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Transferred arc plasma processed mullite from coal ash and bauxite

S. Yugeswaran [a], P.V. Ananthapadmanabhan [b], Akira Kobayashi [a,*], L. Lusvarghi [c]

[a] *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[b] *Laser and Plasma Technology Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India*
[c] *Department of Materials and Environmental Engineering, University of Modena e Reggio Emilia, Via Vignolese, 905, Modena, 41100, Italy*

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Abstract

Coal ash disposal is one of the main problems in thermal power plant unit. Currently, a number of waste management systems are being tried for effective disposal of coal ash. In this paper, coal ash from thermal power plant unit was successfully utilized for synthesis of mullite ceramic by using transferred arc plasma processing (TAP) technique. For this purpose, bauxite was added with coal ash by 0, 25, 50 and75 weight ratio. The compositions were thoroughly mixed by ball milling and were melted in the transferred arc plasma torch at 10 kW input power level for 3 min. Argon was used as plasma forming gas. The phase and microstructure formation of the melted samples were investigated by XRD and SEM images. The results show that the additions of bauxite greatly influenced the phase formation of mullite during the processes.

Keywords: D. Mullite; E. Refractories; Coal ash; Arc plasma

1. Introduction

The possibility of utilization of industrial waste materials such as fly-ash, red mud rejected from aluminium industry, mud from hydrometallurgy zinc plants, etc. has assumed increased research and development thrust. Development of new glass–ceramic products by re-use of fly-ash from domiciliary waste incinerators and coal power plants has been the subject of many investigations [1–9]. Conversion of coal ash to ceramic bricks and zeolites has been studied by various investigators [6–10]. A number of researchers have used coal ash for devitrifying bulk glass samples by a two-stage heat treatment. However, all these conventional methods take long time to produce the composites and also their power consumption is high.

Transferred arc plasma processing is an effective and efficient technology for melting and vitrification of hazardous wastes due to the high temperatures and energy density available in transferred arc plasma (TAP) torch. The present paper deals with transferred arc plasma processing of coal ash to produce mullite-based ceramics for high temperature applications. Mullite ceramics have been extensively studied because of their excellent properties of high melting point (1830 °C), moderate thermal expansion coefficient, high resistance to thermal shock, good chemical stability in various corrosive environments, low thermal conductivity, low dielectric constant, excellent creep resistance and sufficient mechanical strength [11].

There are numerous advantages of the application of TAP for processing of materials and waste utilization. The process is characterized by extremely high temperatures (up to 20,000–30,000 K), excellent arc stability and low environmental impact (low oxides emissions, low percentage of ultra-fine powder). Another advantage of the process lies in the simplicity of generation and control. High power density allows high production rate with evident time savings [12–15]. Also, it is highly cost effective compared to the conventional methods. In this study, coal ash waste from thermal power plant was successfully utilized to prepare mullite ceramic.

2. Experimental procedure

The coal ash used in this investigation was obtained from the Neyveli Lignite Corporation (NLC), Tamilnadu, India and the bauxite was purchased from Carborundum Universal (CUMI) India (P) Ltd. The phase and chemical compositions of the coal ash and bauxite were analyzed by X-ray diffraction (XRD) and

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* Corresponding author. Tel.: +81 6 6879 8694; fax: +81 6 6879 8694.
E-mail address: kobayasi@jwri.osaka-u.ac.jp (A. Kobayashi).

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Table 1
Chemical composition of raw materials.

Constituents	Bauxite	Coal ash
Al_2O_3	57.5	28.97
SiO_2	5.1	60.44
TiO_2	6.4	1.97
Fe_2O_3	3.7	4.49
MgO	1.55	1.03
K_2O	0.21	1.08
P_2O_5	0.33	0.37
CaO	0.59	0.77
Na_2O	0.29	0.27
Others	Balance	Balance

spectroscopic analysis by induction coupled plasma (ICP) method. The chemical compositions of coal ash and bauxite are given in Table 1.

The objective of the present work is to convert coal ash to mullite. Muliite is $3Al_2O_3{:}2SiO_2$ and therefore, the molar ratio of alumina to silica required for mullite formation is 3:2. Coal ash contains about 30 wt.% of alumina and 60 wt.% of silica which correspond to alumina-to-silica molar ratio of 0.3:1. Therefore, the yield of mullite resulting from transferred arc plasma processing of coal ash alone without any addition of alumina is expected to be very low. The idea of adding bauxite is to bring the alumina–silica ratio closer to 3:2. Since coal ash contains about 30% of alumina, the amount of bauxite required to bring the alumina–silica molar ratio closer to 3:2 would be about 50 wt.%. In view of the considerable loss of silica (by volatilization as SiO gas) during transferred arc plasma processing, it was decided to see the effect of lower and higher alumina additions on the phase composition. The amount of bauxite additions was worked out with this logic. Free energy minimization plots for the alumina–silica system illustrates the significance of the relative amounts of alumina and silica on the formation of mullite. It is also seen from free energy minimization studies that the by proper control of alumina–silica ratio, mullite formation can be accomplished.

Transferred arc plasma processing was carried out using coal ash and coal ash mixed with 25, 50 and 75% of bauxite powder. The different samples were designated as T1 (100% coal ash), T2 (75% ash + 25% bauxite), T3 (50% of ash + 50% bauxite) and T4 (25% ash + 75% bauxite). The powder mixture containing different percentages of bauxite was thoroughly mixed in a planetary ball milling for 2 h. The ball to mixture weight ratio was kept at 10:1. The milled powders were melted in the transferred arc plasma torch at 10 kW input power level for 3 min and cooled by a jet of air directed towards the molten sample. The schematic diagram of the TAP system is shown in Fig. 1.

The transferred arc plasma system consists of plasma torch, power supply, gas and water lines. The cathode of the plasma torch is made of a graphite rod 250 mm long and 50 mm diameter. Its end tapers to a conical shape for better electron emission. The cathode is enclosed in a hollow brass cylinder and provisions are made for water circulation (for cooling) and gas flow. The system has multiple inlets for plasma gas at the cathode end. A graphite bowl of 100 mm depth and 50 mm inner diameter serves as the anode and melting bed. The samples were placed in the anode bed and DC arc was struck. The melted samples were cooled by forcing a jet of air on the molten sample. The operating parameters for the experiments are given in Table 2. The different compositions of coal ash–bauxite mixture are labeled as T1, T2, T3 and T4. The weight % of bauxite was 0 in T1; 25 in T2; 50 T3; and 75 in T4.

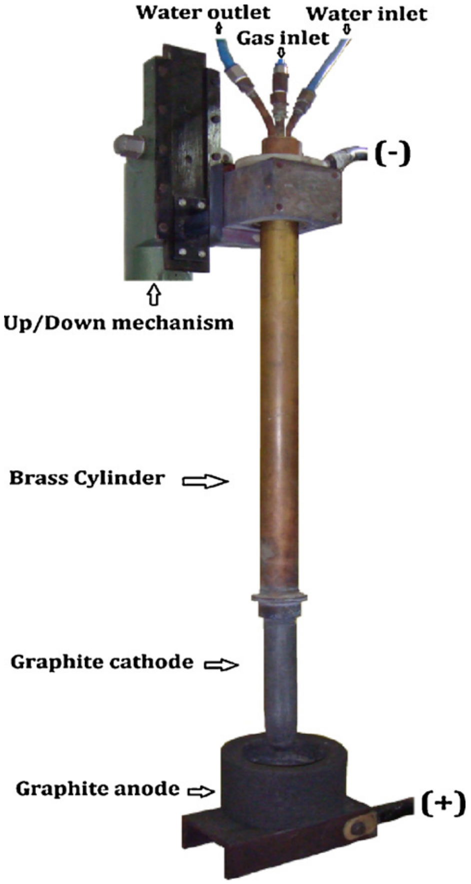

Fig. 1. Sehamatic of TAP torch.

The TAP processed samples were milled down to a few micrometer size powders in agate mortar prior to X-ray diffraction (XRD) analysis. For scanning electron microscope (SEM) investigation, the samples were polished beginning with a set of silicon-carbide papers and final polishing with diamond paste. Then the samples were chemically etched using 30 wt.% HF solution for 30 s. The XRD pattern of the sample was performed using a PW Philips X-ray diffractometer with Cu Kα

Table 2
Operating parameters.

Input power	10 kW
Plasma gas and flow rate	Argon; 10 lpm
Cooling water flow rate	10 lpm
Processing time	3 min
Cooling time	10 min
Cooling medium	Forced air

radiation. The microstructures of the samples were studied by SEM (Philips XL40) and the compositions by EDX spectrometry (EDX, INCA, Oxford Instruments). The density and porosity of the TAP processed samples were measured by Archimedes' principle method.

3. Results and Discussion

3.1. Phase and chemical composition of raw materials

Figs. 2 and 3 show the XRD patterns of raw coal ash and bauxite respectively. The coal ash mainly consisted of quartz and small amounts of potassium aluminium silicate (microcline, microperthite) and calcium aluminium oxides. The XRD pattern of bauxite shows that gibbsite (γ-Al $(OH)_3$) is the main phase combined with small amounts of boehmite (γ-AlO(OH)), nacrite ($Al_2Si_2O_5(OH)_4$), anatase TiO_2 and cristobalite. Chemical composition of the as-received coal ash and bauxite was characterized by ICP spectroscopy and the results are summarized in Table 1. Bauxite is mainly composed of alumina (57.5 wt.%), about 24% water, and small amounts of silica (5.1 wt.%), titania (6.4 wt.%) and ferric oxide (3.7 wt.%). In addition to this, very little amounts of alkali and alkaline-earth metal oxides such as Na_2O, K_2O, MgO and CaO, are also present. The major content of coal ash is SiO_2 (60.44 wt.%) and Al_2O_3 (28.97 wt.%) along with 4.49 wt.% of Fe_2O_3 and very little amounts of other alkali and alkaline-earth metal oxides.

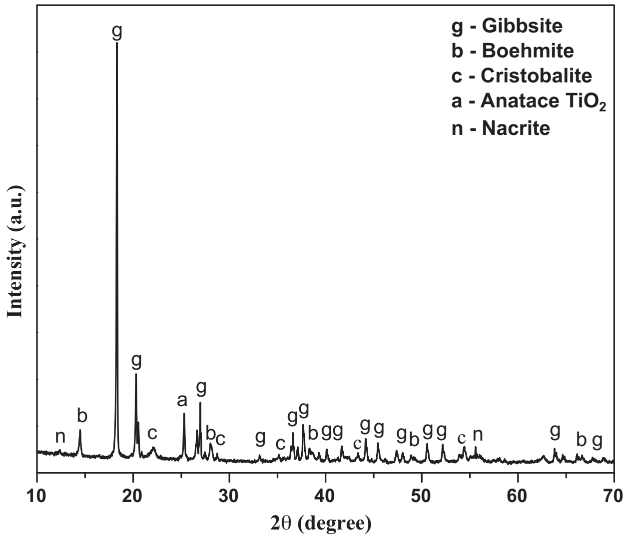

Fig. 2. XRD pattern of natural bauxite.

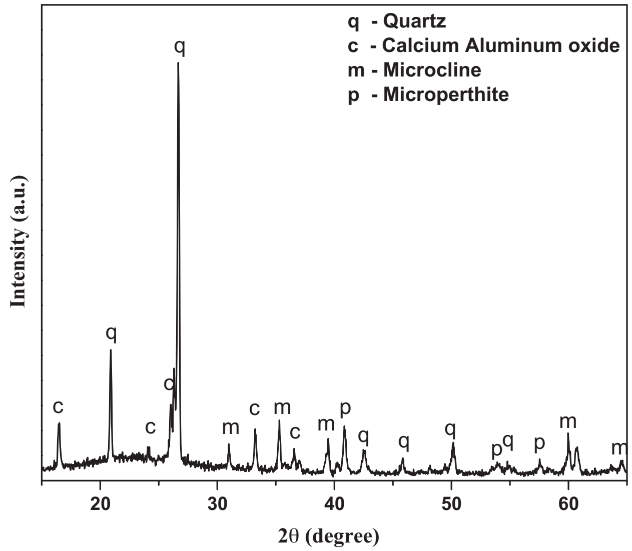

Fig. 3. XRD pattern of as received coal ash.

3.2. Phase and microstructure analysis of TAP processed samples

Fig. 4 shows the XRD patterns of four different compositions of TAP processed coal ash–bauxite mixtures (T1, T2, T3 and T4). The XRD pattern of T1 composition shows mullite as the predominant phase along with quartz in minor amount. In addition, a large broad peak was observed due to the presence of a large amount of silica-based amorphous phase in the processed sample. This is because of the insufficient amount of alumina in coal ash (see Table 2) to completely bind the silica and form mullite during the TAP process. During TAP processing, it was observed that the coal ash initially melted and part of the silica and the alkaline oxides in the ash evaporated due to the high temperature of the plasma arc. The alumina present in coal ash reacted with silica to form mullite. However, the excess silica remained as amorphous silica during the cooling process. This is evident from the broad diffraction peaks seen in the lower two theta side of the XRD spectrum.

The XRD pattern of T2 composition clearly showed sharp mullite peaks along with amorphous silica or aluminium silicates as seen from the broad peaks in the lower two theta end of the pattern. Addition of bauxite (25%) to coal ash increases the amount of alumina favoring increased mullite formation. The XRD pattern of T3, on the other hand, shows only a single phase corresponding to mullite. In this case, the amount of amorphous silica and/or aluminium silicates is much less compared to the sample T1 and T2. Addition of 50% bauxite increases the amount of alumina in the mixture and the weight fractions of alumina and silica are close to their respective theoretical values in mullite. Further, the high temperature of the plasma arc helped in removing a large fraction of the alkali oxides, alkaline-earth oxides and excess silica as volatile species. This resulted in a product that consisted entirely of mullite.

In contrast to the XRD patterns of T1, T2 and T3, XRD pattern of T4 composition shows the presence of sillimanite and small amount of alumina phases along with the predominant mullite phase. In this case, the mullite peaks show shoulder region, which can be resolved to the XRD peaks of sillimanite. The higher alumina content in T4 plays a key role in the solid state reaction between alumina and silica. Fig. 5 shows the comparative XRD pattern of T2, T3 and T4 at 20 to 30° interval of 2θ. The comparative patterns clearly show the splitting of the complex peak at $\sim$26° into those of mullite, sillimanite and alumina.

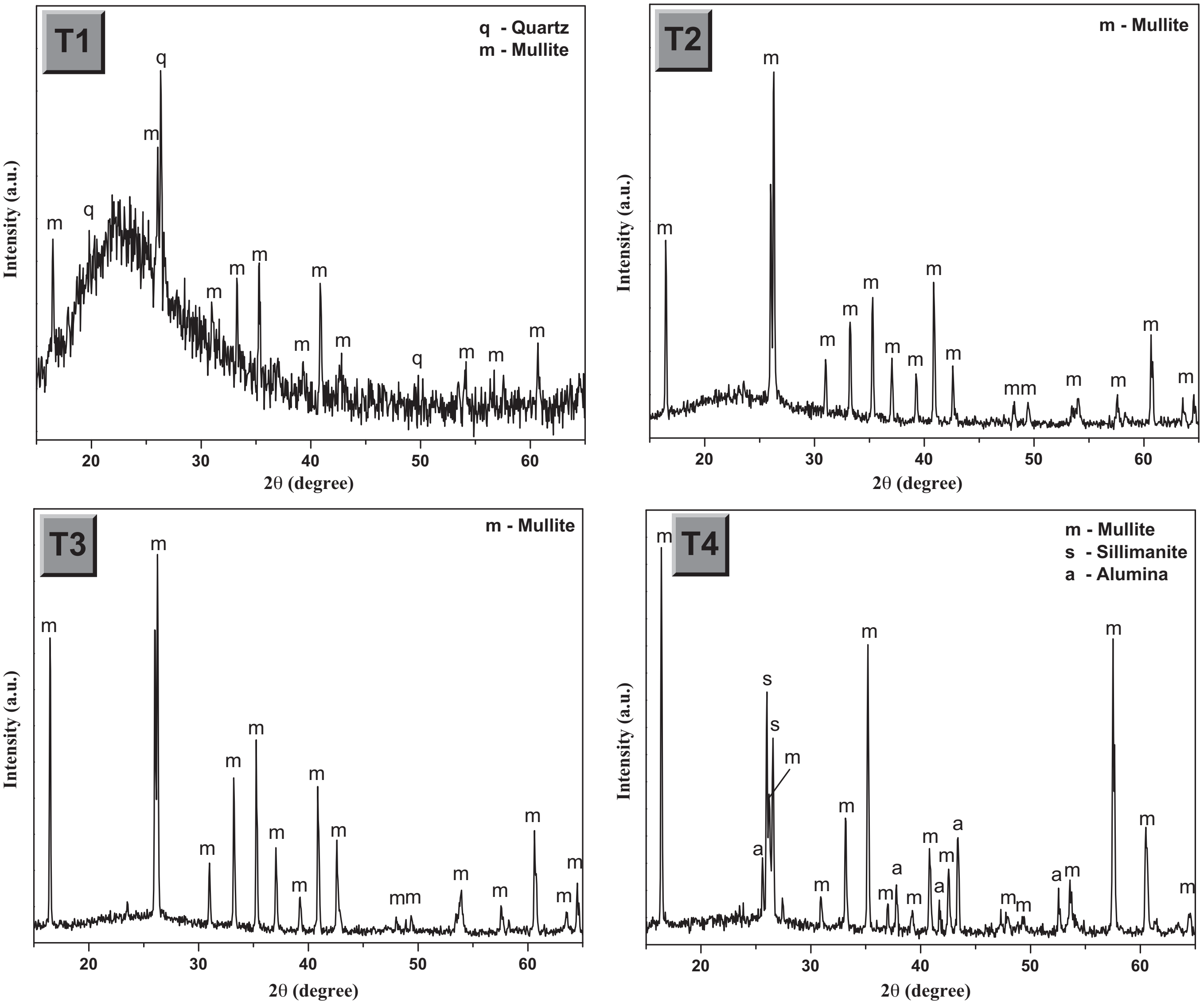

Fig. 4. XRD pattern of TAP processed T1, T2, T3 and T4 samples.

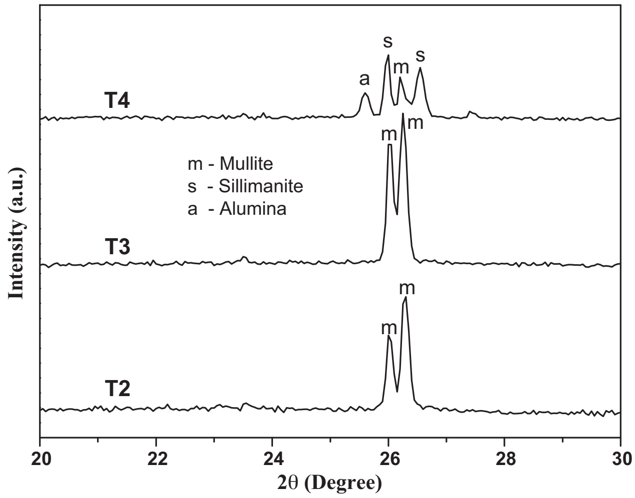

Fig. 5. Comparative XRD pattern of TAP processed T2, T3 and T4 samples.

Fig. 6 shows the SEM images of TAP processed T1, T2, T3 and T4 samples of coal ash and bauxite mixtures. The microstructure of T1 composition i.e. coal ash is more porous compared to all other compositions. During the process, silica in the coal ash gets melted and goes into liquid state; at this stage the small amount of liquid phase alumina reacts with liquid phase silica and forms a mullite phase and free silica are still present in the molten slag. During the solidification, the excess silica solidifies as silica rich amorphous phase with simultaneous release of volatile species as gas. The escape of the volatile matter and differential shrinkage rates of mullite and silica cause pores in the processed samples.

The microstructure of T2 shows like a layered structure with two different colors (dark and light gray color). The structure of the dark and light regions was identified by using EDX analysis with the corresponding SEM image (Fig. 7). EDX spectrum corresponding to the dark gray region shows large concentration of Al compared to the light gray region. Results of EDX

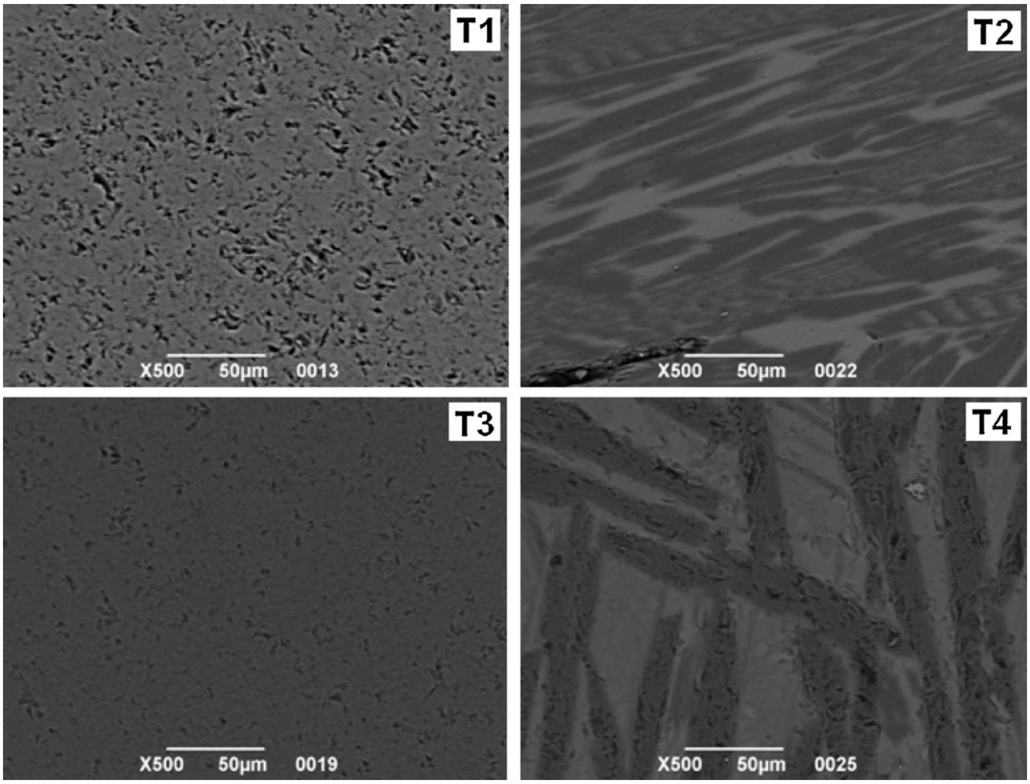

Fig. 6. SEM images of TAP processed T1, T2, T3 and T4 composition.

coupled with that of X-ray diffraction clearly show that the sample consists of mullite and silica or aluminium silicate phase. The spectrum shows that the dark gray colored region represents mullite and light gray region corresponds to silica rich aluminium silicate. However, the presence of silicates is not identified in XRD, because mullite and aluminium silicate have similar structure with their diffraction peaks very near to each other and also because of the lower concentration of sillimanite.

The microstructure of the T3 composition appears with homogeneous equiaxial grains of mullite. The magnified image (Fig. 8) of T3 clearly shows the presence of equiaxial mullite in cubic structure with randomly distributed pores. The equiaxial grain growth of mullite clearly shows that the processed mullite is having more than 72 wt.% Al_2O_3 [16]. Hence the microstructure formation confirms that T3 composition has a suitable ratio to get a single phase mullite with homogeneous structure.

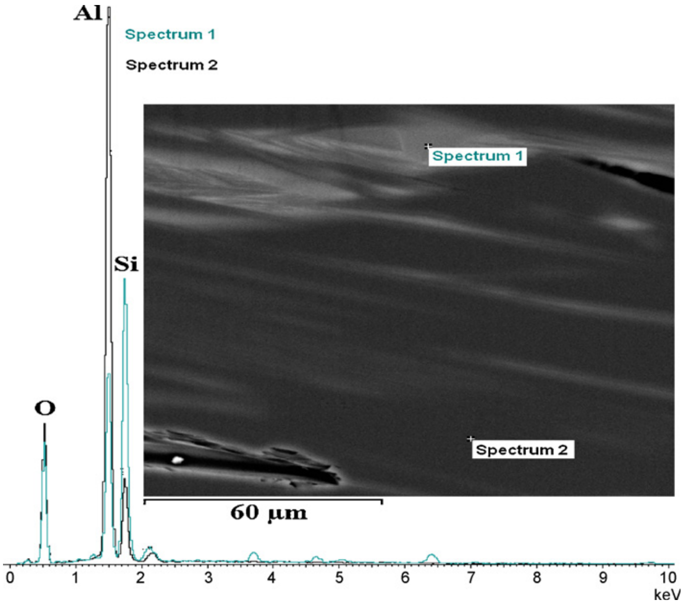

Fig. 7. SEM with EDX images of TAP processed T2 composition.

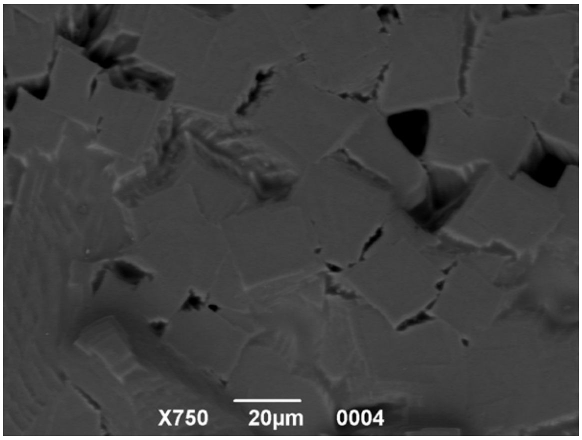

Fig. 8. Magnification SEM images of TAP processed T3 composition.

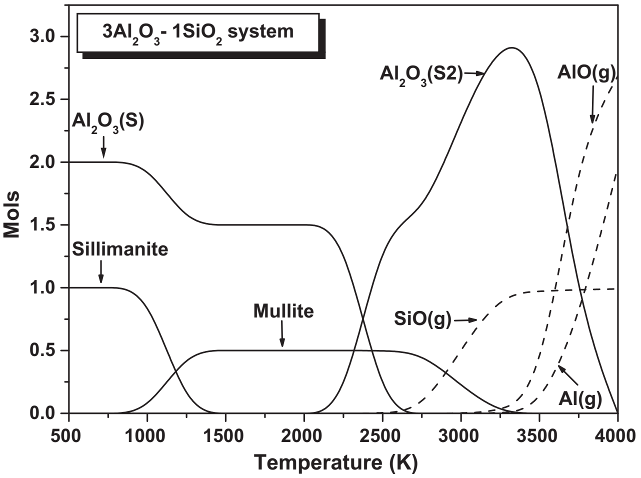

Fig. 10. FEM Plot for $3Al_2O_3$–$1SiO_2$ system.

3.3. Sillimanite formation

During the TAP processes corundum (α-Al_2O_3) crystallizes from the decomposition products of major Al-bearing hydrates, mostly gibbsite and boehmite. Then the corundum (α-Al_2O_3) reacts with quartz to form mullite. One significant finding of the experimental studies is that, mullite is formed in all the cases irrespective of the alumina–silica ratio in the starting material. Further, sillimanite (aluminium silicate, Al_2SiO_5) is also formed although in small amount, along with mullite. In the case of composition T1, where the amount of silica is much higher than that of alumina, sillimanite and silica (excess) are the expected compounds after plasma melting. However, the results show the formation of mullite along with silica admixed with small quantity of sillimanite.

In order to explain these experimental findings, free energy minimization (FEM) plots of the Al_2O_3–SiO_2 system, in different ratios, were developed using CSIRO thermo package [17]. FEM plots were constructed over a wide temperature range from 500 K to 4000 K at 1 atm total pressure. Results of the FEM plots for alumina–silica ratio of 1:3, 3:1 and 3:2 are shown in Figs. 9–11. The FEM plots illustrate the thermal stability of the various phases over different temperature regions. Many of the gaseous species that are not relevant are not shown in the figures; only solid phases and gaseous species that are relevant to this study are shown in the figure.

It is evident from the figures that sillimanite (Al_2SiO_5) is stable only up to 1250 K. Above this temperature; aluminium silicate is converted into mullite and silica. This transformation is greatly aided in presence of alumina (bauxite). This has been experimentally observed in the case of alumina-rich compositions T2, T3 and T4. The amount of mullite depends on the ratio of alumina to silica. For alumina–silica ratio of 3:2, mullite is the only stable compound oxide phase in the temperature range 1250–3000 K. If the amount of alumina is insufficient to bind the silica completely, the product contains amorphous silica and quartz. For the alumina rich mixture, alumina and mullite are formed (Fig. 11). In the case of silica rich mixture silica and alumina are formed. Silica starts dissociating to SiO gas above 2000 K and above 3500 K alumina starts dissociating into gaseous AlO and Al vapour.

The most noteworthy feature of the FEM plots is that below 1250 K, mullite is not stable and dissociates into sillimanite (aluminium silicate) and alumina. The practical significance of

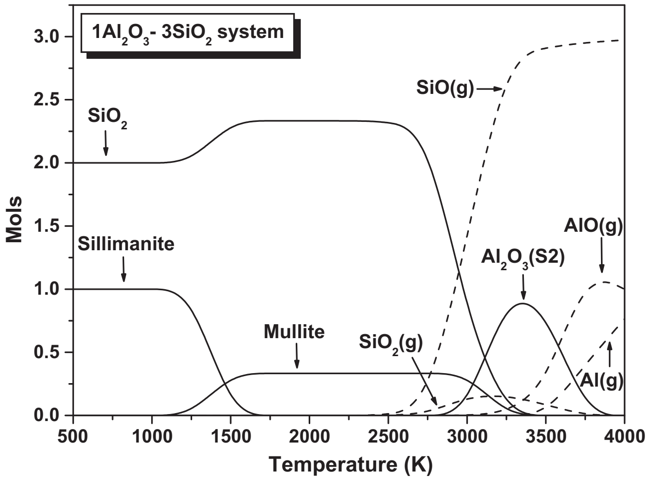

Fig. 9. FEM Plot for $1Al_2O_3$–$3SiO_2$ system.

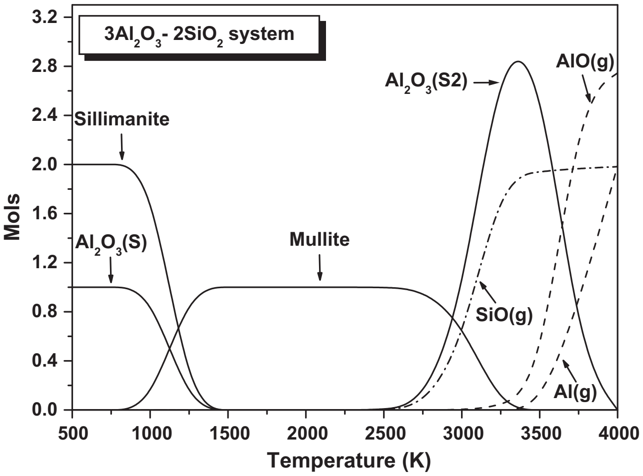

Fig. 11. FEM Plot for $3Al_2O_3$–$2SiO_2$ system.

this is that it is very difficult to synthesize mullite free from aluminium silicate due to the dissociation of mullite to sillimanite and alumina during the cooling cycle. However, if mullite is quenched rapidly from the high temperature zone, sillimanite formation can be avoided.

The high temperature transformation of sillimanite to mullite has been studied experimentally by Tamba et al. [18]. According to these authors, transformation of sillimanite to mullite and amorphous silica starts at 1350 °C and is complete by 1650 °C. These authors did not observe dissociation of mullite to sillimanite and alumina after cooling. This is due to the fact that although, sillimanite is the thermodynamically stable phase below 1250 K, the kinetics of solid state transformation from mullite to sillimanite and alumina is very slow and usually once mullite is formed, it is retained even at lower temperatures.

During the TAP processing of mullite from coal ash (coal ash + bauxite), alumina and silica melt in the plasma arc and form mullite. When the arc is switched off, the surface of the molten chunk cools rapidly. This results in rapid solidification of the product at the surface without the formation of sillimanite. However, inside the molten chunk, the rate of cooling is low favoring the transformation of mullite into sillimanite and alumina as seen from the FEM diagrams. Therefore, the product is always expected to contain sillimanite. Since the amount of mullite in T1 and T2 is low, sillimanite fraction is too low to be detected by XRD. However, sillimanite and alumina could be detected in T4. These observations are matching very well with the experimental results.

In summary, the amount of alumina and silica in the mixture plays a key role in the final product after plasma arc melting. It should be emphasized that the relative concentration of alumina and silica in the sample decides the resulting phases in the TAP processed samples. In the case of T1, the molar ratio of alumina to silica is about 0.3, whereas mullite ($3Al_2O_3{:}2SiO_2$) formation, ideally requires a ratio of about 1.5. However, it should be pointed out that considerable amount of silica volatilizes, thereby shifting the original alumina–silica ratio higher than 0.3. The yield of mullite increases with increasing amount of alumina in the starting composition. The composition T3 containing 50 wt.% of bauxite and 50 wt.% coal ash, after arc melting, yields mullite almost free from silica and silicate impurities. However, when alumina is in large excess, there is a tendency to form alumina and sillimanite, besides mullite.

4. Conclusion

Coal ash from thermal power plant unit was successfully utilized to synthesize mullite ceramic through addition of bauxite by using transferred arc plasma torch at 10 kW input power level with processing time of 3 minutes. The obtained results show that:

(1) The percentage of bauxite added greatly influences the phase composition and the microstructure of the product.
(2) Equal weight percentage of coal ash and bauxite (50:50 wt.%) yields mullite with homogeneous equiaxial grains in cubic structure which is almost free from silica and silicate impurities.
(3) The torch operating parameters prove that the transferred arc plasma processing is one of the promising techniques for efficient utilization of industrial wastes with time and power effectiveness.

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