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Production of alumina fibre through jute fibre substrate

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Alumina fibre has been produced using jute fibre as substrate material at temperatures lower than 1600° C in a reducing atmosphere. Processed jute fibre was chemically pretreated by saturation with $Al_2Cl_6 \cdot 12H_2O$, coked and then pyrolysed to obtain alumina fibre. Chemical pretreatment conditions have been determined by following weight loss measurements of the jute fibre at 0.1 to 0.6 N solutions of NaOH, KOH, NH_4OH, Na_2CO_3, K_2CO_3, HCl and acetic acid. The effect of heat treatment on the jute fibre and jute fibre + aluminium salt has been studied from 150 to 1600° C. Trace elements present (Fe_2O_3, SiO_2, K_2O, Na_2O, CaO, MgO, ZnO, MnO, V_2O_5, P_2O_5, CuO) on heat-treated products have been determined by atomic absorption spectrometry. Optical and scanning electron micrographs of representative samples showing growth mechanism are presented. The effect of copper, nickel and platinum catalysts and fluxing agents such as K_2O and Na_2O in fibre formation has also been examined. Particle size and surface area analyses of intermediate and final products have been carried out. Changes in 2θ values are plotted for various products from X-ray diffraction studies. It is conceived that the porous surface of cellulosic fibrils in the jute fibre adsorbs the $AlCl_3$ molecules which decompose to oxide and are gradually shaped to the fibrous form during the course of thermal treatment in a reducing atmosphere and due to the high surface area.

1. Introduction

Jute fibres, botanically known [1] as *Corchorus capsularis*, are elongate sclerenchyma cells, ranging in length from 20 to 550 mm. They are composed of cellulose, lignin, wax with trace amounts of inorganic oxides. Cellulose pertains to the class of carbohydrates [2] containing about 44% carbon, 6.2% H_2 and 49% O_2. The cell walls of the fibres consist of several layers of fibrillar structure. The very thin outer wall is composed of fibrillae arranged as a network. It encloses the secondary wall which again consists of a number of layers. Out of these, the outer ones consist of fibrillae wound in flat spirals around the fibre axis. Cellulose, H_2 gas and the fibrillae in jute fibre are taken into account in conceiving the fiberization mechanism here.

Potential applications of alumina fibre in aluminium alloy, ceramics and composite materials are well known [3–5]. For the formation of alumina fibre, a vapour-phase mechanism is generally considered to be valid. $AlCl_3$ was used [6] as the basic raw material in many of the previous processes [4] for production of alumina fibre but not using any natural fibre as here. Cellulose pretreated with $NaHCO_3$ and acids, can exchange Na^+ ions [7] which are then exchanged with Al^{3+}. It was shown previously [8] that reducing gases evolved from rice husk, control the fiberization mechanism at least in the initial period for SiC. The middle rib of the rice husk is shown to be structurally firm and to act as a substrate for the formation of SiC whiskers [9]. Catalysts from an external source [10] may not be indispensible for whisker formation, especially as many metallic elements are already present in the rice husk [11]. The present work further confirms these conceptions. The formation of alumina fibre using jute fibre substrate has been found here to be so simple that this process can open up a new dimension for preparing other fibres and from various other plant products.

2. Experimental procedure

Jute fibre obtained after bacterial decomposition and industrial processing was used for this work. The fibre was treated with laboratory grade chemicals: NaOH, KOH, NH_4OH, Na_2CO_3, K_2CO_3, HCl and acetic acid. $AlCl_3$ was prepared from aluminium metal and HCl for which the following chemical reaction can be written

$$2Al + 6HCl + 12H_2O = Al_2Cl_6 \cdot 12H_2O + 3H_2$$

Alkali pretreatments were done in Teflon beakers while acid reactions were conducted in Borosil glass beakers. Reflux reactions were undertaken in stainless steel balloon flasks at 110 ± 2° C.

Reactors for coking as well as pyrolysis were made out of high-alumina bricks. The heat treatment was carried out in muffle furnaces at 1600° C.

Processed jute fibre is first pretreated with chemicals (NaOH) under reflux and then soaked for half an hour in $Al_2Cl_6 \cdot 12H_2O$ solution so that the fibre is

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saturated with the salt solution. The dried aluminous fibre is then packed inside the reactor for heat treatment.

Weight loss experiments were conducted in air at 100 to 350° C for durations varying from 1 to 6 h.

For optical microscopy, a Leitz Metalloplan microscope was used and for SEM analysis, a Jeol JSM 35 CF SEM was employed.

A Philips microprocessor-based X-ray diffractometer (XRD) was used. Atomic absorption and visible spectrophotometers (Varian) were used in this work. Particle size analysis was carried out in a computerized and in-built microprocessor-based Elzone particle size analyser (Particle data Inc, USA), and a Micromeritics (USA) BET surface area analyser was used.

3. Results and discussion

The chemical analysis of the jute fibre used is given in Table I. Cellulose and lignin are the major constituents of the fibre, amounting to 84% and 13%, respectively. The cellulose contains α, β and γ cellulose; pentason, hexason and glucosides. Among the inorganic oxides, SiO_2 is 1.09% and Fe_2O_3 is 0.51%. Leaving aside P_2O_5 (0.16%), all other elements are present only in low amounts. MnO, CuO and V_2O_5 are present in extremely small amounts (1 to 2 p.p.m.). These three elements and Fe_2O_3 are known to be catalysts and may participate in the fiberization mechanism. The fluxing agents, Na_2O, K_2O, CaO, MgO and P_2O_5, are also likely to take part in the reaction mechanism. The role of Fe_2O_3 as a catalyst has already been reported in the formation of SiC whiskers [9].

3.1. Chemical pretreatment

Pretreatment of the jute fibre is required mainly to remove the black particles of bark which remain adhered to the surface. Treatment with alkali has the beneficial effects of increasing the porosity and the creation of active sites for easy access of the aluminium salt. Oxycellulose, alkali cellulose or sometimes alcoholates may be the products after treatment of the cellulose with alkali [2]

$$C_6H_7O_2(OH)_3 + NaOH \rightleftarrows C_6H_7O_2(OH)_2ONa + H_2O \qquad (1)$$

$$2C_6H_7O_2(OH)_3 + 6Na \rightarrow 2C_6H_7O_2(ONa)_3 + 3H_2 \qquad (2)$$

$$C_6H_7O_2(OH)_3 + NaOH \rightarrow C_6H_7O_2(OH)_3NaOH \qquad (3)$$

TABLE I Chemical analysis of jute fibre

Constituent	Content (wt %)
Cellulose	84.29
Lignin	13.17
Wax	0.431
SiO_2	1.09
Fe_2O_3	0.51
Na_2O	0.075
K_2O	0.063
CaO	0.088
MgO	0.047
ZnO	0.058
Al_2O_3	0.013
P_2O_5	0.156
MnO	0.001
CuO	0.002
V_2O_5	0.001

TABLE II Trace elements (wt %) in coked fibre (200 to 500° C)

Constituent	200° C	300° C	400° C	500° C
SiO_2	0.232	0.266	0.371	0.510
Fe_2O_3	0.156	0.196	0.214	0.306
Na_2O	0.075	0.074	0.072	0.071
K_2O	0.063	0.062	0.062	0.060
MgO	0.047	0.047	0.0469	0.0468
ZnO	0.056	0.056	0.057	0.056
MnO	0.001	0.001	0.001	0.001
CuO	0.002	0.002	0.002	0.002

Acids cause the disintegration of macromolecules resulting in a complex mixture of the products of incomplete decomposition of cellulose D-glucose

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad (4)$$

NaOH and KOH will partially eliminate SiO_2 according to the following reaction

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O \qquad (5)$$

SiO_2 present in the initial jute fibre (1.09%) can be partially solubilized by the above reaction. In Tables II to IV, it can be seen that an amount of SiO_2 remains unreacted. Previously, it was observed in the case of rice husk [8] that part of the SiO_2 behaves differently because of the difference in the nature of bonding. SiO_2 bonded to the carbohydrate molecules in rice husk behaves differently from the free SiO_2 present. It appears, therefore, that here also SiO_2 is present in the free form as well as bonded to the –C–H groups.

The weight loss observed after different chemical treatments under reflux for 1 h at concentrations of 0.1 to 0.6 N is summarized in Figs 1 and 2. The percentage of weight loss varies from one reagent to the other. At 0.2 N, NaOH brings about a loss of about 13%, followed by 10% with Na_2CO_3, and nearly 8% with K_2CO_3 and KOH. NH_4OH is a very weak alkali and the loss occurring on treatment with it is just 2.3%. With HCl and acetic acid, the weight loss values found are 5.1 and 4.1%, respectively, at 0.2 N concentration (Fig. 2). As the surface of the jute fibre needs to be conditioned for efficient adsorption of alumina, 0.2 N NaOH was selected for all chemical pretreatments in

TABLE III Trace elements (wt %) in intermediate products (600 to 1000° C)

Constituent	600° C	800° C	1000° C
SiO_2	0.96	1.40	1.44
Fe_2O_3	0.416	0.600	0.658
Na_2O	0.063	0.0571	0.0493
K_2O	0.0593	0.0551	0.046
CaO	0.0825	0.088	0.0825
MgO	0.0447	0.0446	0.0446
ZnO	0.054	0.0419	0.035
MnO	0.001	0.001	–
CuO	0.001	0.001	–

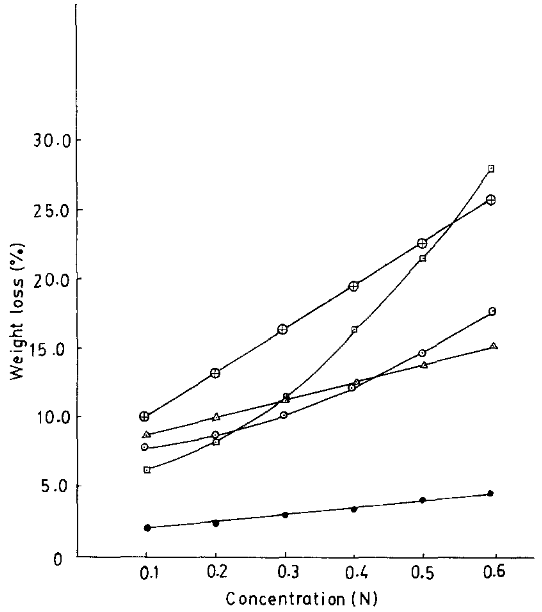

Figure 1 Weight loss on alkali treatment. (△) Na_2CO_3, (⊕) NaOH, (○) K_2CO_3, (□) KOH, (●) NH_4OH.

the formation of alumina fibre. Weight loss measurements made at higher concentrations and for longer durations are not presented here, as these may not be relevant for production of alumina fibre. Acids cannot be used as they have a tendency to char the organic part and thus disintegrate the jute fibre.

3.2. Trace elements

Metals have been reported to act as catalysts [9] in the formation of SiC whiskers and therefore analysis of the metallic elements present at every stage of heat treatment in producing alumina fibre needs to be thoroughly evaluated. The results for trace elements in coked fibre (200 to 500° C), intermediate products (600 to 1000° C) and in alumina fibre (1200 to 1600° C) are tabulated in Tables II, III and IV, respectively. In all 11 elements were detected: silicon, iron, sodium, potassium, calcium, magnesium, zinc, phosphorus, manganese, copper and vanadium. The elements are expressed as oxides. Each oxide varies with increasing temperature. Both SiO_2 and Fe_2O_3 increase on raising the temperature from 200 to 1200° C as the carbonaceous part of the jute fibre slowly escapes on heat treatment. Above 1400° C, there is a decrease in the concentrations of these two oxides. Na_2O and K_2O show the reverse trend in concentration, which decreases with increasing temperature because of their lower melting points than SiO_2 and Fe_2O_3. However, even at 1600° C (Table IV), 6 to 8 p.p.m. oxides are present. CaO has been analysed in products obtained above 600° C. It is found to remain almost unchanged on heating because of its high melting point. The case with MgO is similar. ZnO remains more or less the same up to 600° C, but it decreases above this temperature. The amounts of MnO and CuO, though very small, have catalytic effects similar to Fe_2O_3.

TABLE IV Trace elements (wt %) in alumina fibre

Constituent	1200° C	1400° C	1600° C
SiO_2	1.60	1.32	1.02
Fe_2O_3	0.715	0.458	0.236
Na_2O	0.0217	0.0113	0.006
K_2O	0.0441	0.0147	0.008
CaO	0.088	0.0825	0.082
MgO	0.0443	0.0432	0.0431
ZnO	0.033	0.0293	0.016
MnO	Traces	Traces	–

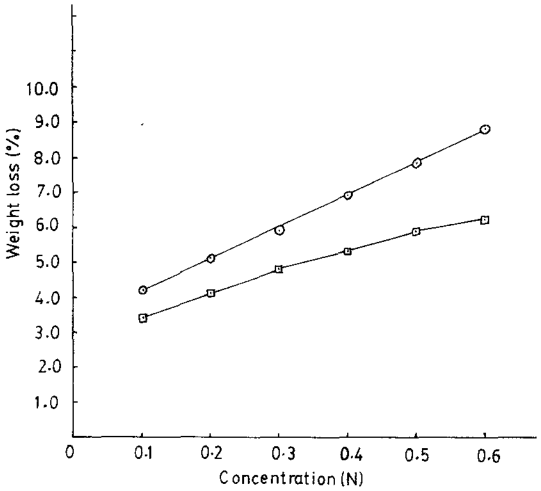

Figure 2 Weight loss on acid treatment. (○) HCl, (□) CH_3COOH.

Because it was possible to obtain alumina fibre without the addition of any metal catalysts from an external source, it is certain that the metals present initially serve this purpose if they participate at all in fibre formation. Oxides such as Na_2O, K_2O, CaO, MgO, P_2O_5 can, on the other hand, impart fluxing effects which are also present above 1400° C. It is therefore established that the ceramic fibre can be formed without metals from external source [10] which was previously considered indispensible [9].

3.3. Yield of products

Jute fibre is fairly thermally resistant and Table V shows that even at 300° C in air for 6 h, the weight loss is not total (83%). Weight loss values of jute fibre in closed containers are tabulated in Table VI. The weight loss at 300° C after 6 h is 75%.

The yields of coking [8], intermediate and final fibre are shown in Tables VII, VIII and IX, respectively. The values are expressed with respect to the composite mixture of jute fibre and aluminium salt and with respect to $Al_2Cl_6 \cdot 12H_2O$ separately. The latter values can be very important and indicate the fibre obtained after each heat treatment. The decomposition takes place as follows

$$Al_2Cl_6 \cdot 12H_2O = Al_2O_3 + 6HCl + 9H_2O \quad (6)$$

TABLE V Weight loss (wt %) on heat treatment of jute fibre in air

Time (h)	150° C	200° C	250° C	300° C
1	5.92	6.30	46.15	65.81
2	6.16	6.93	51.76	69.37
3	6.79	8.40	56.56	72.64
4	7.91	11.62	63.04	76.12
5	10.01	19.11	70.15	79.61
6	14.35	47.74	78.16	83.08

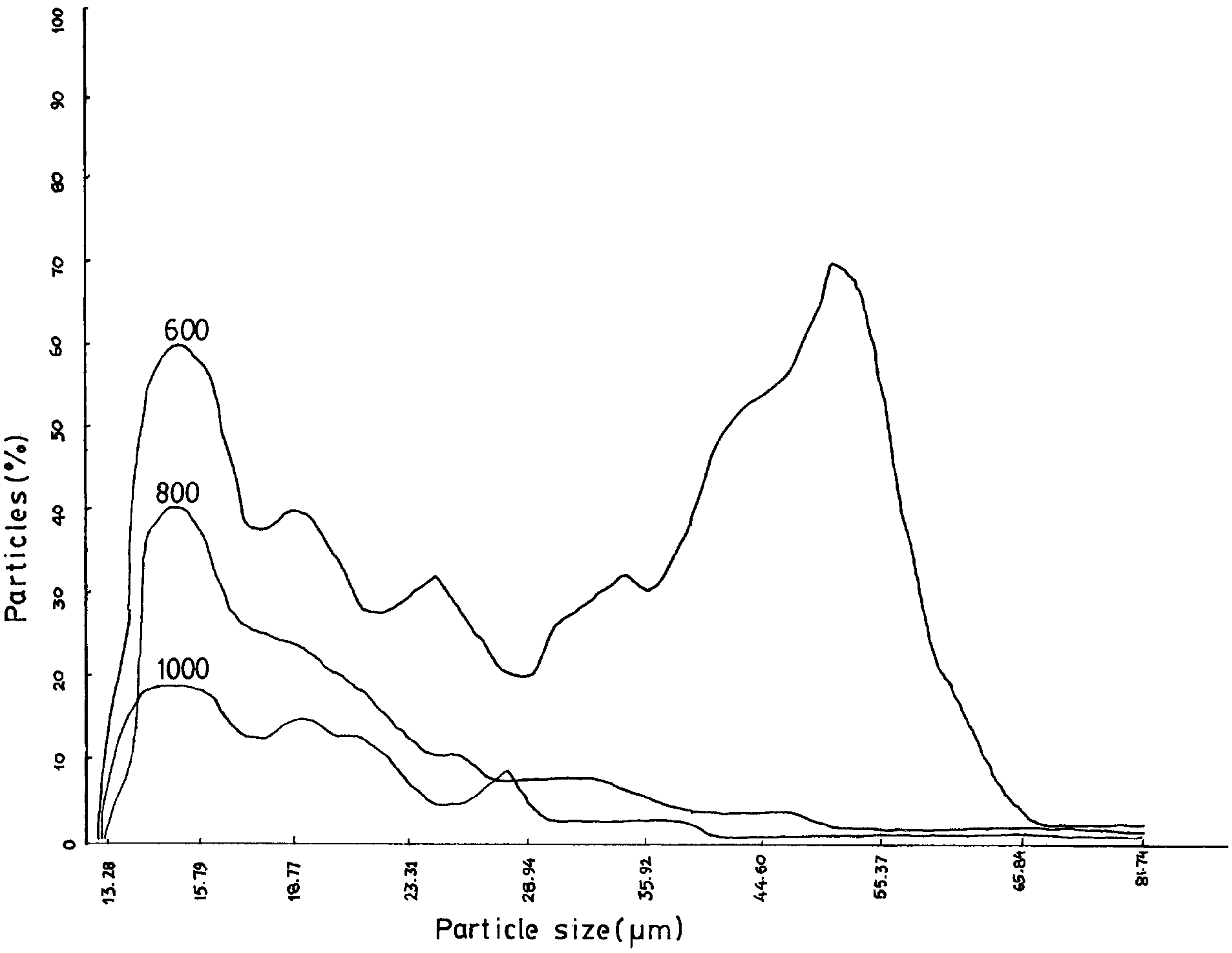

Figure 3 Particle size analysis of alumina fibre (600 to 1000° C).

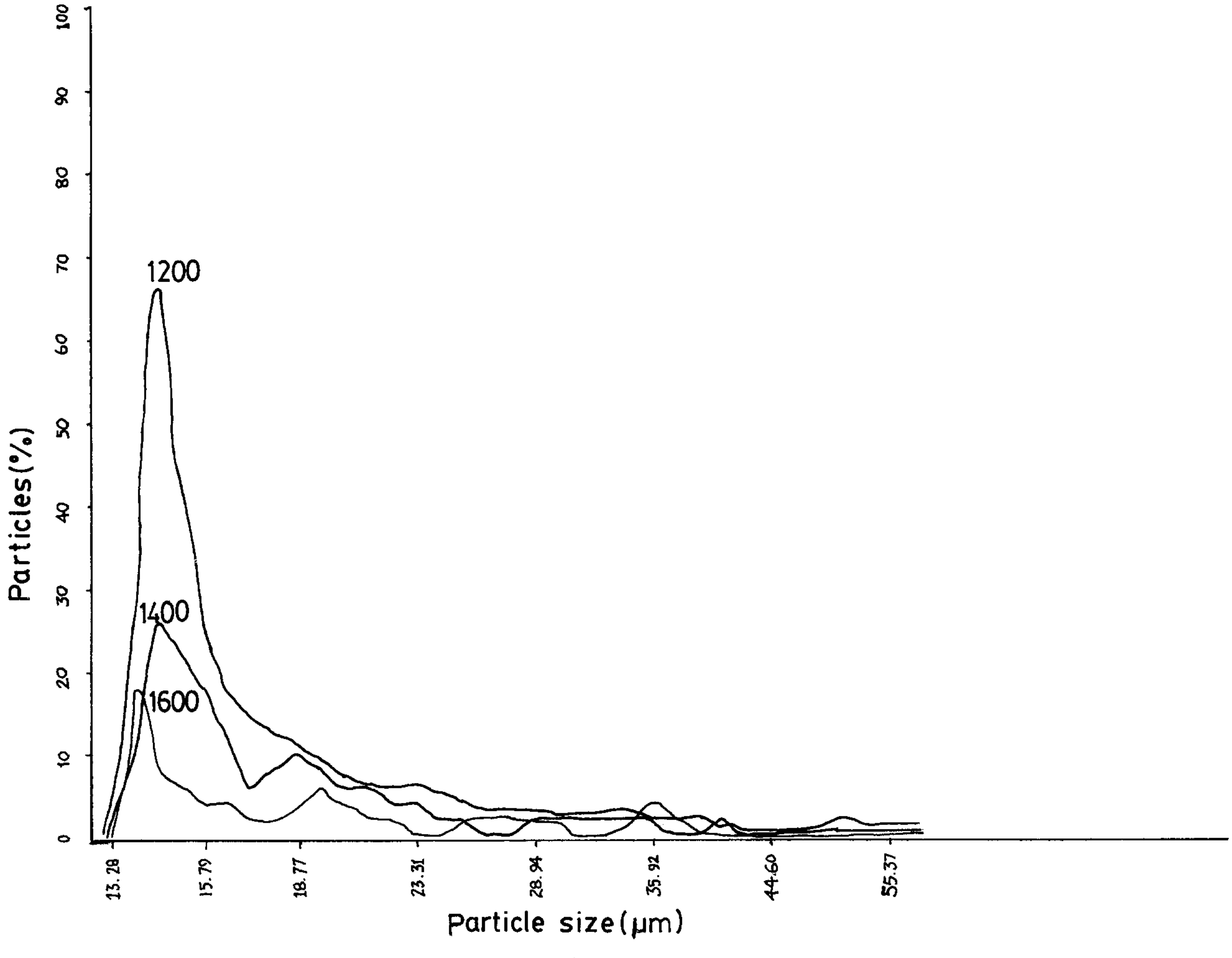

Figure 4 Particle size analysis of alumina fibre (1200 to 1600° C).

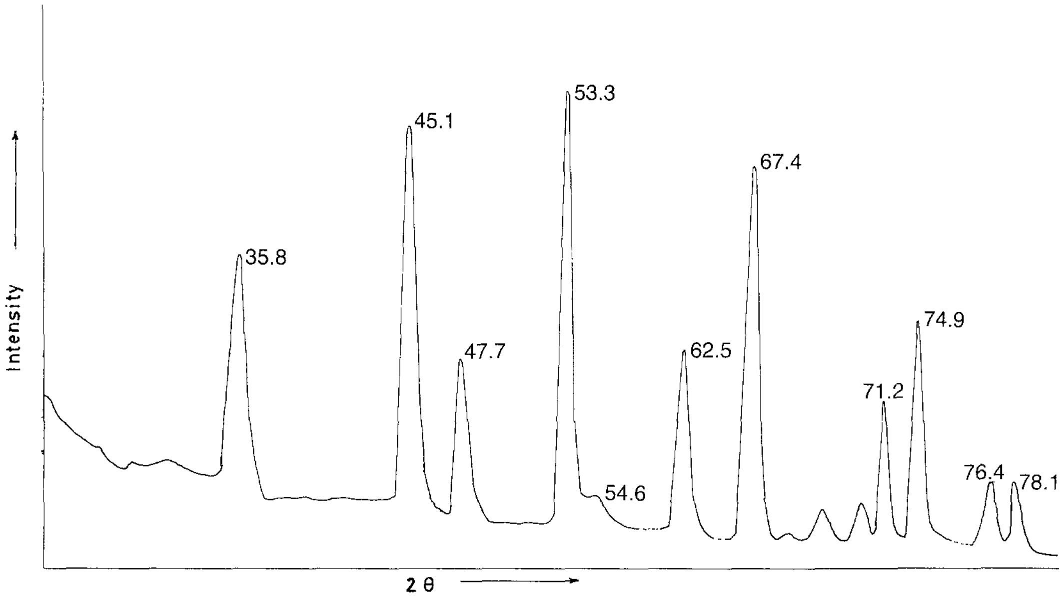

Figure 5 XRD analysis of alumina from $AlCl_3$.

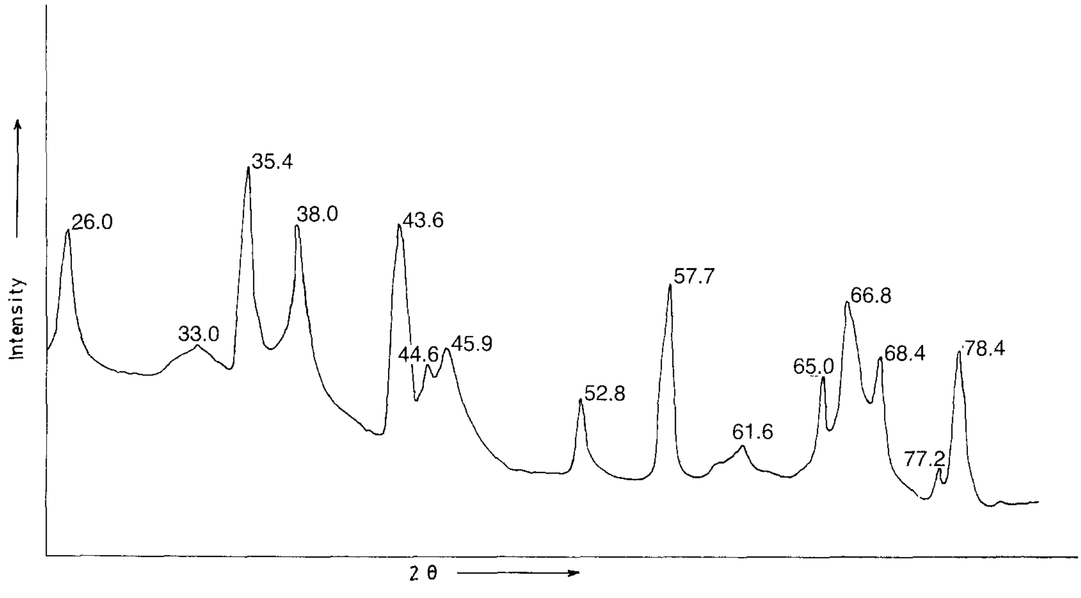

Figure 6 XRD analysis of alumina fibre (1200° C).

It can be seen from the tables that between 300 and 500° C, the yield decreases from 26.5% to 15.8%, while it remains constant around 14.9% in Table VIII and 14.75% in Table IX. After elimination of carbonaceous matter and moisture, there is practically no further loss and therefore the yield remains constant. The presence of nickel, copper, sodium or potassium does not improve the yield.

TABLE VI Weight loss (wt %) of jute fibre on heat treatment in a reducing atmosphere

Time (h)	150° C	200° C	250° C	300° C
1	4.38	5.81	17.37	23.79
2	4.51	6.13	37.23	45.83
3	4.59	6.80	42.37	51.66
4	5.12	7.92	46.76	58.36
5	5.71	10.10	53.16	68.81
6	6.89	14.42	61.83	75.36

3.4. Granulometry analysis

As the alumina particles form fibres they cannot be passed through screens of finer mesh size. Therefore, simple dry sieve analysis (ROTAP) could also be useful in characterizing the fibres. The products obtained at 600, 1000 and 1400° C in the range 25 to 180 μm are given in Table X. In the range 25 and 45 μm, the percentage retained at 600° C is, therefore, higher than that at 1000 and 1400° C. On the other hand, at 150 and 180 μm, the amounts retained in products at 1000 and 1400° C are higher than the product at 600° C.

TABLE VII Yield (wt %) of coked product (300 to 500° C)

Temperature (° C)	Yield with respect to jute and Al salt	Yield with respect to Al salt
300	13.28	26.56
400	9.48	18.96
500	7.90	15.80

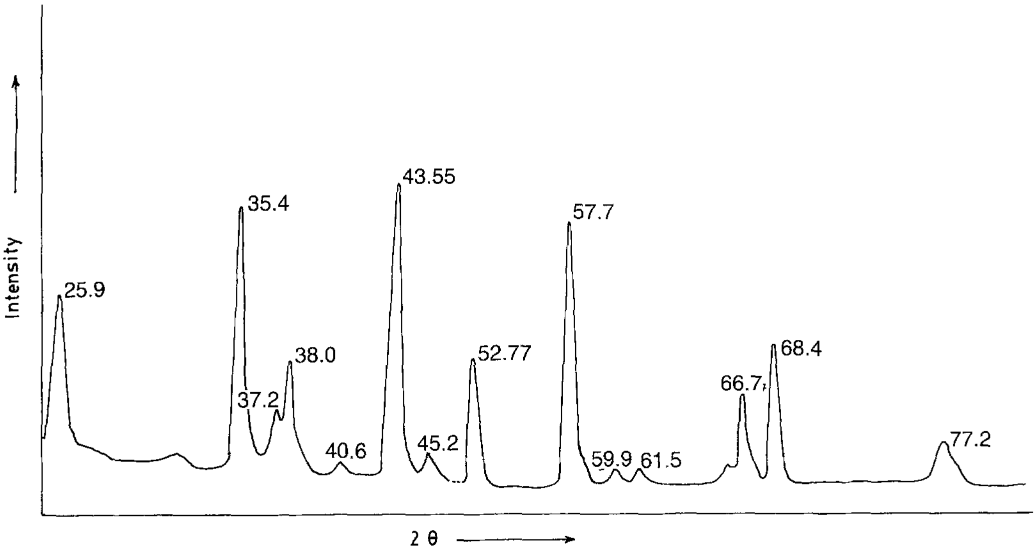

Figure 7 XRD analysis of alumina fibre (1400° C).

Granulometry analysis conducted in an Elzone particle size analyser is plotted in Figs 3 and 4. In Fig. 3, at 600° C, it can be seen that both in the lower and higher ranges, a higher percentage is obtained compared to products at 800 and 1000° C. At 600° C, the texture of the jute fibre seems to be retained, while conversion of aluminium salt to Al_2O_3 proceeds. These two types of behaviour are reflected in the coarser and finer particles, respectively, in Fig. 3. At 800° C, only alumina powder exists and therefore the second peak is not observed. The case at 1000° C is the same, where conversion of powder to fibre is accentuated and the particles become coarser. The peaks of finer fractions sharpen at higher temperatures, and the percentages decrease with increasing temperature.

3.5. Surface area analysis

BET surface area analysis of the heat-treated products are given in Table XI. At 300° C, the surface area is as much as 576 $m^2\,g^{-1}$, and is 374 and 224 $m^2\,g^{-1}$ at 400 and 600° C, respectively. Such high surface areas are quite favourable for fiberization, as the particles will remain adsorbed on the surface of the jute fibre, especially at 300° C and become shaped according to the form of the jute fibre. Such high surface areas could be due to activated carbon and also to the alumina gel. Above 1000° C, the surface areas decrease significantly and come down to less than 1 $m^2\,g^{-1}$ at 1400 and 1600° C. Alpha-alumina is formed at these high temperatures as will be evident from the XRD analysis. One may presume that the reducing atmosphere inside the reactors is highly conducive to increasing the surface area and consequently the fiberization mechanism.

TABLE VIII Yield (wt %) of intermediate product (600 to 1000° C)

Temperature (° C)	With respect to jute fibre and Al salt	With respect to Al salt
600	7.46	14.92
800	7.44	14.88
1000	7.43	14.86

TABLE IX Yield (wt %) of alumina fibre (1200 to 1600° C)

Temperature (° C)	With respect to jute fibre and Al salt	With respect to Al salt
1200	7.41	14.82
1400	7.38	14.76
1600	7.35	14.70

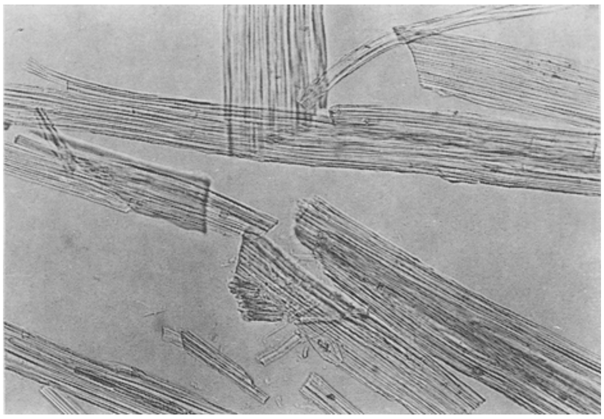

Figure 8 Optical micrograph of fibre formed at 600° C (× 128).

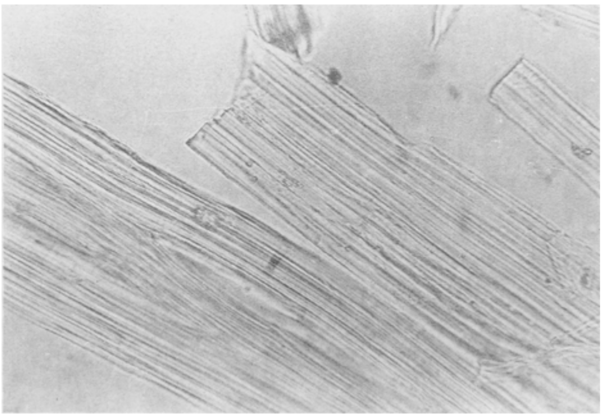

Figure 9 Optical micrograph of fibre formed at 800° C (× 320).

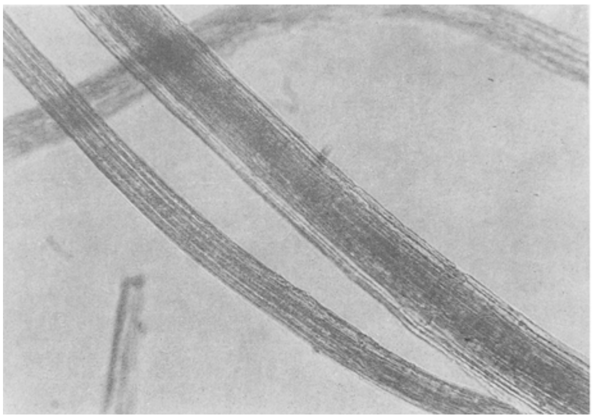

Figure 10 Optical micrograph of fibre formed at 1000° C (× 128).

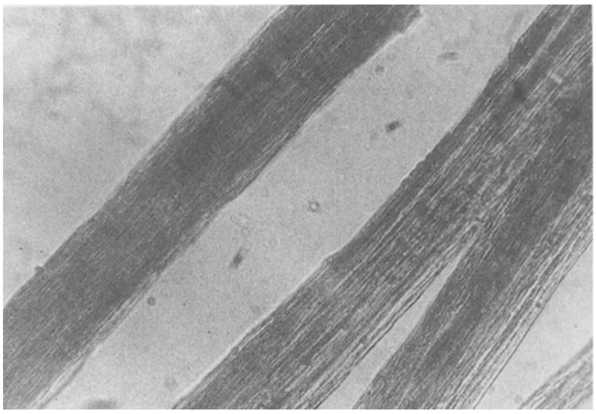

Figure 11 Optical micrograph of fibre formed at 1200° C (× 300).

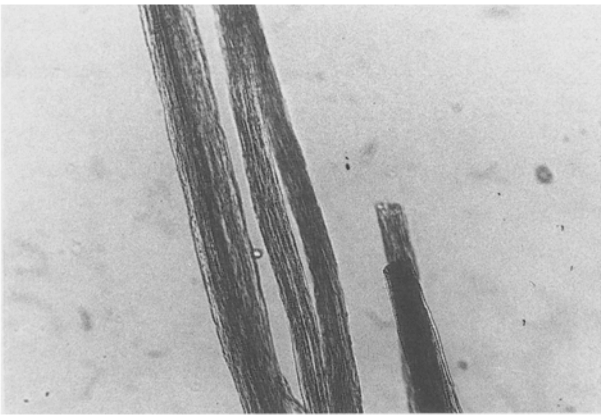

Figure 12 Optical micrograph of fibre formed at 1400° C (× 120).

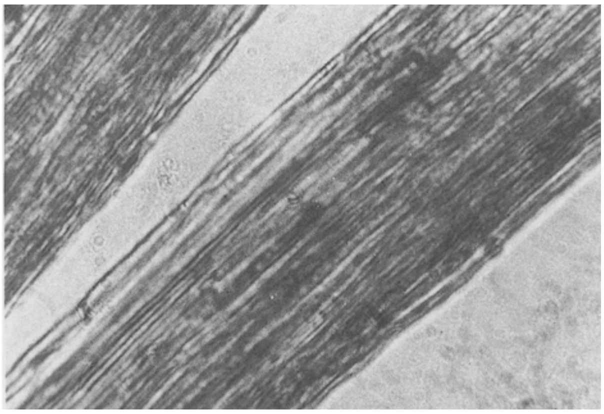

Figure 13 Optical micrograph of fibre formed at 1400° C (× 300).

3.6. XRD analysis

XRD analysis of only three products will be discussed here. Fig. 5 represents XRD analysis of $AlCl_3$ alone, heated to 1400° C and without passing through the jute fibre. The 2θ values indicate that the product is α-alumina. Comparing the 2θ values in Figs 6 and 7, it can be found that there is some variation. Fig. 6 represents alumina fibre at 1200° C and Fig. 7 at 1400° C but using jute fibre substrate. A distinct peak appears at about 26° which is not observed in pure α-alumina (Fig. 5). The 2θ values are also different and at 1200° C, the diffractogram above 2θ values of 60°, some additional peaks appear. It was very difficult to interpret these data as the literature on XRD of fibre products is scant. However, it is evident that the major phase in the present product is α-alumina.

3.7. Microscopic study

The optical micrographs indicate that at no stage is the fibre structure obscure. The transformation of jute fibre structure to the alumina fibre structure seems to occur systematically. Fig. 8 indicates fibre is formed even at 600° C. At 800 (Fig. 9) and 1000° C (Fig. 10) fibrous alumina structure is obvious. The micrograph at 1000° C, however, shows that the fibre is curved and lacks strength. As the temperature is increased to 1200° C, the fibre appears to be stronger (Fig. 11). Fig. 12 shows the fibre obtained at 1400° C. At higher magnification (× 300), the surface seems to be defect-free and the fibres are arranged in bundles, similar to the initial jute fibre (Fig. 13). All these samples are obtained without catalyst. Figs 14 and 15 represent fibre obtained using copper catalyst (× 120 and × 300, respectively), while Figs 16 and 17 show fibres obtained using a nickel catalyst. From the dark colour, it seems that the fibre is dyed and the strength has increased.

Scanning electron micrographs of the products are shown in Figs 18 to 22. The jute fibres are arranged in bundles (Fig. 18). As the fibres had been cut to size, the lengths of the fibres (~ 10 mm) appear to be fairly uniform. On NaOH treatment, the surface is cleaned and at the same time, becomes activated (Fig. 19) which is favourable for the exchange of Al^{3+} ions and then fiberization. Here also, the arrangement of fibres in groups of bundles is obvious. The number of fibres in each bundle is variable: from one to even 10. The cross-sectional views indicate that the tips are attacked more than the surfaces and are not smooth.

TABLE X Granulometry analysis (wt %) of alumina fibre

Temperature (° C)	25 μm	45 μm	53 μm	75 μm	106 μm	150 μm	180 μm
600	12.63	10.76	13.26	11.71	20.32	21.61	8.96
1000	0.95	4.53	15.51	6.16	10.32	16.44	46.09
1400	0.40	2.12	10.16	7.19	14.65	6.44	59.04

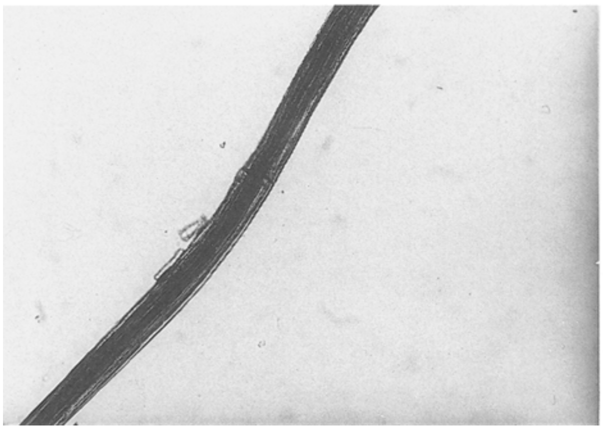

Figure 14 Optical micrograph of fibre formed at 1400° C using a copper catalyst (× 120).

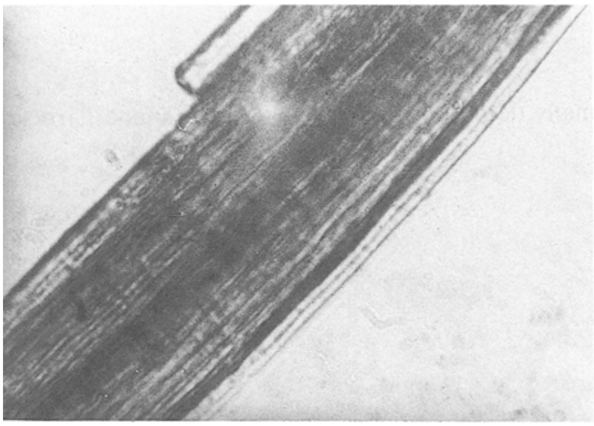

Figure 15 Optical micrograph of fibre formed at 1400° C using a copper catalyst (× 300).

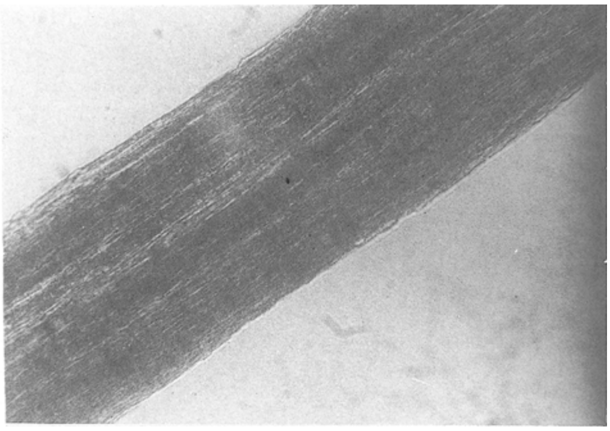

Figure 17 Optical micrograph of fibre formed at 1400° C using a nickel catalyst (× 300).

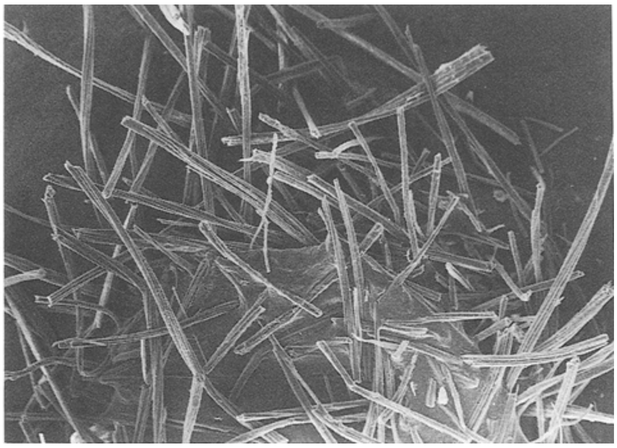

Figure 18 Scanning electron micrograph of processed jute fibre (× 30).

The aluminium chloride solution is presumed to have entered into the fibres through these tips. In fact, Fig. 20 indicates that only a few alumina particles are adhered to the outer surface of the fibre. This micrograph corresponds to the product after $AlCl_3$ treatment followed by heating at 300° C in a reducing atmosphere. The excess alumina particles are observed on the outer surface. As the temperature is 300° C, the major part of the aluminium chloride is decomposed to Al_2O_3. These particles cannot, therefore, be other than alumina. The diameter of each fibre at this stage is 10 to 15 μm.

The surface morphology of the final alumina fibre obtained at 1400° C is presented in Fig. 21. It is interesting to observe that the alumina fibre produced at such a high temperature retains the morphology of the initial jute fibre. These are also arranged in bundles. Fig. 22 shows a higher magnification of the same product which very much corresponds to the form of jute fibre. Therefore, the substrate properties

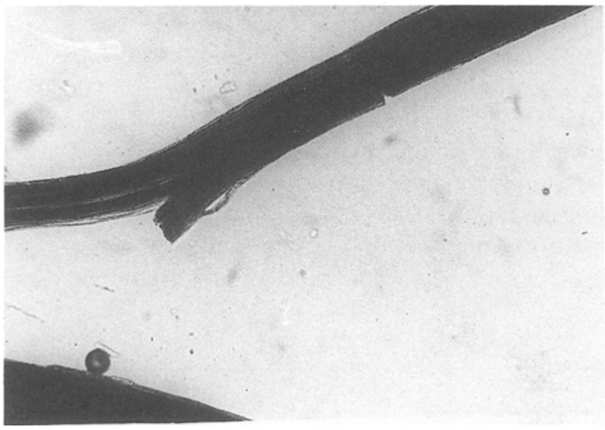

Figure 16 Optical micrograph of fibre formed at 1400° C using a nickel catalyst (× 120).

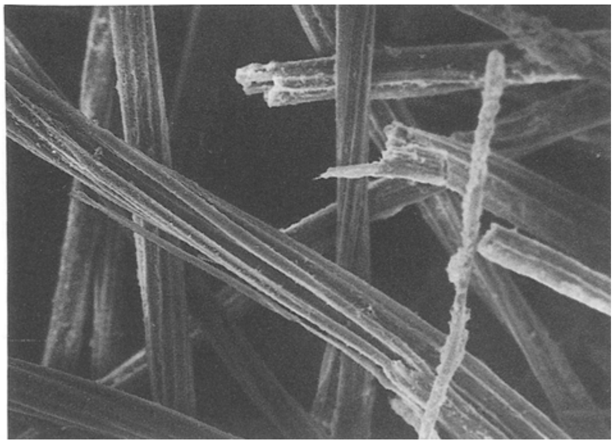

Figure 19 Scanning electron micrograph of NaOH-treated jute fibre (× 135).

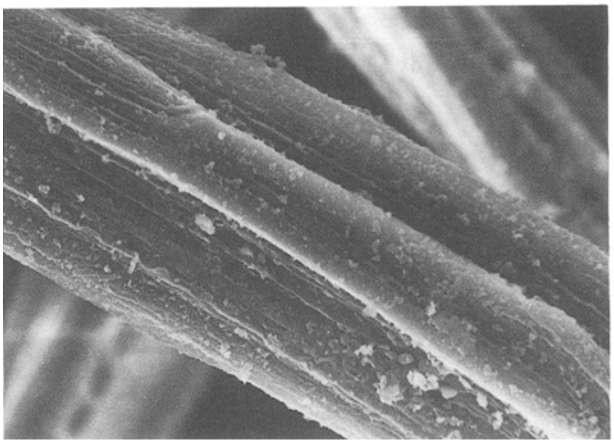

Figure 20 Scanning electron micrograph of alumina containing jute fibre at 300° C (× 705).

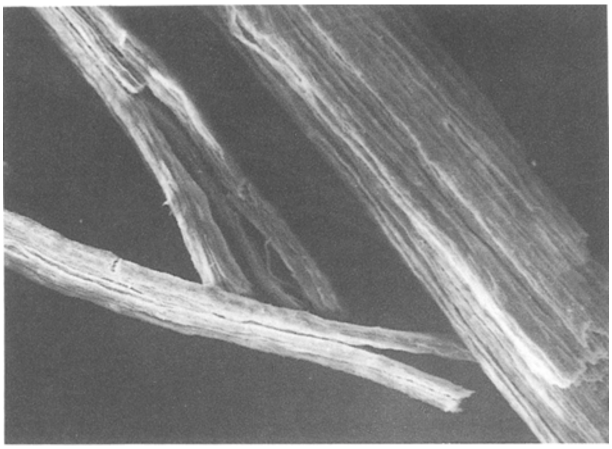

Figure 21 Scanning electron micrograph of alumina fibre formed at 1400° C (× 150).

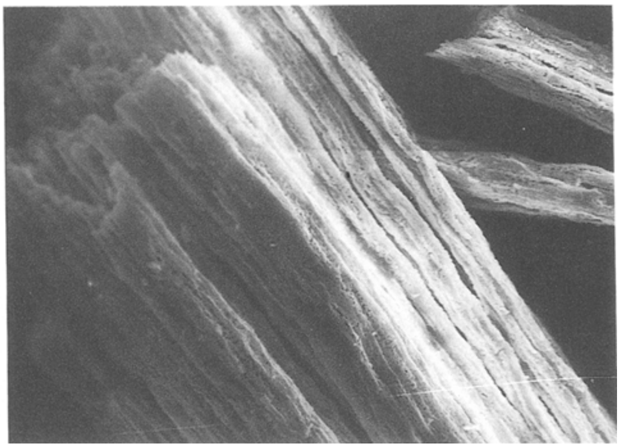

Figure 22 Scanning electron micrograph of alumina fibre formed at 1400° C (× 405).

of the jute fibre [9] for the formation of alumina fibre at all temperatures is obvious. Added nickel and copper fibres have also been examined by scanning electron microscopy. The micrographs are similar to the fibres obtained without any catalyst, the fibre being darker only in the latter cases.

4. Conclusions

Alumina fibre can be produced using jute fibre substrate at temperatures of 1400 to 1600° C. Metal catalysts from external sources are not required for fibre formation. The metals present in the initial fibre continue to remain even at 1600° C and might participate in fiberization. During chemical pretreatment, Na^+-celulose is formed which is exchanged with Al^{3+} ions, finally decomposing to Al_2O_3. The alumina particles are firmly adsorbed on to the surface of the jute fibre because of the high surface area and are finally shaped according to the morphology of jute fibre. The gases evolved from the jute fibre are also helpful in fibre formation.

TABLE XI BET surface area analysis ($m^2 g^{-1}$)

Temperature (° C)	300	400	600	800	1000	1200	1400	1600
Surface area	576	374	224	102	56.0	3.0	1	1

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