Inflight dissociation of zircon in air plasma

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Abstract. Thermal dissociation of zircon can be conveniently carried out in a plasma reactor, which is characterized by high temperature, high energy density and high quench rate. Zirconia is recovered from this partially dissociated zircon by alkali leaching. Dissociation of zircon has been conventionally carried out in argon gas, which is expensive. The present paper reports experimental results on thermal dissociation of zircon in air plasma medium. Process simulation for ‘inflight’ dissociation of zircon in air plasma medium is also presented. The experimental system 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 the system is that it uses air as the working gas to generate the thermal plasma. The system has been used to study in-flight dissociation of zircon in the thermal plasma jet. Dissociation was carried out over 10-25 kW power range. Results of the study indicate that complete dissociation of zircon to ZrO₂ and silica could be accomplished at 25 kW in air plasma.

1. Introduction
Zircon is the raw material for production of zirconia for various refractory applications in metallurgical industries. Zirconia ceramics today compete with metals and alloys in many industrial applications involving high strength, toughness and erosion and wear resistance at elevated temperatures. Most of the processed zirconia is used for 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 many new areas which are growing day by day.

Commercially, zirconia is mainly prepared by the chemical process involving high temperature digestion of zircon with alkali, followed by separation of zirconium oxide from sodium silicate. However, this technique has some drawbacks such as process complexity, environmental pollution and high cost. The above factors are limiting the use of this technique and persuade the invention of alternative technique with cost effectiveness. Thermal plasma technology offers a one-step process for extracting zirconium oxide from zircon sand. Thermal plasma processing has several distinct advantages over conventional methods due to its controlled environmental operations with cost effectiveness. Some of the advantages of thermal plasmas are: (1) availability of high temperature and high energy density which makes 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 [1,2].

Several researchers have studied the properties of plasma-dissociated zircon (PDZ) [3,4]. The first successful preparation of zirconia by plasma dissociation of zircon on a pilot-plant scale was demonstrated by Wilks et.al [5, 6], who used a three-phase arc furnace fitted with carbon electrodes for production of zirconia from of zircon sands. The electricity consumption for the plasma process was estimated to be 1.32 kWh per kg of product, against 9.9 kWh per kg in the classical furnaces.

Zirconium silicate is not stable at temperatures above 1811 K, when it spontaneously dissociates into zirconium oxide and silicon oxide as expressed by the following reaction:

$$\text{ZrSiO}_4 \rightarrow \text{ZrO}_2 + \text{SiO}_2$$

The above reaction is reversible and the oxides recombine to form the silicate on cooling. However, if zircon is heated to temperatures exceeding 1900K and the reaction products are quenched rapidly, the reversible reaction can be prevented. The silica can be separated from the product by acid or alkali leaching to get pure zirconium oxide.

Ananthapadmanabhan et.al [7, 8] have investigated the parametric studies on the plasma processing of Indian zircon. The experiment was carried out by specially developed non-transferred arc plasma torch based 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. During the same period, Syamaprasad et.al [9] studied the preparative and microstructural aspects of plasma-dissociated Indian zircon prepared by specially designed transferred arc plasma torch based plasma reactor (20 kW). The vital parameters involved in the process have been optimized for a high degree of dissociation with maximum feed rate (4-5 kg/h). The processes achieved 90% of phase separation (ZrO2 and SiO2) with two types of spheroids.

Plasma processing, usually, uses argon as the plasma-forming gas, which is quite expensive. In the present work, we have studied plasma dissociation of zircon using air as the plasma-forming gas with a view to make the process cost-effective. The investigations focused on the effect of torch input power on the zircon dissociation. The phase and microstructure of the processed samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. The dissociation percentage (DP) of the processed zircon was estimated by the following expression:

$$\text{DP (\%) } = \frac{I_b}{I_z + I_b} \times 100$$

where $I_z$ and $I_b$ are the intensities of the most intense diffraction peaks of zircon and zirconia respectively.

2. Experimental setup and procedure

2.1 Plasma torch

Figure 1 shows the schematic of 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. 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 powder injection port.
2.2 Characterization of the raw powder

Indian zircon containing 62% ZrO₂, 35% SiO₂, 1% Al₂O₃, 0.15% TiO₂ and 0.15% Fe₂O₃ was used for the present study. The XRD pattern of the raw zircon powder is shown in Figure 2. All the diffraction peaks corresponding to zircon can be identified. The morphology and particle size distribution of the raw zircon particles are shown in figure 3 and 4 respectively. It is seen that the particles are distributed between 100 microns and 300 microns. The surface morphology shows that the particles have irregular shape.
2.3 Plasma dissociation
Two sets of experiments were carried out. The first set of experiments used argon as the plasma gas and zircon as the feed material. In the second set of experiments, air was used as the plasma gas and zircon was the feed material. The plasma torch was connected with 25 kW IGBT DC power source and plasma arc was initiated by injecting the plasma gas (argon or air) into the electrode gap. After obtaining stable plasma jet, zircon powder was fed into the plasma column through the central hole of the cathode. Zircon powder was injected at a controlled feed rate of about 15 g/minute. The dissociated zircon powder exiting the torch nozzle was collected on a flat-bottomed collection vessel kept about 450 mm down the torch nozzle. The torch input current was varied from 150 - 250 amperes and the experiment was continued with fixed air and powder feed rates. The operating parameters and dissociation percentage for the various experimental runs are given in Table 1.

| Parameters                  | Argon plasma | Air plasma |
|-----------------------------|--------------|------------|
| Power (kW)                  | 8.3          | 16         |
| DP (%)                      | 23           | 65         |
| Gas flow rate (lpm)         | 12           | 12         |
| Feed rate (gpm)             | 15           | 15         |

X-ray diffraction of the plasma dissociated was used to estimate the degree of dissociation. XRD results were also compared with SEM and EDX results as well as alkali leaching experiments.

3. Results and discussion
X-ray diffraction (XRD) patterns of argon plasma dissociated zircon at different plasma power are shown in figure 5a. Figure 5b shows the intensities of the most intense diffraction peaks of zircon and zirconia. It is seen from the figure that, the intensities of zircon peaks gradually decrease and simultaneously the intensities of the monoclinic phase of zirconia increase with increasing torch input current. The XRD patterns clearly show that the extent of dissociation increases with plasma power. At 25 kW power, more than about 90% dissociation was obtained. The dissociation percentage of processed zircon was estimated by the relative intensity the x-ray diffraction peak of zircon (at 27.17°) and that of monoclinic phase zirconia peak (at 28.39°).

![Figure 5. XRD pattern of argon plasma dissociated zircon at different input power](image-url)
X-ray diffraction patterns of plasma-dissociated zircon in air plasma medium at different input power to the torch are shown in figure 6. It is seen from the figure that the percentage of zircon dissociation increased with increasing torch power. Complete dissociation could be achieved in this case at 25 kW. The variation of degree of dissociation of zircon with power is shown in figure 7. The effect of input power is evident from the figure. Increasing torch power increases the plasma temperature leading to increased heat transfer from the plasma to the particles, thus leading to higher degree of dissociation.

SEM photographs of plasma processed zircon at various power levels are shown in figure 8. Particle morphology gives a clear indication of the extent of dissociation. In the case of zircon processed in argon plasma at 8.3 kW, majority of the particles are irregular indicating the presence of unreacted zircon particles. As the input power is increased, the degree of dissociation increases and consequently the number of spherical particles also increases. As the particle temperature increases beyond the dissociation temperature, zircon dissociates into zirconium oxide and silica particles. As these particles exit the plasma jet, they are rapidly quenched and the molten drops of liquid retain the spherical shape due to surface tension effect. In the case of completely dissociated zircon, all the particles are spherical. These results are in perfect agreement with those of X-ray diffraction.

Figure 6. XRD pattern of air plasma dissociated zircon at different input current

Figure 7. Variation of extent of dissociation with power
The EDX spectrum of the surface of a typical as-dissociated zircon particle is shown in figure 9. Zr, Si and oxygen peaks are clearly identified. The plasma-dissociated zircon is seen to consist of well-developed polygonal grains with spherulitic growth of zirconia in a silica matrix. The EDX spectrum (Figure 10) of plasma dissociated zircon (25 kW, argon) after leaching with NaOH shows intense Zr peak along with weak Si peak, as expected.

Figure 8. Surface morphology of dissociated zircon

Figure 9. EDX spectrum of dissociated zircon
Degree of dissociation estimated by XRD was also compared with results obtained by alkali leaching of the plasma processed product followed combined with gravimetric analysis. The plasma-dissociated product was treated with 50% solution of NaOH (boiling point 150°C). About 10 gram of the processed material was treated with 50% NaOH solution for about three hours, allowed to cool and then diluted with water. The residue was separated by filtration and then washed thoroughly to remove the alkali, dried at 200 °C and then weighed. The difference in the weight of the product before alkali treatment and after treatment represents the amount of free silica present in the plasma-dissociated product. The free silica resulting from dissociation is leached out as sodium silicate, which can be separated from the insoluble residue that is a mixture of undissociated zircon (if any) and zirconium dioxide. The quantity of NaOH used was in excess of that required to leach out the total silica present in the sample.

Results for 25 kW-processed zircon samples are summarized in Table 2. Since the zircon sand processed at 25 kW in air plasma is seen to be completely dissociated (Figure 6), the % of free silica leached out should be about 32%. In the case of the sample processed in Ar plasma at 25 kW also, the % silica is expected to be more than 25%. However, it is seen from Table 3 that the amount of silica leached out is considerably lower than the theoretically expected value. This suggests that there is considerable loss of silica from the surface of the particles as they traverse the plasma jet due to vaporization.

4. Discussion
Results of the investigations clearly show that the input power and the processing environment significantly affect the course of the dissociation reaction. It is observed that increase in the input
power to the plasma results in increased extent of dissociation. This is true in all the experiments irrespective of the plasma gas. This observation has also been confirmed in earlier studies by Ananthapadmanabhan et al [8] and Syamaprasad et al [9]. The observed trend in variation of dissociation % is closely connected with the variation in the plasma temperature. The mean temperature of the plasma at the nozzle exit can be calculated by the following energy balance equation [10].

\[ P_o = \int_{300}^{T_p} m C_p \, dT \]  \hspace{1cm} (3)

In the above equation, m is the mass flow rate of the plasma gas. Cp is the specific heat capacity of the gas and \( T_p \) the mean plasma temperature at the exit of the nozzle. The gas flow rate used in our experiments was 12 liters per minute of argon in the first set of experiments and 12 liters per minute of air in the other set of experiments. The powder was fed gravimetrically without any carrier gas. An average torch efficiency of 45% has been assumed in the calculations. The values of \( C_p \) at different temperatures for argon and air used in the calculation have been taken from the thermodynamic and transport properties calculated by Murphy and Arundell [11]. Table 3 lists input power and nozzle exit temperature under different operating conditions.

**Table 3. Plasma gas temperature at the nozzle exit**

| Input power (kW) | Argon plasma temperature (K) | Input power (kW) | Air plasma temperature (K) |
|------------------|------------------------------|------------------|---------------------------|
| 8.3              | 11990                        | 9.8              | 6490                      |
| 16               | 13610                        | 19               | 7910                      |
| 25               | 14950                        | 25               | 10040                     |

The degree of dissociation listed in Table 1 for different power levels shows the influence of the plasma medium on the dissociation reaction. It is observed that, irrespective of the plasma medium, the extent of dissociation is more the higher the plasma power. However, at lower power levels, the degree of dissociation is higher in argon plasma than that observed in air plasma. It is found that there was hardly any dissociation when the input power was 8.3 kW. For the same input power using argon as the plasma-forming gas, the extent of dissociation was found to be about 23%. As the input power increases, the trend is reversed. The dissociation slowly increased to about 18% at 9.8 kW and at 19 kW, it increased to 67%, compared to 65% in the case of 16 kW argon plasma medium. Complete dissociation was observed at 25 kW.

This is due to the fact that the temperature of air plasma is comparatively lower than argon plasma jet due to its polyatomic nature. However, the recombination of the atomic species downstream of the plasma jet results in an extended plasma zone. Although the average temperature is lower than that observed in argon gas, the extended plasma zone leads to higher degree of dissociation. It is also observed that the thermal conductivity of air in the temperature region, 6000-10,000K is higher than that of argon leading to higher heat transfer coefficient and consequently enhanced dissociation of zircon in air plasma.

The present studies have considerable technological implications. The use of air as the plasma processing gas would lead to significant cost savings. Further, a substantial fraction of silica is removed in-flight, thus, leading to additional cost benefits. The results of these studies can be valuable input for commercialization of the process.

5. **Conclusion**

Zircon was successfully dissociated using hollow cathode plasma processing torch by using air as the plasma forming gas. Experiments showed that maximum dissociation percentage was obtained at 25
kW with 15 gpm feed rate and 12 lpm gas flow rate. The results showed that the air plasma gives comparatively higher percentage of dissociation than argon plasma.

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