NANOCRYSTALLINE CERAMIC SiC, TiC AND SiC-TiC POWDERS PRODUCED IN A RF-INDUCTION PLASMA

H.-D. Klotz[1], R. Mach[1], F. Oleszak[1], K. Szulzewsky[2], W. Kramer[2],
E. Schierhorn[3]

[1] TU Berlin, Institut für Nichtmetallische Werkstoffe / Plasmachemie
Rudower Chaussee 5, D-12489 Berlin

[2] WITEGA Angewandte Werkstoff-Forschung g.GmbH Adlershof
Rudower Chaussee 5, D-12489 Berlin

[3] BAM, Unter den Eichen 87, D-12200 Berlin

ABSTRACT

The objective of this work is to study the high temperature plasma synthesis of nanoscale SiC, TiC and SiC-TiC composite powders through vapor phase reactions between C_2H_4 and the tetrachlorides of silicon and titanium. The experiments are carried out in an Ar/H_2 r.f. inductively coupled plasma at plate power of 30 kW and atmospheric pressure. Special attention is given to the powder properties and composite composition in regard to ceramic processing. The composites were black in color, composed of mostly crystalline SiC and TiC in different amounts according to reaction route.

1. INTRODUCTION

Over the last years, there has been a steady grown interest in nanoscale powders for ceramic processing. The advances of nanoscale powders ($<$ 100 nm diameter) include lower sintering temperature, novel properties as a result of ultrafine grain structures with high grain boundary area per unit volume, and superplastic deformation of high density ceramics. Recent studies on nanocomposite ceramics having two or more nanoscale phases, have clearly demonstrated the importance of a second phase on the properties. One of the most important nonoxide ceramic is SiC. In order of increasing fracture toughness and thermal shock resistance SiC ceramics reinforced with TiC were studied. Additionally, it was found that the corrosion resistance of SiC-TiC ceramics increases with increasing TiC content. For composite powder processing, gas phase routes (CVD, laser and plasma processing) have used often. The thermal plasma route provides improved chemical homogeneity, control over stoichiometry, and purity. It is important to note that thermal plasma synthesis offers the potential for mass production. Furthermore, in rf induction torches, the absence of electrodes allows the use of cheap but corrosive starting materials like chlorides.

Thus in this paper first result on the plasmachemical preparation of nanocrystalline SiC and TiC as well as SiC-TiC composites from $SiCl_4$ and $TiCl_4$ are reported.

2. EXPERIMENTAL PROCEDURE

A homemade r.f. induction plasma of standard design, the geometry and dimensions of which has been previously described [1], was used. But in the present work, the torch was powered by a 60 kW, 4 MHz generator. Briefly, the magnetic field is provided by a three turned copper coil of 60 mm i.d., the plasma confinement tube of 46 mm i.d. is made of quartz and cooled by compressed air. The reactants $SiCl_4$, $TiCl_4$ as well as $SiCl_4/TiCl_4$ mixtures were fed by a peristaltic displacement pump into a stainless steel heating system, evaporated at 200 °C, diluted with the H_2-carrier gas heated to the same temperature, and injected immediately into the plasma tail. The injection distance in regard to the last turn for the chlorides and C_2H_4 was 80 and 110 mm, respectively. The operating conditions are given in Table 1.

Table 1: Operating conditions

power supply	N, f	30 kW, 4 MHz
central gas	H_2	10 slm
swirl gas	Ar	80 slm
carrier gas	H_2	5 slm
quenching gas	H_2 / Ar	110 slm
run 1	$SiCl_4$ C_2H_4	5 - 25 g/min 0.5 - 3 slm
run 2	$TiCl_4$ C_2H_4	10 - 20 g/min 1 - 2 slm
run 3	$SiCl_4 + TiCl_4$ C_2H_4	5 - 20 g/min 1 - 2 slm

Continuously efficient collecting, without destroying the unique characteristics of plasma generated powders, is not simple. An inert powder handling is necessary often because (amorphous) powders, especially nitrides, tend to oxydize very rapid and some times plasma powders are extremely pyrophoric (metal powders). An electrical filter like the electrostatic fume precipitation in industrial plants was tested. The basic idea is charging and separating the particles by a negative wire corona. The collecting electrode (on earth) consist of a hohned stainless steel tube 1,7 m in length and 80 mm i.d. in the axis of which a 0.25 mm diameter stainless steel wire is tightened by a weight, negative high voltages was 1...40 kV and 1 - 5 mA. Till now, test conditiones were: gas feed rate 3 - 13 m^3/h, gas temperature 100 - 250 °C, gas velocity 0.2 - 0.8 m/s, residence time 2 - 9 s, mass flow 25 - 35 g/m^3, and corona current 1 mA.

In the first experiments, inside the tube a growing powder sheath in flow direction was observed. According to operating conditions and powder composition some times the wire was surroundet with powder too. If that powder sheath has reached the filter exit, more and more powder leaves the filter and the voltages, at the beginning of about 20 kV at 1 mA, breaks down to 1 - 5 kV, some times sparks occur. Only few milligrams have fallen down into the bunker where as the rest sticked fast to the electrodes. Optimization of the filter is under investigation.

3. RESULTS AND DISCUSSION

3.1. SiC powders

Plasmachemical production of nanoscale SiC powders has been reported by several workers [2, 3, 4]. From these results it is obviously that plasma SiC is suitable for ceramic processing. In experiments of run 1 maximum powder yield was about 300 g/h. The C/Si ratio has been changed from 0.7 to 4.0 , the H/C ratio of the reacting system was in the range of 10 to 30. Hydrogen in excess acts three fold: raising plasma temperature, reducing free carbon, and improving carbides formation. In all cases SiC was synthesized, but if understoichiometric carbon was used Si appears in the X-ray diffraction pattern, where as at C/Si ratios greater 1.8 crystalline forms of carbon occur allways. According to EDX, IR and XPD proper SiC powders were obtained with C/Si ratios of 1.3 to 1.8, here the carbon content in the powders nearly corresponds to the theoretical value for SiC. The oxygen content is about 3 wt%, some times less; chlorine portion is allways lower than 0.1 wt%. From SEM investigations mean particles size ranges from 20 to 50 nm.

The SiC powders preparated are highly crystallized, crystallisation degree varies in the range of 30 - 70 % according to reaction route, crystallite size is around 15 nm. All reaction routes of run 1 result in β-SiC as main phase (Fig. 1). Some times, week, broad signals at 2 θ around 25.6 degr. appear in X-ray diffraction pattern. In agreement with that, HREM images schows filament like carbon fibres with d values of 0.33 - 0.35 nm. Additionally, at small angle side of the sharp peak of plane (111) a small diffuse peak is observed, steeply rising from small angle side and a tail towards larger angles, and at the large angel side of the (111) peak a broad tail occurs. Both is explained by overlapping signals of α-SiC (peak of plane (101)), stacking faults, highly disordered polytypes of β-SiC, and not resolved signals of α-SiC peak of plane (103), respectively. Hexagonal SiC was identified by CBED and HREM measuring d values of 0.235 nm. In all HREM micrographs of both α-SiC and β-SiC ($d \sim 0.25$ nm) the crystals are surrounded by an amorphous layer

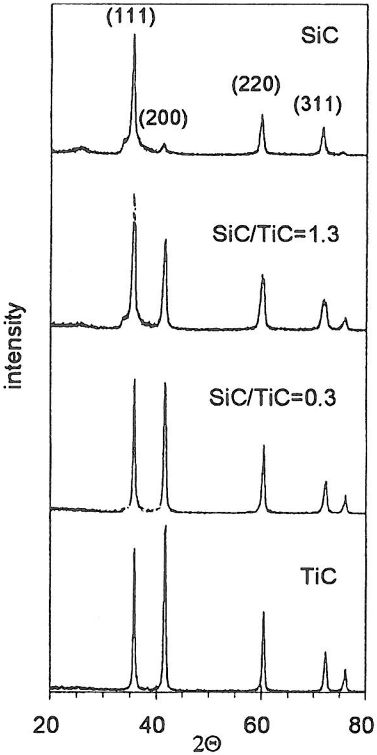

Fig.1: X-ray diffractograms of nanoscale SiC, TiC, and SiC-TiC composites

assumed to be characteristically for plasma generated crystalls. In TEM (Fig. 2) and HREM cubic SiC appears mostly as irregularly shaped SiC-agglomerates of 40 - 100 nm, few crystals of 0.2 μm were found also. The marked streaks caused by stacking faults and/or disordered cubic polytypes are assumed to be typically for plasma β-SiC.

It should be noted that the formation of α-SiC may be important for sintering because a more homogeneous texture and a higher fracture toughness due to traces of α-SiC were observed.

3.2. TiC powders

TiC powders have been preparated also in a variety of thermal plasmas using different titanum sources like Ti, TiO_2 and $TiCl_4$ [5, 6, 7, 8]. Referring to SiC-TiC production it was of great interest to compare the properties of composite components fabricated under the same reaction conditions. Independent on different reaction routes of runs 2 (maximum powder yield about 300 g/h) a high crystalline (about 90%) TiC was observed allways, what is quite different from SiC formation. Like SiC, proper TiC was produced with C/Ti ratios in the range of 1.3 to 1.8, the carbon content in the powders determind by EDX varies between 20.5 and 19.2 wt%. That is in good agreement with chemical analysis according to which the content of free carbon is less than 1 wt%. The oxygen content in the TiC powders is in the same range to that of SiC, but chlorine content is an order of magnitude higher (about 3 wt%). The chlorine can be removed by heating at temperatures less than 1000 °C. It is assumed that the high chlorine content arrises from adsorbed HCl or partially dissociated $TiCl_4$. Particle size distribution of TiC powders by SEM is some what narrow shaped compared with that of SiC ones resulting in mean particles sizes of 15 - 30 nm. Crystallite size from XPD gives values of 30 nm, e.g. under the same reaction conditiones the crystallite size of TiC is about double the size of SiC ones. TEM (Fig. 2) and HREM photographs show high symmetrical TiC single crystals with 4 or 6 fold forms of 15 - 100 nm, all crystals are also surrounded by an amorphous layer too and the calculated d value is 0.25 nm like SiC. From EELS investigations it is concluded, that most of the TiC is stoichiometric, but some unstoichiometric forms as Ti_2C, Ti_2C_3 and Ti_5C_2 could be detected. TiO_2 was not detectable neither by EELS nor XPD and IR.

3.3. SiC-TiC composites

All reactions of run 3 result in SiC-TiC composites, the content of main elements is given in Table 2. The composite powders are soft, fluffy and black, like their components. Mean particle size varies in the range of 10 - 50 nm, all particles are mostly smaller than 100 nm. Some exceptions may be due to large SiC crystals. Oxygen content of the composites is always less than 5 wt%. According to the (Si + Ti)/C ratio, free carbon amounts to 5...10 wt%. Chlorine impurities of about 1 wt% can be removed by heating in hydrogen atmosphere. SEM indicates the produced powders to be a homogeneous mixture of the SiC and TiC components described above. Neither Ti_XSi_Y nor $Ti_XS_YC_Z$ were detectable by EELS and XPD.

Table 2: Composite composition according to EDX

ratios of precursors (wt%)		main components / wt%		
$SiCl_4$ / $TiCl_4$	(Si + Ti) / C	Si	Ti	C
0.8 - 4.5	1.8 - 5.7	20 - 45	15 - 75	20 - 45

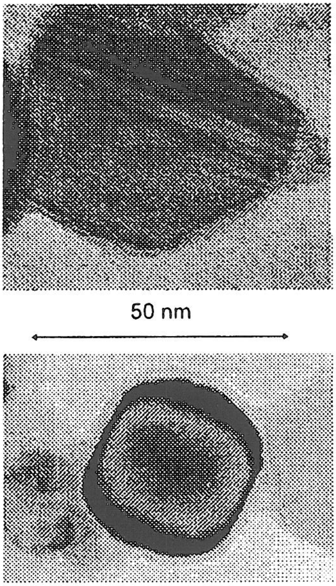

Fig. 2: TEM photographs of typic β-SiC (at the top) and TiC crystals.

Contrary to SiC-Si_3N_4 composites [1], in SiC-TiC powders the composition can not be evaluated from the bonds of the main components by IR. Where as in the IR spectra of plasma-SiC a sharp well defined band in the range of 870 - 890 cm^{-1} appears, TiC causes only very week signals (1/10 or less of that from SiC) and broad not well defined bands over the range of 900 to 500 cm^{-1}. Consequently band position and shape of the composites are very close to that of SiC, allowing for rough estimation of the Si-C bonds concerned to indicate the SiC portion in the powder only.

Total composite composition was calculated from element composition by EDX, but some assumption had to be done. The values in Fig. 3 were estimated assuming that all Ti forms stoichiometric TiC and O_2 is bond as SiO_2. The crystalline composition of SiC-TiC powders is computed from X-ray diffraction pattern using the intensity ratios of the peaks of plane (111) and

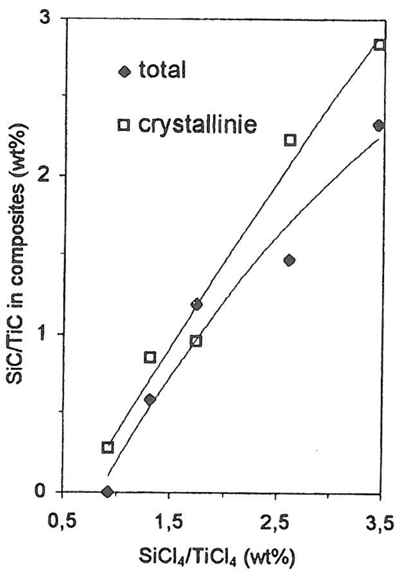

Fig.3: SiC-TiC composite composition in dependence on starting mixtures, (Si+Ti)/C=0.8

(200) after calibration with Powder Diffraction File and mixtures of TiC and SiC produced under the same plasma and feeding conditions. This procedure becomes necessary because in the diffraction pattern the peaks of TiC and SiC were not resolved. Both monocarbides crystallize in a cubic form of the zinc blende typ and their lattice parameters are very close. Additionally, in X-ray analysis there is a peak broadening caused by the fine crystal size and amorphous components.

The crystalline SiC/TiC ratio in composites, calculated in that manner is compaired with the total ones by EDX in Fig. 3; from which it is obviously, that SiC-TiC composite powders can be produced in all compositions of interest in regard to ceramic processing. According to powder composition the specific surface area of composites is in the range of 38 - 45 m^2/g by BET, in good agreement with mean particle size assuming spheres. According to that, the highly crystallized powders should be easily sinterable.

4. REFERENCES

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5. ACKNOWLEDGEMENTS

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