mu 943/6) and the German Fonds of Chemical Industry for financial support of this research. Also we like to thank Prof. G. Roewer and his coworkers (Freiberg University of Mining and Technology, Department of Inorganic Chemistry) for valuable advice and discussions of the results and for the synthesis of the investigated polysilanes.

## References

1. H.-P. MARTIN, E. MÜLLER and U. DACHSELT, *J. Mater. Sci.* (in press).
2. H.-P. MARTIN, E. MÜLLER, R. RICHTER, G. ROEWER and E. BRENDLER, *ibid.* **32** (1997) 1381.
3. H.-P. MARTIN, Ph.D. thesis, TU Bergakademie Freiberg, Faculty of Engineering Science, 1994.
4. H.-P. MARTIN, E. MÜLLER and E. BRENDLER, *ibid.* **31** (1996) 4363.

*Received 22 November 1997*
*and accepted 6 October 1998*