

Chemical Bonding of Silicon Carbide

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Abstract

The effect of several variables such as the type of binder and additive, the temperature, time, furnace atmosphere, particle size and forming pressure, on the strength of chemically bonded SiC specimens was studied. It was shown that the highest compressive strength (43.67 MPa at 500°C) can be obtained by using optimum amounts of orthophosphoric acid and aluminium hydroxide as binder and additive respectively. Various stages in the structural development were followed by DTA, XRD and SEM/EDX analysis. It was shown that by using aluminium hydroxide and kaolin additives, phosphate bonding could be preserved at the specimen surfaces up to 1450°C.

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1 Introduction

The chemical bonding, especially phosphate bonding, of various materials has been the subject of extensive research studies over many decades and the topic has been well reviewed by Kingery¹ and Cassidy.^{2,3} But among the refractory materials, the chemical bonding of SiC has attracted relatively little attention. The information presented in the literature in this case mainly concerns silicon carbide containing castables and monolithics. As such, they are mostly technically oriented, with little systematic information concerning the bonding mechanisms and effects of various parameters on the strength and stability of bonds. Cassidy² has mentioned the application of phosphate bonded silicon carbide refractories in steam generating boilers, and quoted the aluminium-phosphate containing products as possessing the best properties. According to this author, the phosphate bonded high alumina and SiC products exhibited radically

different thermo-mechanical behaviour. In the case of SiC products the modulus of rupture increased up to 1100°C then decreased, whereas alumina products showed continuous decrease of MOR in the 800–1200°C range. This behaviour has been attributed to the formation of silico-phosphates in the case of phosphate bonded SiC bodies. Reed⁴ has named $\text{SiO}(\text{PO}_3)_2$ as a reaction product of silicate compounds with phosphoric acids above 250°C, which is in accordance with Cassidy's report.¹ Sheets *et al.*⁵ used a mixture of SiC powders, aluminium phosphate and ammonium fluoride to produce SiC castables. They obtained relatively strong bodies, but encountered the problem of bloating during heating of their specimens. The preheating of SiC powders was suggested as a possible solution to the problem. Dhupia *et al.*⁶ has discussed the use of SiC monolithics for waste incinerators and concluded that the strength of SiC mixes can be sharply increased through the addition of phosphate binders. They compared the dry and fluid phosphate bonded specimens, and claimed that at 100°C dry phosphate bonded mixes had strengths equivalent to those achieved by fluid phosphate bonded mixes at 1200°C, but the exact composition of the binders has not been disclosed. Emblem⁷ and Singer and Singer⁸ have mentioned the application of ethyl silicate bonds in silicon carbide bodies.

The lack of sufficient scientific information in this field encouraged the present study of the subject.

2 Experimental Procedure

2.1 Starting materials

The starting materials, α -SiC, (Carborundum Co Ltd.) aluminium hydroxide, alumina and silicon were reagent grade, (Merck) powders. The acids used were analytical grade 65% nitric acid, 98% sulphuric acid and 85% orthophosphoric acid (Merck) solutions.

2.2 Specimen preparation and testing

The acid solutions were added on the basis of 3–7 ml to 100 g of dry powder and were thoroughly mixed.

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The mixtures were pressed at 73.28 MPa into discs of 30.18 mm diameter and 25 mm thickness. The particle size distribution of the SiC powder is shown in Fig. 1. This powder was used in all experiments except those in Section 3.5, where the influence of different SiC powder particle sizes was investigated.

The pressed specimens were heated to various predetermined temperatures and soaked for times ranging from 4 to 8 h. The compressive strength of specimens was determined using the methods described in ASTM C133-84.

2.3 Study of reaction sequences and identification of phases

Differential thermal analysis (DTA, Shimadzu-50) was used to follow the reaction sequences of specimens. The heating rate used was 10 K min^{-1} . The identification of phases at different stages of heating was carried out by X-ray diffractometry (XRD, Jeol JDX-8030). Scanning electron microscopy (SEM, S 360 Cambridge) was used to observe the microstructures. The phase compositions of different zones in the microstructures were determined by using an energy dispersive X-ray analyzer (EDX) attached to SEM.

3 Results and Discussion

3.1 The effect of different binders

Figure 2 shows the effect of various acids used as binders, on the compressive strength of specimens. It may be concluded that the orthophosphoric acid is the most effective binder. The experiments showed that the optimum amount of each acid was about 5 ml (for 100 g of dry powder). Excessive amounts had no further effect on strength values. In the case of orthophosphoric acid, the maximum compressive strengths that could be obtained at

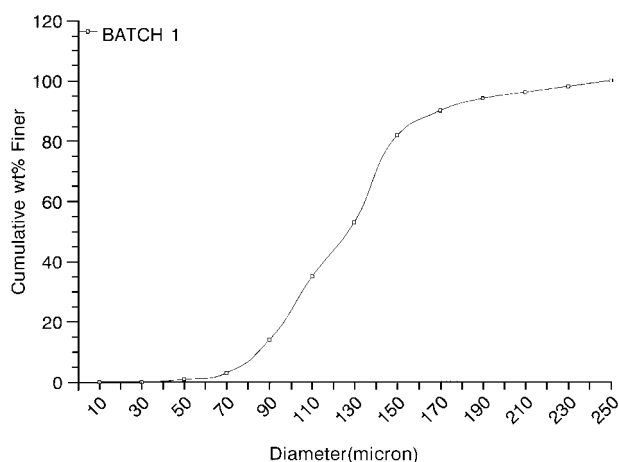


Fig. 1. Particle size distribution of SiC powder used as the main raw material.

500 and 1450°C were 4.4 and 15.15 MPa respectively. A drop in strength values was observed in all phosphate bonded specimens over the 1000–1250°C interval. This behaviour will be discussed later.

In Fig. 3 the effect of orthophosphoric acid and di-ammonium hydrogen phosphate binders on the compressive strength of specimens is compared. Since there is a relatively small difference between the effects of these two binders, it was decided to use the orthophosphoric acid as a binder in all the remaining experiments.

3.2 The effect of time

From Fig. 4 it may be seen that increasing the soaking time at 500°C from 4 to 6 h nearly doubles the compressive strength but a further increase to 8 h has little effect. Therefore a soaking time of 6 h was chosen for the rest of this work.

3.3 The effect of atmosphere

In order to study the effect of atmosphere some of the specimens containing 3 ml of orthophosphoric

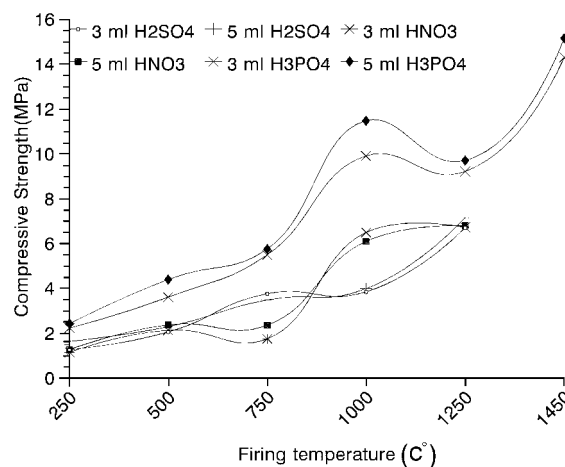


Fig. 2. Compressive strength versus soaking temperature for various binders.

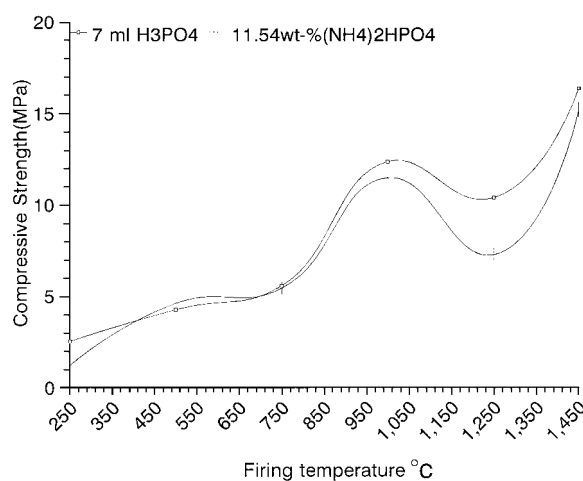


Fig. 3. Compressive strength versus soaking temperature for phosphoric acid and di-ammonium hydrogen phosphate.

acid were placed into refractory saggars, covered with a bed of coke and then heated in the usual way. The results are shown in Fig. 5. It may be concluded that the reducing atmosphere adversely affects the phosphate bonding. It is known that in the case of heat treatment of SiC powders in oxidizing atmospheres, an amorphous SiO₂ layer forms on the particle surfaces. This layer reacts with phosphates to form the silico-phosphate phases responsible for bonding of particles. In the absence of this layer, the phosphate bonding is not possible.

3.4 The effect of forming pressure

From Fig. 6 it is obvious that the increase of forming pressure has a marked effect on the strength of specimens. For example a pressure increase from 51.5 to 109.87 MPa causes an almost 8 fold increase in compressive strength of specimens heat treated at 1000°C.

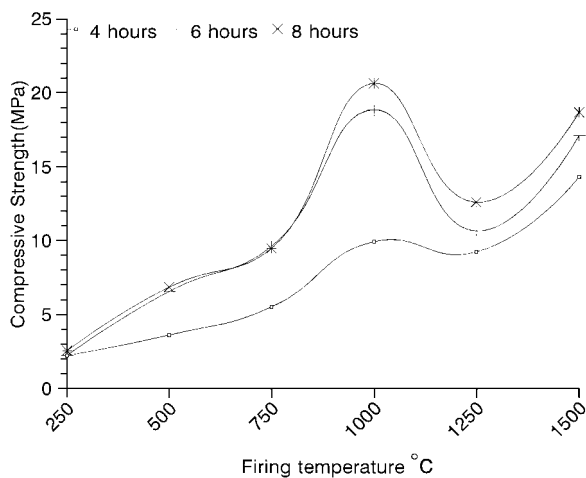


Fig. 4. Compressive strength versus soaking temperature for different times.

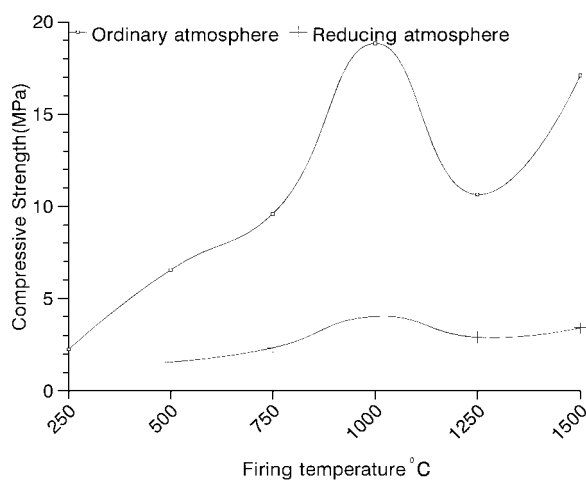


Fig. 5. Compressive strength versus soaking temperature for ordinary and reducing atmospheres.

3.5 The effect of particle size distributions

Figure 7 exhibits the strengths of 4 series of specimens with different particle size distributions. The size distributions are shown in Fig. 8. It is seen that an increase in the fine fractions (which increases the amount of the amorphous SiO₂ surface layers), as well as a broadening of the particle size distribution, (resulting in more efficient packing), increase the strength values.

3.6 The effect of additives

Figures 9–11 represent the effects of Al₂O₃, Al(OH)₃, kaolin and silicon additives on the compressive strengths of phosphate bonded SiC specimens. From Fig. 9 it may be concluded that Al(OH)₃ is a more effective additive than alumina. On adding 5 wt% Al(OH)₃, a strength of 43.67 MPa can be obtained after heating at 500°C, some ten times greater than found in specimens prepared without additives.

An interesting feature of the specimens containing alumina and Al(OH)₃ was the fact that they did not exhibit the marked drop in strength in the

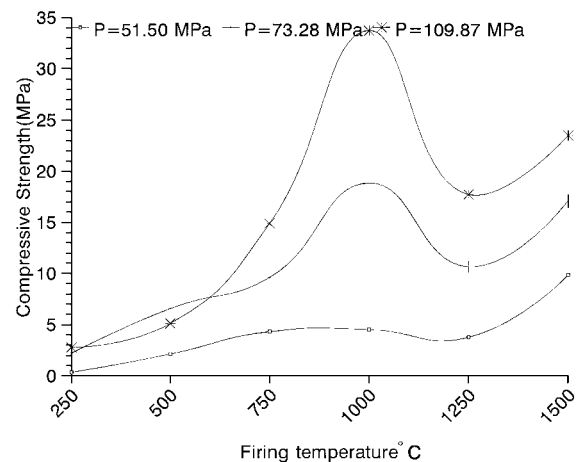


Fig. 6. Compressive strength as a function of soaking temperature at different forming pressures.

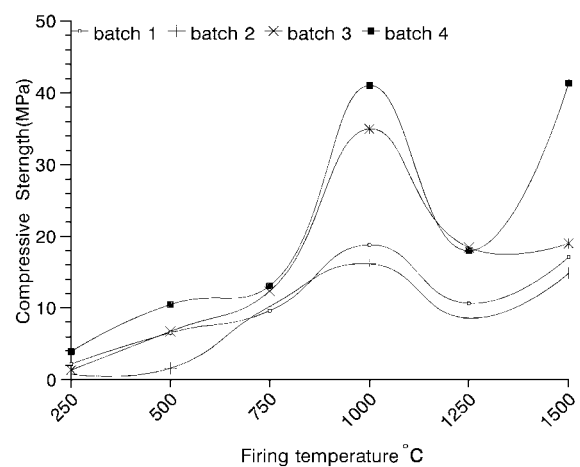


Fig. 7. Compressive strength versus soaking temperature for SiC powders of various particle size distributions.

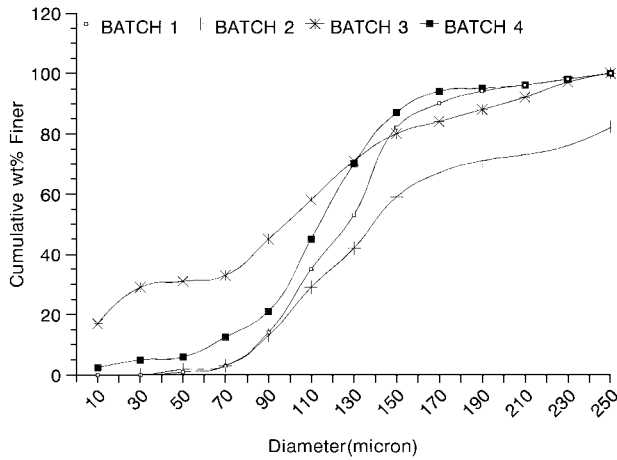


Fig. 8. Particle size distributions of various SiC powders.

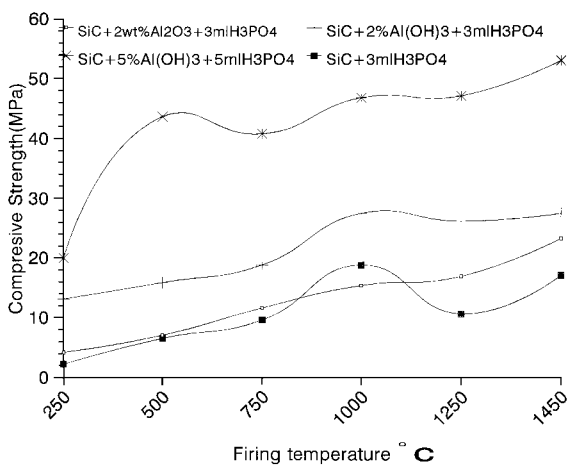


Fig. 9. Compressive strength versus soaking temperature for phosphate bonded specimens containing Al_2O_3 and $\text{Al}(\text{OH})_3$ additives.

1000–1250°C interval. This is an indication of the fact that the bonds formed in the presence of Al_2O_3 and $\text{Al}(\text{OH})_3$ (alumino-silico phosphates), were more stable at high temperatures. In the case of the kaolin additive (ZT-Zedlitz Kaolin), lower strengths were obtained at 500°C but the strength was retained in the 1000–1250°C interval (Fig. 10). The effect of Si is shown in Fig. 11. The maximum strengths obtainable at 500°C were lower and the higher temperature strength drop was also found (silico-phosphate bonding). On the basis of these tests, $\text{Al}(\text{OH})_3$ was chosen as the most effective additive.

3.7 XRD results

Although most bonding phases in chemically bonded bodies have amorphous structure, some crystalline phases can appear during formation of bonds or their subsequent destruction and devitrification. In this experiment an attempt was made to identify the possible crystalline phases formed during heating of phosphate bonded SiC specimens,

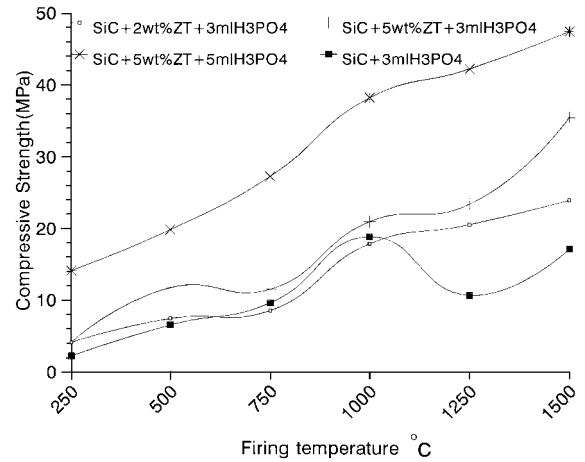


Fig. 10. Compressive strength versus soaking temperature for phosphate bonded specimens containing kaolin additive.

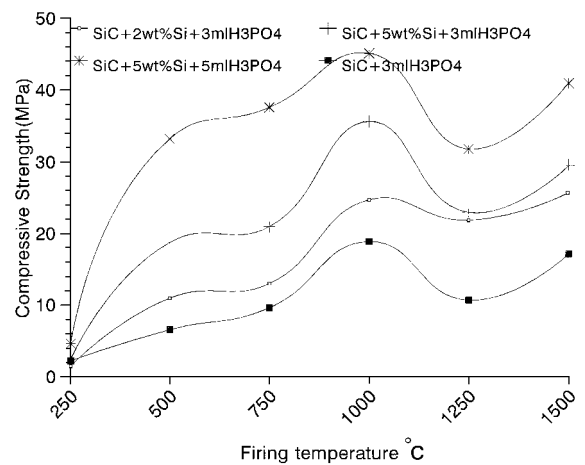


Fig. 11. Compressive strength versus soaking temperature for phosphate bonded specimens containing silicon additive.

up to 1000°C. The sole crystalline phase was identified as α -SiC. This was attributed to the small concentration of possible crystalline phases. Hence, in a separate experiment, the content of orthophosphoric acid was raised to 30 wt% and after soaking the specimens at 500, 1000 and 1250°C for 6 h they were furnace cooled and analyzed by XRD. Figure 12 presents the crystalline phases obtained at different temperatures and Table 1 summarizes the results. It may be seen that at 1250°C the content of crystalline phases has increased giving rise to a marked drop in the strength values. (Section 3.1, Fig. 2).

3.8 DTA results

Figure 13 exhibits the DTA traces of various specimens. In the case of $\text{SiC} + \text{H}_3\text{PO}_4$ specimens [Fig. 13(a)] the major endothermic and exothermic peaks appeared at 126 and 1074°C respectively. The low temperature signal may be associated with the evolution of water from the acid solution. The exothermic peak at 1074°C may be related to the destruction of the phosphate bond, producing

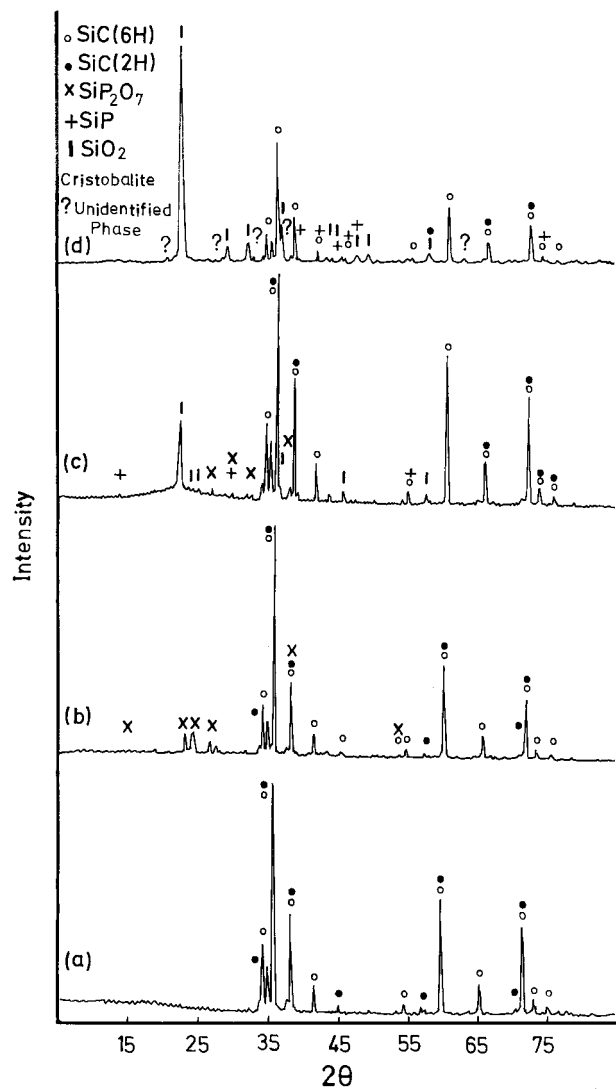


Fig. 12. XRD traces of SiC + 30 wt% H₃PO₄ specimens held at (a) 25°C, (b) 500°C, (c) 1000°C and (d) 1250°C for 6 h.

Table 1. Crystalline phases identified in SiC + 30 wt% H₃PO₄ specimens after soaking at different temperatures for 6 h

Temp. °C	Crystalline phases
500	α-SiC + SiP ₂ O ₇
1000	α-SiC + cristobalite + SiP + SiP ₂ O ₇
1250	α-SiC + cristobalite + SiP + SiP ₂ O ₇ + an unidentified phase

the marked decrease in strength observed at 1000–1250°C. Figure 13(b) reveals the behaviour of specimens consisting of SiC + Al(OH)₃ + H₃PO₄ during the course of their heating up to 1300°C and Fig. 14(a) and (b) show the DTA traces of the Al(OH)₃ and Al(OH)₃ + H₃PO₄ additives respectively. The endothermic effects at 112, 244 and 333°C [Fig. 13(b)] are attributable to the water evolution from phosphoric acid and to the phase transitions of Al(OH)₃ respectively. The major exothermic peak observed at 1195°C may be associated with the partial destruction of the bonding phases due to the crystallization.

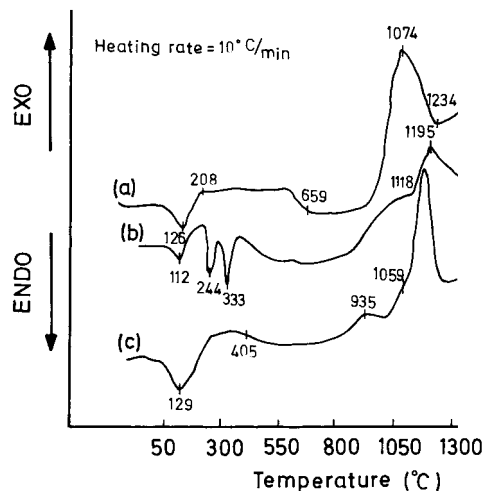


Fig. 13. DTA traces of (a) SiC + H₃PO₄, (b) SiC + Al(OH)₃ + H₃PO₄, (c) SiC + Kaolin + H₃PO₄.

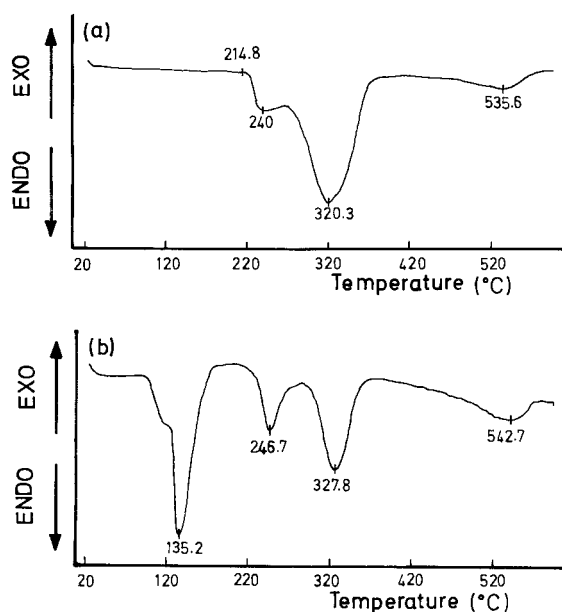


Fig. 14. DTA traces of (a) Al(OH)₃, (b) Al(OH)₃ + H₃PO₄ specimens.

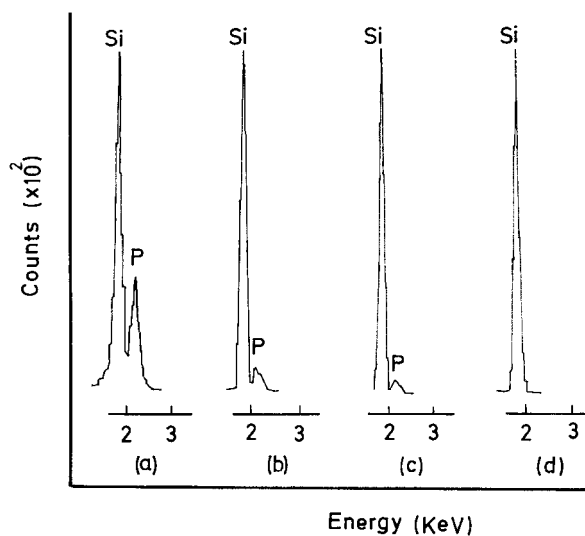


Fig. 15. EDX spectra for SiC + 3 ml H₃PO₄ specimen, held for 6 h at (a) 500°C, (b) 1250°C, (c) 1450°C (specimen interior) and (d) 1450°C (specimen surface).

Figure 13(c), which presents the DTA trace of SiC + kaolin + H₃PO₄ specimens, in addition to the peaks discussed earlier, shows an exothermic peak

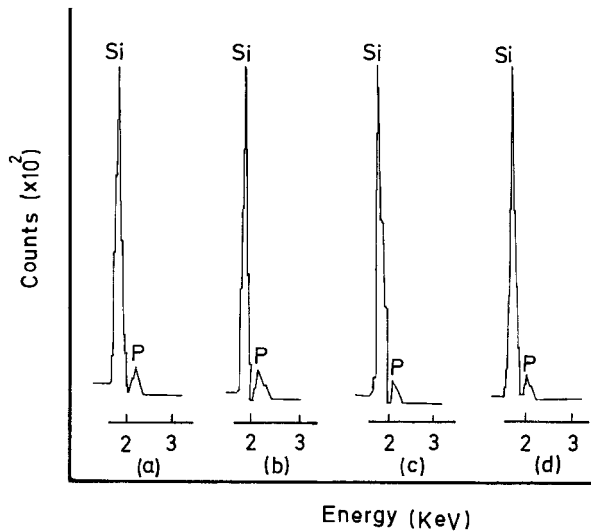


Fig. 16. EDX spectra for SiC + 3 ml H₃PO₄ + the indicated additive, held at 1450°C for 6 h, (a) 2 wt% Kaolin, specimen interior, (b) 2 wt% Kaolin, specimen surface, (c) 2 wt% Al(OH)₃, specimen interior and (d) 2 wt% Al(OH)₃, specimen surface.

at 935°C related to the phase transformation in kaolin.

The DTA results presented herein show a higher stability for aluminosilico-phosphate amorphous phases (formed in the presence of Al(OH)₃ and kaolin) in comparison with silico-phosphate phases. This effect is explainable in terms of the roles of the aluminium and phosphorus ions in silicate glass structure, as discussed by McMillan.⁹ The aluminium ion occupies the centre of a tetrahedral AlO₄ group which takes part in the glass network and this group bears an excess unit negative charge. When phosphorus is present in the glass the excess negative charge of AlO₄ can be neutralized by becoming linked to a PO₄ group having an excess positive charge. The double bond between oxygen and phosphorus is, therefore, unnecessary in this case. In addition to this the radii of the aluminium and phosphorous ions (0.5 and 0.34 Å respectively) are such that when these ions occupy the centres of adjacent tetrahedral groups, the overall atomic spacing for the two groups will be quite close to that for an adjacent pair of SiO₄ groups in which

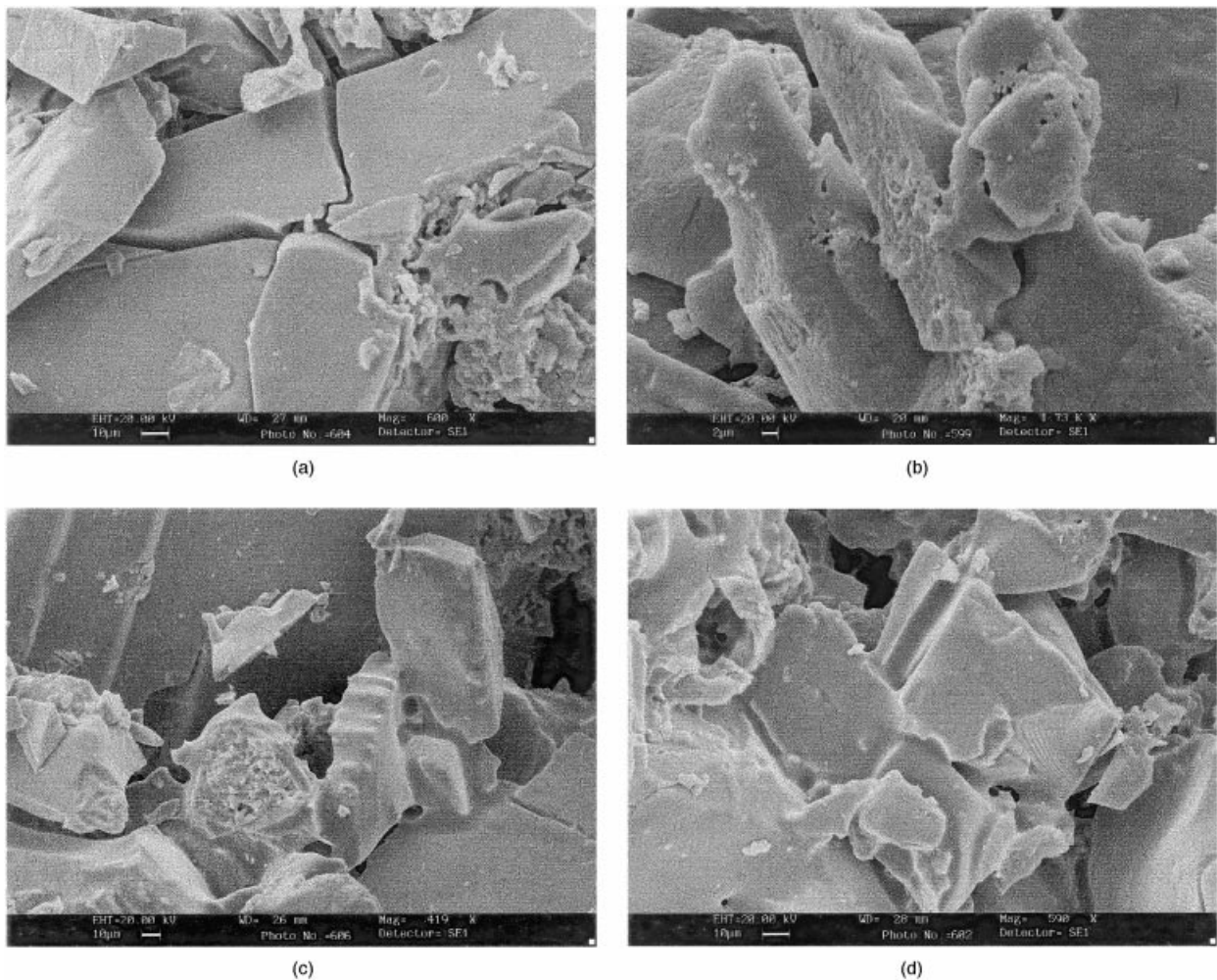


Fig. 17. Typical SEM micrographs for SiC + 5 ml H₃PO₄ specimens, heat treated at 1450°C for 6 h, (fractured surfaces). (a) without additive, specimen surface. (b) without additive, specimen interior. (c) with 5 wt% Al(OH)₃ additive, specimen surface. (d) with 5 wt% Al(OH)₃ additive, specimen interior.

the central ion, Si^{4+} , has radius of 0.41 Å. Thus, both from the point of view of ensuring electro-neutrality and from considerations of the size of tetrahedral groups participating in the network, linking together of AlO_4 and PO_4 groups would tend to stabilise the phosphate tetrahedra within the silicate network. Thus, the addition of Al_2O_3 to P_2O_5 - SiO_2 glasses, suppresses phase separation and crystallization tendencies of these glasses and increases their chemical resistance.

3.9 Microscopic examinations

Figure 15(a)–(d) shows typical EDX Spectra of $\text{SiC} + 3 \text{ ml H}_3\text{PO}_4$ specimens at different temperatures. It may be concluded that the phosphate bonding was preserved at 500 and 1250°C. At 1450°C although the bond was preserved in the specimen interior, it was destroyed at the specimen surface. Figure 16 indicates that in the case of $\text{SiC} + 3 \text{ ml H}_3\text{PO}_4 + 2 \text{ wt\% kaolin}$ and $\text{SiC} + 3 \text{ ml H}_3\text{PO}_4 + 2 \text{ wt\% Al(OH)}_3$ specimens the phosphate bonding can be preserved at 1450°C both at the surface and interior of specimens, confirming the higher stability of the alumino-silico-phosphate bond discussed before.

Figure 17(a)–(d) show typical SEM micrographs of $\text{SiC} + 5 \text{ ml H}_3\text{PO}_4$ specimens with addition of 5 wt% Al(OH)_3 and without it, heat treated at 1450°C for 6 h, confirming the above deductions.

4 Conclusions

1. It was proved that orthophosphoric acid is a more effective binder for SiC in comparison with H_2SO_4 and HNO_3 acids and its optimum amount is about 5 ml (in a concentration of 85 wt%).
2. Decreasing the coarse fraction ($> 150 \mu\text{m}$), increasing the fine fraction ($< 150 \mu\text{m}$) and broadening of particle size distribution may bring about a more than 2-fold increase in the compressive strength of phosphate bonded SiC specimens heat treated at 1000°C.
3. Phosphate bonded SiC specimens normally exhibit a continuous increase in compressive strength in 250–1000°C range, following with a marked drop in the 1000–1250°C interval, after which the course of strength increase is

restored up to 1450°C. The addition of Al(OH)_3 and kaolin increases the stability of silico-phosphate amorphous bonding phase by converting it to alumino-silico-phosphate thus giving rise to the elimination of the strength drop interval.

4. The optimum heat treatment time is about 6–8 h for phosphate bonded SiC specimens in all temperatures.
5. By nearly doubling the forming pressure (from 51 to 109 MPa) an 8-fold increase in the compressive strength of phosphate bonded SiC specimens, heat treated at 1000°C, may be achieved.
6. By using 5 wt% Al(OH)_3 as an additive, the compressive strength of phosphate bonded SiC specimens heat treated at 1000°C may be increased almost by a factor of 4.
7. A reducing atmosphere may decrease the compressive strength of phosphate bonded SiC specimens more than four times, in comparison to an ordinary atmosphere.
8. The use of Al(OH)_3 or kaolin additives gives rise to the preservation of the resultant phosphate bond at 1450°C at the specimen surfaces, which otherwise would be destroyed in the absence of these additives.

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