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Preparation of pressureless-sintered $SiC-Y_2O_3-Al_2O_3$

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Sintering additives were prepared from aluminium hydroxide and yttrium hydroxide. These additives were soluble in water and resulted in a binder. A β-SiC powder was mixed with the additive solution and sintered at 2150° C without pressure. The oxides formed from the additive promoted sintering. The sintered body contained no pores. Aluminium, silicon, and yttrium oxide were precipitated in the sintered body.

1. Introduction

The aim of sintering is to easily and economically produce a shaped body with high strength and toughness, good thermal shock and oxidation resistance, and other dominant properties. These properties depend, slightly or dramatically, on a dispersed second phase. Silicon carbide bodies have not been obtained by pressureless sintering without a sintering aid. The second phase can be formed with an aid, but it does not invariably form. An SiC body with boron and carbon is single phase [1, 2] and shows a strength [3] similar to that of single-crystal SiC [4] at high temperature. Although a primary disadvantage of ceramics is their lack of toughness, the fracture energy of a ceramic can be increased by the second phase [5–8]. The sintering aid plays an important role in changing the ceramic properties.

This paper concerns the pressureless sintering of an SiC body with Y_2O_3 and Al_2O_3. Part of these results were reported previously [9]. A generally approved sintering process begins by mixing an SiC powder and a sintering-aid powder. Sintering should take place after the SiC surface has reacted with the aid. In special instances, if the reaction is lengthy, a sintered body might not be obtained in an ordinary time span, but if the SiC powder is covered with the sintering aid, the reaction proceeds rather rapidly and uniformly. In the present investigation, Al_2O_3 and Y_2O_3 were transformed into water-soluble additives, A and Y. When the SiC powder was mixed with the additive solution, it became coated with the additive, which left an oxide film on the surface of the powder after firing. Moreover, the additives made a viscous solution. Green bodies moulded from the SiC powder and the additive solution were strengthened by the binding force of the additive without organic polymers. The additive thus played the role of both sintering and moulding aid.

2. Experimental procedure

A sintering additive (additive A) was synthesized from $Al[iso\text{-}OCH(CH_3)_2]_3$ (Wako Chemicals Industries Co., Shudo, Higashiku, Osaka, Japan) which was reagent grade, because aluminium oxide does not dissolve in acids. Aluminium isopropoxide (30 g) was dissolved in 120 ml benzene; 200 ml 1 N HCl solution was added to this solution. The reaction mixture was stirred for 4 h at room temperature; the aqueous and benzene layers were then separated. Evaporation of the aqueous solution yielded a light yellow residue, which was vacuum-dried and produced 20 g of additive A. Another additive (additive Y) was prepared from Y_2O_3 (Nippon Yttrium Co. Ltd, Shimorenjaku, Mitaka, Tokyo, Japan). Yttrium oxide (9 g) was dissolved in 180 ml of 2 N HCl; when 30 ml ammonia solution was added, $Y(OH)_3$ precipitated. This product was filtered and washed with distilled water several times. The washed hydroxide was reacted with 260 ml HCOOH solution (pH 2). The reaction mixture was stirred for 6 h at room temperature and evaporated under reduced pressure, leaving a white residue. Vacuum drying of the residue yielded 18.5 g of additive Y. Additives A and Y were dissolved in distilled water and then were mixed with β-SiC powder (Ibiden Co., Ogaki, Gihuken, Japan); average size of 0.28 μm and specific surface area of $17.5\,m^2\,g^{-1}$). The mixture was dried and ground to fractionate the granule size under 150 μm using an agate mortar and pestle. The granule was moistened in a desiccator saturated with water, and then pressed in a steel die at 40 MPa. The pressed sample was heated from room temperature to 500° C at $1.7°\,C\,min^{-1}$ in air, and 500 to 1400° C at $3.3°\,C\,min^{-1}$ in nitrogen to remove volatile materials. Sintering above 1400° C was done in an induction furnace using a graphite crucible with a cap to suppress evaporation of volatile materials. A hole leading to the bottom of the graphite cap allowed the temperature to be measured pyrometically near the sample. The heated samples were fired in two ways: 1400 to 2100° C at $3.3°\,C\,min^{-1}$, at 2100° C for 0.5 h; 1400 to 2050° C at $6.7°\,C\,min^{-1}$, and 2050 to 2150° C at $1.7°\,C\,min^{-1}$.

The bulk density of the green body was calculated from the dimension and weights of bodies heated at 500° C. The bulk density of the fired body was determined by the same method. The bulk density and apparent porosity of the sintered body without pores

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TABLE I Elemental analysis of additive A

Element	Analytical (wt %)	Atomic ratio
Al	18.8	4
Cl	30.4	5
H	4.34	26
O*	46.1	17

*O = 100 − (Al + Cl + H).

TABLE II Elemental analysis of additive Y

Element	Analytical (wt %)	Atomic ratio
Y	36.0	4
C	12.4	10
H	2.62	26
O*	49.0	31

*O = 100 − (Y + C + H).

were obtained by an immersion method using water. Firing shrinkage was determined by measuring the difference in size of bodies heated from 500 to 2100° C. Thermal analyses (TG and DTA) were carried out in a Shinku-Riko TGD-3000. The sample was placed in a platinum crucible and heated at a rate of 3° C min^{-1} in nitrogen. Finely powdered aluminium oxide was used as a reference material. Powder diffraction patterns were obtained for powdered specimens by using a Rigaku X-ray diffractometer DMG-S2 with Cu$K\alpha$ radiation. Sample bars (30 mm × 4 mm × 3 mm) were tested for flexural strength in three-point bending (span 20 mm). The cross-head speed in the Shimazu Autograph tester was 0.5 mm min^{-1}. The electrical resistance of a sample about 30 mm long was measured by the four-probe d.c. method with a constant current of 10 μA at room temperature. A Hitachi S-570 scanning electron microscope was used for observation of the sample.

Elemental analysis for aluminium and yttrium was conducted by absorption spectrophotometry, using xylenol orange and chromazurol S. Hydrogen and carbon contents were determined using an analytic carbon and hydrogen instrument (Yanagimoto MC-2). Chlorine in additive A was converted to hydrogen chloride by combustion of the sample, and titration with mecury (II) nitrate solution.

3. Results

Additive A was synthesized from an Al(iso-$C_3H_7O)_3$ and hydrochloric acid and contained aluminium, chlorine, oxygen and hydrogen. Additive Y was prepared from Y_2O_3 and formic acid and consisted of yttrium, carbon, hydrogen and oxygen. Analytical results for additives A and Y are shown in Tables I and II. The atomic ratio for each element in the tables was calculated from the analytical values. The thermal behaviour of the additives was investigated by differential thermal analysis (DTA) and thermogravimetry (TG) in the temperature range 20 to 900° C, as shown in Figs 1 and 2. Oxide residues of additives A and Y were 37 and 46 wt %, respectively. The DTA and TG curves of Fig. 1 show the thermal decomposition of additive A; adsorbed water vaporized above 120° C. Decomposition and elimination of a hydroxyl group and chlorine took place at 164 and 206° C. Above this temperature, the additive was substantially free of hydrogen and chlorine. An average molecule of additive A, estimated from the raction with HCl and the atomic ratio in Table I, is assumed to contain four aluminium atoms, five chlorine atoms, three oxygen atoms, and five hydroxyl groups. Nine water molecules were adsorbed on additive A. The amount of Al_2O_3 was calculated to be 35 wt %, consistent with the residue of 37 wt %. The atomic ratio in Table II

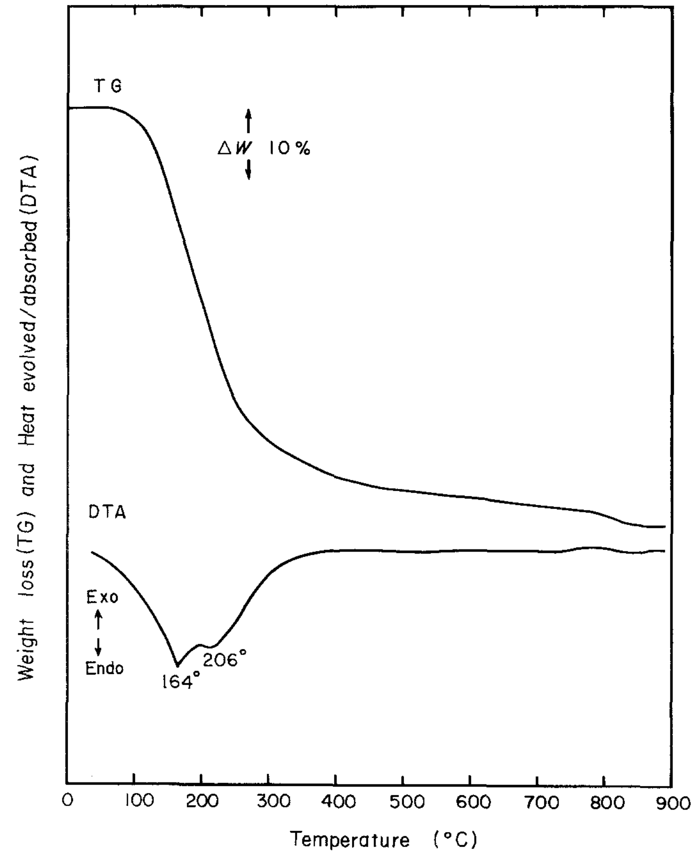

Figure 1 TG and DTA curves of additive A in nitrogen.

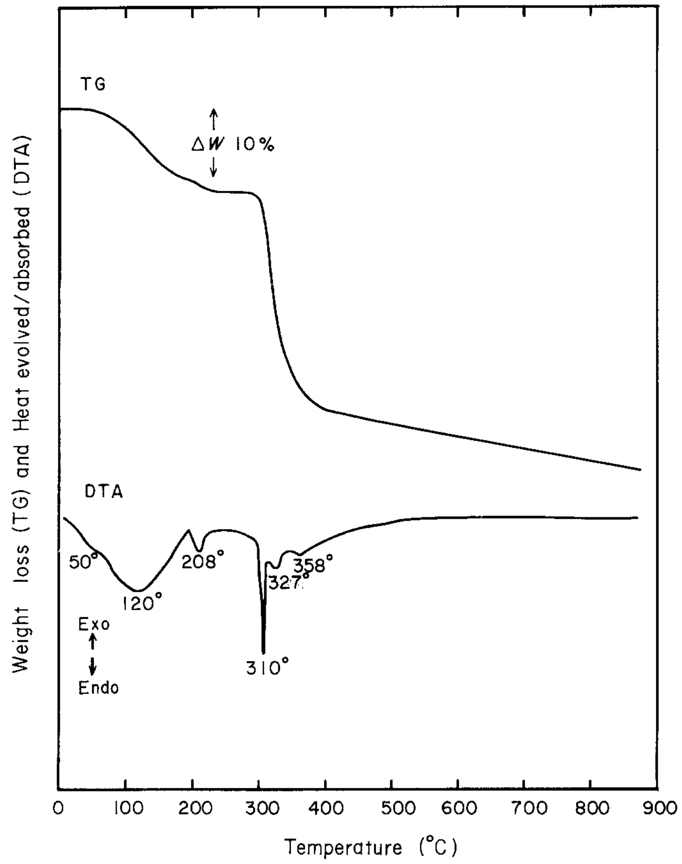

Figure 2 TG and DTA curves of additive Y in nitrogen.

and the reaction with HCOOH suggest that additive Y might consist of four yttrium atoms, four oxygen atoms, six -OOCH groups, and two hydroxyl groups. Four formic acids and eight water molecules were adsorbed on the structure. The amount of yttrium oxide calculated from the formula was 45 wt %, which corresponded to the residue heated at 900° C. The DTA and TG curves of Fig. 2 reveal the elimination of the adsorbed molecules and the decomposition of the hydroxyl and -OOCH group. An endothermic peak at 120° C depended on the vaporization of water and formic acid. The hydroxyl group and the -OOCH group decomposed at 208, 310, 327 and 358° C. Additive Y virtually became the composition of Y_2O_3 above 500° C.

Additives A and Y were water soluble, and the resultant solution was viscous, like an organic polymer. The binding ability of additive A and Y was investigated by consulting the density of green bodies fired at 500° C to remove volatile materials. Fig. 3 is the plot of bulk density against amount of binder prepared from 50 wt % each of additives A and Y. The bulk density was values calculated by subtracting the weight contribution of Al_2O_3 and Y_2O_3 which were formed at 500° C. The green body was bound by the additive binder. Bulk density increased remarkably with a 5 to 15 wt % increase in additives; however, 15 to 20 wt % additives did not produce an increase. When the powders lacked sufficient binder, the green body did not achieve a high density. The body cracked with more than 15 wt % additives, but 10 wt % resulted in a high density and a good working strength of 20 MPa.

The green bodies with 10 wt % additives were fired at 2100° C to examine the sintering capability of the additive. The fired bodies shrank in proportion to their varying bulk densities, as illustrated in Fig. 4. The body produced with additive Y was not sintered, although a small shrinkage was observed. The SiC grain in this body grew as large as that of the powder heated at 2100° C. The shrinkage was explained by the growth. Considerable grain growth took place in the body with additive A, but did not accompany densification. Shrinkage and bulk density increased with the mixing of additive A and Y. A maximum shrinkage value was attained when 40 wt % additive A was mixed with 60 wt % Y. On the other hand, bulk density reached a maximum value with 50 wt % of each

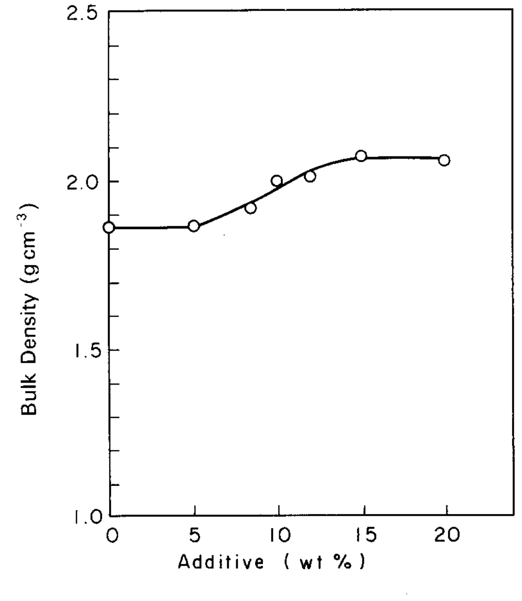

Figure 3 Bulk density of green body fired at 500° C as a function of amount of additive prepared from same weights of additives A and Y.

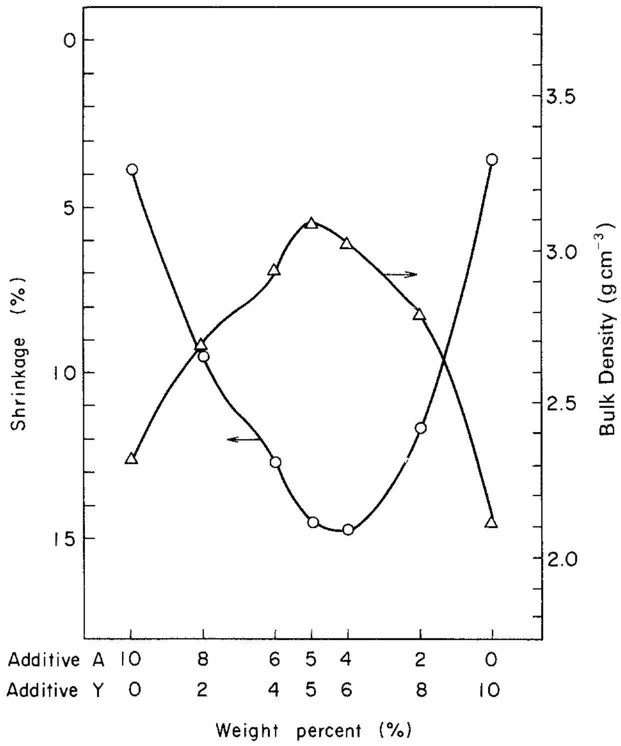

Figure 4 Shrinkage and bulk density as a function of mixing ratio of additives A and Y; 90 wt % SiC and 10 wt % total additives were fired at 2100° C for 0.5 h.

additive. A concrete mixing ratio was not obtained from these results, but an appropriate ratio would be from 40 to 50 wt % additive A. A dense body has not yet been obtained using this amount of additive.

The temperature dependence of sintering was investigated using 5 wt % additive A, 5 wt % additive Y, and 90 wt % β-SiC powder. The shrinkage from 1400 to 1600° C was due to reaction and crystallization of the two additives, and occurred in Si_3N_4 powders with these additives which did not sinter. The sintering began above 1600° C, as shown in Fig. 5. Changes in bulk density and shrinkage show that the sintering stopped at > 2000° C. The optimum additive amount and sintering temperature were derived by further synthetic attempts at synthesis.

A dense body can be prepared at 2150° C by mixing 10 wt % additive A (4.3 wt % Al_2O_3) and 15 wt % additive Y (8.1 wt % Y_2O_3). Because the additive comprises more than 15 wt %, the body tends to crack during sintering due to gas evaporation. Half of the additive was mixed with the SiC powder and heated to 1000° C to remove the gas. The heated mixture was then ground and mixed with the other half of the additive to avoid such cracking. The green body with optimum additive was heated to 2150° C to produce dense SiC. The bulk density was not always an efficient monitor of densification. Because the density of second phases is lower than that of the SiC, it is effective for observing a polished surface. A scanning electron micrograph (SEM) of the dense SiC is shown in Fig. 6. The SiC body constituted an SiC matrix and a dispersed second phase. No pores were found in this body. The SiC matrix was columnar. A white second phase was dispersed among the matrix grains, and did not assume a specific shape. The large size of the white phase was near 50 μm. A second phase under 10 μm was dispersed in the surface area of the body heated at 2000° C. In this case, the surface became dense, but the core was still sintering. Sintering accompanied grain growth.

X-ray diffraction patterns of heated bodies with optimum additive are shown in Fig. 7. The mixture of additives A and Y was 10 and 15 wt %, which corresponds to the composition of $3Y_2O_3$–$5Al_2O_3$ (yttrogarnet). Compounds formed at 1500° C were not identified. Two oxide compounds, yttorgarnet and $Al_2Y_4O_9$ [10], were evident in the range 1600 to 1900° C, and compounds were unidentified which corresponded to diffraction bands (2θ = 32.1, 33.3, 33.7, 44.3). The amount of yttrogarnet was small. Al_2O_3 and Y_2O_3 were not confirmed between 1500 and

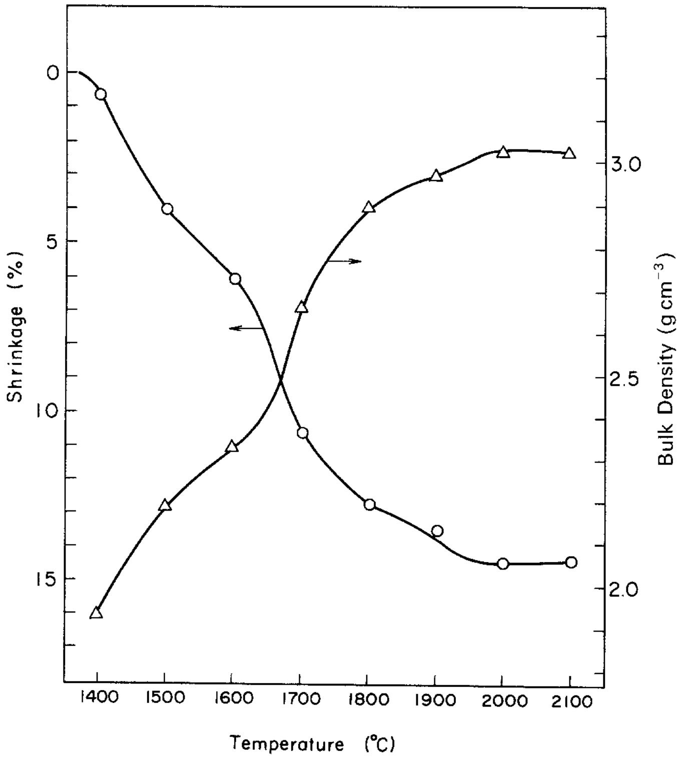

Figure 5 Shrinkage and bulk density as a function of firing temperature; the green body was formed from 90 wt % SiC, 5 wt % additive A and 5 wt % additive Y.

Figure 6 Scanning electron micrograph of a dense SiC body prepared at 2150°C from 75 wt% SiC, 10 wt% additive A (4.3 wt% Al_2O_3) and 15 wt% additive Y (8.1 wt% Y_2O_3).

TABLE III Properties of dense SiC sintered at 2150° C

Property	Observed value
Bulk density	3.11 $g\,cm^{-3}$
Apparent porosity	0%
Flexural strength	470 MPa
Electrical resistivity	$9.7 \times 10^{-3}\,\Omega cm$

2150° C. All compounds formed at > 1900° C decomposed above 2000° C, producing aluminium, silicon and an yttrium compound. Aluminium and silicon were confirmed in the samples prepared at 2000 and 2150° C in Fig. 7. The yttrium compound may be an oxide, but its crystal structure is inconsistent with that of any known yttrium oxide. A diffraction band (2θ = 34.1) of the body sintered at 2150° C, located at the position corresponding to SiC polytypes, disappeared from the oxidized sample. A compound, which was unstable in the presence of oxygen, such as metal, was precipitated, but was not identified. The starting material of β-SiC retained a cubic structure up to 2000° C, but after densification this changed to a hexagonal structure (4H-SiC).

The bulk density, apparent porosity, electrical resistivity, and flexural strength of the dense body are shown in Table III.

4. Discussion

Additive A was prepared from Al(iso-$OC_3H_7)_3$, a compound which dissolves in benzene and ether. As soon as the benzene solution of Al(iso-$OC_3H_7)_3$ came into contact with water, aluminium hydroxide precipitated. The hydroxide reacted immediately with HCl in the HCl solution. Additive Y was also synthesized from yttrium hydroxide. As the hydroxide neither dissolved in water nor produced a viscous solution, it was hard that this was mixed with ceramic powders and strengthened the green body, in comparing the use of additives A and Y. It is assumed that properties of the hydroxide and the additive are characterized by a molecular structure. Most transition metal hydroxides are insoluble, but if the monomolecules of a hydroxide do not bind to each other, the hydroxide should be soluble. The investigation of hydroxide structure was limited exclusively to solid compounds. The idealized structure of $Al(OH)_3$ can be described as a system of octahedral $Al(OH)_6$ coordination groups, each sharing three edges [11]. The sharing structure forms a kind of insoluble polymer. In water the polymer structure may resemble the solid structure. This polymer reacts with acids to produce rather small molecules. Aluminium hydroxide reacts with various amount of acid [12]; alumina sol was prepared by adding a small amount of acid. The sol

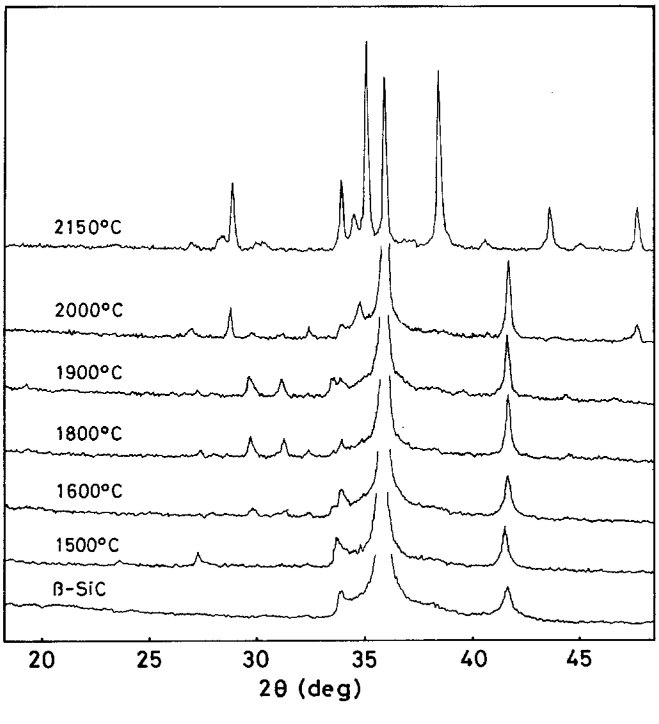

Figure 7 X-ray diffraction patterns. The starting material was β-SiC. 75 wt% SiC, 10 wt% additive A and 15 wt% additive Y were fired at 2150° C and 1500 to 2000° C for 0.5 h.

was not, however, a suitable binding aid. The sol was gelled and pyrolysed to produce a transparent alumina [13] and glasses [14]. Additive A was the product reacted with a rather large amount of acid, and did not have the same properties as the sol. It is assumed that the average molecule of additive A is smaller than that of the sol and relates to the viscosity. The reaction of yttrium hydroxide and HCOOH was not tested for various products. As the amount of HCOOH decreased to less than that of additive Y, yttrium hydroxide remained. These viscous additives tightly bound the SiC powders. The organic binding aid is essential for forming green bodies. Prior to sintering, it is necessary to remove the constituent. This binder-removal process is very time consuming. It was unnecessary to remove the binder of the additives. At the same time, the surface of the powder was uniformly coated with the sintering aid.

A dense SiC body can be synthesized using water-soluble additives A and Y. The addition of only Al_2O_3 resulted in grain growth at 2100° C. The Al_2O_3 was reduced by SiC above 2000° C. Aluminium was effective for grain growth, but not for sintering. Below 2000° C, Al_2O_3 was slowly reduced and remained for some time. The pressureless sintering of SiC was carried out by adding Al_2O_3 and took more than 15 h at 1900 and 2000° C [15]. Yttrium oxide depressed the grain growth, and a combination of Al_2O_3 and Y_2O_3 promoted rapid sintering. $Al_2Y_4O_9$ was the main compound produced from the additives between 1600 and 1900° C. The amount of Al_2O_3 in the compound was less than that in the starting composition. Part of the aluminium should have reacted with the SiC. Lange [16] reported the hot-pressing of SiC powder with Al_2O_3. He suggested that the densification of SiC was responsible for the liquid phase of an alumino-impurity silicate derived from Al_2O_3 and SiO_2 on SiC. A eutectic composition between SiC and Al_2O_3 was said not to exist, but this has not been confirmed. The β-SiC powder was not complete stoichiometric compound of silicon and carbon but contained small amounts of oxygen [17]. Aluminium oxide may react with the SiC–oxygen compound more easily than does SiC to produce an unidentified compound. $Al_2Y_4O_9$ and the unknown compound aided sintering of SiC between 1600 and 2000° C. There is no evidence that these compounds melt in this temperature range. The solid state sintering may control the densification up to 2000° C. Even when the compounds melted, near 2000° C, holding at that temperature for a few hours did not produce dense SiC. Final densification was caused by the liquid phase of aluminium and silicon which occurred above 2000° C. This aluminium and silicon was produced by the decomposition of $Al_2Y_4O_9$ and the gradual reaction with SiC. The liquid phase was confined to the sintered body below 2150° C, but left pores in the body above this temperature due to evaporation.

Flexural strength was not very high, taking into account the apparent porosity. The size and shape of the second phase decreased the strength. The white second phase was constituted of the unknown yttrium oxide. Considering the angular and irregular shape, this oxide was in the process decomposing from $Al_2Y_4O_9$ and reacting with the β-SiC. To control the size and shape, and to increase the strength, it is necessary to change the β-SiC powder. The electrical resistivity was less than that of the SiC body sintered with boron and carbon. The low resistivity was based on aluminium.

5. Conclusions

1. The sintering additives A and Y (small molecules prepared from aluminium hydroxide and yttrium hydroxide) were effective for use as binder.
2. The additive was transformed to oxide by heating.
3. 10 wt % additive A (4.3 wt % Al_2O_3) and 15 wt % additive Y (8.1 wt % Y_2O_3) were the optimum amounts for sintering the β-SiC powder.
4. The densification of SiC was achieved at 2150° C, the bulk density and the apparent porosity were 3.11 $g\,cm^{-3}$ and 0%, respectively.
5. The sintered SiC was constituted of the SiC matrix and the second phase of aluminium, silicon and yttrium oxide.
6. The flexural strength and the electrical resistivity were 470 MPa and $9.7 \times 10^{-3}\,\Omega\,cm$.

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