Synthesis of ceramic materials from waste residues

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Abstract. In the frame of a wide research program devoted to the matter recovery from waste by means of thermal processes, particular efforts have been put into the study of biomasses and waste residue of peculiar composition, which could be used as precursors of ceramic materials.

Rice shells are waste biomasses coming from the purification process of rice, which show a high carbon and silica content. The exploitation of these peculiarity promoted a series of experimental activities, aimed at the production of ceramic materials through high temperature carbothermal synthesis reactions. The synthesis products were characterized by X Ray Diffraction (XRD) and scanning electron microscopy (SEM) and the data confirmed the production of ceramic silicon nitride (Si_3N_4) at high yield and purity, under the adopted process parameters.

Introduction

Current EU waste policy is based on a series of "guidelines", fully oriented towards the environment protection through the adoption of a concept known as the waste hierarchy. This model gives the highest priority to the waste prevention and is aimed at the accomplishment of a management strategy which encourages waste recycling as secondary raw materials or as energy sources.

Among the thermal treatments, the development of new technologies potentially alternative to the traditional waste-to-energy processes is gaining particular attention, due to political reasons and to the favorable media scene; anyway, apart from any other motivation, pyrolysis or gasification processes, applied to biomass or waste, are definitely highly advantageous, in terms of energy efficiency increase, of reduction of gaseous emissions to be depurated, of enhancing of solid residue inertization [1-2].

The properties of the process solid residue (char) strongly depend upon the nature of the starting materials and the process conditions; when a high carbon content is present, the char can be used as solid fuel or as secondary row material. In view of favoring the material recovery rather then the energy production, char has been employed as substrate for active carbon production, but its utilization in carbothermal synthesis for the achievement of high added value products, such as ceramics (Si_3N_4, SiC, TiC, NbC, ecc.), seems promising.

Silicon nitride is an advanced ceramic material with attractive properties for structural and functional applications. It has excellent wear and corrosion resistance and remarkable high temperature mechanical properties and due to its low thermal expansion coefficient and high thermal conductivity, has an excellent thermal shock resistance. For these reasons, it has been used for the manufacturing of structural parts of gas turbines, engines and high temperature systems. There are several method for Si_3N_4 synthesis, but the most common is the direct nitridation of Si metal powders at temperature ranging from 1200 to 1500°C:

$$3Si(s) + 2N_2(g) \rightarrow Si_3N_4(s) \quad (1)$$

or the carbothermal reduction of silica in N_2 gas:

$$3SiO_2(s) + 6C(s) + 2N_2(g) \rightarrow Si_3N_4(s) + 6CO(g) \quad (2)$$

The reaction takes place at temperature ranging from 1200 and 1700°C, through a gas-solid mechanism which proceeds in two steps and brings to the formation of gaseous SiO as reaction intermediate.

Morphology and dimensions of nitride are influenced by the characteristics of starting carbon and from the process conditions, but generally the main product is α- Si_3N_4, the more reactive phase [3].

Rice husks is a by-product of the rice milling process and is mainly composed of organic material and silica; due to the composition, this material is particularly interesting in view of its energy exploitation as renewable fuel and as a low cost source of the main precursors for the production of high added value ceramics. In this frame, the present paper describes the results obtained for the synthesis of silicon nitride powders by means of rice husks pyrolysis and the characterization of the process products; the experimental tests were conducted in two steps, that is the preliminary low temperature pyrolysis of rice husks, and the further high temperature carbothermal synthesis of the solid residue.

Materials and methods. Synthesis reactions have been performed both on the original rice husk (without any pre-treatment) or after size reduction. Low temperature pyrolysis tests have been conducted on a Lenton tubular furnace (LTF 12/600/610) at 600°C in nitrogen atmosphere (flow rate of 1 l/min), with a solid residence time of 1 hour. Nearly 20 g of sample were used for each test; during the treatment, the effluent gas was headed for the cleaning system, composed of an ice-jacketed condenser trap dedicated to the oil condensation, and of a basic scrubber (1M sodium hydroxide solution) for acid removal.

Ceramic synthesis were conducted on a bench scale high temperature tubular furnace (Nabertherm 120/300/1800); the tests were carried out at temperatures ranging from 1500 to 1600°C, with residence time of nearly 1 hour, in nitrogen atmosphere (flow rate of 50 l/h) with the samples in alumina crucibles.

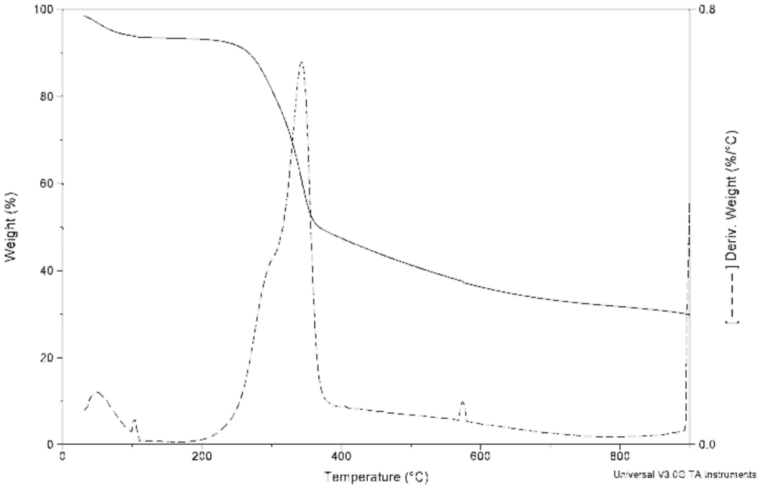
A TA Instrument TG 2950 system was used to analyze the macro-component composition (proximate analysis) of the starting mixture and to verify the presence of carbon in the synthesis products; pure nitrogen was used as inert purge gas, at a constant flow rate of 100 $cm^3\ min^{-1}$, for proximate analysis, while air was used as oxidizing agent for carbon determination.

Ultimate analysis was obtained with a Thermo Quest EA 1110 analyzer. Such an analysis gives simultaneously the weight percent of carbon, hydrogen, nitrogen and sulphur in the samples; oxygen determination can afterwards be obtained by difference. Initial ash content was evaluated by incineration at 1000 °C.

The products were characterized using scanning electron microscopy (SEM) (Zeiss microscopy) and X ray diffraction (XRD) (MPD-X'PERT Philips diffractometer).

Results and discussions. The decomposition profile of rice husk, from thermogravimetry-differential thermogravimetry (TG-DTG), at heating rate of 10 °C/min, is shown in Figure 1, where is noticeable that the decomposition is practically complete at nearly 400°C [4].

Fig.°1, Rice hush thermograph, showing a ramp at 10°C/min in N_2 to 900°C, followed by air combustion



The proximate and ultimate analyses of the sample are presented in Table 1.

Table 1, Ultimate and proximate analyses

	[% w/w]		[% w/w]
C	49.4	Moisture	6.7
H	6.2	Volatile	61.3
N	0.3	Fixed carbon	18.0
S	0.4	Ash	13.7
O	43.7		
PCS		17370 kJ/kg	

The macrocomponent analysis of the material shows a significant organic content amount and a high ash content, in comparison with other biomasses: the ash are almost exclusively composed of silica and, together with the fixed carbon, form the char (nearly 30% of the mixture).

As above underlined, the process has been developed by preliminary conducting the pyrolysis of rice husk at low temperature and by further using the solid residue of the process, the char, for the high temperature synthesis of the ceramic material.

The pyrolysis tests, conducted at 600°C in nitrogen atmosphere, gave a char yield of nearly 32%, in line with the expected results obtained from the proximate analysis of the starting material. The chars have been characterized and the proximate analysis data are reported in Table 2.

Table 2, Proximate analysis of char from rice husk pyrolysis

	[% w/w]
Volatile	32.9
Fixed carbon	29.6
Ash	37.5

According to the experimental data, the carbon/silica weight ratio of the char is nearly 0.8 (considering that the ash is just silica); such a value is definitely higher than the stoichiometric value of the two reagents of reaction (2) (which is 0.4), but is certainly adequate to allow high conversion rates.

The char samples were put in recrystallized alumina crucibles and heated at 5°C/min to the predetermined temperature (1500 and 1600°C), held there for 1 hour and then cooled in flowing N_2. The continuous nitrogen flow provides for the presence of a reactant (the nitrogen indeed, according

to reaction1) and promotes silicon nitride formation. Nevertheless, the gas flow must be relatively low, to prevent gaseous SiO (the intermediate of the reaction) to be swept away from the hot zone. On the other hand, the carrier gas flow should be sufficient to remove the CO gas produced in the overall reaction. Consequently it has been judged that a flow of 0.8 l/min was adequate for getting the proper compromise among the different aspects [5].
After the synthesis, the excess carbon was oxidized by firing the products in air at 700°C, which allowed the removal of a volatile fraction of nearly 50% for each sample.
Powder X-ray diffraction analysis (XRD) was utilized for the characterization of the ceramic products; according to the next figures (figures 2a and 2b), which show the XRD patterns of the products, all the salient peaks can be attributed to silicon nitride [6-7]. Essentially α-Si_3N_4 accounts for most of the peaks, while β phase is low represented; anyway α/β ratio normally influences the sintering behavior and the high value encountered is certainly qualifying for high tech applications.
prerequisito per applicazioni di alta tecnologia.

Fig.°2a –XRD pattern of rice husk

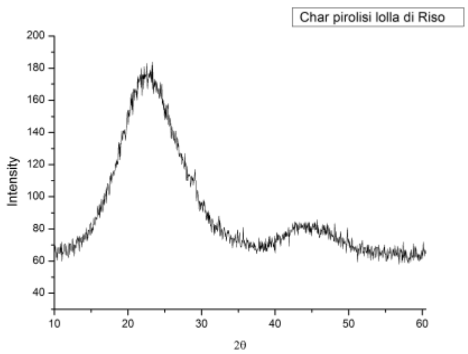
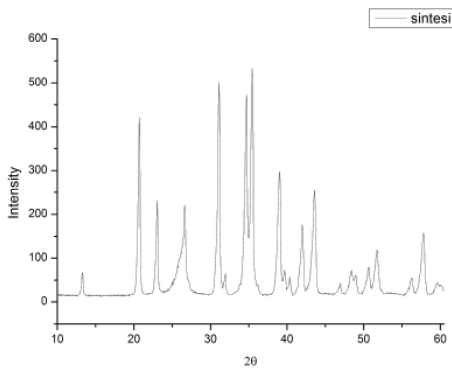


Fig.°2b –XRD pattern of synthesis product obtained at 1500°C



All the synthesized samples were examined by SEM and the corresponding photographs (see Figures 3a and 3b) reveal the existence of two main morphologies, that is aggregates of hexagonal shape grains and elongated fibers of needle-like growth. This last morphology becomes predominant at higher synthesis temperatures [3].

Fig.°3a, SEM photograph of the powder produced at 1600°C – grains

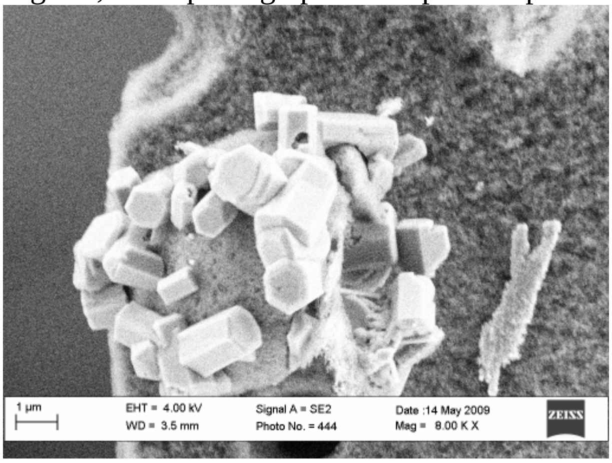
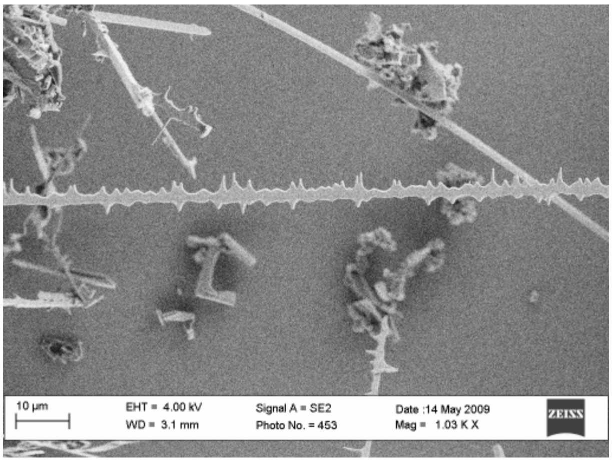


Fig.°3b, SEM photograph of the powder produced at 1600°C – fibers



Summary

The carbothermal reduction at high temperature of a process by-product, such as the char coming from the rice shell pyrolysis, under nitrogen atmosphere, brings to the synthesis of silicon nitride, an advanced ceramic material which has excellent wear and corrosion resistance and remarkable high temperature mechanical properties.

The characterization of the synthesis products, conducted at various temperatures and at different milling grade of the starting materials, confirms the ceramic nature of the materials and shows a variable morphology according to the process conditions.

The obtained results encourage the growing interest towards the matter recovery from waste and open up new scenarios within the research field of low cost sources for the production of high added value materials [8-9].

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