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SiC–YAG sintered composites from hydroxy hydrogel powder precursors

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Abstract

Yttrium hydroxide and aluminium hydroxide hydrogel were derived from yttrium nitrate and aluminium nitrate through hydroxy hydrogel route in which SiC particles were kept dispersed. The gel-like mass was heat treated at 900°C in ambient atmosphere followed by heat treatment at 1400°C in Ar atmosphere. The specimens were then sintered in the temperature range of 1800–1950°C in Ar atmosphere with 30 min soaking. The phases were identified by XRD analysis. Microstructure of the sintered materials were analysed by scanning electron micrograph. With this new method of preparation of powder precursors, the process of sintering was easier and almost theoretical density was achieved with moderate hardness. The mechanism of densification was postulated to be a solid-state initiated liquid phase sintering and the overall process of which was activated by the reactive species formed from hydroxy hydrogel powder precursors.

Keywords: A. Precursors; Hydroxyhydrogel; Densification; Reactive

1. Introduction

The fabrication of dense SiC ceramics requires a sintering additive because of the extremely low self-diffusivities in the strongly covalently bonded SiC structures [1,2]. An effective additive promotes densification and creates an atmosphere which inhibits the decomposition of SiC at sintering temperature. There are several works devoted to the study of processing [3–5] and mechanical properties [5–12] of SiC platelet reinforced Al_2O_3 matrix. In those works, the composites were sintered by hot pressing, a technique that only allows the fabrication of pieces with simple geometry that require extensive machining. In addition, the hot pressed composites have shown anisotropic mechanical and wear behaviour due to the preferred orientation of the platelets with respect to the hot pressing direction [4,6,13]. Consequently, it is important to consider other sintering routes such as pressureless and gas pressure sintering, which can be used to develop isotropic components.

The usual sintering additives used for SiC are alumina + yttria with an alumina:yttria weight ratio > 1 [14]. Typically 5–15 wt% of the sintering additives were used. The higher the amount of sintering additives, the higher is the sintering rate [15]. Other sintering additives are $MgO + Al_2O_3$ [16], other rare earth metal oxides + Al_2O_3 [17], Al_2O_3 [18], sialon [19], or yttria + aluminium nitride [20].

The sintering temperature is reported to be ~1900°C [16,17,21–23] in Ar and ~2100°C [14,17] in N_2 sintered mostly by hot pressing. Considerable weight losses of the sample were always observed. A higher weight loss in N_2 atmosphere than in Ar atmosphere was also reported and the use of closed containers and a powder bed reduced the weight losses [23,24].

Many researchers have used alkoxide as a starting material for sintering purpose which gave suitable sintering aid during sintering. On the other hand, inorganic salts have also been used as starting materials [25–31] mostly via the homogeneous precipitation route which was also characterised by easy control of precipitation rate.

In the preparation of sintering aids from inorganic precursors with the homogeneous precipitation method, it is not easy to prevent the coalescence of particles. A number of efforts have been made to prevent the coalescence. Matijevic and co-workers [25,26] prevented coalescence of particles by using dilute dispersions and/

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or adding surfactants. However, it is still rather difficult to prevent the coalescence, especially when coated layers are thick and dispersions are not sufficiently dilute.

The method was also used later by Garg and De Jonghe [32] for the preparation of Si_3N_4 coated with yttria and yttria-alumina precursors. For particulate composites, the reinforcement phase was coated with the required thickness of the matrix phase by controlled heterogeneous precipitation in a suspension of particles. The coated powders were then collected, compacted by normal ceramic powder forming methods and densified by conventional pressureless sintering. Sacks et al. [33] employed an alternative method based on the use of coated powders. They prepared amorphous coating on core particles in order to take advantage of the easier densification of the coating by viscous flow. After densification, the amorphous phase could be crystallised or reacted with the core particles to produce a crystalline product.

It has been shown that it is possible to pressureless sinter SiC with additions of Al_2O_3 and Y_2O_3, and it was also demonstrated that those additives made it possible to reduce the sintering temperature to well below 2000°C [34–36]. Dissociation of SiC in the presence of metal oxides at higher temperature was the main factor for weight losses which retarded densification of SiC. Use of threaded crucible and powder bed partially reduced the weight loss. A higher temperature was necessary for sintering where additives form liquid but at higher temperature dissociation of SiC was more. Hydroxy hydrogel route is promising for ceramic powder preparation. Powder prepared by this method likely to be much reactive and pure, hence the formation of YAG is expected at relatively lower temperature which later may act as sintering aid thus retarding dissociation of SiC.

2. Experimental[1]

Commercial SiC (characteristics of which are given in Table 1), AR grade aluminium nitrate, yttrium nitrate and ammonia (1:1 v/v) were used as raw materials. A suspension of SiC was prepared in deionised water having 50 gm/l solid content with suitable deflocculant. A solution of 0.2 M aluminium nitrate and yttrium nitrate was also prepared in deionised water. Aluminium nitrate and yttrium nitrate were allowed to interact in SiC suspension with ammonia. The gel-like mass that was formed was allowed to age overnight for complete reaction and network formation. The material was filtered and the residue was initially air dried followed by heat treatment at 900°C in ambient atmosphere. The dried mass was ground and bars were prepared uniaxially followed by isostatic pressing at 250 MPa. The bars were fired at 1100, 1200, 1300 and 1400°C in Ar atmosphere with 2 h hold. In final firing schedule, the isopressed bars were packed with packing materials in a threaded graphite crucible and fired at the temperature range of 1700–1950°C in GPS ASTRO furnace with 30 min hold. The phase analysis was done by XRD and the microstructures of fracture surfaces were analysed by scanning electron microscope. Bulk densities were measured by Archemedes's method. The fired bars were polished with 1 μm diamond paste in PEDEMAX-2 (Struers, Denmark) for evaluation of mechanical properties. Hardness of the samples was measured by Leitz Miniload Hardness Tester.

Table 1
Chemical analysis and characteristics of starting SiC powder

Constituents	SiC	Al_2O_3	Fe_2O_3	Si	C
% by wt	98.8	0.07	0.08	0.15	0.50

[1] The process is protected in India by patent application No. 375/DEL/98.

3. Results and discussion

Yttrium nitrate and aluminium nitrate were taken in such amounts that will give Y_2O_3:Al_2O_3 in the mole ratio of 3:5 (Fig. 1) in their oxide state. Five batches of SiC, Y_2O_3 and Al_2O_3 with different Y_2O_3 and Al_2O_3 contents were prepared keeping mole ratio of Y_2O_3 and Al_2O_3 constant. In Table 2 amount of different constituents are given for different batches.

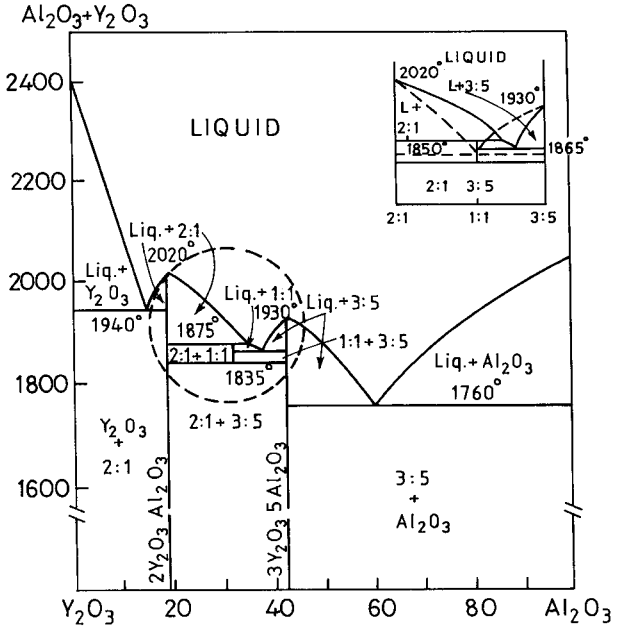

Fig. 1. Equilibrium phase diagram in Y_2O_3–Al_2O_3 system.

Table 2
Composition of different batches on the basis of oxide formed after heat treatment at 900°C and resulting SiC and YAG in vol%

Batch no.	Wt. of SiC (gm)	Wt. of Y_2O_3 (gm)	Wt. of Al_2O_3 (gm)	Vol% of SiC	Vol% of YAG
Y-1	90	5.70	4.29	92.71	7.29
Y-2	85	8.56	6.44	88.91	11.09
Y-3	80	11.42	8.58	84.97	15.03
Y-4	75	14.27	10.73	80.92	19.08
Y-5	70	17.13	12.87	76.74	23.26

Volume changes of the specimens fired at 1200, 1300 and 1400°C in Ar atmosphere were calculated on the basis of the volume of the specimens pre-fired at 900°C. The volume shrinkages were due to collapse of gel structure [37]. Fast volume shrinkage between 1300 and 1400°C indicated maximum collapse of gel structure after which the changes were negligible. Volume contractions were not due to sintering is obvious as with increasing SiC content, shrinkages were progressively lesser (Fig. 2).

Due to removal of gel water during heat treatment, a loss in weight was observed which caused lowering in bulk density. On the other hand volume shrinkage due to collapse of gel structure caused increase in bulk density. The increment of bulk density calculated on the basis of the density of the specimens fired at 900°C are shown in Fig. 3. Increment of bulk densities increased with increase in temperature for all specimens.

The X-ray diffraction patterns of 10, 20 and 30% YAG containing specimens fired at 1200, 1300 and 1400°C in Ar atmosphere are shown in Fig. 4. From XRD patterns it was observed that the formation of YAG phase started at 1200°C for all specimens and increased with increasing temperature. At 1400°C, no free Al_2O_3 and Y_2O_3 were detected and only YAG phase was found to be present along with SiC for 30 wt% YAG containing specimen. Trace amount of Al_2O_3 was detected for specimens with higher SiC content ($\geqslant$80%) at 1400°C. This might be due to dilution of the Y_2O_3–Al_2O_3 in the system resulting into retarded reactions. But the formation of YAG phase was initiated at about 1400°C when Al_2O_3 and Y_2O_3 powders were mixed in solid state (Fig. 5). A large amount of free Al_2O_3 and Y_2O_3 were also detected in specimens prepared by solid state mixing process. Thus it may be concluded here that the present method of preparing powder precursors is superior to the solid oxide mixing process in relation to YAG phase formation.

The specimens on heat treatment (1400–1950°C) primarily yielded the monoxides of silicon, carbon, aluminium and yttrium. On subsequent reaction the carbides of silicon and aluminium were formed along with some carbon from SiC and CO when YAG does not take part

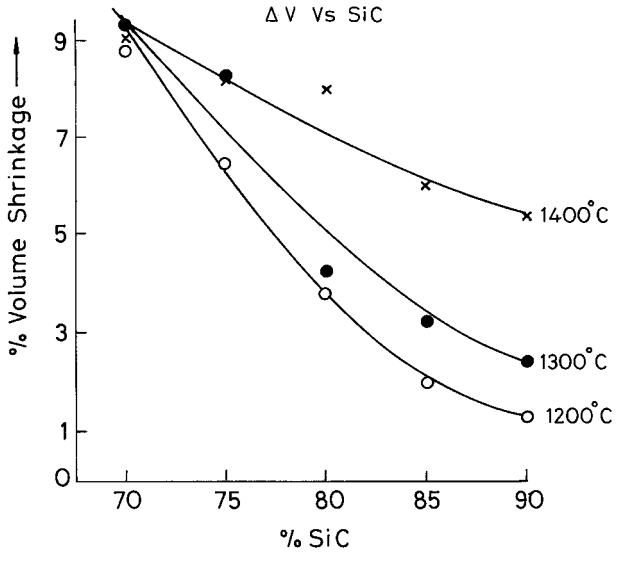

Fig. 2. Volume shrinkages of the specimens due to collapse of gel structure during heat-treatment at 1200, 1300 and 1400°C in argon in relation to SiC content.

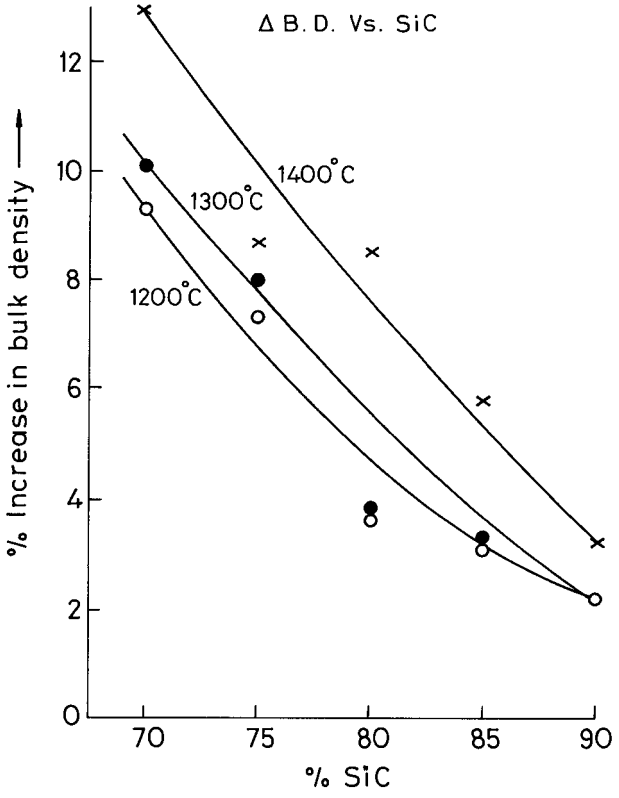

Fig. 3. Increment in bulk densities at 1200, 1300 and 1400°C pre-heat treatment in argon with increasing SiC content.

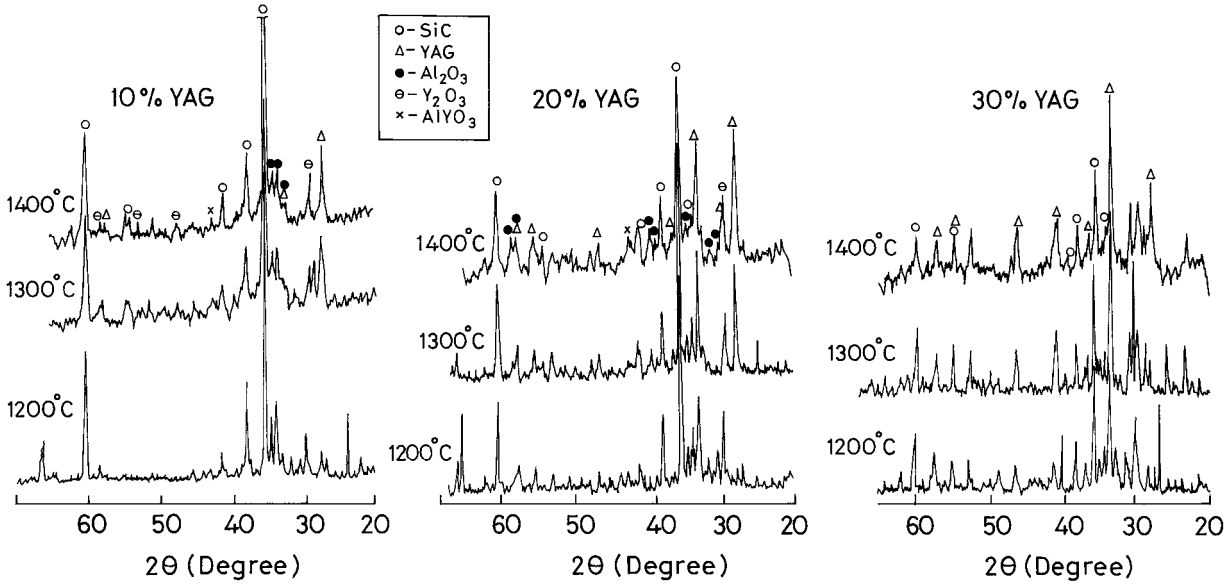

Fig. 4. Phases present in pre-heat treated specimens (pre-heat treated at 1200, 1300 and 1400°C in argon).

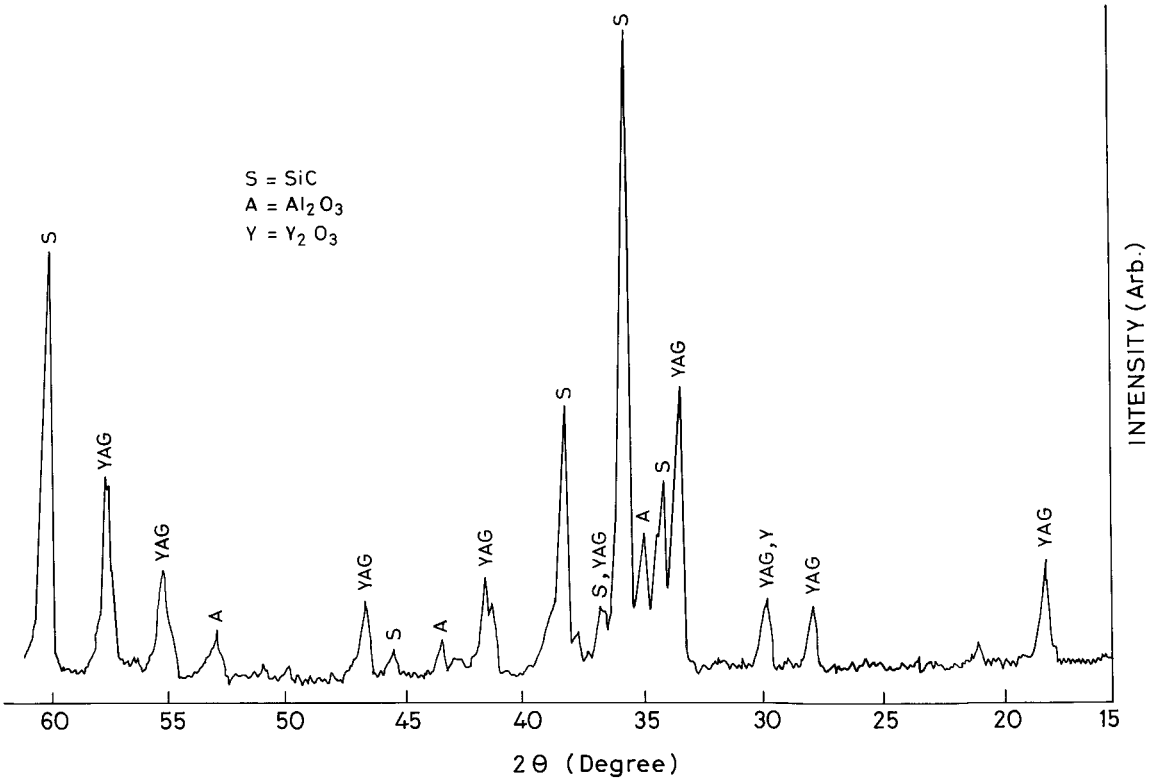

Fig. 5. XRD analysis of fired compacts (fired at 1400°C in argon) prepared by solid-mixing of Al_2O_3 and Y_2O_3 powder.

in the reaction. The final products on reaction with YAG were

$$Y_3Al_5O_{12} + CO + C \leftrightarrow 3AlYO_3 + 2AlO + CO \quad (1)$$

$$Y_3Al_5O_{12} + 2CO + 2C \leftrightarrow 3AlYO_3 + Al_2O + 4CO \quad (2)$$

$$Y_3Al_5O_{12} + 4CO + 3C \leftrightarrow 3AlYO_3 + Al_2OC + 6CO \quad (3)$$

The formation of volatile species impart porosity inside the body which was likely to impede densification [38]. The 'native' surface silica layer of SiC may lead to the formation of a SiC-network [39] and this could subsequently break up with the formation of SiO and

CO. So, two counteracting mechanisms may be operative in the system where pores retard molecular movements and at the same time defects in the SiC structure increase the same in it thereby increasing the chemical activity. This may explain the simultaneous increase in the weight loss and increase in densification. Densification at lower temperature was indicative of enhanced molecular movement favouring volume diffusion.

During sintering above 1500°C several polymorphic and polytypic changes of SiC might take place and when YAG was used as additive both α and β-SiC changed to 6H and 4H type [40,41]. The effect of Al [42], Y, O etc. on stabilisation of phases of SiC [40] should also be considered. Yttrium orthoaluminate ($YAlO_3$), one of the three congruent melting compound reported in the Al_2O_3–Y_2O_3 system formed by the reactions (1)–(3), might decompose at high temperature into $Y_3Al_5O_{12}$ (YAG) and $Y_{4.67}(SiO_4)_3O$ [43]. The overall process was likely to enhance volume diffusivity resulting in substantial densification at below 1800°C due to the distabilisation of SiC structural network resulting in increase of molecular movement. However, the above process might have been catalysed by very small amount of liquid phase formed in the temperature range of 1700–1800°C (Fig. 6) as SiC powder was associated with a thin layer of SiO_2.

Al_2O_3 and SiO_2 which caused decomposition of SiC, retarded densification and sintering process. These oxides in effect are responsible for the weight losses. When percent weight loss was plotted against temperature (Fig. 7), weight losses were found to increase with increasing temperature of sintering. Maximum weight loss of specimens were noted at 1850°C. But when specimens were fired at 1950°C weight loss was less. At 1850°C, the weight loss i.e. decomposition reactions dominated over sintering but when the specimens were fired at 1950°C, sintering of specimens partially suppressed the decomposition of SiC by reducing available surface area for the reaction resulting into less weight loss due to formation of liquid. With specimens containing ⩽15% YAG, the continuous increase in weight loss might be due to insufficient liquid phase.

At 1400°C no change in porosity was observed with increasing amount of YAG (Fig. 8). At temperatures ⩾1850°C, a decrease in porosity was found for all the specimens containing ⩾20% YAG. A minimum porosity of 3.85% was achieved at 1950°C for specimen containing 30% YAG.

XRD analysis of specimens fired at 1950°C showed SiC and YAG as the main phases. In Fig. 9 XRD pattern of 30 wt% YAG containing specimen fired at 1950°C is shown where SiC and YAG were detected and no Al_2O_3 or Y_2O_3 was found. Assuming complete conversion of Al_2O_3 and Y_2O_3 into YAG, theoretical density of fired

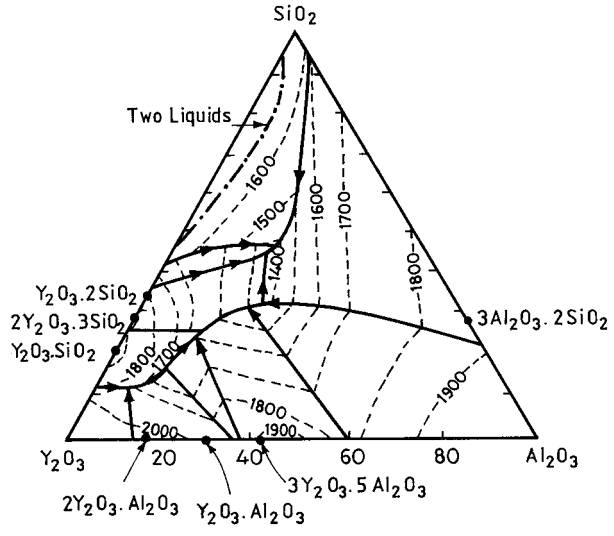

Fig. 6. Equilibrium phase diagram in Al_2O_3–Y_2O_3–SiO_2 system.

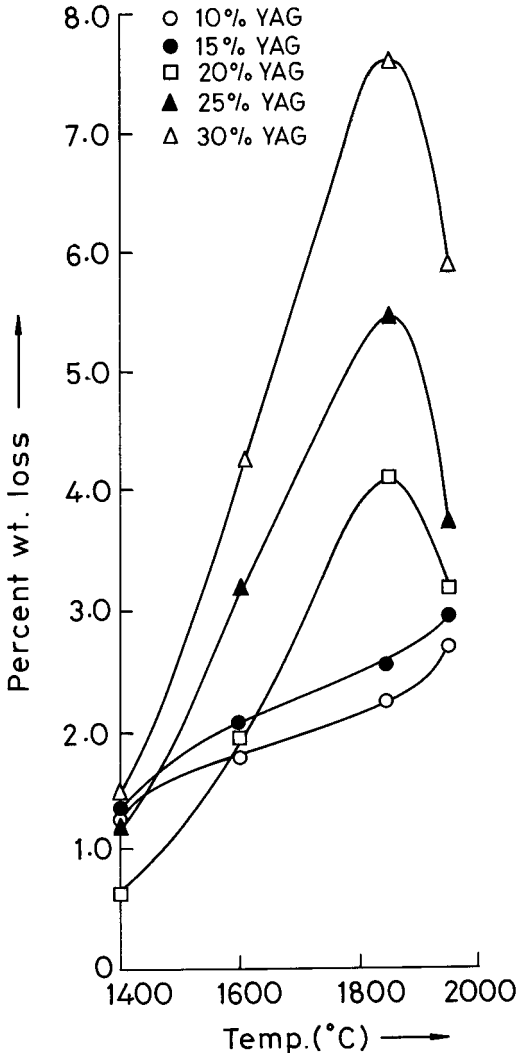

Fig. 7. Weight losses of the sintered compacts with sintering temperature and content of YAG (specimens were kept at sintering temperature for 30 min).

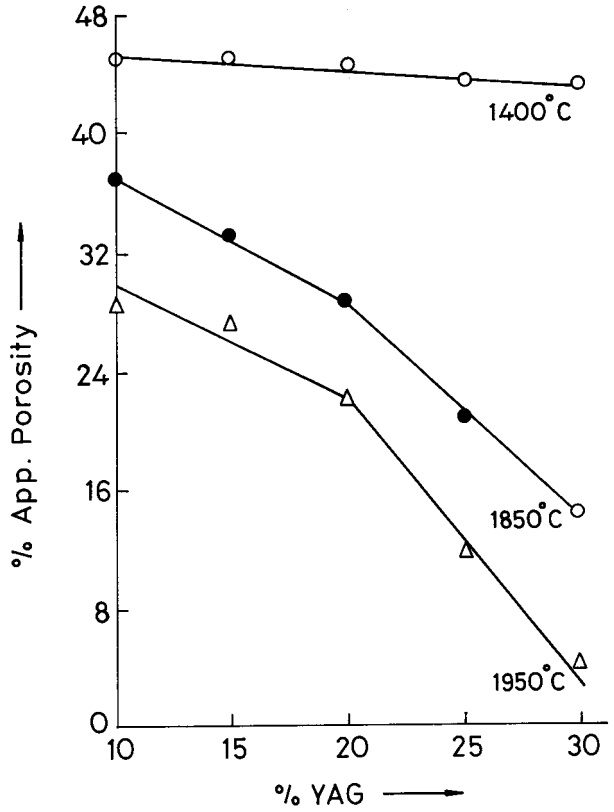

Fig. 8. Porosities of sintered compacts sintered in the temperature range 1400–1950°C.

specimens was calculated and by measuring density of fired specimens, the percentage of theoretical density (TD) achieved was also calculated.

A sharp increase in density (Fig. 10) was observed for all specimens in the temperature range of 1850–1900°C. Beyond 1900°C, the increment in density was small. A maximum of 98.6% TD was achieved at 1950°C for 30% YAG containing specimen in the present study. This comparatively low value could be due to the coarseness of initial SiC powder.

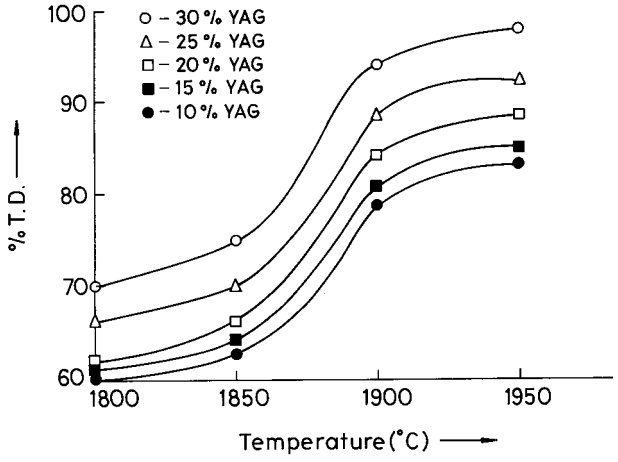

Fig. 10. Percent TD (assuming the presence of only SiC and YAG) in sintered compact in relation to the temperature of sintering.

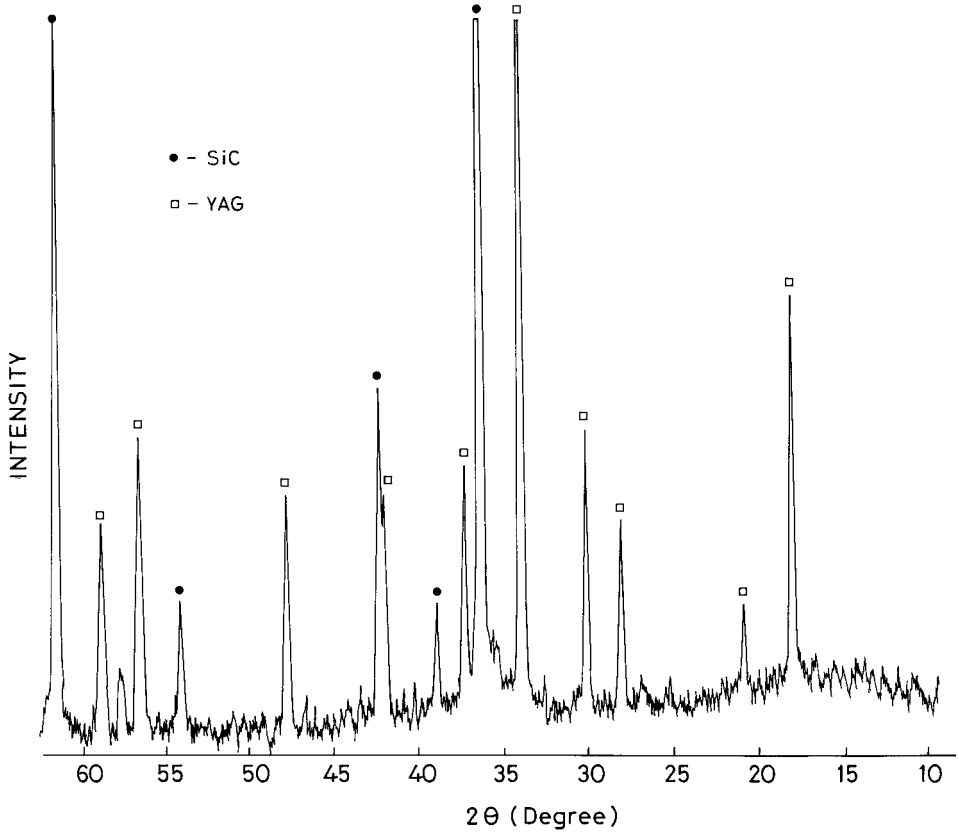

Fig. 9. XRD of sintered compact (30 wt% YAG) sintered at 1950°C.

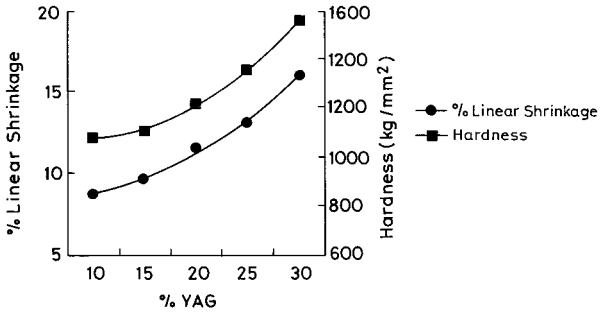

Fig. 11. Variation of hardness in sintered compacts and linear shrinkage in relation to YAG content.

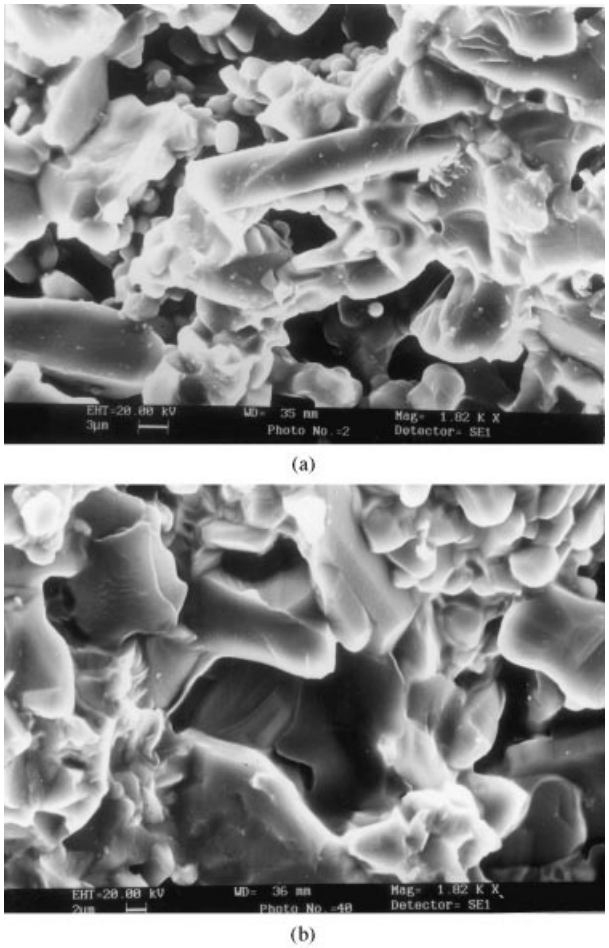

Fig. 12. Scanning electron micrographs of fracture surface, sintered at 1950°C showing grain growth of SiC with increasing YAG content (a, 10 wt% YAG; b, 30 wt% YAG).

The flexural strength of the specimens measured by three-point bending tester were considerably high (Y-1, 244.8 MPa, Y-2, 267.9 MPa, Y-3, 282.6 MPa, Y-4, 325.4 MPa and Y-5, 342.1 MPa). Microhardness (measured by indentation) of specimens sintered at 1950°C was found to be related to the extent of sintering (Fig. 11) as it was found to increase almost in a similar path to that of shrinkage of the specimen. Both shrinkage and hardness of specimens were found to be strongly related to the amount of yttrium aluminium garnet in the microstructure. Hardness values of SiC–YAG composites, thus, were less than sintered silicon carbide.

The scanning electron micrograph of fracture surfaces showed (Fig. 12) uniform distribution of YAG phase into SiC-matrix. The grain growth of SiC was found with increasing amount of YAG and with increasing temperature of sintering.

4. Conclusion

1. SiC–YAG sintered composites could be prepared by hydroxyhydrogel powder precursors at 1900–1950°C in argon atmosphere and the method was found to be a better available process than those using oxides as raw materials.
2. Flexural strength of the sintered compacts were considerably higher but the hardness was moderate.
3. Hardness of the sintered materials were dependent on the extent of sintering which was more with more YAG in the specimens.
4. Sintering could be explained on the basis of solid state phenomenon followed by liquid phase sintering.

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