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The Physical, Thermal and Phase Identification Studies of Zirconia–Flyash Material

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Abstract: The addition of zirconia in different proportions to one of Indian flyash has been studied for its sintering characteristics. The sintered product has been characterised for physical, thermal properties and phase identification studies. The density was increased with zirconia content and the per cent linear shrinkage remained almost constant. As observed, the major phase was zircon($ZrSiO_4$) in these materials. The other phases were mullite, faylite, quartz and cristobalite. As the amount of zirconia increased in the matrix, the free silica was consumed by zirconia to form zircon. At 25% zirconia content, there was no free silica present. The thermal expansion studies revealed the decrease of per cent change in length with the addition of zirconia up to 25% in flyash matrix. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Flyash is a by-product of thermal power stations during the combustion of coal. It is available in very large quantities. It is a finely divided residue with particle size varying from 0.5 micron to 100 microns. It is refractory and abrasive in nature. The chemical composition of flyash varies with the source of coal used. But the major constituents of flyash are silica, alumina, iron oxide, calcia, etc., which constitute up to 95–98% of the total composition. The minor constituents are alkalies, magnesia, titania. It also contains trace amounts of elements like vanadia and manganese oxide.[1]

A country like India produces nearly 70–75 million tonnes of flyash every year. Due to the stringent environmental regulations, the disposal of such flyash wastes is a major problem. A lot of effort has been put to produce bricks, tiles, concretes, etc. from flyash. An emphasis has also been given to produce wear resistant tiles using flyash as a raw material. The details have been compiled elsewhere.[2] Efforts are also on to develop value added ceramic materials using flyash as a raw material.

Zirconia is a versatile material which finds application in all the major fields of ceramics such as refractories, structural ceramics, electronic ceramics, etc. The martensitic transformation of zirconia plays an important role in designing structural ceramics. A lot of work has been carried out and published. There were few reviews on zirconia ceramics reported in the literature.[3–5]

To the best of our knowledge, for the first time an attempt has been made here to add zirconia into flyash matrix in various proportions and study the properties like physical, thermal and phase identification. Unlike in zirconia–alumina composite which has been well studied by various authors,[6–8] here zirconia takes part in the reaction with the matrix material, i.e. flyash to form new phases. A correlation of properties has been carried out in this study. The microstructural and mechanical properties are under study by the author and will be published later.

2 EXPERIMENTAL

The flyash used in this experiment was obtained from Raichur thermal power station, Karnatak, India. The chemical composition of the powder is

Table 1. Chemical composition of flyash used in the present work

SL. No.	Chemical composition		Wt %
1.	Silica	(SiO_2)	57.00
2.	Alumina	(Al_2O_3)	29.30
3.	Iron oxide	(Fe_2O_3)	06.50
4.	Calcia	(CaO)	03.90
5.	Magnesia	(MgO)	01.10
6.	Potassium oxide	(K_2O)	00.30
7.	Sodium oxide	(Na_2O)	00.21
8.	Titanium dioxide	$(TiO)_2)$	00.13
	Loss on ignition	(LOI)	0.00

given in Table 1. The average particle size (D_{50}) value of this material was found to be 3.76 microns and with a specific gravity of 2.4.

The zirconia used in this experiment was that of our institute prepared by a solution method. 3 mole % yttria (Y_2O_3) was used in zirconia as a stabilising agent. This powder was pure and had an average particle size of <0.5 microns.

Stoichiometric compositions of zirconia were added in flyash. Different batches having 0, 5, 10, 15, 20 and 25% of zirconia in flyash were dispersed in an alcohol medium with a suitable dispersant. Each mixture was pulverised separately in a Fritsch pulverisette for 8 h using alumina bowls and alumina balls. The slurry was mixed with 2 wt% polyethylene glycol (PEG-4000) binder in solution form and again pulverised for 1 h. Then the mixture was dried to get back the powder and was sieved to form soft granules. The soft granules were used for compaction. The batches were named as F-0, F-5, F-10, F-15, F-20 and F-25 for the samples containing 0, 5, 10, 15, 20 and 25% zirconia in flyash matrix, respectively.

The granulated powders were uniaxially pressed at different pressure to make pellet and bar shapes. Five pellets of 25 mm diameter and 5 mm thickness were used for densification studies including shrinkage measurement. Rectangular bars of approximate green dimension of $60\times6\times5\,mm^3$ were fabricated for thermal expansion measurement studies.

The samples were dried at 110°C for 12 h prior to firing in an open tunnel kiln at $1255\pm5°C$. The fired samples were used for characterisation studies. The density and porosity measurements were carried out by standard Archimedes principle. The linear shrinkage was calculated by dimensional method. The X-ray diffraction studies were carried out on ground powder of the sintered pellets by a Rigaku X-ray diffractometer, Japan. The thermal expansion studies were carried out by a Harrop dilatometer, UK.

3 RESULTS AND DISCUSSION

The green density of the zirconia–flyash materials is given in Fig. 1. There was an increasing trend of green density observed with the addition of zirconia in flyash. This was obvious due to the fact that the density of zirconia is higher compared to that of flyash. As the zirconia content increased in the matrix, following the rule of mixture the density was also found to be increased. The similar trend was also observed in the fired densities of the samples. It was also found from the density measurements that, barring F-10 and F-15, all other samples were fully densified with no porosity. There was nearly 0.3% of apparent porosity found in F-10 and F-15 samples (Table 2). The percentage linear shrinkage of all these compositions did not vary to a great extent (Fig. 2). This may be due to the fact that all the samples were densified to near theoretical density at that sintering temperature.

The percentage elongation vs temperature of zirconia–flyash samples showed increasing trend of the values with the rise in temperature. This was because of the stretching of the bond with the application of temperature. The per cent elongation vs temperature curves were lowered in value with the addition of zirconia in flyash matrix (Fig. 3). This was explained on the basis of formation of increasing amount of zircon as the major phase with the addition of zirconia. The linear thermal expansion coefficient value of zircon was in the range of $4.5–6.0\times10^{-6}\ K^{-1}$ from room temperature to 1000°C. In the same temperature range, cristobalite had the value of $6.0–8.0\times10^{-6}\ K^{-1}$ and that for mullite is $5.0–7.0\times10^{-6}\ K^{-1}$.[9] From the above data it was obvious that, as the amount of zircon increased in the matrix with the addition of zirconia, the linear thermal expansion coefficient values dropped down proportionately. The phase formations had been confirmed by XRD analysis.

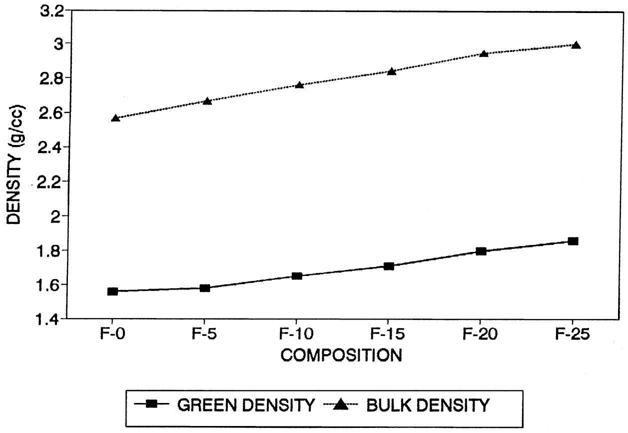

Fig. 1. Variation of density of zirconia–flyash material.

Table 2. Properties of zirconia–flyash material

Composition	GD (g cc^{-1})	BD (g cc^{-1})	O.P. (%)	L.S. (%)	T.E.C×E-6 at 1000°C (/°K)	Major phases
1. F-0	1.56	2.57	0	17.8	NA	Q, C, M,H,F
2. F-5	1.58	2.67	0	18.2	5.75	Z,Q,M,C,H,F
3. F-10	1.65	2.76	0.3	17.8	5.38	Z,Q,M,C,F,H
4. F-15	1.71	2.84	0.3	17.2	4.78	Z,Q,M,C,F,H
5. F-20	1.80	2.95	0	17.2	4.60	Z,Q,M,C,F,H
6. F-25	1.86	3.00	0	18.2	4.41	Z,Q,M,C,F,H

N.B: Q=quartz, C=cristobalite, Z=zircon, M=mullite, F=faylite, H=hematite, NA= not available, GD=green density, BD= bulk density, O.P.=open porosity, T.E.C.=thermal expansion coefficient, g cc^{-1}=gram cubic centimetre^{-1}.

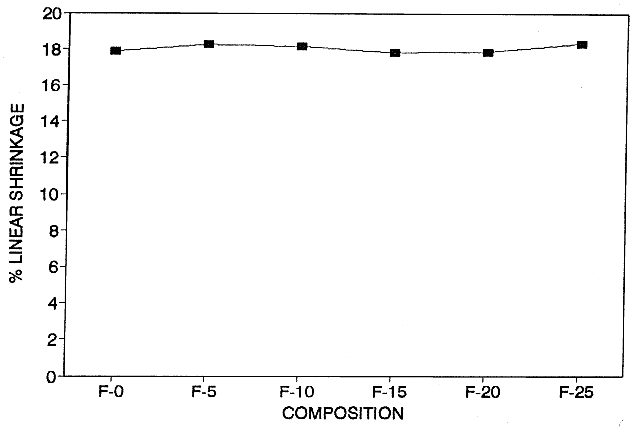

Fig. 2. Variation in per cent linear shrinkage of zirconia–flyash material.

The X-ray diffraction pattern of various compositions are compared in Fig. 4. The pure flyash without any additives (F-0) showed mullite, quartz, cristobalite and hematite as the major phases. The mullite was formed by the reaction of alumina and silica. Since the quantity of silica in flyash was of the order of 57%, the remaining silica appeared in the pattern as quartz and cristobalite. The formation of the cristobalite depends on the sintering temperature and the duration of soaking at the peak temperature. F-5, F-10, F-15, F-20 and F-25 are the XRD patterns compared with that of F-0.

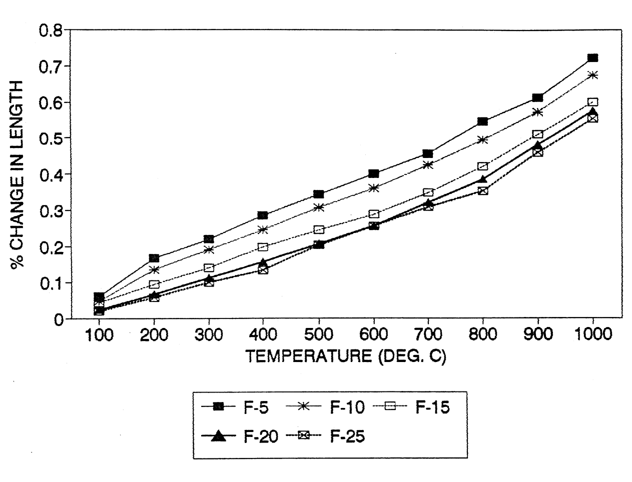

Fig. 3. Variation in per cent change in length of zirconia–flyash material.

In F-5 it was observed that the reaction between zirconia and silica occurred leading to major phase as zircon ($ZrSiO_4$). In some 2θ values, these peaks were found to be overlapped with either quartz or hematite peaks. As the zirconia content increased in the flyash matrix it was observed that the intensity of zircon peak were enhanced and that of cristobalite peaks were reduced. In F-25 composition, there was no peak of cristobalite at $2\theta = 21.98$. This result indicated the non-availability of free silica at F-25 composition. It was also implied that the total silica content of 57% were exhausted at F-25 after reacting with both alumina and silica forming mullite and zircon phases, respectively. The mullite peak intensities were also reduced with the addition of zirconia. This result revealed the possibility of faster reaction between zirconia and silica compared to that of alumina and silica. The peak at $2\theta = 20.02$ which was earlier identified as quartz peak in F-0, was found to increase with the increase in zirconia additions. On investigations, it was found that there was a peak of zircon present in this 2θ range. As the zirconia content increased in the matrix, the tendency of forming zircon increased and thus intensity got enhanced. So, there may be a possibility of overlapping of both the peaks. A similar situation was also observed at $2\theta = 26.6$ as depicted in Fig. 4. There were also a few other zircon peaks that appeared with increasing intensity from F-5 to F-25 compositions, which were not seen in F-0.

Besides the major zircon and mullite peaks, the other main peaks were that of iron silicate or faylite. The formation of faylite was due to the reaction of free silica with the iron oxide of flyash. The other peaks were of very low intensity, which may be due to the formation of trace amount of calcium aluminate and magnesium aluminate spinel.

In a nutshell, the XRD pattern comparison of F-0 to F-25 samples revealed that, there was a strong interaction of alumina, zirconia and iron oxide with silica to form mullite, zircon and faylite, respectively. The proportion of these phases depended upon the amount of additives present in

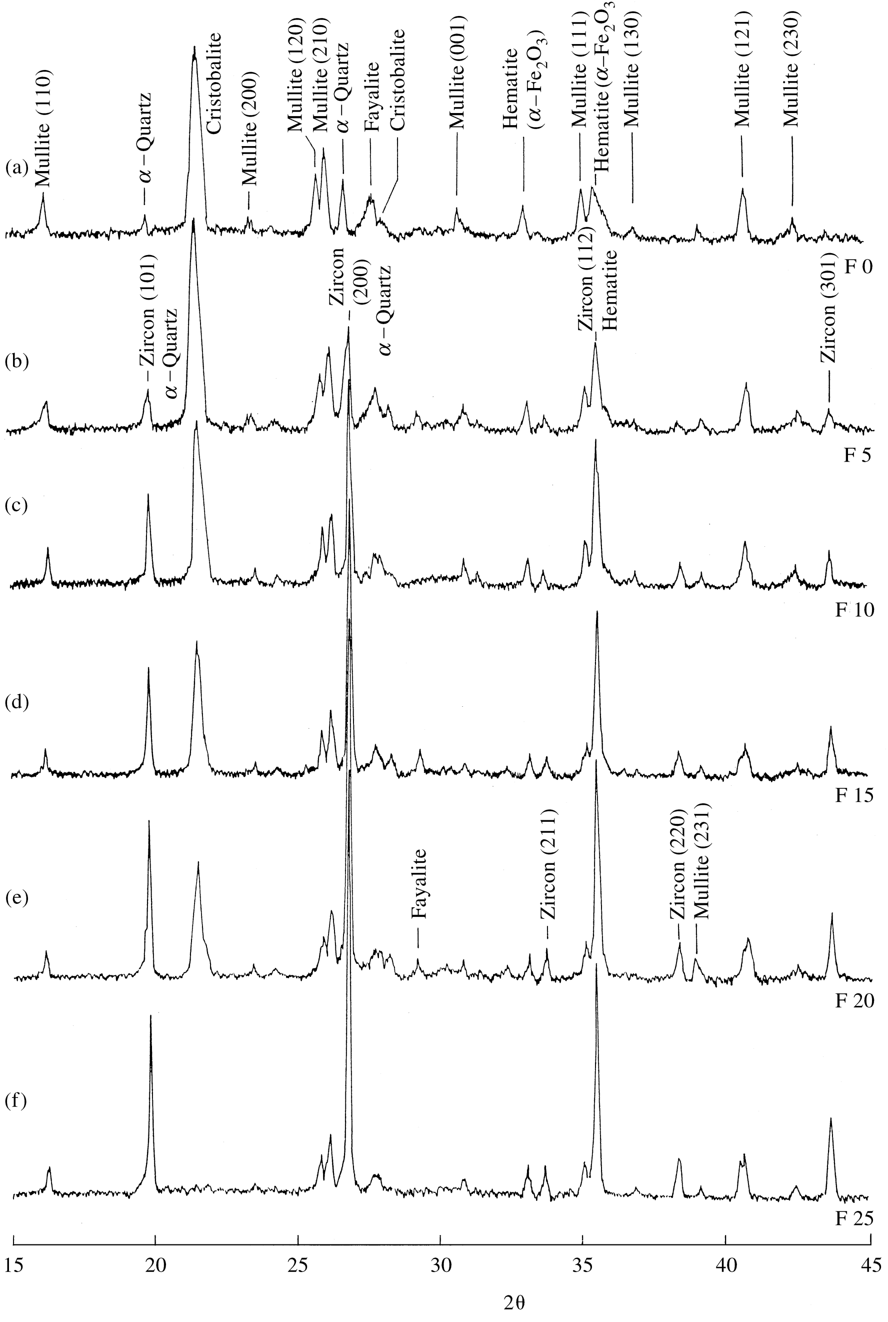

Fig. 4. XRD patterns of zirconia–flyash materials.

flyash matrix, keeping other factors constant. Table 2 summarises the properties of zirconia–flyash materials studied in this work.

4 CONCLUSIONS

An attempt has been made for the first time to study the properties of flyash with the additions of zirconia as a second phase material. The physical, thermal and phase identification studies of these materials were reported here for various compositions of zirconia–flyash materials. The density was found to be increasing and the per cent linear shrinkage remained almost constant with the additions of zirconia up to 25 wt% in flyash matrix. The per cent elongation of these materials showed a downward trend with the addition of zirconia. The major phase from XRD pattern was confirmed to be that of zircon. Other phases were mullite, faylite, quartz and cristobalite. The studies on the mechanical properties, abrasion resistance properties and microstructural characterisation of these materials are under progress.

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