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Synthesis of SiC from rice husks catalysed by iron, cobalt or nickel

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The synthesis of SiC (both powder and whiskers) was carried out from rice husks with and without the use of catalysts (iron, cobalt and nickel). The introduction of the catalyst increased the reaction rate, the yield becoming up to three times that for the uncatalysed reaction, and increased the proportion of β-phase from 95% to 99%. The general behaviour of the three catalysts was very similar, although nickel was the most effective from the point of view of reaction rate, and cobalt in producing larger crystal size. Analysis of the evolution of reaction rate, morphology of the whisker formed, evolution of gases during reaction, crystal size and intermetallic phases, led to a reaction mechanism based on the formation of an M–Si–C liquid phase which is essential for the nucleation and growth of the SiC whiskers.

1. Introduction

Silicon carbide is a commonly used ceramic material with attractive properties such as high strength, stiffness, good wear and corrosion resistance, etc., some of which are characteristic of typical covalently bonded materials [1–3]. The industrial manufacture of SiC is by the Acheson process, carbothermal reduction of silica sand with green petroleum coke; however, this process uses a very high temperature (around 2400 °C) and the product has a large grain size (> 1 mm), which requires extensive grinding to reduce the powder to sinterable size. In order to optimize the production of submicrometre SiC particles, several authors have used fine starting materials, reaction mixtures prepared by sol–gel techniques or laser- or plasma-driven chemical vapour deposition [4–11]. As the most easily scalable process is the carbothermal reduction of silica, a large effort has been made to improve the control of SiC particle size by the appropriate control of the size of carbon and silica particles in the reaction mixture.

Because the main problem of the carbothermal reduction process is the particle size of reactants and the need for an intimate contact among them, it is not surprising that a great deal of attention has been paid to the use of rice husks as a starting material for the production of SiC [12]. Rice husks consist of a cellulosic component that can be easily converted to carbon upon pyrolysis, and silica (up to 28% in some varieties [13]). With the very high surface area and intimate contact available from carbon and silica in carbonized rice husks, it is possible to form silicon carbide at relatively low temperatures [14].

Although the main industrial aim is the preparation of high-quality sinterable SiC powder at a reasonable cost, the last few years have seen a growing interest in SiC whiskers because they provide an effective means of reinforcement for modern metal and ceramic matrix composite materials, with high strength and stiffness values combined with a large aspect ratio. Whiskers are usually defined as single crystals of very high aspect ratio, i.e. ratio of length, l, to diameter, d, with $l/d > 10$, for a diameter in the range $0.01\ \mu m < d < 10\ \mu m$. Many manufacturing routes for producing SiC whiskers have been described in the technical and patent literature [15], the most popular being: (i) pyrolysis of gaseous sources of silicon or silicon and carbon (e.g. silanes, carbosilanes, etc.), usually involving hydrogen as carrier gas, and (ii) carbothermal reduction of artificial or natural silica/carbon mixtures. The possibility of preparing SiC whiskers from rice husks has been reported by several authors [12, 14, 16], but the mechanism of growth and the influence of catalysing the reaction by metals have not been thoroughly studied.

The aim of the present work was to investigate the possibility of producing high-quality SiC powder and whiskers from rice husks; the study includes the analysis of the role played by transition metals (iron, cobalt and nickel) as catalysts of the process and an elucidation of the mechanism involved.

2. Experimental procedure

The raw material used for the synthesis of SiC was rice husks from Valencia (Spain), with 11.5% humidity and 14.6% ash content. The ash was mainly constituted by silica (98%), the rest of the inorganic components being calcium, potassium and magnesium with traces of iron. The catalysts were introduced by incipient wet impregnation (minimum volume of solution) with nitrates of iron, cobalt and nickel dissolved

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in ethanol. Metal loading was determined by atomic absorption spectroscopy after 24 h digestion of the dry sample with a 1 : 1 $HCl:H_2O$ solution.

The synthesis was carried out in two steps. The first one was the pyrolysis under a nitrogen flow (90 ml min^{-1}, minimum purity 99.999%) of the raw material in an horizontal furnace, and the second one the thermal treatment (1400–1500 °C) of the resulting char in a high-temperature horizontal furnace under a 90 ml min^{-1} flow of argon (purity 99.999%).

The determination of the SiC formed was carried out as follows: combustion (12 h in an air flow at 800 °C) of the unreacted carbon and digestion of the residue for 48 h in a 1 : 1 $HCl:H_2O$ solution to eliminate the remaining catalyst; the resulting residue was treated with a HF/HNO_3 solution in a platinum crucible to eliminate the silica and the final product was SiC.

Identification of products was carried out by X-ray diffraction (JSO Debye-Flex 2002 from Seifert) fitted with a copper cathode and a nickel filter and using a 2° min^{-1} scanning rate. Particle size was determined by line broadening analysis, using the Scherrer equation. The morphology of the product was carried out by scanning electron microscopy (JSM 840, from Jeol) fitted with a Link QK 200 dispersive X-ray analyser.

3. Results and discussion

SiC obtained in the catalysed reaction differs from that obtained in the uncatalysed reaction and thus, although a mixture of crystals and whiskers is obtained in both cases, the catalysed reaction produces whiskers which exhibit a different morphology (Fig. 1), with the appearance of VLS growth [17]. However, the crystals/whiskers ratio is very similar in the uncatalysed and catalysed reactions, with 15%–20% whiskers. There is, however, an increase in crystal size for the catalysed reaction and a decrease in the α/β ratio of the forms of SiC, from 5/95 in the uncatalysed to 1/99 in the catalysed reaction. On the other hand, the catalysed reaction leads to the formation of two new phases: (i) silicides of iron, cobalt and nickel, and (ii) graphite.

The effect of the different variables used in the catalysed synthesis is now analysed.

3.1. Method of catalyst introduction

Two different methods of introduction of the metal salts were attempted:

(i) impregnation of the raw material, as described by Lee and Cutler [14]. The rice husks were treated for 1 h with a 10 w% solution of the metal chloride (precursor: solution ratio, 1 : 10); a 9 w% solution of ammonium hydroxide was then added and the reaction continued for another hour. After filtration, the product was washed with distilled water, dried at 100 °C and kept until use;

(ii) impregnation of the char obtained by carbonization of the rice husks, using the same method as in (i).

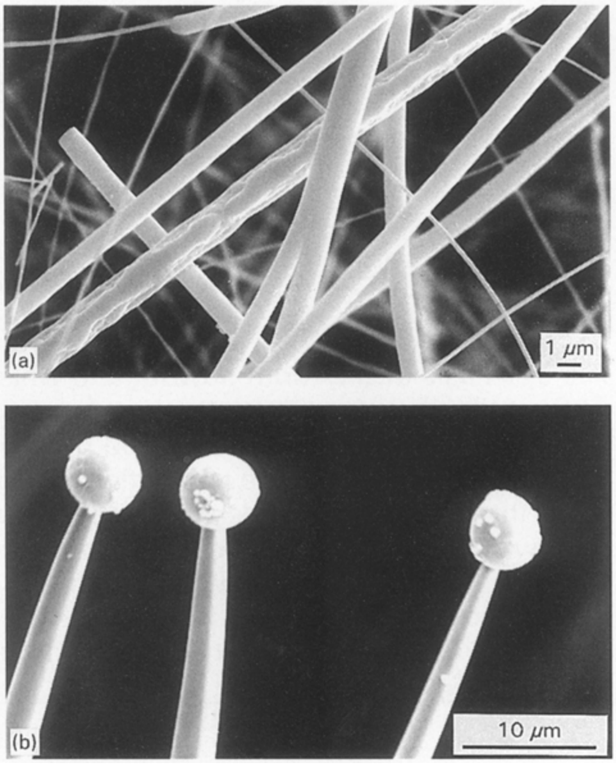

Figure 1 (Scanning electron micrographs of SiC whiskers prepared from rice husks: (a) uncatalysed, and (b) nickel-catalysed reactions.

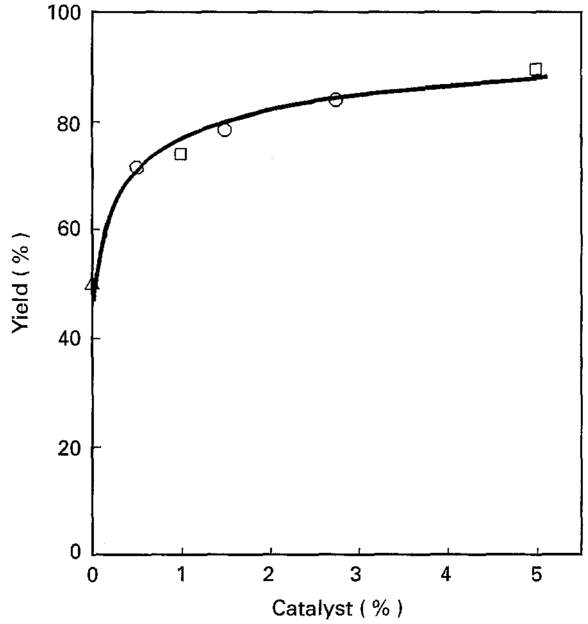

Figure 2 Evolution of SiC yield (1400 °C, 5 h) as a function of iron loading: (○) rice husks; (□) carbonized rice husks.

In order to test the efficiency of the two methods of introduction of the catalyst, preparation of SiC was attempted with the two types of impregnated material and the results in Fig. 2, for the particular case of iron as catalyst, show that there is no effect on the yield of the reaction for different catalyst loadings. One could perhaps expect better results for the case of the catalyst impregnated in the char, because this will have a larger porosity and surface area than the raw husks, thus allowing for a better dispersion of the metal. This

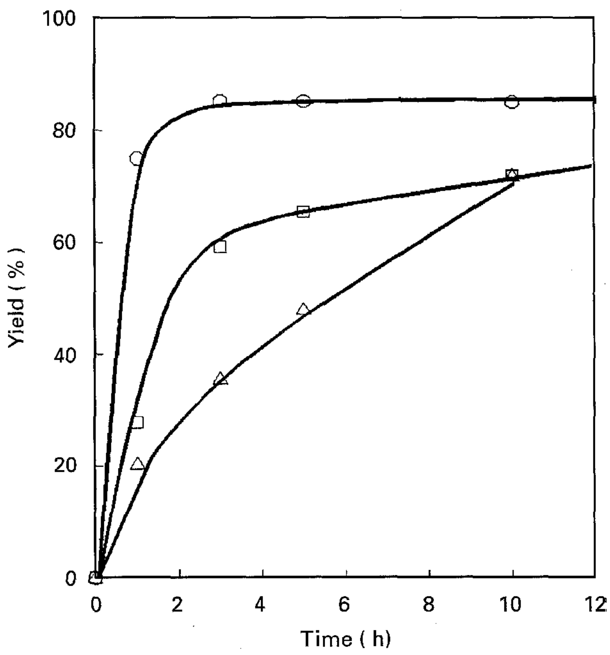

Figure 3 Evolution of SiC yield as a function of residence time at 1400 °C: (○) 1% Fe; (□) 5% Fe; (△) uncatalysed.

is not the case in practice, because the high temperature of the reaction (1400 °C) would sinter the catalyst. In fact, the catalyst must pass through a liquid state, as shown by the occurrence of metal silicides. As no difference could be detected between the two methods of impregnation, impregnation of the char was selected for the rest of the work because of its experimental simplicity.

3.2. Catalytic effect

The catalytic effect of iron in the synthesis of SiC, mainly the reduction in reaction temperature and the modification in morphology, has already been shown by previous authors [14, 18]. However, a more detailed study is needed to obtain better insight into the effect of the catalyst on the process and into the reaction mechanism.

Figure 3 shows the evolution of yield at 1400 °C as a function of reaction time. The yield increases considerably with the introduction of the catalyst (iron), the reaction being faster for 5% Fe than for 1% Fe, so that the yield for the former after 1 h reaction is larger than for 10 h in the latter or in the uncatalysed reaction. Although for the uncatalysed and the 1% Fe reactions the yield after 10 h is relatively similar, the effect of the catalysts is very clear for shorter reaction times, when 1% Fe produces a larger yield. A comparison of the three reactions at 1400 °C indicates that the approach to the maximum yield becomes shorter as the catalyst loading increases from 1% to 5% Fe, 3 h being sufficient for 5% Fe, when it is not yet reached even after 10 h for 1% Fe.

In order to determine the effect of the catalyst at different temperatures, the results for 5 h reaction can be compared in Table I, where it is shown that the differences between the three reactions (uncatalysed, 1% Fe, 5% Fe) become less important as the reaction temperature increases from 1400–1475 °C. On the other hand, the data for 1% and 5% Fe do not differ greatly, the effect of reaction temperature being less important as the metal loading increases from 1%–5% (it is very important for the uncatalysed reaction). What is clear from Fig. 3 is that iron catalyses the synthesis of SiC when present in the right proportion and that, as shown in Table I, a 5% Fe loading makes the reaction almost independent of temperature.

The results for cobalt and nickel as catalyst are given in Table I. For the former, the behaviour is similar to iron, the main difference being that the 5% loading is less effective than in the case of iron, not only because the total yield is lower but also because the approach to the maximum yield is slower. The effect of temperature is also similar for iron and cobalt, although for the latter the differences between 1% and 5% loading are smaller. Although the behaviour for nickel is relatively similar to iron and cobalt, there are some significant differences. Thus, Table I shows that the effectiveness of 1% and 5% are now more similar, but (as with cobalt) with a slower approach to maximum yield than in the case of iron; however, the maximum yield is larger than for the other two catalysts. On the other hand, 1% Ni is more effective than the equivalent loadings of iron or cobalt, very probably due to a better distribution in the original char. Another difference is that the effect of reaction temperature for 1% and 5% Ni is practically the same (the data evolve in a parallel way), this indicating that the increase in yield produced by the increase in reaction temperature is almost independent of catalyst loading (in the range covered here).

The effect of the catalysts on the morphology of the SiC obtained is also rather similar. Figure 4 shows the evolution of crystal size as a function of reaction time for 1400 °C. There is always an increase in crystal size

TABLE I Yield of SiC for the uncatalysed and catalysed syntheses

Treatment	SiC yield (%)						
	Fe		Co		Ni		Uncatal.
	1%	5%	1%	5%	1%	5%	
1400/1 h/Ar	27.8	75.0	38.1	76.0	47.9	77.9	11.0
1400/3 h/Ar	59.4	84.2	62.6	78.7	72.7	82.7	28.4
1400/5 h/Ar	65.5	85.2	67.9	82.3	79.2	86.3	39.4
1400/10 h/Ar	72.1	86.1	72.0	84.1	82.0	88.0	65.8
1450/5 h/Ar	82.0	89.5	80.4	89.2	84.0	91.8	75.0
1475/5 h/Ar	84.9	91.8	83.7	92.1	86.5	94.5	80.2

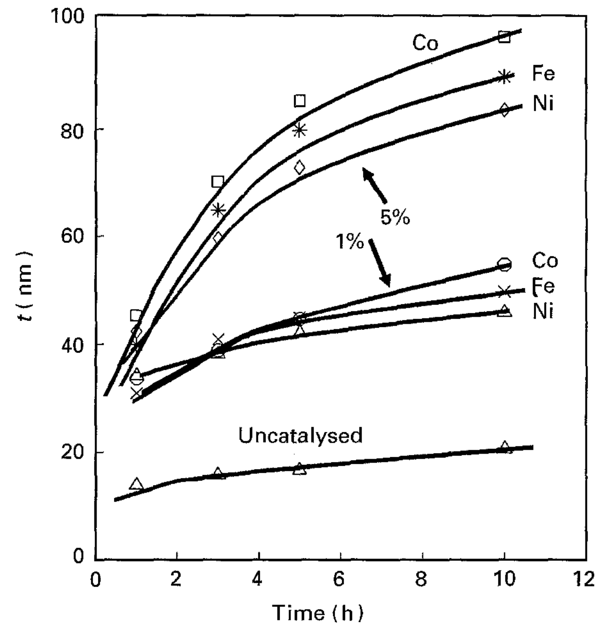

Figure 4 Evolution of SiC crystal size as a function of residence time (1400 °C).

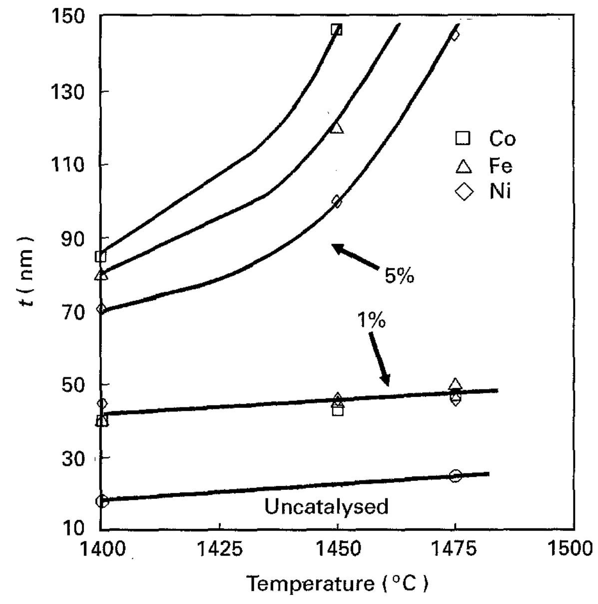

Figure 5 Evolution of SiC crystal size as a function of reaction temperature (5 h reaction) : (□) cobalt, (△) iron, (◇) nickel.

as reaction proceeds, which is more noticeable when a catalyst is used and even more for large catalyst loadings, but the effect of the catalyst in the crystal size does not follow the same sequence as the yield, because the largest effect is now observed for cobalt. The differences are more clearly shown when the reaction temperature is changed. As Fig. 5 shows, the effect of increasing temperature is similar for the 1% loading and for the uncatalysed reaction (with larger crystal size for the former), but for 5% metal there is an exponential increase in crystal size with increasing temperature, again the largest effect being for cobalt and the minimum for nickel. These results indicate that the selection of type of metal, metal loading and reaction temperature allows a control of both the yield of SiC and crystal size.

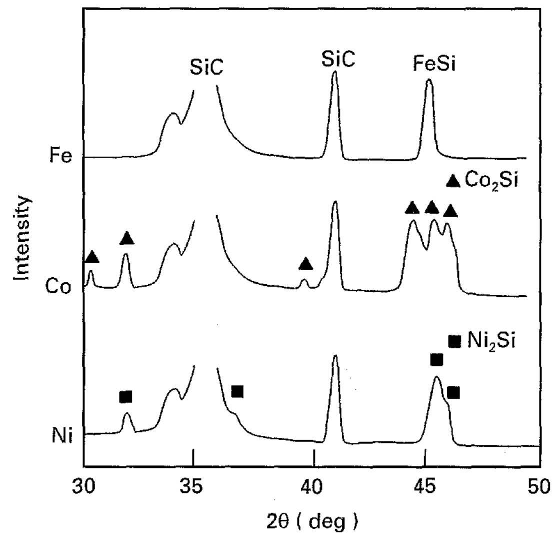

Figure 6 XRD diffractograms of samples prepared at 1400 °C (5 h reaction) catalysed by iron, cobalt and nickel (5% loading).

As stated above, the catalysed reaction produces two additional phases, metal silicides and graphite. X-ray diffraction permits the determination of the metal silicides formed during the reaction. As Fig. 6 shows, there is a solid-solution "Fe–Si" for the iron catalysts, different from the Fe_3Si phase described by other authors [12, 19], whereas for cobalt and nickel the phases are Co_2Si and Ni_2Si, respectively. The amount of these phases is almost independent of the reaction temperature and residence time and is only a function of the metal loading. This seems to indicate that the phases are produced in the first stages of the formation of SiC. The unreacted silica is in the form of crystobalite, as in the uncatalysed reaction.

The presence of graphite as reaction product is not well defined, but very probably it may occur as a consequence of the precipitation of the carbon dissolved in iron as the sample is cooled down [20, 21]. If this is the case, because the SiC is already formed before cooling down, there will not then be any modification in the reaction rate.

3.3. Reaction mechanism

Several mechanisms have been proposed for the synthesis of SiC, but in all of them there is an initial stage with the formation of silicon monoxide

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \qquad (1)$$

There are some doubts with respect to the next stages because there are several possibilities

$$SiO(g) + 3CO(g) = SiC(s) + 2CO_2(g) \qquad (2)$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \qquad (3)$$

$$SiO(g) + C(s) = Si(s) + CO(g) \qquad (4)$$

$$Si(s) + C(s) = SiC(s) \qquad (5)$$

The more generally accepted mechanism is the reaction of silicon monoxide with carbon (Reaction 3) and then the point is to elucidate the way in which the

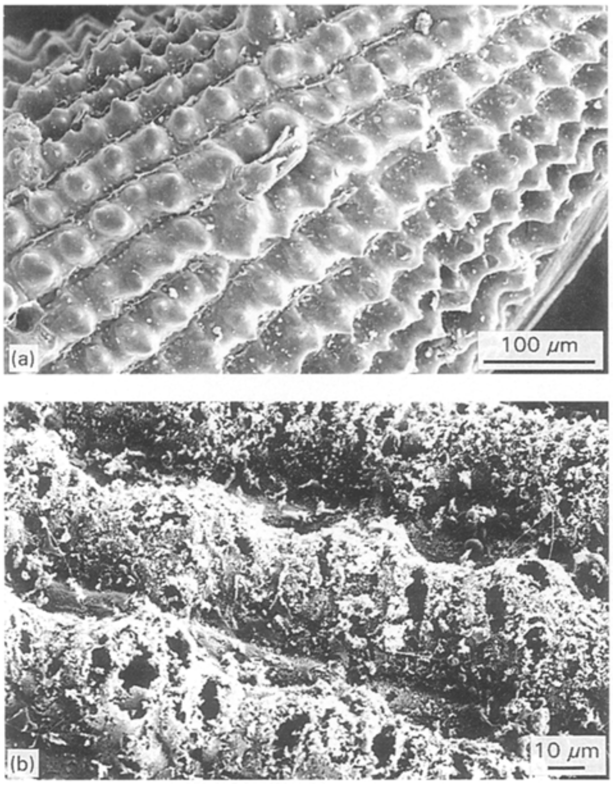

Figure 7 Scanning electron micrographs of rice husk surface reacted at 1400 °C for 10 h: (a) uncatalysed; (b) iron catalysed.

mechanism is affected by the catalyst. There are two possible solutions:

(i) the catalyst produces a localized decrease of the CO produced, because the metals favour the disproportionation of CO to give CO_2 and carbon [22]. The CO_2 could react again with carbon to produce CO, as shown by the increase in porosity observed for the catalysed reaction (Fig. 7). This solution would be in agreement with the experimental data of Bechtold and Cutler [23], which indicate that the activation energy does not change with the introduction of the catalyst. This would mean that there has been an increase in the number of active sites where the reaction may take place;

(ii) formation of an intermetallic phase M–Si which, at the reaction temperature, is in liquid state and where the carbon is dissolved to form a supersaturated solution from which the solid-phase SiC is removed [17, 18].

In order to elucidate the best alternative to explain the experimental results, one has to summarize the above results and some other additional experimental data, to complete the information needed:

(a) the SiC whiskers exhibit a morphology typical of VLS growth;

(b) the spherical end of the whiskers is composed of the catalyst and silicon (Fig. 8); no carbon can be detected with the type of dispersive X-ray analyser used;

(c) intermetallic phases (FeSi, Co_2Si and Ni_2Si) are detected by XRD;

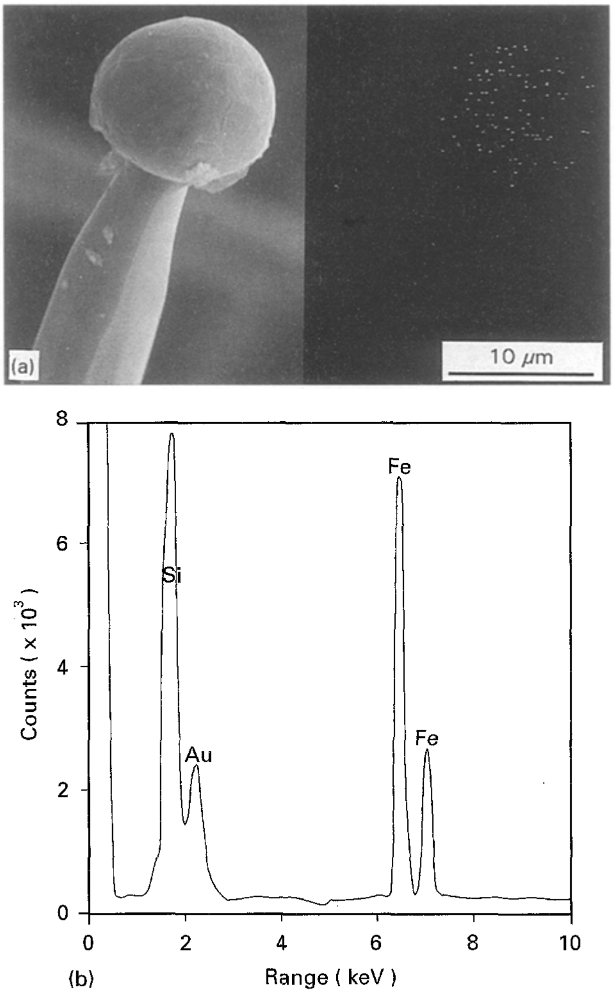

Figure 8 (a) Scanning electron micrographs of SiC whiskers prepared at 1400 °C, 5 h, 5% Fe. (b) X-ray dispersive analysis of spheres of (a).

(d) there is a larger porosity in the surface of the carbonized rice husks after a catalysed reaction;

(e) the temperature-programmed reaction (Fig. 9) shows the evolution of gases during reaction, with a low-temperature evolution of NO, CO and CO_2 due to the decomposition of the metal precursor and a partial reduction of the metal oxide formed. The evolution of CO at 900 °C is due to the reduction of the metal oxide and the evolution of CO and CO_2 at higher temperatures is produced by the formation of SiC.

With these results and taking into account other previously published [16, 17, 18, 24], the second alternative given above seems to be more complete although it cannot explain the loss of high-temperature CO_2 or the larger porosity of the sample in the catalysed reaction.

The consequence of the above results is a reaction mechanism based on the formation of SiC through the formation of metal silicides as an intermediate stage, and could be summarized in the following steps:

(i) decomposition of the metal precursor with the formation of the metal oxide and its reduction by carbon, including the possibility of the formation of

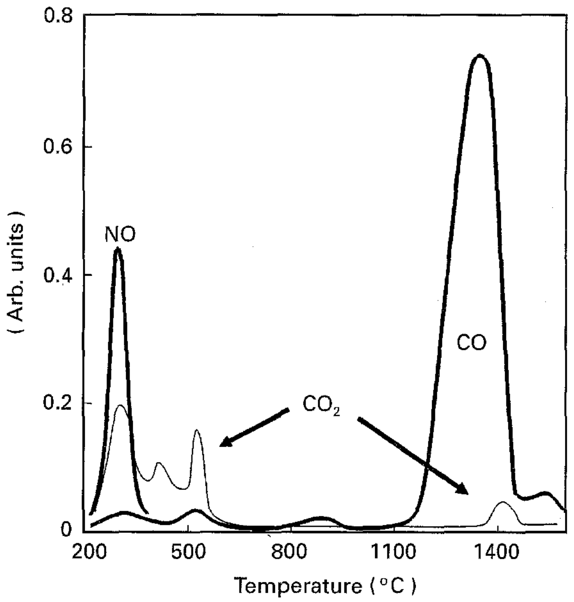

Figure 9 TPR profiles of 5% Ni carbonized rice husks.

the corresponding metal carbide (at $T < 1000\,^{\circ}\mathrm{C}$)

$$M(NO_3)_x = M_2O_x + xNO \tag{6}$$

(ii) formation of SiO by reduction of silica by carbon

$$SiO_2 + C = SiO + CO \tag{7}$$

(iii) silicon monoxide reacts with carbon to produce SiC as in the uncatalysed reaction, or it reacts with CO in the surface of the catalyst to yield CO_2, carbon and silicon, which are dissolved in the liquid metal

$$SiO + 2C = SiC + CO \tag{8}$$

$$SiO + 3CO + Fe(Si^s, C^s) = 2CO_2 + Fe(Si^{ss}, C^{ss}) \tag{9}$$

(iv) SiC is produced by segregation of silicon and carbon from the supersaturated solution of iron,

$$Fe(Si^{ss}, C^{ss}) = SiC + Fe(Si^s, C^s) \tag{10}$$

The CO_2 formed reacts with carbon to produce CO and consequently, the amount of CO_2 detected is very small.

This mechanism combines the two possible routes in the synthesis of SiC catalysed by metals: ease of disproportionation of CO and formation of SiC through an intermediate silicide. One cannot ignore the possibility of SiC also being formed by reaction of silica with the graphite produced, but the reaction rate observed is larger than that obtained for only graphite [25] and consequently this cannot be, by itself, the only responsible for the increase in reaction rate.

4. Conclusions

1. The synthesis of SiC from rice husks is confirmed to be feasible, with a yield of 84% after 5 h reaction at 1475 °C, 15%–20% of the products being whiskers.

2. Iron, cobalt and nickel are good catalysts for the synthesis of SiC, the yield for the same experimental conditions used in the uncatalysed reaction being 94% for 5% Ni and 90% for 5% Fe and Co. The effect of the catalyst is more noticeable for short reaction times, when the yield increases up to three-fold with respect to the uncatalysed reaction.

3. The increasing order of catalytic activity is Ni > Co > Fe > uncatalysed, whereas for SiC crystal size is Co > Fe > Ni > uncatalysed.

4. The reaction mechanism is based on the formation of an M–Si–C liquid phase which is needed for the nucleation and development of SiC whiskers.

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