Journal of the European Ceramic Society 17 (1997) 373–376
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0955-2219/97/$17.00
PII: S0955-2219(96)00106-9

Electrophoretic Forming of Silicon Carbide Ceramics

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(Received 15 September 1995; accepted 10 June 1996)

Abstract

Electrophoresis is the movement of particles suspended in a liquid under influence of an electric field. Electrophoretic forming of silicon carbide (SiC) requires the simultaneous deposition of SiC and sintering aids such as carbon and boron. The incorporation of the sintering additives was studied in two ways: co-deposition of a boron-containing SiC powder and carbon black, as well as the co-deposition of SiC, boron carbide and carbon black. A high final density after sintering (>95%) was obtained with the two approaches. © 1996 Elsevier Science Limited.

Introduction

Silicon carbide (SiC) has strong potential for use as tubes for heat exchangers and other high-temperature structural applications. It has a low density, good strength retention at high temperatures and excellent oxidation resistance.

Electrophoretic deposition of ceramic powders has been given quite some attention as a forming route for ceramics during the last decade.[1–4] It combines the advantages of a wet processing route, with the ease of production of complex shapes in a short time. The process consists of applying an electric field to a suspension of a ceramic powder in a liquid. Due to charge redistribution between the liquid and the solid phase, the particles carry a charge and therefore move and deposit under the influence of the electric field.

Electrophoretic forming of SiC, however, requires the simultaneous deposition of silicon carbide and sintering aids, since the high amount of covalent binding in SiC makes it impossible to obtain high densities using a normal sintering process if no sintering additives are present. Most processing of SiC is done by incorporation of boron and carbon,[5–7] although high densities have been achieved in the presence of oxides[8] and with the combination of aluminium and carbon.[9]

The first part of this work describes the simultaneous deposition of a boron-containing silicon carbide powder and carbon black, whereas a second part deals with the co-deposition of SiC, boron carbide and carbon black.

Experimental Procedure

The co-deposition of a boron-containing SiC and carbon black requires a medium in which both SiC and the carbon black are similarly charged. Since both powders can be expected to have an acid surface, a basic medium was used consisting of a mixture of acetone and n-butylamine. Acetone is basic by itself, but the addition of the amine reinforces the basic behaviour of the medium. Hence the particle charge is negative. The amine concentration was adapted so that a good stability was obtained.

Suspensions with varying carbon black and SiC concentrations in a mixture of n-butylamine (10 vol%) and acetone were prepared, and deposits formed by applying an electric field of 103 V cm^{-1} for 5 min. Polyvinylbutyral (10 g l^{-1}) was added to the suspensions to increase the green strength of the deposits. The deposits were dried, removed from the electrode and subsequently heated to 800°C in air to determine the carbon content (loss on ignition[10]). In order to account for oxidation of the silicon carbide, a deposit from a suspension with no carbon black was submitted to the same treatment.

Table 1. Loss on ignition and free carbon incorporation from carbon black as estimated from the loss on ignition data after correction for the oxidation of SiC

Carbon black concentration in suspension (wt%)	*Loss on ignition (wt%)*	*Free carbon from carbon black incorporation (wt%)*
0	−2·1 ± 0·3	0 ± 0·3
3	0·3 ± 0·2	2·4 ± 0·2
6	3·0 ± 0·1	5·1 ± 0·1
9	5·7 ± 0·2	7·8 ± 0·2

Another series of the same suspensions was prepared for deposition of samples for sintering tests; After drying and removing of the electrodes, the samples were pyrolysed under a nitrogen flow (1 h, 650°C) to remove the binder and sintered under argon (0·1 MPa) at 2050°C for 30 min.

Co-deposition of SiC, carbon black and boron carbide is possible from butanol with addition of polyvinylpyrrolidone (PVP). Suspensions with varying concentrations of the three powders involved were prepared and samples for sintering test obtained by deposition at 672 V cm^{-1}. After drying, the samples were burned out under argon at 450°C for 30 min, followed by sintering under argon at 2050°C for 30 min.

The green and final densities were determined by Archimedes' displacement method in water. The samples were lacquered with a lacquer with known density to prevent penetration of the water.

Results and Discussion

System 1

With too little or too much n-butylamine, the suspensions were unstable, resulting in the rapid formation of a sediment. Concentrations above 5 and below 15 vol% of n-butylamine in acetone gave reasonable-to-good stability, so that it was decided to use 10 vol% of n-butylamine.

The results from the loss on ignition test (Table 1) show that a correction of the loss on ignition data is appropriate: samples with no extra carbon incorporation gain weight during the treatment. This weight gain can be attributed to oxidation of silicon carbide. With the assumption that all increase in weight comes from the reaction:

$$SiC + 2O_2 = SiO_2 + CO_2 \qquad (1)$$

the formation of only 0·07 wt% (0·04 mol%) of SiO_2 can explain the observed weight increase. After correction of the data for SiC oxidation, the free carbon incorporation is almost equal to the carbon black concentration in suspension, indicating that both powders deposit with an equivalent deposition rate (Fig. 1).

The final density shows a maximum around 1·5 wt% of carbon black in suspension (Fig. 2). Taking into account that the silicon carbide powder itself contains 1·81 wt% of free carbon, 1·5 wt% of carbon black in suspension corresponds to a free carbon content of 3 wt%.

The role of carbon as a sintering additive is still under debate.[11] There have been suggestions that carbon could create silicon vacancies and increase the diffusion rate,[12] but most arguments suggest that the primary role of carbon is to reduce the native oxide layer on the SiC particles. It seems especially important that enough free carbon is present to prevent the oxide layer being reduced by the silicon carbide itself.

The overall reaction can be written as:

$$SiO_2 + 3C = SiC + 2CO \qquad (2)$$

Hence, stoichiometrically, 3/2 mole of carbon is necessary for every mole of oxygen. The SiC powder used contains typically 0·8 wt% of oxygen and therefore 1·20 wt% of free carbon would be enough to reduce all native oxide to SiC. This SiC powder is developed for direct use without the addition of sintering aid and therefore contains

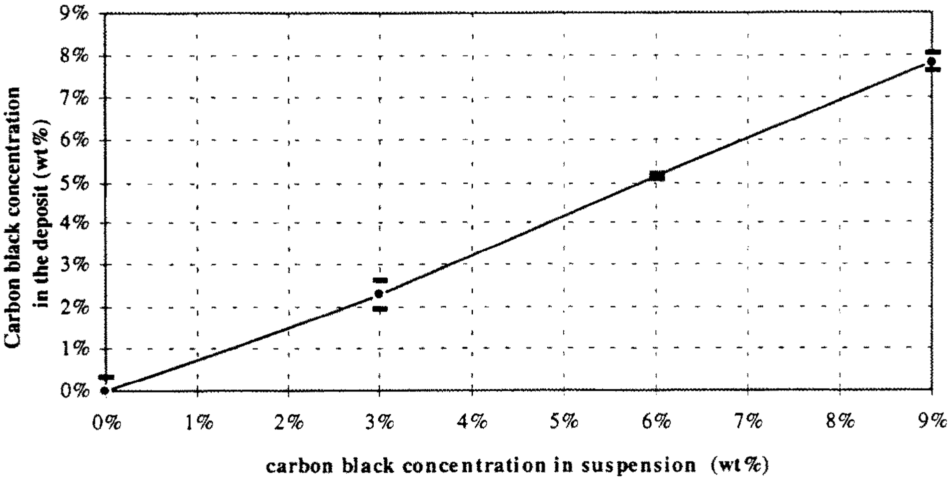

Fig. 1. Carbon black concentration in the deposits as a function of the carbon black concentration in suspension.

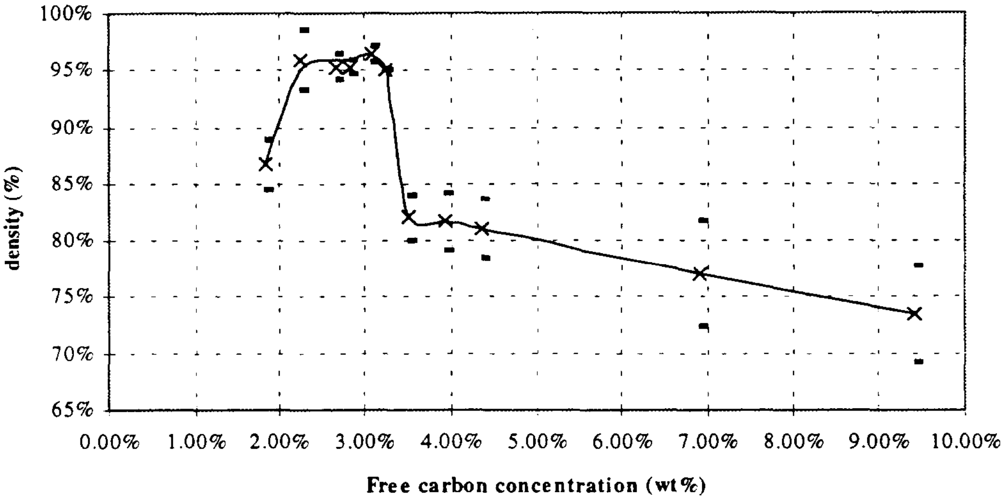

Fig. 2. Density after sintering at 2050°C (30 min) as a function of the free carbon concentration of the deposits.

typically 1·20 wt% of free carbon. Analysis of the batch used in our experiments revealed that the oxygen content was only 0·78 wt% with a free carbon content of 1·81 wt%. So, theoretically, the free carbon content should be high enough for sintering. However, it seems necessary to use a certainexcess of free carbon, as is frequently encountered in the literature.

System 2

The suspensions of SiC, carbon black and boron carbide in butanol with PVP are stable and deposition occurs on the anode, meaning that the particles are negatively charged.

The incorporation of boron carbide and carbon black as a function of the suspension concentration was not determined, but the sintering results show that co-deposition occurs. Whereas the final density is around 50% of the theoretical value for suspensions with only carbon black or only boron carbide present as sintering aid, which is equal to the density obtained from suspensions with only the SiC powder, the final density increases to an average value of 90% when both additives are added to the suspension (Fig. 3).

Further tests showed that 1 wt% of boron carbide was enough to obtain a high density, and that 3 wt% of carbon black is necessary (Table 2). The maximum density obtained was 96%.

Conclusions

The electrophoretic deposition of SiC is possible and a high density is possible by simultaneous deposition

Table 2. Density after sintering for deposits from suspensions with carbon black and boron carbide concentrations as indicated

B_4C concentration (wt% of solids)	*Carbon black concentration (wt% of solids)*	*Average final density (% of theoretical density of SiC)*
1	1	86
1	3	96
10	3	90

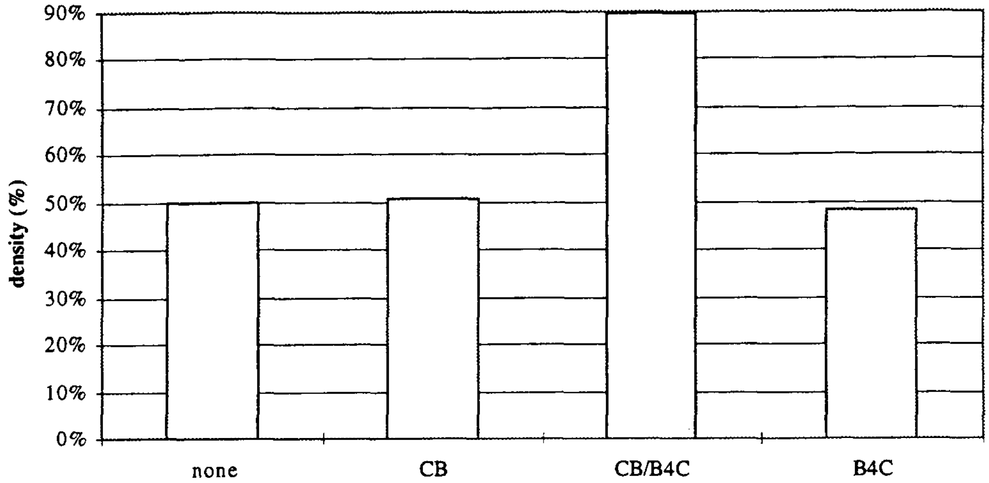

Fig. 3. Average density after sintering for four types of deposits: (none), only SiC in the suspension; (CB), SiC and carbon black in the suspension; (B4C), SiC and boron carbide in the suspension; (CB/B4C), SiC, boron carbide and carbon black in the suspension.

of a silicon carbide powder and sintering aids (boron and carbon)

Boron can be incorporated by using a boron-containing powder or co-deposition of a boron carbide powder.

The lower density obtained at high carbon black concentration indicates that a too high a carbon concentration inhibits full densification of the silicon carbide.

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