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Synthesis of Alumina from In-Flight Sillimanite Dissociation through a Hollow Cathode Plasma Torch[†]

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Abstract

An experiment was undertaken to synthesize alumina from in-flight sillimanite dissociation through a thermal plasma medium. To accomplish this a unique hollow cathode plasma torch was designed and an air plasma was generated and thermal dissociation of sillimanite was carried out. The experimental setup consists of a central hollow graphite electrode which acts as the cathode, and a graphite anode. The material to be processed is fed centrally through the cathode. The unique feature of this system is that it uses air as the working gas to generate the thermal plasma. Experiments were carried out at 150 to 250 Amp. current levels with fixed gas flow rate and powder feed rate. The results obtained indicated that it was impossible to obtain alumina through a single step process from direct sillimanite dissociation due to the formation of mullite phase. Hence as a second step, the mullite was mixed with carbon, again dissociated in the air plasma and alumina was obtained. This confirms that the additional carbon has played a vital role in alumina–silica phase separation.

KEY WORDS: (Thermal plasma), (Dissociation), (Sillimanite), (Mullite), (Alumina), (In-flight)

1. Introduction

Generally alumina is used in refractories, pigments, colours, glazes, opacifiers, abrasives and structural applications in hot extrusion dies, wire drawing dies, cutting tools, automotive engine components, thread guides, bearings and innumerable new areas which are increasing day by day. It is prepared from minerals through various kinds of physical and chemical processes. From the available natural resources, sillimanite is also a mineral for alumina production. Sillimanite is the byproduct generated during the extraction of rare earth compounds from beach sand minerals. Numerous investigators have successfully promoted this mineral as a value added product through different kinds of physical and chemical routes[1-3]. However, notable works in sillimanite have not been conducted using thermal plasma processing technology.

On the other hand several researchers have successfully utilized the thermal plasma technology for mineral processing for more than 50 years[4,5]. For example, the first successful preparation of zirconia by plasma dissociation of zircon on a pilot-plant scale was demonstrated by Wilks et.al[6,7], who used a three-phase arc furnace fitted with carbon electrodes for production of zirconia from zircon sands. Similarly, Ananthapadmanabhan et.al[8,9] have investigated the parametric studies of the plasma processing of Indian zircon. The experiment was carried out through a specially developed non-transferred arc plasma torch based on a plasma chemical reactor. The authors pointed out that the dissociation percentage can be strongly affected by torch input power, plasma and carrier gas flow rate, location of powder feed port.

Based on the above research reports, the present investigation was undertaken to synthesize alumina from in-flight sillimanite dissociation sand through hollow cathode plasma (HCP) processing torch. Air was used as plasma forming gas in order to achieve cost effectiveness. Thermal plasma processing has several distinct advantages over conventional methods due to its controlled environmental operations and cost effectiveness. Some of the advantages of thermal plasmas are: (1) availability of high temperature and high energy density which makes it easier to process high-temperature materials; e.g., ceramic oxides and refractories; (2) independent control of crucial process parameters like input power, process gas flow rate, or reactive environment; (3) attainability of very high cooling rate (as high as million deg/s is possible); (4) Increased reaction kinetics by several orders of magnitude due to the high temperature in the plasma medium[10,11].

Thermal plasma technology offers a two-step process for extracting alumina from sillimanite sand. The phase and microstructure of the processed samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. The dissociation

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percentage (DP) of the processed sillimanite was estimated by the following expression:

$$\mathrm{DP}\,(\%) = \frac{I_b}{I_a + I_b} \times 100 \qquad (1)$$

where I_a and I_b are the intensities of the most intense diffraction peaks of initial and processed feedstock phases respectively.

2. Experimental Setup and Procedure

2.1 Plasma torch

Figure 1(a) and **(b)** shows the schematic and photographic images of the hollow cathode plasma processing torch used for this study. The torch consists of a graphite nozzle, 20 mm inner diameter and 100 mm length. The hollow cathode is made of graphite with 15 mm outer diameter and 70 mm length.

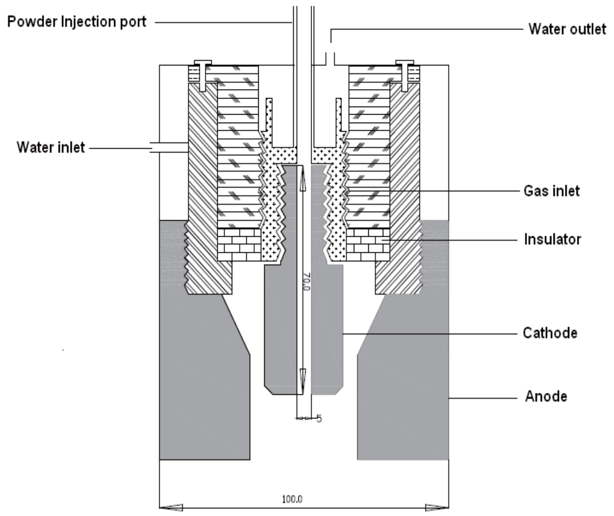

Fig. 1(a) Schematic of plasma processing torch.

Fig. 1(b) Photographic images of electrodes and HCP torch.

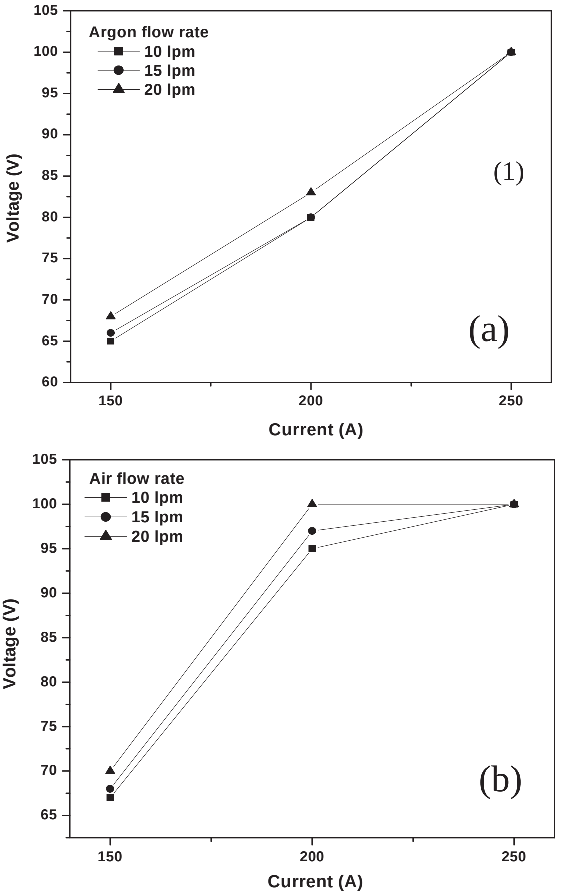

Fig. 2 I-V Characterization of HCP torch for different gas flow rates: (a) Argon; (b) Air.

Both the electrodes are held in water-cooled brass holders and the electrodes are insulated from each other. Vortex gas flow is established by passing the plasma gas through the holes drilled in the insulator parallel to the walls to stabilize the plasma jet, while the centre hole (5mm diameter) in the cathode acts as the powder injection port.

2.2 I-V Characterization of HCP torch

The current and voltage (I-V) relationship of the hollow cathode plasma processing torch was measured manually using a digital ammeter and a voltmeter. Air and argon gases were used as plasma forming gas for comparative purposes. All the measurements were done for the power source only, because the measurement at the electrode terminal was not accurate due to the arc fluctuation. I-V relations of the torch for different argon and air flow rates are shown in **Fig. 2 (a)** and **(b)** respectively. In argon and air plasma cases, the voltage increases normally with respect to increasing current.

The increasing plasma forming gas flow rate did not play a major role in voltage development due to limitation of the power supply and the dimension of the torch. The effect of gas flow rate on the voltage development of the torch was very small for argon and air plasma cases.

2.3 Characterization of raw sillimanite

Two types of sillimanite sands are available from the Indian Rare Earths Limited, OSCOM (O) variety, which is yellowish due to the presence of the ferrogeneous coating on them, and QUILON (Q) which contains some amounts of zircon. For the present study Q grade sillimanite sand was used, whose chemical composition is given in **Table 1**.

The XRD pattern, SEM image with corresponding EDX spectrum and the particle size distribution plot of the raw sillimanite sand (Q) are given in **Figs. 3, 4** and **5** respectively. The results showed that the raw sillimanite sand is crystalline in nature with irregular surfaces. The particle size distribution result showed that the average particle size is 300-400 microns.

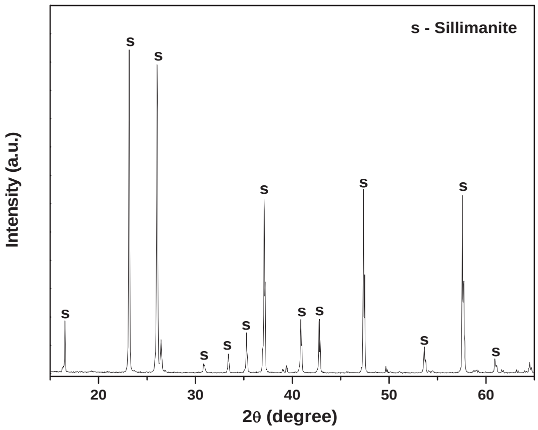

Fig. 3 XRD pattern of raw sillimanite powder.

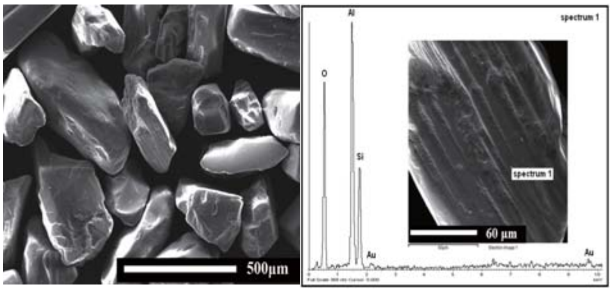

Fig. 4 SEM and EDX spectrum of raw sillimanite powder.

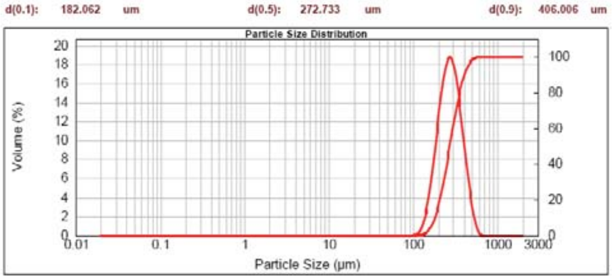

Fig. 5 Particle size distribution of raw sillimanite powder.

Table 1 Chemical compositions of raw sillimanite.

Oxides in sillimanite sand (Wt. %)						
Al_2O_3	SiO_2	TiO_2	Fe_2O_3	ZrO_2	Na_2O $+K_2O$	CaO
59.30	37.10	0.40	0.50	1.50	0.50	0.60

3. Results and Discussion

3.1 Plasma dissociation

In this case two steps of experiments were carried out to synthesize alumina from sillimanite. In the first step raw sillimanite was used as the feed material. In the second step processed sillimanite (mullite) with carbon was used as the feed material. The plasma torch was connected with a 25 kW IGBT DC power source and the plasma arc was initiated by injecting the plasma gas (air) into the electrode gap. After obtaining a stable plasma jet, feedstock powder was fed into the plasma column through the central hole of the cathode. Feedstock powder was injected at a controlled feed rate of about 15 g/minute. The dissociated feedstock powder exiting the torch nozzle was collected on a flat-bottomed collection vessel kept at about 600 mm below the torch nozzle. The torch input current was varied from 150 -250 Amp. and the experiment was continued with fixed air and powder feed rates. The typical operating parameters are given in **Table 2**.

3.2 Phase and microstructure formation

Generally sillimanite sand on heating in the temperature range from 1300 ºC to 1700 ºC decomposes to mullite and silica. Decomposition temperature depends on the particle size and impurity level of the raw materials. In this case, feedstock particle size and the presence of impurity were relatively higher and consequently it might have enhanced the dissociation processes in-flight within the plasma medium as per the following reaction mechanism[12].

$$3(Al_2O_3.SiO_2) \rightarrow 3Al_2O_3.2SiO_2+SiO_2 \qquad (2)$$

Figure 6 shows the dissociation percentage of sillimanite as a function of plasma torch input current. The resulting pattern clearly shows that the increasing plasma torch input current concurrently increases the dissociation of sillimanite into mullite due to the increase of plasma medium temperature. However, the present temperature was not enough for complete removal of silica in the sillimanite phase structure, but the surface morphology and the structural orientation of sillimanite were changed due to partial removal of silica in sillimanite during in-flight reaction with air plasma. Hence the partial loss of SiO_2 in Al_2O_3-SiO_2 phase structure can easily produce mullite phase. Mullite and sillimanite are closely related structurally, both being members of the mullite family. The general formula of the mullite family is $Al_{4+2x}Si_{2-2x}O_{10-x}$.

Table 2 Typical Operating parameters.

Parameters	**1^{st} step**	**2^{nd} step**
	Sillimanite dissociation	Mullite dissociation
Input current (A)	150-250	150-250
Voltage (V)	65-100	65-100
Air flow rate (lpm)	15	15
Feed rate (gpm)	15	15

The *x*-value of sillimanite ($Al_2O_3.SiO_2$) is $x= 0$, while 3/2-mullite ($3Al_2O_3.2SiO_2$, i.e., stoichiometric mullite) and 2/1-mullite ($2Al_2O_3.SiO_2$) correspond to *x*-values of 0.25 and 0.40, respectively[13)]. The common feature of both structures is edge-sharing [AlO_6] octahedra, forming chains parallel to the crystallographic *c* axis. Octahedral chains are cross linked by [(Al, Si) O_4] tetrahedral double chains. Al and Si are ordered over the tetrahedral sites in sillimanite but disordered in mullite.

Figures 7 and **8** shows the XRD and SEM image of HCP torch processed sillimanite at 250 Amp. input current. The pattern confirmed that the complete phase changes occurred from sillimanite to mullite during the process. However the pattern appears slightly amorphous in nature due to the presence of silica. The spherical nature of the processed powders concurrently increases with increasing torch input current due to the increase in plasma temperature. This kind of spheroidization nature is one of the unique processing advantages of thermal plasma processing. The above results clearly show that the single step HCP torch processing was not adequate to produce alumina from in-flight sillimanite dissociation due to the lack of torch input power and residence time of the in-flight particles.

To overcome the above constraints, second step was used to produce alumina from mullite disassociation, which is derived from sillimanite dissociation at 250 Amp. In this case, fine carbon powder was added to mullite in a 2:1 mole ratio and was thoroughly milled by ball milling for 15 hours which dramatically reduced the size of the mullite powders. Then the carbon added mullite feedstock was again processed in the HCP torch at different current levels. Generally the addition of carbon can reduce the dissociation temperature due to the formation of SiO and CO gases, which has already been confirmed by the author's previous zircon dissociation work[14)]. During the process the carbon reacts with SiO_2 in mullite through the following mechanism:

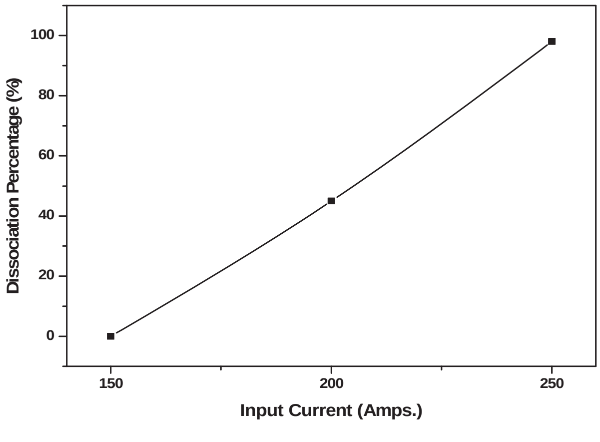

Fig. 6 Dissociation percentage of sillimanite as a function of input current.

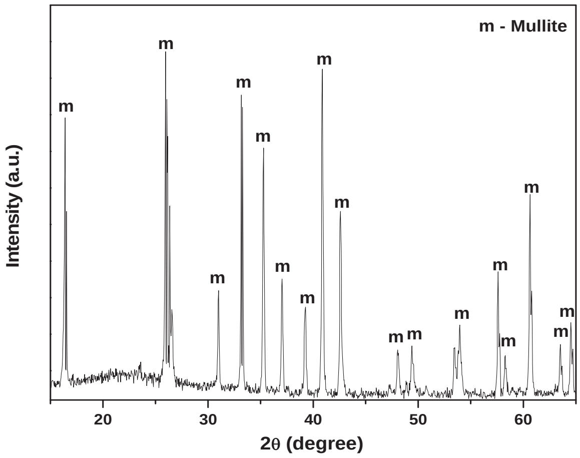

Fig. 7 XRD pattern of HCP torch processed sillimanite at 250 Amp.

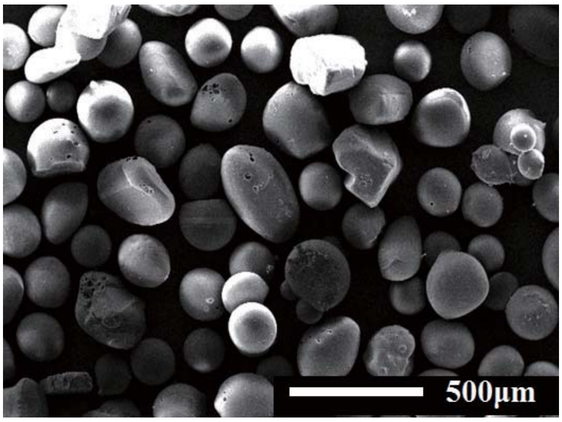

Fig. 8 SEM image of HCP torch processed sillimanite at 250 Amp.

$$3Al_2O_3.2SiO_2 \text{ (mullite)} + 2C \rightarrow$$
$$3Al_2O_3 \text{ (alumina)} + 2SiO \text{ (gas)} + 2CO \text{ (gas)} \qquad (3)$$

For without carbon

$$3Al_2O_3.2SiO_2 \text{ (mullite)} \rightarrow 3Al_2O_3 + 2SiO_2 \qquad (4)$$

The above reaction mechanisms directly depend on the plasma temperature and reactive species of the plasma medium; here air was used as plasma forming gas. The polyatomic nature of the air provides relatively more.

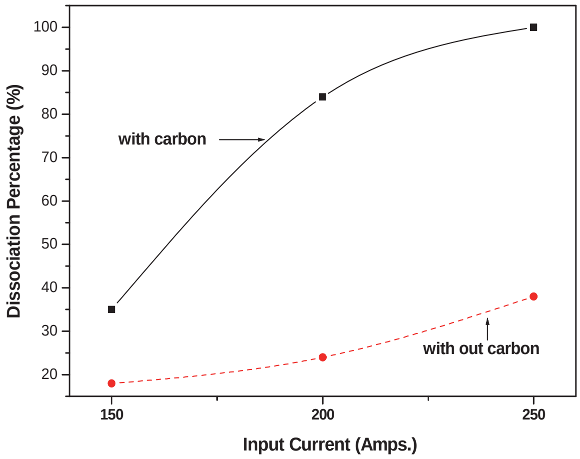

Fig. 9 Dissociation percentage of mullite as a function of input current.

Figure 9 shows the dissociation percentage of the mullite feedstock with and without addition of carbon as a function of torch input current. The dissociation percentage of carbon added mullite predominantly increases with increasing torch input current compared to the mullite without carbon due to the catalytic character of the carbon. The added carbon can easily react with SiO_2 in mullite and consequently produces SiO and CO gases exothermically which enhances the plasma zone temperature. Hence the SiO_2 from mullite was completely removed in the form of gases which gave maximum percentages of alumina. On the other hand in the mullite without carbon mixed, SiO_2 could not be completely removed due to the lack of plasma zone temperature even at high operating power level (250 Amp.). Hence the above results strongly confirm that the addition of carbon can play a crucial role in mullite dissociation in-flight in the high temperature plasma zone.

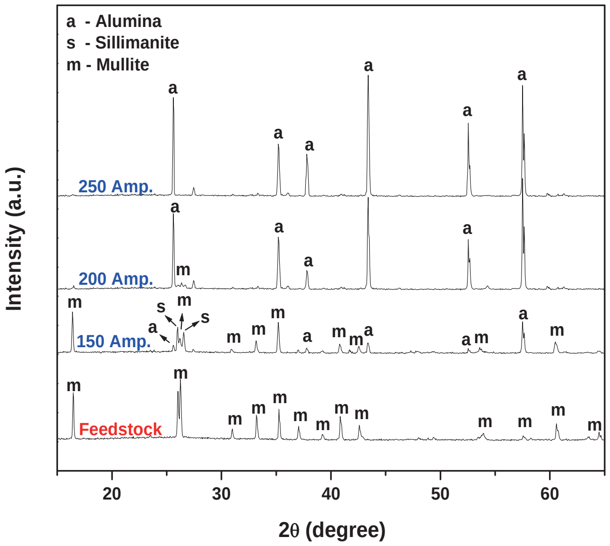

Fig. 10 XRD pattern of HCP torch processed mullite at selected input currents.

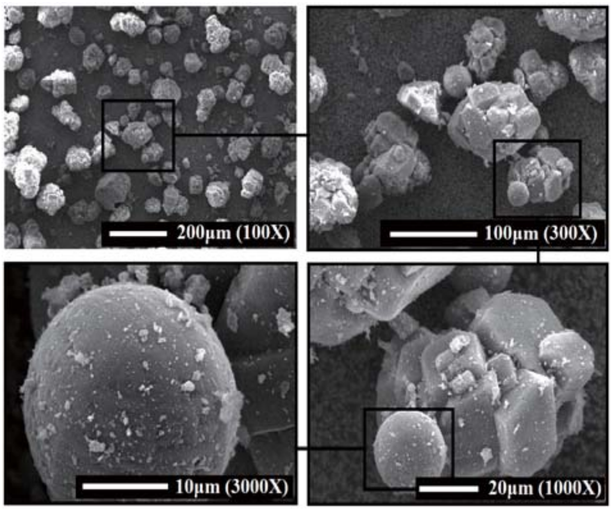

Fig. 11 SEM image of HCP torch processed alumina from carbon added mullite.

The XRD pattern of the HCP torch processed carbon added mullite dissociation is shown in **Fig.10**. At lower current level (i.e. 150 Amp.), the pattern appears with the combinational presence of alumina, mullite and small amount of sillimanite due to the deficiency of plasma zone temperature to remove SiO_2 in the form of gases, but it can lead to the phase separation in mullite. This is primary for the formation of sillimanite phase along with alumina and mullite. At 200 Amp., the maximum percentage of (84%) alumina was obtained due to the high temperature of plasma. Similarly at 250 Amp., the absolute yield of alumina was obtained from mullite due to the complete removal of SiO_2.

The SEM images of HCP torch processed alumina from mullite dissociation at 250 Amp. are shown in **Fig.11**. The surface morphology of processed alumina powders appeared nearly spherical in shape with an average size of ~100 micron. The individual spherical shape consists of a number of discs with an average size of ~20 micron. During processing, the molten droplets of small sized feedstock particles joined together to form a spherical structured ball with interlocked discs. Generally high temperature plasma processing produces these kinds of microstructures due to the complete melting of the in-flight particles[15)].

4. Conclusion

The HCP processing torch was successfully utilized to synthesize spherical alumina particles from sillimanite sand through a two step process. The first step leads to the complete phase transformation from sillimanite to mullite phase at 250 Amp. current level of the torch due to the partial removal of silica in sillimanite.

On the contrary, the second step cannot lead to the complete phase transformation from mullite to alumina phase due to the inadequate plasma zone temperature.

However, addition of 2 mole carbon to the mullite plays a catalytic role and predominantly enhances the mullite dissociation during in-flight and contributes to the complete phase transformation from mullite to alumina phase.

The surface morphology of processed alumina powders appeared nearly spherical in shape and consisted of a number of individual discs. However the results clearly indicated that the current HCP torch power was not adequate to produce alumina from sillimanite sand in a single step process without the addition of carbon.

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