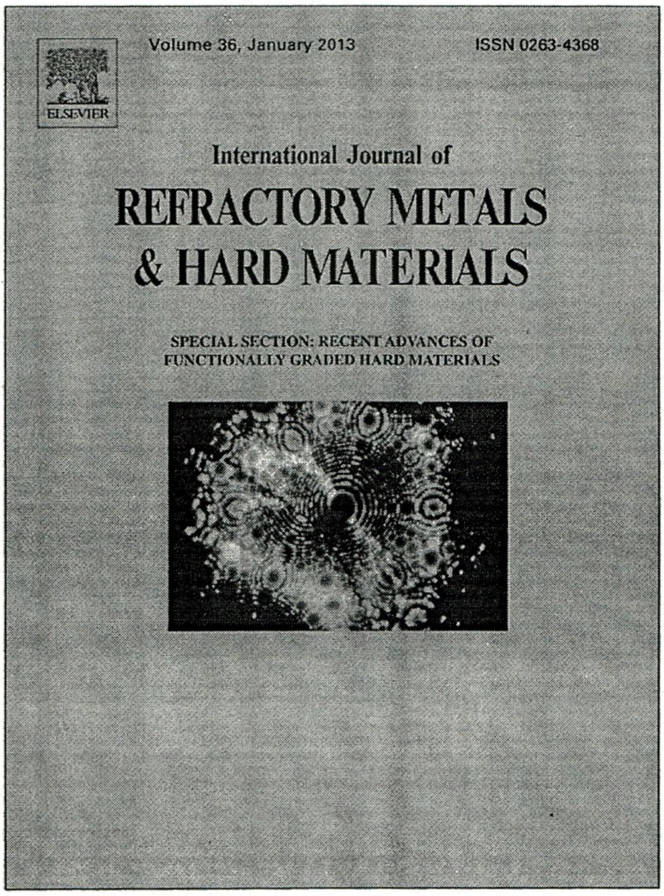
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Carbothermal reduction of sillimanite in a transferred arc thermal plasma reactor

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ABSTRACT

Conversion of sillimanite to value-added ceramic materials was investigated by transferred arc plasma processing using nitrogen as the plasma gas. Plasma processing was carried out using sillimanite and sillimanite–carbon mixtures at different power levels. The products were characterized by XRD, SEM and FTIR techniques. Thermodynamic analysis using free energy minimization principle was used to predict the products formed and also analyze the experimental results. The results of these investigations showed that sillimanite can be converted to mullite, or alumina and silicon carbide by careful choice of the operating conditions and sillimanite–carbon ratio.

1. Introduction

Mullite, alumina and alumina–silicon carbide composite (Al_2O_3–SiC) are of high industrial interest because of their wide range of applications. Mullite ($3Al_2O_3.2SiO_2$) is a promising candidate material for high temperature applications due to its high strength at elevated temperature, low thermal expansion, improved thermal shock and good chemical stability [1]. Aluminum oxide is becoming increasingly important for a wide range of industrial uses including engineering ceramics, catalysts, etc. [2–6]. The mechanical properties such as strength and toughness of Al_2O_3 can be improved by the incorporation of SiC in the Al_2O_3 matrix. Al_2O_3–SiC composites have been studied to improve the high-temperature mechanical properties and wear resistance of alumina [7–12]. Usually, mullite and alumina products are synthesized from various alumina and silica precursors through techniques such as co precipitation, sol–gel, hydrothermal and chemical vapor deposition. However, the products produced from high-purity reagents/precursors are expensive and not commercially viable for bulk refractory applications [13–15]. The Al_2O_3 and Al_2O_3 containing reactants traditionally used for the preparation of mullite are widely produced from bauxite ore. A gradual depletion of naturally occurring high alumina raw materials has made a serious challenge to the refractory industries to keep on continued production of such refractory, which is in high demand. In view of this it has become imperative to find alternate sources for synthesis of mullite refractory.

Recently, beach sand sillimanite (BSS) has been identified as an alternative low-cost raw material for the production of mullite and alumina. Sillimanite sand is abundantly available in nature and only a very small percentage is being used in refractory industries and the rest remains unused as waste. Sillimanite sand, which typically contains 50–60% Al_2O_3, decomposes to mullite and amorphous silica on heating in the temperature range of 1300–1700 °C depending on the particle size and impurity level etc. The dissociation reaction of sillimanite can be written as [6]

$$3(Al_2O_3.SiO_2) \xrightarrow[1300\,^{\circ}C-1700\,^{\circ}C]{} 3Al_2O_3.2SiO_2 + SiO_2. \qquad (1)$$

The utilization of this mineral will contribute to environmental safety and to preserve valuable naturally occurring mineral reserves for alumina. India is one of the few countries in the world that has significant deposits of beach sands [16]. Beach sand sillimanite, a by-product generated in large amount during the separation of rare earth oxide is presently not used in refractory industries or other applications. Although a number of authors have studied the thermal transformation of sillimanite to mullite [17,18], the work on beach sand sillimanite is limited. Attempts have been made by few authors [19,20] for effective utilization of beach sand sillimanite to produce mullite/mullite–alumina composites.

The carbothermal reaction involves high temperature reaction, where carbon is used as a reducing agent. The reaction has been found quite effective in reducing several oxides to lower oxides, metallic oxides to metals and even to metallic carbides and oxycarbides

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[21]. It is normally carried out in an inert gas atmosphere of argon or nitrogen to prevent oxidation of carbon. Panda [7] has reported the carbothermal reduction of sillimanite ($A1_2O_3.SiO_2$), which yields powder mixture of SiC(w) and alumina, which is subsequently used for the preparation of $A1_2O_3$–SiC(w) composite bodies by hot-pressing or atmospheric sintering.

Although transferred arc plasma processing and non-transferred arc plasma processing have been used for various material processing applications, the literature on the use of thermal plasmas for processing sillimanite is scanty. The advantages of transferred arc plasma processing include high enthalpy, high temperature and high reactivity. Further, a wide range of reactive plasma environment can be provided to synthesize a variety of ceramic materials. The processing time is relatively short compared with other competitive techniques and the method is capable of handling bulk production [22–26]. The objective of the present work is to carry out carbothermal reduction of beach sand sillimanite through transferred arc plasma processing for producing value added products such as mullite, alumina and alumina–silicon carbide. In this work, the effect of concentration of carbon in the sillimanite and plasma power on the carbothermal reduction of sillimanite is investigated. The obtained products have been characterized using X-ray Diffraction (XRD) technique, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy.

2. Experimental details

The experimental system used to treat the sillimanite consists of a reactor chamber, transferred arc plasma torch, a 40 kW DC power supply, master control console, gas feeding system, water cooling arrangement and exhaust gas vent. The plasma torch is mounted on top of the reactor which is water-cooled. The transferred arc plasma torch consists of a cylindrical graphite crucible with 120 mm depth and 60 mm inner diameter that serves as the anode. The cathode is made of graphite rod of 250 mm long and 50 mm diameter. Its end is tapered to a conical shape for better electron emission. The cathode is enclosed in a hollow brass cylinder and it has provisions for water circulation (for cooling) and gas flow. The material to be processed was placed in the anode crucible bed and the arc was initiated by shorting the cathode and the crucible wall. The arc was rotated suitably within the crucible to heat the charge placed in the crucible. Nitrogen gas was used as a plasma forming gas.

The beach sand sillimanite (Q grade), which contains 60% of Al_2O_3 and 37% of SiO_2 was obtained from Indian Rare Earths Limited (IREL), Mumbai, India. The particles of raw sillimanite powder are irregular blocky and angular (Fig. 1). The particle size of the sillimanite powder is in the range of 200–400 μm. Activated carbon powder obtained from E-Merck was used as the reducing agent. The main purpose of the addition of carbon to sillimanite is to facilitate the conversion of sillimanite to mullite by removing the excess silica as SiO gas. Also, by using the appropriate amount of carbon, sillimanite can be converted to alumina and silicon carbide. The uniform mixture of sillimanite–carbon samples were prepared using the planetary ball milling system (Insmart, India) with single corundum bowl and balls with different diameters. The powder to ball ratio was kept at 1:10 by weight and the bowl rotating speed was fixed at 200 rpm. The ball-milled powder was mixed with required quantity of ethanol using an agar mortar and the final mixtures were pelletized. Transferred arc processing studies were carried out using sillimanite pellet and sillimanite–carbon pellets containing 0.3, 3.0 and 5.0 moles of carbon in the mixture. The sillimanite–carbon mixture in the form of pellet was used for plasma processing to avoid splashing of the powder particles during the plasma process.

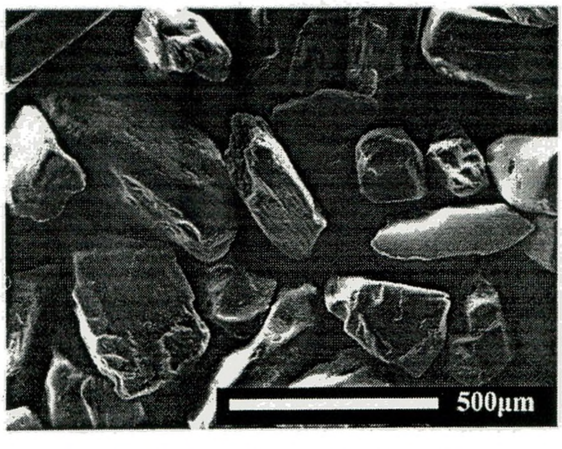

Fig. 1. SEM photograph of raw sillimanite powder.

Before initiating the arc, the reaction chamber was tightly closed and purged with nitrogen gas for 10 min. The plasma arc was initiated using argon and then nitrogen was introduced. Later, plasma arc was maintained with nitrogen gas only. Initially, the plasma arc strikes between the tip of graphite cathode and wall of graphite anode and later the arc randomly spreads in all direction and melts the powder. The molten material forms a slag while cooling. The slag was removed from the crucible and used for phase characterization, microstructural and spectroscopic analyses. The important plasma process parameters used in this work are given in Table 1.

Thermal dissociation of sillimanite in Ar–N_2 plasma was studied by using free energy minimization (FEM) technique for the system Al_2SiO_5–Ar–N_2. FEM plots were developed using the CSIRO thermo package [27]. FEM plot for the system Al_2SiO_5–Ar–N_2 is shown in (Fig. 2a). It is seen that sillimanite is stable until about 1250 K, above which it decomposes into mullite ($Al_6Si_2O_{13}$) and silica. Mullite is stable up to 2750 K and it dissociates into alumina (liquid) and $SiO_{(g)}$ above 2750 K. SiO_2 also dissociates into $SiO_{(g)}$ and oxygen gas above 2750 K. Alumina is stable up to 3500 K. When the temperature exceeds 3500 K, alumina dissociates into sub-oxides, such as AlO, Al_2O, and Al vapor. It is seen from the figure that sillimanite can be converted to mullite by careful control of the processing temperature in the range 1500–2750 K. However, it is nearly impossible to get silica-free mullite from thermal dissociation of sillimanite. Although alumina is formed above 2750 K, the temperature range over which alumina is stable is narrow (2750–3500 K).

The free energy minimization (FEM) plots for the system Al_2SiO_5–C–Ar–N_2 with sillimanite-to-carbon ratio of 1: 3 is shown in Fig. 2b. The addition of carbon to sillimanite influences the course of the reaction and the resulting products. Thermal dissociation of Al_2SiO_5 system starts above 1250 K. During the dissociation, Al_2SiO_5 solid phase is converted to mullite ($Al_6Si_2O_{13}$) and SiO_2. However, the temperature region of stability of mullite is very narrow and above 1500 K, mullite is not stable. It dissociates into alumina and silica above 1500 K. The silica formed is immediately converted to SiC. Alumina and SiC are stable upto 2250 K.

Above 2000 K, the reduction of alumina to Al_2O gas and Al vapor starts. At 2500 K, alumina is totally reduced to Al and Al_2O vapor species. At the same time, SiC is also progressively transformed to SiO gas and CO gas. At 2750 K and above, Al and SiO are the major species with minor amount of Al_2O, and Si gas. Carbon is totally present as CO gas. It is found that alumina and carbon are stable in the narrow

Table 1
Operating parameters.

Input power	4.5 and 6 kW
Plasma gas and flow rate	Nitrogen; 4 lpm
Processing time	3 min
Cooling medium	Nitrogen
Powder quantity (sillimanite)	50 g

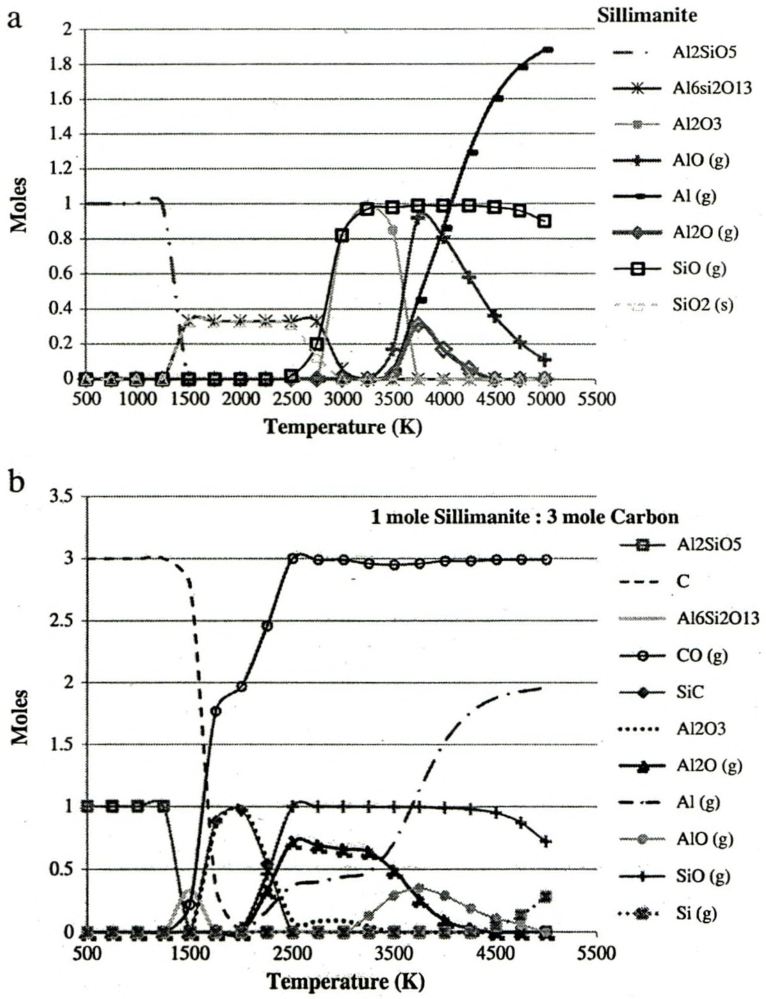

Fig. 2. a. Free-energy minimization plot for the Al_2SiO_5 system. b. Free-energy minimization plot for the Al_2SiO_5-C (1:3) system.

temperature zone of 1750 to 2250 K. In other words, by careful control of the processing conditions to regulate the temperature in the range of 2000–2250 K, sillimanite can be converted to alumina and SiC.

3. Results and discussion

It was noted during initial trial experiments that when the arc power was maintained at 3 kW, conversion of sillimanite to mullite was not complete even after long processing time (6 min). However, complete conversion could be achieved at 4.5 kW and 3 minute processing duration. Therefore it was decided to carry out all the experiments at 4.5 and 6 kW power and time duration of 3 min. In all the experiments, it was ensured that the arc is moved across the crucible for 3 min and the slag is then allowed to cool naturally. The product was then characterized for phase composition. The charge was kept constant at 50 g for all the experiments.

Fig 3 shows the XRD patterns of raw sillimanite and the products treated for 3 min at 4.5 kW and 6 kW of transferred arc plasma. It is evident that sillimanite is completely converted into mullite at both the power levels. As discussed earlier (Fig. 2a), sillimanite dissociates into mullite and silica on heating to high temperatures (>1500 K). It is interesting to note that the silica peaks are not present in the XRD patterns of the treated products. This may be due to the evaporation of the silica during arc plasma processing when it is exposed to high temperature plasma environment. Also, there is a possibility of silica being present as amorphous silica. The material treated at higher power level shows higher crystallinity. The results indicate that the input power of 4.5 kW and the three min processing time are enough to transform sillimanite powder into mullite.

Fig. 4 shows the XRD pattern of the products obtained from the plasma processing of sillimanite with 0.3 moles of carbon (sillimanite mixed with carbon in the ratio of 1:0.3 gram molar ratio). The chosen power levels are 4.5 kW and 6 kW and the processing time is fixed to 3 min. There is negligible difference between the XRD patterns of products obtained from plasma processing sillimanite and sillimanite with 0.3 moles of carbon. The product obtained could be identified as mullite. The addition of carbon in limited quantity facilitates to reduce silica as SiO gas, which escapes with the off gas. The net result is mullite free of silica. It should be noted that although sillimanite is converted to mullite by simple thermal treatment, the product contains silica. The addition of carbon in limited amount leads to 'insitu' removal of silica resulting in high purity mullite.

The amount of carbon in the reaction mixture significantly affects the final product formed. As the carbon content is increased, formation of alumina and SiC is favored. In order to completely convert

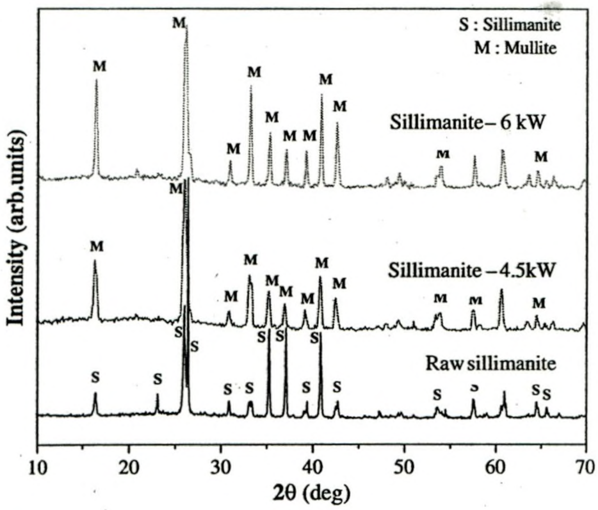

Fig. 3. XRD pattern of raw sillimanite sand and plasma processed sillimanite powder.

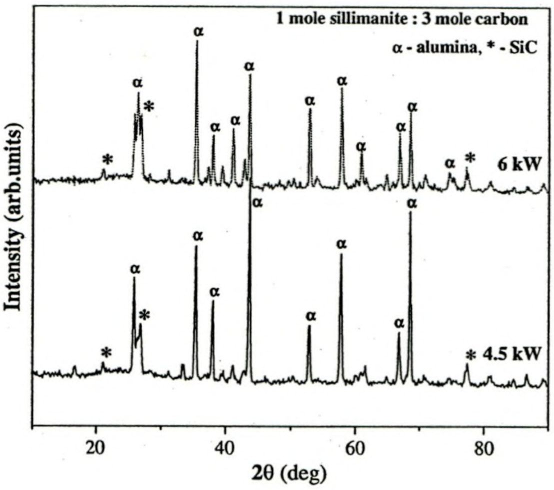

Fig. 5. XRD pattern of plasma processed sillimanite with 3.0 moles of carbon.

sillimanite to alumina and SiC, transferred arc plasma processing of sillimanite was carried out with 3 and 5 moles of carbon. Fig. 5 shows the X-ray diffraction pattern of plasma processed sillimanite containing 3 moles of carbon; α-alumina is seen as the major phase. Diffraction peaks of SiC can also be seen. Ideally, 3 moles of carbon are sufficient to convert sillimanite to alumina and SiC as shown below:

$$Al_2SiO_5 + 3C = Al_2O_3 + SiC + 2CO.$$

However, splashing of fine carbon powder from the reaction mixture during arc plasma processing can lead to loss of carbon. This can lead to insufficient amount of carbon present in the reactant mixture to convert all the Si into SiC. Therefore, experiments were carried out with sillimanite containing 5 moles of carbon. X-ray diffraction of the product, illustrated in Fig. 6 shows α-alumina and SiC as the major phases. The intensities of the diffraction peaks of SiC have increased considerably compared to Fig. 5, indicating that sufficient carbon was available to form SiC.

The presence of SiC in the product was also confirmed by the results of FTIR spectrum of the product. The FTIR spectra of the raw sillimanite and the product obtained from the plasma processing of sillimanite mixtures (sillimanite with 3 and 5 moles of carbon) are shown in Fig. 7. The absorption peak at 1175 cm^{-1} in the raw material clearly indicates that this mineral is sillimanite [28]. The total absence of this peak in the plasma processed sillimanite mixture confirms the complete dissociation of sillimanite. The pronounced absorption band at ~810 cm^{-1} in the products treated with plasma for sillimanite mixtures corresponds to stretching vibrations of silicon carbide bonds [29].

The experimental findings are seen to agree with the predictions based on thermodynamic analysis. The addition of carbon is found to have a remarkable influence on the course of the reaction and also on the product formed. By adding carbon in sufficient amount, sillimanite can be converted completely into alumina and SiC. Free energy minimization study of sillimanite–carbon system clearly indicates that above 2500 K, SiO(g), Al_2O(g), AlO(g) and Al(g) and CO gas are the major species present. Therefore, care should be exercised to control the processing conditions so that the reaction temperature does not exceed 2500 K.

In summary, results of the investigations showed that the nature of the product obtained by transferred arc plasma processing of sillimanite depended on the sillimanite–carbon ratio. By careful control of the processing conditions, sillimanite can be converted to mullite,

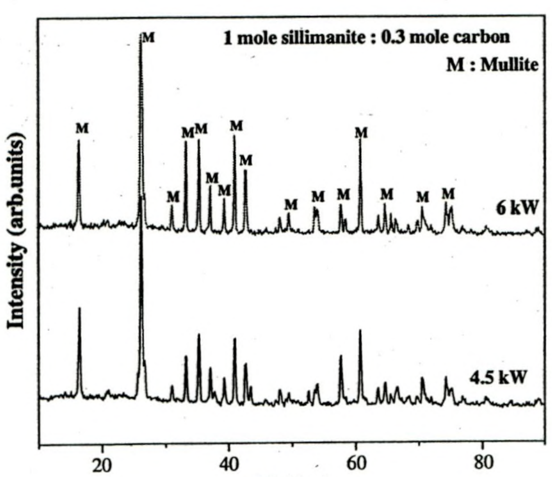

Fig. 4. XRD pattern of plasma processed sillimanite with 0.3 moles of carbon.

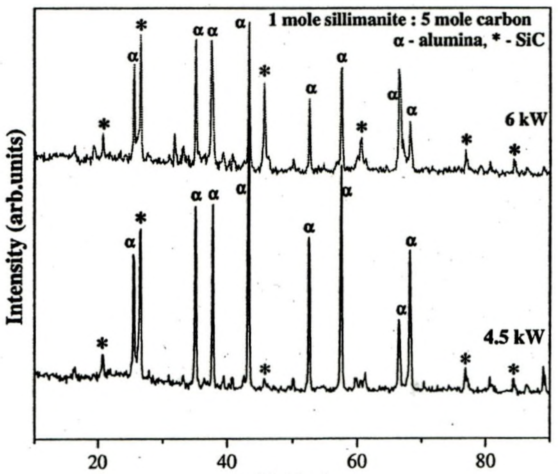

Fig. 6. XRD pattern of plasma processed sillimanite with 5.0 moles of carbon.

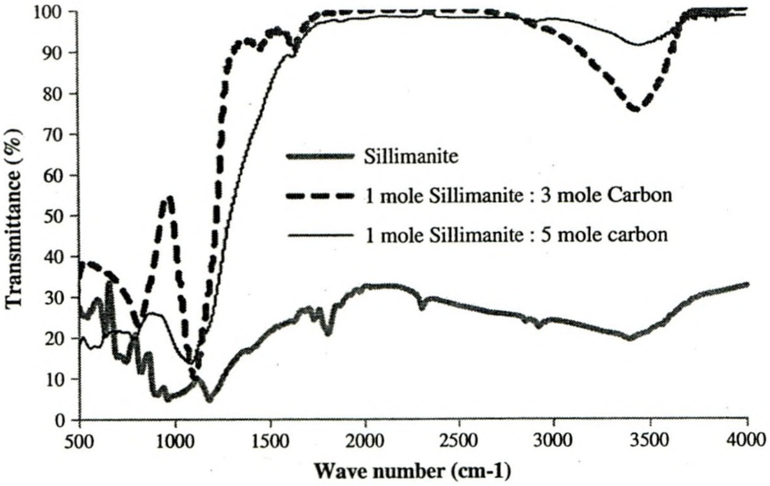

Fig. 7. FTIR spectra of sillimanite and plasma processed samples.

or alumina and SiC. Arc plasma melting of sillimanite at 4.5 kW and 6 kW without any carbon resulted in mullite admixed with silica, which can be removed 'in situ' by controlled addition of carbon. By increasing the carbon content in the reaction mixture, sillimanite could be converted to alumina and SiC, which have potential applications in the ceramic industry.

4. Conclusion

Transferred arc plasma route was used to convert sillimanite to industrially useful products like mullite, alumina and silicon carbide. Free energy minimization studies were carried out to get the favorable temperature conditions for formation of mullite, alumina and SiC. The FEM results were used as the guideline for the experimental studies. Sillimanite could be converted to mullite by arc processing of pure sillimanite or sillimanite containing carbon sufficient to remove silica as SiO. By adding the appropriate amount of carbon and careful control of the processing conditions, sillimanite could be converted to alumina and silicon carbide.

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References

[1] Schneider H, Okada K, Pask JA. Mullite and mullite ceramics. UK: Wiley; 1994.
[2] Ye R, Li JG, Ishigaki T. Controlled synthesis of alumina nanoparticles using inductively coupled thermal plasma with enhanced quenching. Thin Solid Films 2007;515(9):4251-7.
[3] Levin I, Brandon D. Metastable alumina polymorphs: crystal structures and transition sequences. J Am Ceram Soc 1998;81(8):1995-2012.
[4] Fincke JR, Swank WD, Haggard DC. Plasma spraying of alumina: plasma and particle flow fields. Plasma Chem Plasma Process 1993;13(4):579-600.
[5] Singh J, Van B. Structure of alumina supported platinum catalysts of different particle size during CO oxidation using in situ IR and HERFD XAS. Catal Today 2010;155(3–4):199-205.
[6] Tripathi HS, Banerjee G. Effect of chemical composition on sintering and properties of $Al_2O_3 \pm SiO_2$ system derived from sillimanite beach sand. Ceram Int 1999;25(1):19-25.
[7] Panda PK, Mariappan L, Jaleel VA, Kannan TS, Duboisb J, Fantozzib G. Carbo therma1 reduction of sillimanite. J Mater Chem 1996;6(8):1395-400.
[8] Kimura I, Hotta N, Matsuda G, Saito N, Yasukawa S. Preparation of SiC–Al_2O_3 composite powder. J Mater Sci Lett 1987;6:1359-60.
[9] Wei C, Becher PF. Development of SiC-whisker-reinforced ceramics. Am Ceram Soc Bull 1985;64(2):298-304.
[10] Tiegs TN, Becher PF. Sintered Al_2O_3–SiC-whisker composites. Am Ceram Soc Bull 1987;66(2):339-42.
[11] Tiegs TN, Becher PF. Thermal shock behavior of an @alumina–SiC whisker composites. Am Ceram Soc Bull 1987;70(5):109-11.
[12] Chokshi AH, Porter JR. Creep deformation of an alumina matrix composite reinforced with silicon carbide wishkers. J Am Ceram Soc 1985;68:144-5.
[13] Basu SN, Ping Hou, Sarin VK. Formation of mullite coatings on silicon-based ceramics by chemical vapor deposition. Int J Refract Met Hard Mater 1998;4(6):343-52.
[14] Li DX, Thomson WJ. Kinetic mechanisms for mullite formation from sol–gel precursors. J Mater Res 1990;5(9):1963-9.
[15] Okada K, Otsuka N. Characterization of the spinel phase from SiO_2-Al_2O_3 xerogels and the formation process of mullite. J Am Ceram Soc 1986;69(9):652-6.
[16] Kumar S, Das SK, Daspoddar PK. Thermo-mechanical behaviour of low cement castables derived from mullite aggregates synthesised from beach sand sillimanite. Ceram Int 2003;29(2):139-44.
[17] Schneider H, Majdic A. Preliminary investigation on the kinetics of high temperature transformation of sillimantie to 3/2 mullite plus silica acid comparison with the behaviour of and alusite and kyanite. Sci Ceram 1981;11(1):191-6.
[18] Wilson HH. Mullite formation from sillimanite group of minerals. Am Ceram Soc Bull 1969;48(b):796-7.
[19] Tripathy HS, Banerjee G. Synthesis and mechanical properties of Mullite from beach sand sillimanite: effect of TiO_2. J Eur Ceram Soc 1998;18:2081-7.
[20] Tripathy HS, Das SK, Mukerjee B, Ghosh A, Banerjee G. Synthesis and thermo-mechanical properties of mullite alumina composite derived from sillimanite beach sand: effect of ZrO_2. Ceram Int 2001;27(8):833-7.
[21] Khalafalla SE, Haas LA. Carbothermal reduction of liquid siliceous minerals in vacuum. High Temp Sci 1970;2:95–109.
[22] Ananthapadmanabhan PV, Sreekumar KP, Venkatramani N, Kameswaran R, Dias CC, Mishra SC. Particle morphology and size distribution of plasma processed aluminium Powder. Bull Mater Sci 1996;19(3):559-64.
[23] Chazelas C, Coudert JF, Jarrige J, Fauchais P. Synthesis of ultra fine particles by plasma transferred arc: influence of anode material on particle properties. J Eur Ceram Soc 2006;26:3499-507.
[24] Ananthapadmanabhan PV, Vijay M, Thiyagarajan TK, Sreekumar KP, Selvarajan V, Yu J, et al. In-Flight formation of nano-crystalline titanium dioxide powder in a plasma jet and its characterization. Plasma Sci Technol 2010;12(4):426-32.
[25] Vijay M, Selvarajan V, Sreekumar KP, Yu J, Liu S, Ananthapadmanabhan PV. Characterization and visible light photocatalytic properties of nanocrystalline TiO_2 synthesized by reactive plasma processing. Sol Energy Mater Sol Cells 2009;93:1540-9.
[26] Ramachandran K. Numerical modelling of plasma spray process. J Phys Conf Ser 2010;208:012052.
[27] Turnbull AG, Wadsley MW. The CSIRO thermochemistry system. Version 5: IMEC; 1988.
[28] Roy R, Francis EE. On the distinction of sillimanite from mullite by infrared technique. Am Mineral 1953;38:725-8.
[29] Chen L, Goto T, Hirai T. Preparation of silicon carbide powders by chemical vapor deposition of the SiH_4–CH_4–H_2 system. J Mater Sci 1989;24:3824-30.