RF induction plasma synthesis of Si_3N_4-SiC composite powders from different silanes and silane mixtures

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ABSTRACT

Nanoscale Si_3N_4-SiC composite particles in the range below 100 nm were synthesized by an RF induction plasma. Systems of silane, different chlorinated and/or methylated silanes as well as silane mixtures in combination with ammonia and a hydrocarbon (C_2H_4) have been studied. The composition of composite powders changed with both the reactant mixture and the chemical nature of the Si-carrier, so the carbon and nitrogen content of the powder could be controlled in a wide range. The as produced powders consist of intimately mixed Si, C, and N atoms, the crystalline phases are of β-SiC structure and some times Si. Heat treatments result additionally in α-Si_3N_4 structure.

1. INTRODUCTION

The major advances in nanoparticle derived ceramics may arise from the large grain boundary volume. A contemporaneous discovery with new properties was the superplastic deformability of these fine grain structures. Superplastic deformation rates in fine grain size materials are proportional in the inverse square or cubic of grain size. Thus, a reduction in grain size to 10 - 20 nm would yield strain rates for direct plastic forming of ceramics in a manner akin to metals. At Osaka University, Niihara and co-worker have shown that when the nanoscale is retained, nanocomposites of metaloxides-SiC and Si_3N_4-SiC have superior mechanical properties relative to their coarser grained counterparts as well as the single phase materials [1].

In many technical systems, components with excellent mechanical properties and corrosion resistance at high temperatures are needed. One of the most promising nonoxide structural ceramic for these applications is Si_3N_4 reinforced by SiC.

So, economical production of such nanoscale, complex shaped composite powders become more and more important. One of the promising techniques is the thermal plasma route. The induction plasma torch offers a large plasma volume which

provides sufficient residence time for complete reactions at high yields. Some researches have worked on plasma processing to fabricate Si_3N_4-SiC composite powders [2-5]. From their results, it is clear that the process needs to be improved in starting materials, reactive flow rate, and in powder structure obtained.

The paper reports our continued studies in preparation of nanoscale Si_3N_4-SiC composites by an RF induction torch.

2. EXPERIMENTAL

The composite powders were produced by vapor phase reactions at atmospheric pressure in an Ar/H_2 RF induction plasma generated by plate power of 3.9kW and frequency of 3.8 MHz. The plasma torch of standard design previously described in detail [6] was used without any remarkable changes. The reactants $SiCl_4$, $Si(CH_3)_4$, SiH_4, $SiCl_3CH_3$ as well as C_2H_4 and NH_3 were injected radial into the tail flame 75, 105 and 120 mm respectively, downstream the three turned induction coil. Three types of experiments were performed: Combination of methylated silanes and ammonia without any additional carbon donator (run 1 and 2); mixtures of nonmethylated silanes, ammonia, and C_2H_4 as carbon donator (run 3 and 4); and mixtures of unchlorinated silanes (run 5) as well as chlorinated silanes (run 6) plus ammonia, in each case the methyl groups of one silane component act as carbon donator. Reaction parameters are listened in Table 1. Mass flow controller checked all gas feeding rates. A tube pump drove the liquid silanes into an oven, after evaporation and

Table 1: Reaction systems for Si_3N_4-SiC composite synthesis

run	starting system		molar mixtures		
	reactants	feed rates	N / C	N / Si	C / Si
1	$Si(CH_3)_4$ NH_3	0.25 - 4.5 mol/h 300 - 900 l/h	3 - 40	3 - 150	4
2	$SiCl_3CH_3$ NH_3	0.2 - 2.5 mol/h 20 - 600 l/h	0.3 - 50	0.3 - 50	1
3	$SiCl_4$ C_2H_4 NH_3	0.8 - 4.5 mol/h 15 - 240 l/h 300 - 900 l/h	1.5 - 30	8 - 20	0.3 - 5
4	SiH_4 C_2H_4 NH_3	0.9 - 3 mol/h 15 - 240 l/h 60 - 900 l/h	3 - 30	3 - 30	1.2
5	3 SiH_4 + $Si(CH_3)_4$ NH_3	0.9 mol/h 60 - 600 l/h	3 - 30	3 - 30	1.2
6	$SiCl_4$ + $SiCl_3CH_3$ NH_3	0.8 - 3.5 mol/h 60 - 900 l/h	1.5 - 60	0.8 - 30	0.5

dilution with H_2 that mixture was fed into the reaction zone of about 4000 K. SiH_4 was injected as commercial mixture of 5% SiH_4 in Ar. The reacting system is quenched by adding cold gases in the converging nozzle at the exit of reaction zone. This results in accelerating the gas flow simultaneously the temperature drops. Measured and calculated cooling rates are in the order of 10^6 K/s or more. Such high quenching rates favour the formation of nanoscale particles in a narrow size range.

The fabricated composites were collected in a stainless steel filter having pores of 5 µm. Standard powder characterization techniques applied were FT-IR, XPD, SEM and EDX. In the case of chlorinated silanes, analysis were performed on powders from which the by-product NH_4Cl (20 - 80 wt% in as produced powders) was removed by heat treatment (4 hrs, 900 °C, Ar atmosphere).

3. RESULTS AND DISCUSSION

According to IR and EDX investigations, in all runs Si_3N_4-SiC composite powders were produced. The element distribution in the composites is summarized in Table 2. As indicated earlier [6] the oxygen content in nanoscale plasma powders correlates with the portion of amorphous phases. Different reaction routes result in different composite composition (Fig. 1). Rising N/C ratios in the starting system cause rising N/C ratios in the composites. But this is not the only decisive factor, additional the N/C ratio in the composites is strongly determined by the chemical nature of the Si-carrier. Combination of Table 2, Fig. 1 and 2 clearly demonstrates the production of Si_3N_4-SiC composites in all compositions of interest.

Table 2: Composite composition (wt %)

run	Si	C	N	O
1	60 - 64	23 - 32	1 - 10	3 - 5
2	58 - 65	10 - 25	12 - 32	1 - 5
3	35 - 60	2.5 - 10	25 - 45	1.5 - 10
4	80 - 85	5 - 8	2 - 10	2 - 5
5	75 - 85	8 - 12	2 - 10	2 - 5
6	30 - 62	3 - 30	20 - 40	3 - 10

Fig. 2 shows SiC portion in dependence on reaction route. The measured content of crystalline SiC is compared with that calculated SiC portion, which is maximum possible in the composites. The last was obtained by assuming that all carbon detected by EDX forms SiC. Both different kinds of SiC determination agree very well in tendency, and from the differences of the corresponding values it can be concluded, that the SiC portion in the composites is crystallized in a high degree. Furthermore it can be clearly seen in Fig. 2 that the higher the C/Si ratio in the precursor the higher the SiC content in the composites, in very good agreement with IR-spectra [7].

Preformed Si-C bonds in methylated silanes results in composites with high C content. Accordingly, the colour of these composites varies from light grey (run 2) to

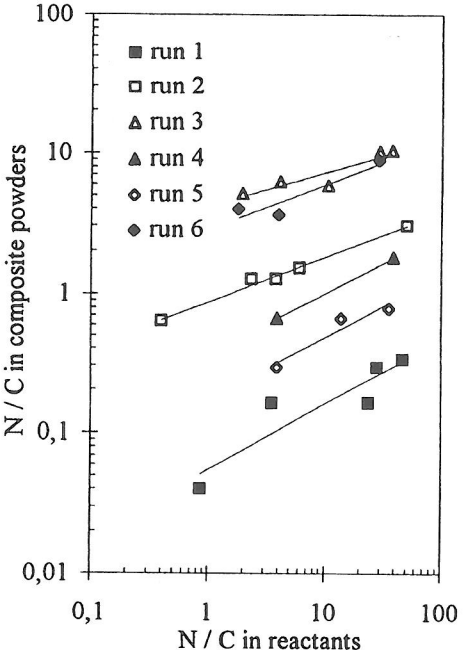

Fig.1: Composite powder composition in dependence on starting mixtures and reaction route

dark grey (run 1). Neither pregraphitic structures nor any forms of crystalline Si_3N_4 are detectable by XPD, the only crystalline component in the composites is SiC. In the case of run 1 β-SiC could be identified only, where as in the XPD pattern arising from run 2 signals of α-SiC and highly disordered polytypes of β-SiC occur additionally. Crystallite size in these composites amounts to 10 - 20 nm, where as in the composites from run 1 the crystallite size is very small, about 3 - 4 nm. Mean particle size determined by SEM is in the order of 10 - 25 nm for both runs.

Composites generated from run 3 appear dirty white till light grey coloured. Small amounts of β-SiC occur in the XPD pattern. Only in the case of nitrogen in high excess, traces of α-Si_3N_4 could be detected, but composites containing both crystalline Si_3N_4 and SiC were not observed. In general, the powders were amorphous to a high degree always. Mean particle diameter estimated by SEM of around 100 nm seems to be very large. It is assumed that these values arise either from agglomerates (not resolved by SEM) or from polymers (in agreement with the low Si content).

SiH_4 as precursor (run 4) results in yellow-brown composite powders. In XPD diffractograms peaks of Si (crystallite size 10 - 15 nm) and little amounts β-SiC (crystallite size about 8 nm) occurred. Crystalline Si_3N_4 was not observed in the as produced composites. Contrary to run 3, in composites produced from run 4 the content of crystallized particles is clearly higher.

Si_3N_4-SiC composite production was investigated from two types of silane mixtures, the chlorine free system SiH_4 + $Si(CH_3)_4$ (run 5) and mixtures of chlorinated silanes $SiCl_4$ + $SiCl_3CH_3$ (run 6). Composites obtained from run 5 are very similar to that ones from run 4 in regard to colour and crystal phases. Only the crystallite size of β-SiC is some what smaller (about 5 nm). But the N/C ratio as well as the Si portion in the composite (Fig. 2) is clearly smaller than in the composites generated from SiH_4 as unique Si-carrier. This indicates an improved SiC formation caused by the $Si(CH_3)_4$ component in agreement with its favoured SiC production (Fig. 1).

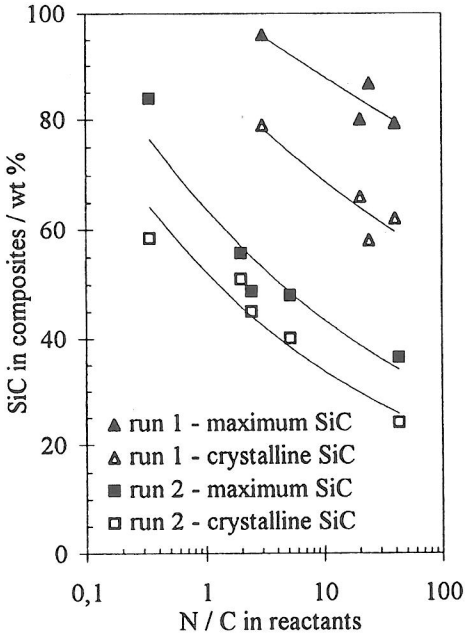

Fig.2: Comparision of the crystalline and maximum possible SiC in composite particles produced from methylated silanes.

Mixtures of chlorinated silanes and NH_3 (run 6) result in light grey composites. The only crystalline component is β-SiC. Crystallinity varies in the range of 1 - 25% in dependence on flow rate, lower flow rate results in higher crystallinity.

It is generally noticed, that composites fabricated from SiH_4 (runs 4 and 5) contain a relative high amount of crystalline Si. For nitridation of Si, the as synthesized powders from runs 4 and 5 were heat treated for 4 hrs at 1400 °C under flowing nitrogen, typical results are summarized in Table 3. It should be mentioned, that annealing in nitrogen results in a marked compositional change, i.e. increasing N and decreasing Si where as C remains nearly constant. A nearly complete conversion of Si to α-Si_3N_4 could be achieved under the given heating conditions accompanied by increasing weights of 15 - 30 %; β-Si_3N_4 was not obtained. But the lattice constant of α-Si_3N_4 in annealed composites is different from that of pure α-Si_3N_4, assumed to be caused by C incorporation. XPD pattern in Fig. 3 are typically for the annealing procedure of run 5.

Table 3: Effect of annealing (1400°C, N_2, 4h) on composite powder composition

powder processing			element content (wt %)				crystalline phases
run	N / C	procedure	Si	C	N	O	
4	3	as produced	80.0	5.4	9.6	5.0	Si, β-SiC
		annealed	63.4	5.0	30.4	1.2	α-Si_3N_4
5	3	as produced	85.5	8.6	2.5	3.4	Si, β-SiC
		annealed	63.6	13.5	20.1	2.7	α-Si_3N_4, β-SiC
5	30	as produced	76.3	10.7	8.4	4.6	Si, β-SiC
		annealed	66.7	10.6	20.2	2.5	α-Si_3N_4, β-SiC

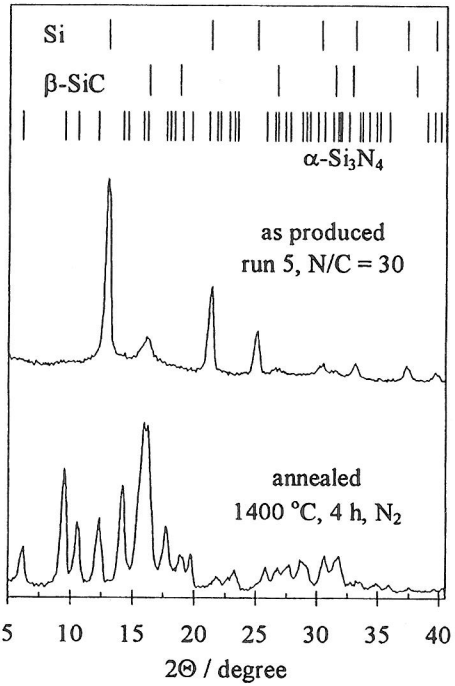

Fig.3: XRD pattern of as produced and annealed composite powders.

In all XPD pattern of as produced composites, SiC peaks are shifted in relation to pure SiC also. At the present stages it seems most likely that the direction of shifting depends on reaction route (C/N ratio as well as kind of silicon carrier) and/or reaction conditions (flow rates). Never the less, the shift shows the change in lattice constant suggesting that the crystal structure in the composite powder is different from that in pure SiC powder. That agrees very well with analytical TEM investigations according to which SiC_XN_Y crystals were traceable. Doubtless, the SiC phase in the composite powders contains nitrogen and it was proposed [8], that the N atoms were tetrahedral surrounded by four Si atoms in β-SiC crystallites. All analytical investigations indicate an intimate mixing of Si, C, and N atoms in the particles of the Si_3N_4-SiC composite powders.

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5. ACKNOWLEDGEMENTS

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