DEVELOPMENT OF CORUNDUM/MULLITE COMPOSITES FROM FLY ASH AND ALUMINA MIX BY REACTION SINTERING

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Abstract

Composites of corundum/mullite have been developed from mixtures of fly ash and alumina by reaction sintering at 1600°C. The physico-mechanical properties of the composites have been evaluated. The microstructural evolution of the composites was investigated by scanning electron microscope(SEM). The spherical corundum crystals were found reinforced with randomly oriented acicular mullite matrix leading to dense microstructure and consequently improved mechanical, wear resistant and refractory properties. The reasons of the improved properties have been discussed in the paper.

Key Words: Mullite, Corundum, Composites, Microstructure, Properties

Introduction

Mullite has become a very important material for advanced structural and functional ceramics. The reasons are some of its outstanding properties like low thermal expansion, low thermal conductivity and excellent creep resistance but exhibits low strength and fracture toughness[1-3]. To enhance the mechanical properties of mullites ceramics, development of mullite-matrix composites has taken place. The addition of various alumina grains in mullite matrix composites to form ceramic composites with better strength and toughness has become widely recognised as a method for producing materials for structural applications.

Commercial mullite is prepared from the mixture of kaolin and alumina by reaction sintering method[4]. Mullite from various starting materials has been intensively investigated by many workers[5,6]. Synthesis of mullite from mixture of fly ash and alumina was reported by several authors[7-9]. They observed that these mullites have comparable properties with that of pure commercial mullite. Use of fly ash for the development of hard sintered wear resistant products was also reported by some workers[10,11].

The approach selected to synthesize corundum/mullite composites was reaction sintering. Mullite($3Al_2O_3.2SiO_2$) is a single crystal phase composed of 72 wt% of alumina and 28 wt% of silica[12]. The composition of fly ash falls in the range of 12 to 27 wt% alumina and 31 to 63 wt% of silica[13]. The additional alumina added to fly ash to make up the deficiency and under the appropriate sintering conditions, the fly ash and alumina mixture can react to form corundum/mullite composites.

Experimental

The starting materials used to provide necessary Al_2O_3 and SiO_2 for the desired phase were fly ash and calcined alumina. The raw materials were wet milled intimately in a pot mill for specific duration to a fineness of around 5μm. The slurry obtained was then dried, powdered and homogenised. The prepared powder was compacted using 300 to 350 kg/cm^2 pressure. The compacted samples were again dried and sintered at 1600°C with 2 hours soaking. The rate of heating was kept constant at 6°C/min.

Laboratory Process Flow-Sheet

Raw Material
Fly Ash + α-Al_2O_3
↓
Wet Milling
↓
Sieving
↓
Drying
↓
Homogenisation
↓
Powder
Preparation
↓
Compaction
↓
Drying
↓
Sintering
↓
Characterization

The chemical analysis and physico-mechanical properties such as hardness(Mohs scale), linear shrinkage, bulk density(Archimedes method), flexural strength (three point load), fracture toughness, % apparent porosity(ASTM C373) and compressive strength(ASTM C377) were evaluated by the standard procedures. The particle size after milling was measured with the help of sedigraph. The erosion rate was determined by the volume loss of material in cm^3/kg of erodent at 45^0 impact angle. Abrasion rate was measured on Morgan Marshal abradability index. X-Ray Diffraction (XRD) data were obtained with a diffractometer using Ni filtered $Cu(K_\alpha)$ radiation. Scanning Electron Microscopy(JEOL JSM 840) has been carried out on the fractured surface of sintered specimen to study the crystal morphology.

Results and Discussion

The bulk chemical composition of the raw materials used are given in Table-1.

Table - 1
Chemical Compositions of the Raw Materials

Constituents	Raw Materials (Wt %)	
	Fly ash	Alumina
SiO_2	59.82	-
Al_2O_3	27.79	99.5
Fe_2O_3	4.46	<0.05
CaO	1.44	-
MgO	0.63	-
TiO_2	0.02	-
L.O.I	3.21	0.2

The particle size distribution of the fly ash and clay mixture after 12 hours of ball milling is given in Fig.1. It can be observed from the figure that more than 95% of particles are smaller than 5 microns. The majority of the particle belongs to the size range of 1 to 4 microns. This very fine particle distribution has contributed towards attaining the bulk density of the composites near the theoretical density values.

Fig.2 shows the XRD pattern of corundum/mullite composites. The major phases identified are mullite and corundum.The mullitization started at the interface between pressed pellets of alumina and silica present in the raw mix. The mullite crystal grows as a result of movement of SiO_2 into Al_2O_3 zone and a glassy phase was also formed due to diffusion of Al_2O_3 into SiO_2. The excess of alumina present in the composition has given rise to the corundum phase. Both primary and secondary mullite have been formed. The primary mullite has come from the host fly ash while the secondary mullite has formed by reaction sintering of free SiO_2 present in fly ash and Al_2O_3.

The mullite formation started at the lower temperatures but major mullitisation has taken place at 1600°C. The reaction sintering at 1600°C is the result of presence of impurities like Fe_2O_3, TiO_2, CaO etc. in fly ash. Further, additives played a significant role in promoting the sintering at lower temperatures. Johnson and Pask[14] also observed that addition of small amount of Fe_2O_3, TiO_2 and CaO to Al_2O_3-SiO_2 mixtures enhanced the crystal growth.

The microphotographs taken on the fractured surface is given in Fig.3. The spherical corundum grains are uniformly dispersed throughout the mullite matrix. The needle shaped mullite crystals are randomly oriented and interlocked together giving rise to very compact microstructure. Dekeysen[15] also reported that when mullite is formed in the presence of small amount of intergranular glassy phase, it always exhibits an acicular or elongated morphology.

The mechanical and refractory properties of the presently developed composites are presented in Table 2.

Table - 2
Physico-mechanical & refractory properties of the corundum/mullite composites.

Physico-Mechanical Properties		
Bulk Density	:	2.89 g/cc
Apparent Porosity	:	0.56%
Hardness (Mohs Scale)	:	9
Compressive Strength	:	990 MPa
Flexural Strength	:	197 MPa
Fracture Toughness	:	3.58 $MPam^{1/2}$
Erosion Rate	:	0.015
Abradability Index	:	22.21
Refractory Properties		
P.C.E.(Pyrometric Cone Equivalent) Value	:	36
Linear Shrinkage	:	12.8%

Data of the above table shows that the bulk density of the composites (2.89 g/cc)has achieved almost 95% of the theoretical density. The low apparent porosity at 1600°C has resulted both from the crystalline structure of mullite corundum crystals and glass phase matrix kept rigid by a lattice of secondary mullite in which the crystals of primary mullite grows as closely knitted long needles. This dense net of mullite crystals and the viscous glassy phase occupied the pore spaces and reduced the porosity.

The hardness of the composite is 9 on Mohs scale which is equal to corundum and next to diamond. Comparing with mullite, there is not much improvement in compressive and flexural strength. This may be due to presence of impurities which leads to glass formation and consequently low strength properties. However, an improvement in fracture toughness value(3.58 MPa $m^{1/2}$) was obtained as compared to mullite which is 2.73 M Pa $m^{1/2}$ as reported by Ismail et al. [16]. The erosion and abrasion resistant results confirm the suitability of these composites for wear resistant applications.

The pyrometric cone equivalent of 36 and %linear shrinkage of 12.8 indicate that the composites can be used for high temperature refractory applications.

Conclusions

On the basis of the present study, the following conclusions can be drawn:

1. Fly ash can be used as one of the raw materials for the development of corundum/mullite composites.
2. The presently developed composites consist of spherical shaped corundum crystals and needle shaped mullite which are reinforced together.
3. These composites show improved mechanical and refractory properties.
4. These composites can be used for structural, wear resistant and high temperature applications.

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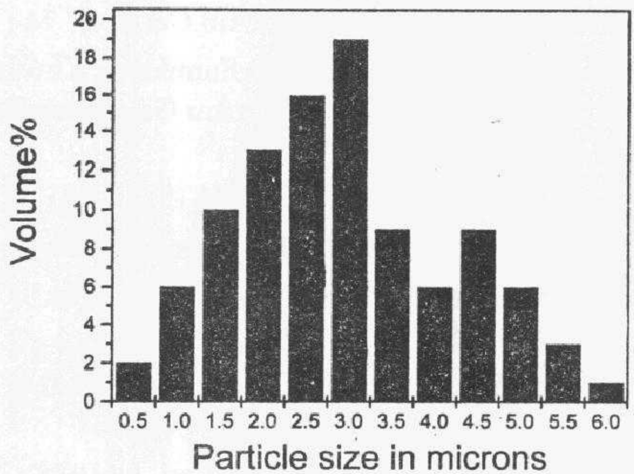

Fig.1 - Particle size distribution of fly ash & clay mixture after ball milling.

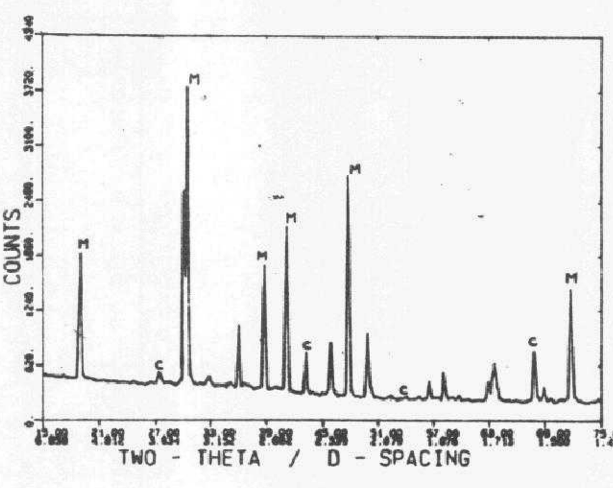

Fig.2 - XRD pattern of corundum/mullite composition

Fig.3 - SEM of fractured surface of composites