

IN-SITU FABRICATION OF CERAMIC MATRIX COMPOSITES BY RH-SHS TECHNIQUE

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A rapid heating self propagating high temperature synthesis (RH-SHS) technique is developed for the fabrication of in-situ Al_2O_3 - SiC_w composites. The adiabatic temperature for the system is calculated to be 2375 K. The green compacts are heated rapidly ($\approx 300 - 400$ K/min) from room temperature to various soaking temperatures (T_s) ranging from 1473 to 2023 K either in air or argon atmosphere. Two exothermic reactions are observed successively during synthesis. XRD analyses show that the reduction of SiO_2 proceeds through aluminothermic route and a holding time of ≈ 30 minutes at T_s is sufficient for the completion of reactions. SiC is observed to be present in the form of β - SiC_w and the size and proportion of the whiskers depends upon the soaking time and temperature. Dimensional stability of the sintered products indicates the possibility of near net shape fabrication of composites using this technique.

INTRODUCTION

Ceramic matrix composites are important for their high temperature applications and excellent mechanical strength at elevated temperatures. Besides being light in weight they also exhibit excellent resistance to wear and corrosive environments. Among the various composites fabricated so far, Al_2O_3 - SiC_w has been investigated extensively [1-3]. However, the health hazard associated in handling the carcinogenic SiC_w and the making of homogeneous composites using conventional powder processing route are the major problems. These drawbacks can be overcome to a major extent by in-situ composite fabrication. Amongst the methods of in-situ fabrication of Al_2O_3 - SiC composites [4-8], the synthesis of the same by the self propagating high temperature synthesis (SHS) routes appears to be attractive [6-8]. In SHS, the reaction is initiated at a localised zone by some external energy source such as heating coil, laser beam, electrical arc etc. Exothermic heat generated during chemical reaction helps the reaction front to propagate through the reactants and thus makes the process energetically self sustaining.

In this paper, the synthesis of Al_2O_3 - SiC_w composites by a rapid heating self propagating high temperature synthesis (RH-SHS) technique is discussed. The role of atmosphere, soaking temperature (T_s) and time on the synthesis of composites is reported.

EXPERIMENTAL METHODS

Appropriate amounts of SiO_2 (98 % purity), Al (99 % purity) and C (90 % purity) powders were taken in a stainless steel container and milled for 6h. Approximately 6.0 g milled powder mixture were pressed to 2.5 cm diameter pellets at a pressure of ≈ 100 MPa. Polyvinyl alcohol (PVA) was used as binder. The green pellets were oven dried at 383 K for 3h. The SHS was carried out in an indigenously designed and fabricated small graphite furnace (schematically shown in figure 1). The furnace had a maximum heating rate of 500 K/min. The details of the experimental conditions employed are given in Table 1.

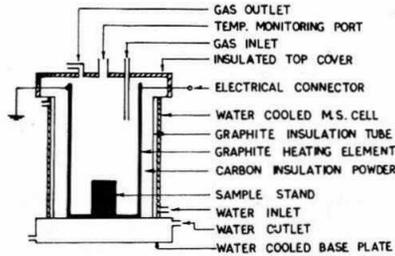


Figure 1. Schematic of the graphite furnace

Table - 1 Experimental conditions for the samples

Sample	Heating Rate (K/min)	Soaking Temperature (K)	Soaking Period (min)	Atmosphere
A	400	1723	0	Air
B	400	1723	10	Air
C	300	1473	0	Argon
D	300	1473	10	Argon
E	300	1473	20	Argon
F	300	1473	30	Argon

A radiation pyrometer was used to measure the furnace temperature. The samples were furnace cooled to room temperature after the completion of soaking and were further decarburised in air at 1123 K for 3h. Decarburised samples were characterised with the help of XRD, SEM and EDS. Ni-filtered $\text{Co-K}\alpha$ radiation was used for the XRD analysis. Fractured surfaces of the pellets were studied by SEM/EDS.

RESULTS AND DISCUSSION

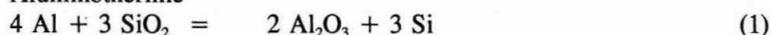
In SHS, the propagation of the reaction front depends on the physical characteristics of the samples and the heat sink existing around the samples. In conventional SHS, a limited heat energy (confined in a small zone) is supplied through an external source to initiate the combustion reaction. Inadequate high temperature soaking due to heat loss by conduction and radiation hinders the sintering of the products.

In RH-SHS technique, as the samples are heated rapidly a sharp thermal gradient is established across the samples. Once, the edge of the sample attains the reaction initiation temperature (T_i), SHS reactions set in. The reasons for adopting rapid heating schedule are as follows:

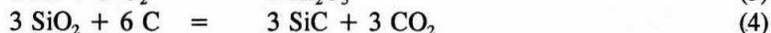
- (a) On slow heating, aluminium (melting point of 933 K) will remain liquid for longer period and will enhance the segregation before the SHS reaction is initiated ($T_i > 1036$ K). Since the reaction temperature is attained very fast in the present scheme, aluminum segregation is reduced.
- and (b) Dissipation of exothermic heat generated by SHS reaction to sinks around the samples may result in insufficient densification. Rapid heating of furnace minimises the temperature difference between samples and surroundings.

The reduction of SiO_2 and formation of SiC may take place through the following schemes.

(i) Aluminothermic



and (ii) Carbothermic



In scheme (i), two reactions (1 & 2) are exothermic, whereas, in scheme (ii), the reaction 4 is endothermic. In the absence of free oxygen in the furnace, aluminothermic reduction of SiO_2 should be predominant and in oxygen atmosphere the formation of SiC may proceed through the reaction 4.

The propagation of the flame front is observed to be completed within 7-10 seconds in the present study. Thermal analyses of the powder compacts indicates the exothermic reaction initiation temperature is ≈ 993 K. It has also been noticed that the combustion reactions proceed in two distinct stages. The first stage is associated with a considerable temperature rise possibly due to highly exothermic oxidation reaction of aluminum. The adiabatic temperature of stoichiometric mixture is calculated to be around 2375 K. The second stage is initiated after completion of the first stage and is marked by moderate temperature rise, probably due to the mild exothermic reaction of SiC formation. Typical XRD patterns of samples c and f are shown in figure 2 (a & b) and details of the XRD analyses of the samples are summarised in Table 2.

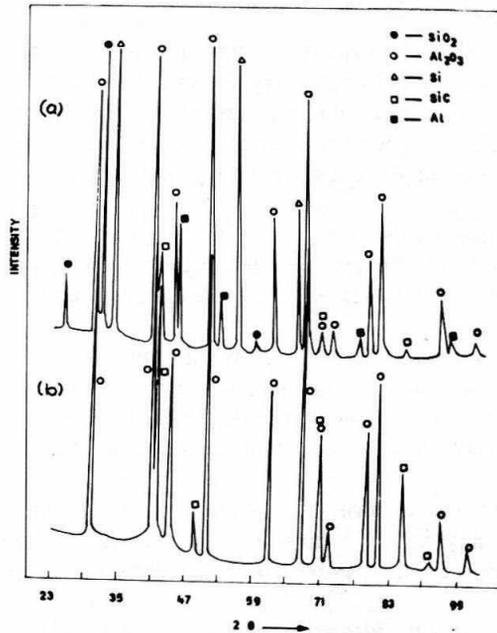


Figure 2 XRD patterns of the samples C (a) and F (b)

Table - 2 XRD analysis of fabricated pellets

Sample	Phase					Peak Ratio	
	Al	SiO ₂	Si	Al ₂ O ₃	SiC	Si/SiC	Al ₂ O ₃
A	✓	✓	✓	✓	✓	2.70	0.11
B	x	x	✓	✓	✓	1.26	0
C	✓	✓	✓	✓	✓	9.0	0.38
D	x	x	✓	✓	✓	1.47	0
E	x	x	✓	✓	✓	0.14	0
F	x	x	x	✓	✓	0	0

Presence of metallic Si in the samples A, B, C, D and E, as evident from the figure 2 and table 2 confirms the aluminothermic reduction of SiO₂. Some amount of unreacted SiO₂ and metallic aluminium are also detected in the samples (A) and (C). A soaking time of ≈ 10 mins is observed to be sufficient for the complete reduction of silica. In air treated samples, the Al at the surface of the pellets may undergoes aerial oxidation, hindering aluminothermic reduction of SiO₂. Hence a less amount of Al is expected for

the air treated sample (A) than argon treated sample (C). It is also evident from table 2 that the relative amount of unreacted Si decreases and on the other hand, the proportion of SiC increases with the increase in soaking period. From the XRD analysis it has also been observed that the amount of SiC is more in the air treated samples than the argon treated samples. This can be attributed to the higher processing temperatures for the former. These observations are in accordance with the expectations. XRD analysis of the sample F shows the presence of α -Al₂O₃ and β -SiC phases only (Fig. 2) indicating that a soaking period of \approx 30 mins is required for the completion of reactions.

SEM images of the samples A, B, C and F are presented in figure 3 (a, b, c and d). Silicon carbide in samples A, B and F is found as whiskers. Whisker formation in the sample C is observed to be not prominent possibly due to low temperature processing and no soaking (Fig. 3c). The amount and size of the whisker is observed to increase with the processing temperature and time as evident from figure 3 (a, b and d). EDS analyses have indicated that the growth of SiC_w is prominent in the alumina rich surroundings.

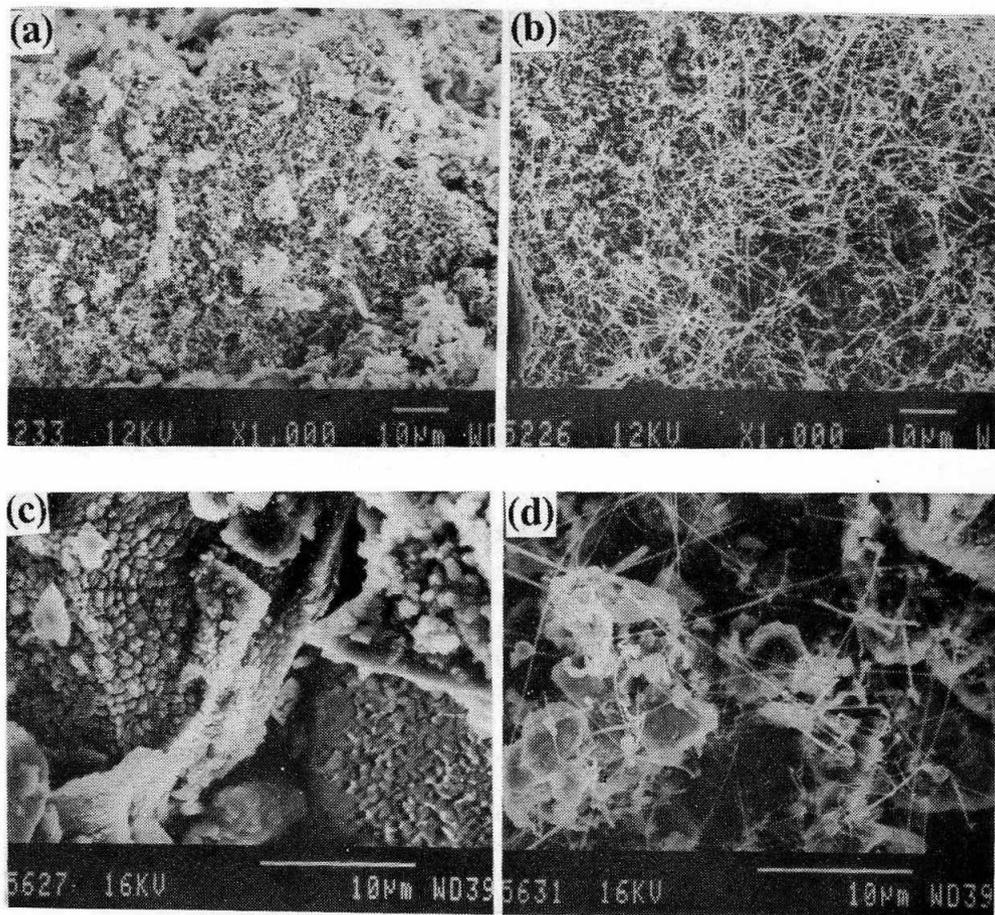


Figure 3 SEM images of the samples A (a), B (b), C (c) and F (d)

The photograph of fabricated composite pellets shown in figure 4, indicates that the shape of the pellets remains unaltered after the RH-SHS. This also suggests the aluminothermic reduction of SiO_2 because a large volume of gas evolution during carbothermic reduction would result in deformed, porous product. Hence, the present process appears to be useful for near net shape fabrication of composites.



Figure 4 Photograph of samples A and B.

CONCLUSIONS

The RH-SHS process is found to be a viable technique for the fabrication of composites. Reduction of SiO_2 is found to proceed through aluminothermic route both in air and argon atmosphere. A soaking period of 30 mins is observed to be sufficient for the completion of reaction. The amount and size of the SiC whiskers are observed to increase with processing temperature and time. Retention of the shape of the pellets after treatment indicates the possibility of near net shape fabrication of composite through RH-SHS.

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