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Synthesis of SiC and Cristobalite from Rice Husk by Microwave Heating

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ABSTRACT In the present work rice husks were exposed to microwave energy at different atmospheres in order to promote the reaction between carbon and silica. From the X-ray diffraction patterns it was possible to detect SiC and/or α-cristobalite as products from that reaction. X-ray fluorescence analysis was used to provide a quantitative impurity determination. Scanning and transmission electron microscopy were performed on selected samples to provide a full microstructural characterization.

INTRODUCTION

Rice husk is a by-product originated from the agricultural industry. Since the rice world production is estimated to be 500 millions of tons per year [1], it is also possible to estimate the rice husk yielding as 50 to 100 millions of tons. The composition of rice husk is known to be rich in carbon and amorphous silica [2]. Therefore this material has been extensively investigated as a precursor to produce ceramic materials, mainly silica based compounds [3], silicon carbide [4] and silicon nitride [5]. Rice husk has also been used commercially to produce silicon carbide whiskers which are widely used as reinforcement of ceramics and metal alloys [6].

Several processing methods have been investigated to produce SiC, Si_3N_4, and SiO_2 from rice husk. Electrical furnaces [7] and plasma arc reactors [8] have been used and demonstrated their advantages and drawbacks. Microwave has not yet been considered as an energy source in the decomposition of rice husk. This kind of energy has already been used to sinter ceramic materials [9], in the drying processes [10], joining materials [11], and to induce the reaction between carbon and silica [12]. Materials can absorb, be transparent, or reflect microwaves depending on their nature. Therefore microwaves can be considered a selective energy. It can heat some materials without affecting others at the same time. Dielectric constant and loss factor are the most important properties to be considered when a material is thought to be "microwaved". This work investigates the use of microwave energy on rice husk to decompose it and to produce silica and silicon carbide.

EXPERIMENTAL PROCEDURES

Rice husk samples were washed in distilled water, dried at 110 °C for 3 h, and weighted before exposing them to 2.45 GHz microwave energy. A conventional kitchen microwave oven rated to 900 W was modified for that purpose. The turntable was removed and an additional hole was drilled to allow an argon flow. Porcelain crucibles were used to contain the samples and they were involved with a ceramic fiber mantle. When an inert atmosphere was required, a pyrex container was used externally to restrict the samples to an argon atmosphere. The oven power was selected according to a pre established setup. Table 1 shows a typical setup adopted to avoid a crucible thermal shock.

Table 1. Oven power setup.

Time (min)	Power (%)
3	20
3	50
30	90

The temperature was measured by a pyrometer Minolta Cyclops model S40 focused on the bottom of the crucible.

After "microwaving", samples located on the bottom part of the crucible were separated from the rest. Samples from the bottom are the ones close to the point where the temperature was measured. They are also less contaminated with oxygen since they are far from the top where the probability of contamination is higher.

Samples were then heat treated in an electric furnace at 700 °C in air for 4 h to burn all residual free carbon. Finally the samples were ground in a mortar with a pestle.

X-ray diffraction and scanning electron microscopy were performed in selected samples by using an Rigaku X-ray diffractometer model DMAX 100 and a Philips Scanning Electron Microscope model XL-30 respectively. X-ray Fluorescence analyzes were performed to determine the product composition by using a Rigaku X-ray spectrometer model RIX 3000.Transmission electron microscopy was performed in selected samples in order to determine the crystalline structure of the product with whisker's shape. A JEOL model JEM 200 C transmission electron microscope was used for that purpose.

RESULTS AND DISCUSSION

Fig. 1 shows sample temperature as a function of exposing time at 90% microwave power.

Five distinguished regions can be noticed. In the first region volatilization of organic matter occurs as the sample absorbs energy which helps to degrade organic chains. A slightly temperature raise is observed. The second region indicates a microwave absorption by the sample, and the temperature is quickly raised. In the third region a phase transformation occurs where amorphous silica becomes α-cristobalite as it will be shown later. In the fourth region α-cristobalite and silica absorb microwave energy and the temperature is raised quickly again. The last region is related to the reaction between carbon and silica resulting SiC according to the following:

$$SiO_2(s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO_2\ (g) \qquad \text{Eq. 1}$$

Different features, such as heating rates, and energy absorption in the regions, are due to the presence of different compounds, consequently, different dielectric constants and loss factors.

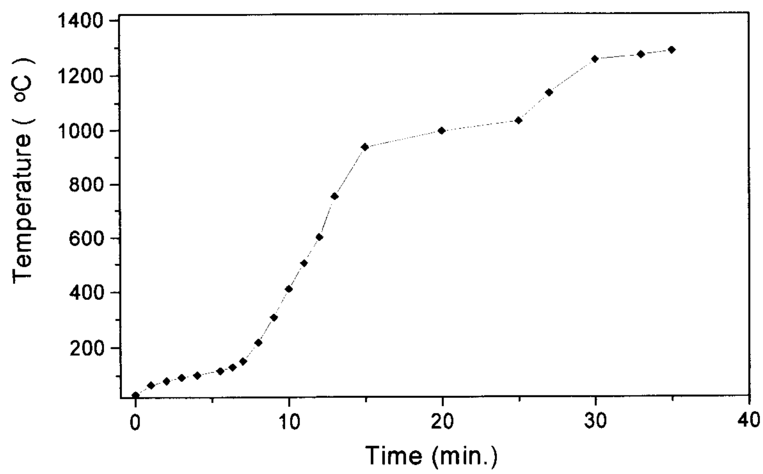

Fig. 1 - Temperature versus exposing time at 90% microwave power.

Table 2 shows the impurity concentration in this sample determined by X-ray fluorescence analysis. Similar results were obtained for others samples.

Table 2: Impurity Concentration in Materials after Microwaving.

Elements	Concentration (wt%)
P	0.070
S	0.045
Mn	0.053
Fe	0.029
Al	0.010
Mg	0.010
K	0.003
Ca	0.003

It is noticed that the total impurity concentration is less than 0.25 wt%. The relatively low concentration of K can be explained by its loss. This element has been detected early in concentrations varying from 0.2 to 0.8 wt% [13]. This element is important since it melts at a relatively low temperature and helps the contact between silica and carbon. If K is removed previously by an acid leaching process, the contact surface between carbon and silica is reduced and the grow of SiC whiskers is prevented [14]. In the present work acid leaching was not performed and the K was kept during the heat treatment. Although K is eliminated in the process, apparently a high concentration of whiskers is still obtained.

Fig. 2 shows the X-ray diffraction (XRD) pattern for a sample microwaved up to 900 °C in air. A halo due to amorphous silica is seen and no crystalline phases have been observed.

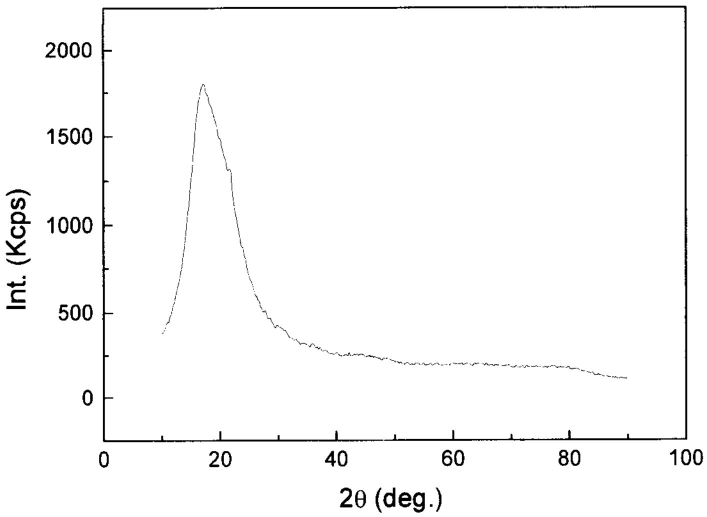

Fig. 2 - XRD pattern from samples heated up to 900 °C.

Fig. 3 shows X-ray diffraction patterns from rice husks "microwaved" at temperatures above 1060 °C in argon. At 1060 °C only XRD peaks corresponding to SiC have been observed superposing the amorphous halo. Above that temperature XRD peaks corresponding to α-cristobalite can also be seen. Therefore for those temperatures it is possible to occur the transformation of amorphous silica to α-cristobalite.

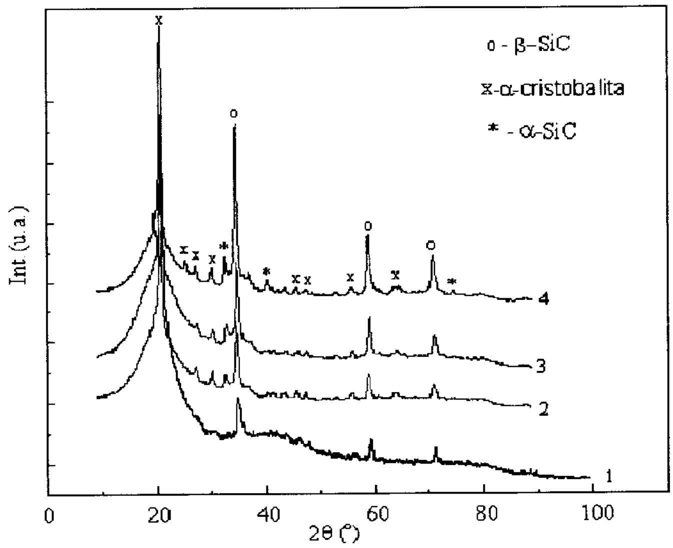

Fig. 3 - XRD patterns from samples heated above 1060 °C. 1) 1060 °C; 2) 1225 °C; 3) 1370 °C; 4) 1395 °C.

In order to analyze the influence of the temperature during the microwave exposition on the produced SiC, the ratio (Fs) between all SiC XRD main peak heights and the background was determined .

Fig. 4 shows Fs as a function of heating temperature.

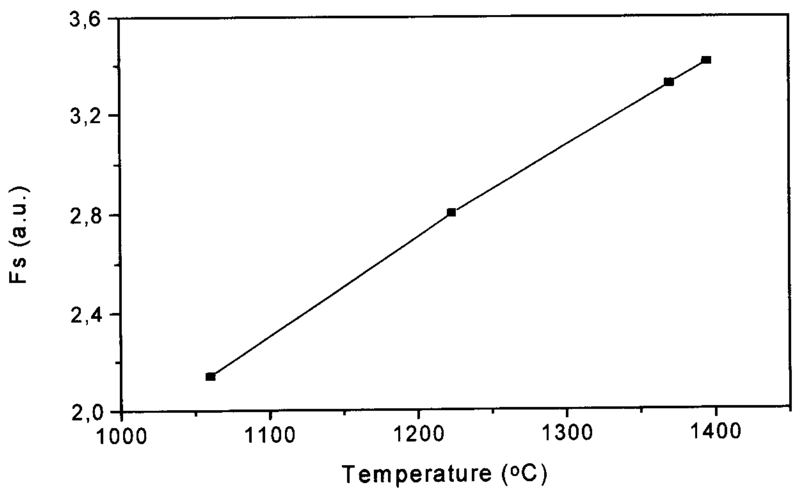

Fig. 4 - Fs as a function of temperature.

It is noticed that the amount of SiC increases as the final temperature is raised. The amount of amorphous silica that reacts with carbon also increases.

Fig. 5 shows microstructural features of rice husk samples microwaved at different temperatures during 35 min in argon. At 1060 °C (Fig. 5A) it is observed the formation of SiC whiskers and large particles corresponding to amorphous silica. At 1220 °C (Fig. 5B) SiC whiskers are still depicted and some morphologically modified silica particles can be seen. Spherical particles seems to be formed from the later ones. The α-cristobalite has been formed. At 1370 °C (Fig. 5C) SiC whiskers can still be seen and a larger number of small spherical particles are shown. More α-cristobalite has been formed according to the XRD pattern and the amount of SiC whiskers is also increasing. At 1395 °C (Fig. 5D) a larger amount of SiC whiskers is observed compared with samples treated at lower temperatures. Some silica is still observed.

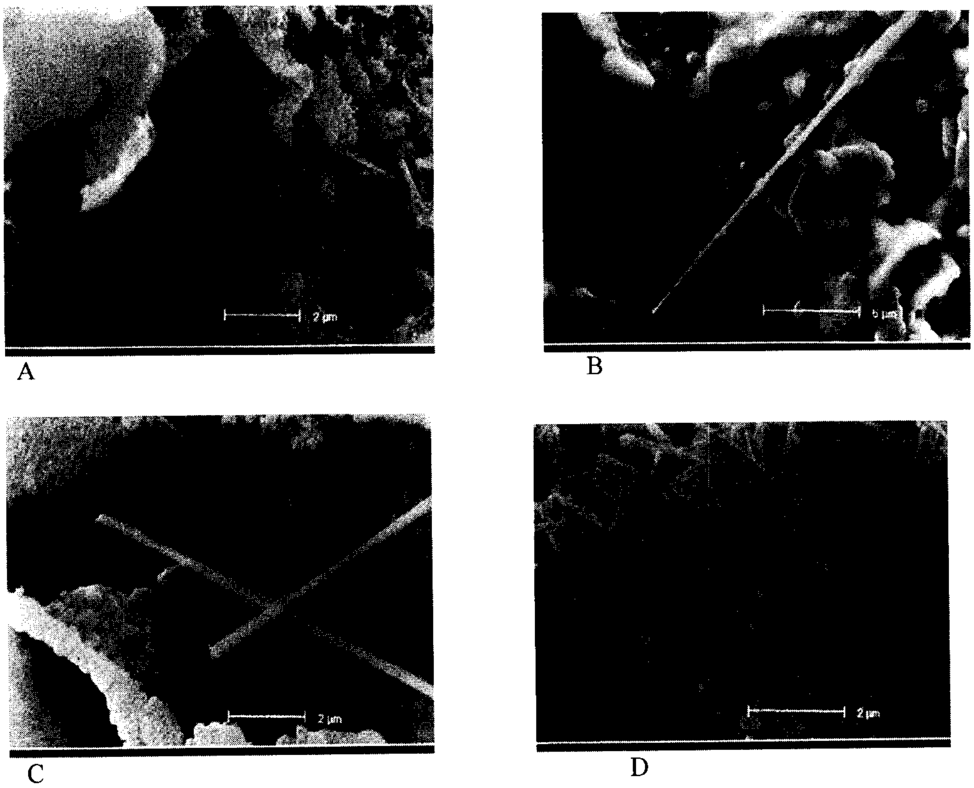

Fig. 5. Scanning electron microscopy from microwaved rice husks: A) 1060 °C; B) 1225 °C; C) 1370 °C; D) 1395 °C.

Fig. 6 shows a transmission electron micrograph of a SiC whisker (Fig. 6A) with its corresponding electron diffraction pattern (Fig. 6B). In the micrograph it is observed lines originated from twins phases as reported early by other work [15]. From the electron diffraction pattern it was possible to identify the SiC whisker crystalline structure as being β-SiC.

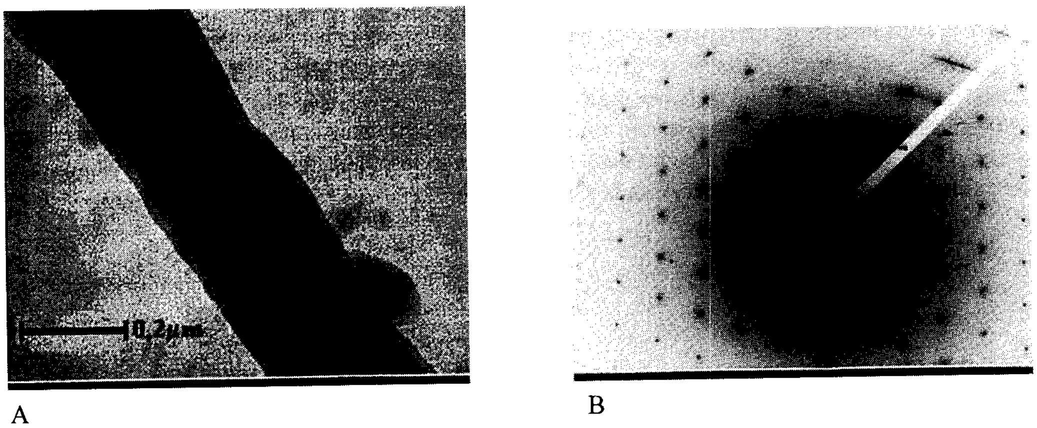

Fig. 6 - Transmission electron microscopy from microwaved rice husks: A) SiC whisker. B) Electron Diffraction Pattern.

CONCLUSIONS

Microwaves can be used to pyrolyze rice husks. As the raw material absorbs microwaves, different compounds are formed with different dielectric properties. Therefore different heating rates have been observed during the process. Organic matters are decomposed, silica reacts with carbon to form β-SiC whiskers and amorphous silica is transformed to α-cristobalite. Silicon carbide twin phases have been detected in whiskers by TEM.

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