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Corrosion of SiC fibres with HNO_3

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The corrosion of SiC fibres with HNO_3 has been studied. Characterization has been carried out by means of infrared spectroscopy, scanning electron microscopy and adsorption of nitrogen and benzene. Corrosion attack changes the specific surface area of the fibres and increases the surface roughness along the fibres. The microstructure of the fibres is not modified by the attack. The surface heterogeneity of the original fibres shows a different feature when the fibres have been corroded; the distribution of active sites on the surface of the fibres is changed by acid attack.

1. Introduction

For many years researchers have sought to develop tough ceramics whose performance characteristics retain the best properties of their parent ceramics and have the additional quality of not being susceptible to fracture during impact or under stress in the presence of a notch. The addition of fibres to ceramics has been known for many years to be one approach for achieving this goal. The development of fibre-reinforced cements is undoubtedly the best-known example of this technology. Extension of this concept into higher-performance ceramic matrices has not been nearly as successful.

Whereas the state of the art in ceramic-fibre-reinforced ceramic composites has advanced dramatically in the last decade, the overwhelming majority of the experimental work has utilized silicon carbide fibres or whiskers as the reinforcement. Next to graphite, SiC shows the most attractive physical properties from the reinforcement standpoint, namely high strength and high elastic modulus. Although strong, tough composites have been fabricated using SiC reinforcement in oxide matrices such as glasses [1] glass–ceramics [2], and ceramics [3], this success is attributable to the presence of a carbon-rich layer that forms on the surface of the fibre during high-temperature densification of the matrix, providing a chemical barrier to inhibit reaction between the fibre and the matrix. An excellent review on this subject is given by Prewo *et al.* [4].

SiC fibres are extensively used in ceramic-matrix composites where a hard environment is present, such as high temperatures or corrosion, and a high resistance to wear is required. These composites have found application in heat engines, as cutting tool tips and in the aerospace industry. The particular advantages of SiC fibres over classical fibres (glass fibres, etc.) have been demonstrated in many industrial applications [5].

As a general rule, the mechanical properties and the corrosion resistance of ceramic- and metal-matrix composite materials are closely related to the chemical reactions that occur at the fibre–matrix interface during their elaboration and use [6]. A thorough understanding of interface chemistry is thus important in the development of these materials.

The strength of high-modulus ceramic fibres is governed by flaws on the surface and within the bulk of the filament. The more severe a flaw, the lower the strength of that section of material. If these flaws are assumed to be distributed randomly along the fibre, then a long length is more likely to contain a serious defect than a short length. A long fibre will thus appear statistically weaker than a short one [7].

The present paper reports the results of an experimental investigation focused on the primary corrosion that occurs between silicon carbide fibres and HNO_3 at boiling point for 2 h.

2. Materials and characterization

The SiC fibres used in this work were the well-known Nicalon type (Nippon Carbon Co.); the detailed fabrication process has been described in the literature [8]. Corrosion attack on the SiC fibres was carried out with HNO_3 of purity grade.

Characterization of original and corroded SiC fibres was carried out by means of scanning electron microscopy, infrared spectroscopy, and adsorption of nitrogen or benzene. The scanning electron microscope used in this work was the Siemens Autoscan. The infrared spectra were measured using a Perkin-Elmer spectrometer model 580 B by the KBr pellet method. Spectra were recorded and stored in a data station. Two home-made apparatuses based on the chromatography methods of Nelsen and Eggertsen [9] and Conder and Purnell [10] were used to measure the adsorption of nitrogen and benzene, respectively. Specific surface areas were obtained from the adsorption of nitrogen. Surface energy distribution functions were obtained using the equation proposed by Rudzinski *et al.* [11] for the adsorption isotherms of benzene at 30 °C.

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3. The corrosion process

The corrosion of the Nicalon fibres was carried out in a vessel (Pyrex glass) provided with a reflux refrigerant. 2 g of fibres were introduced into the vessel and then immersed in 0.5 l of conc. HNO_3, closing the vessel with refrigerant.

A magnetic stirrer was used for stirring the acid–fibre system. This system was heated up to the boiling temperature of the acid and held at this temperature for 2 h. The specimens were then washed several times with distilled water and dried in a vacuum oven at 120 °C for 17 h. After that, they were stored in a vacuum desiccator until measurements were done.

4. Experimental results and discussion

4.1. Scanning electron microscopy

The features of the original and corroded Nicalon fibres as determined by electron microscopy are shown in Figs 1 and 2. The surface of the original fibre is smooth and relatively free of surface roughness (Fig. 1); one could expect a low surface area. All fibres were of similar diameter.

On the other hand the corroded Nicalon fibres (Fig. 2) show a significant surface roughness caused by the corrosion by HNO_3 acid. That roughness is not the same in all fibres, showing that there exist fibres with a poor resistance to the acid. In the corroded fibres it can be seen that the corrosion process has taken place along the fibres but not in particular zones; this result confirms that the resistance of all the fibres is not the same. This behaviour may originate in the production process of the fibres and/or in their composition; both factors play a critical role in the process of corrosion of Nicalon fibres in acidic media. With the relative surface roughness of the corroded fibres an increase in the specific surface would be expected.

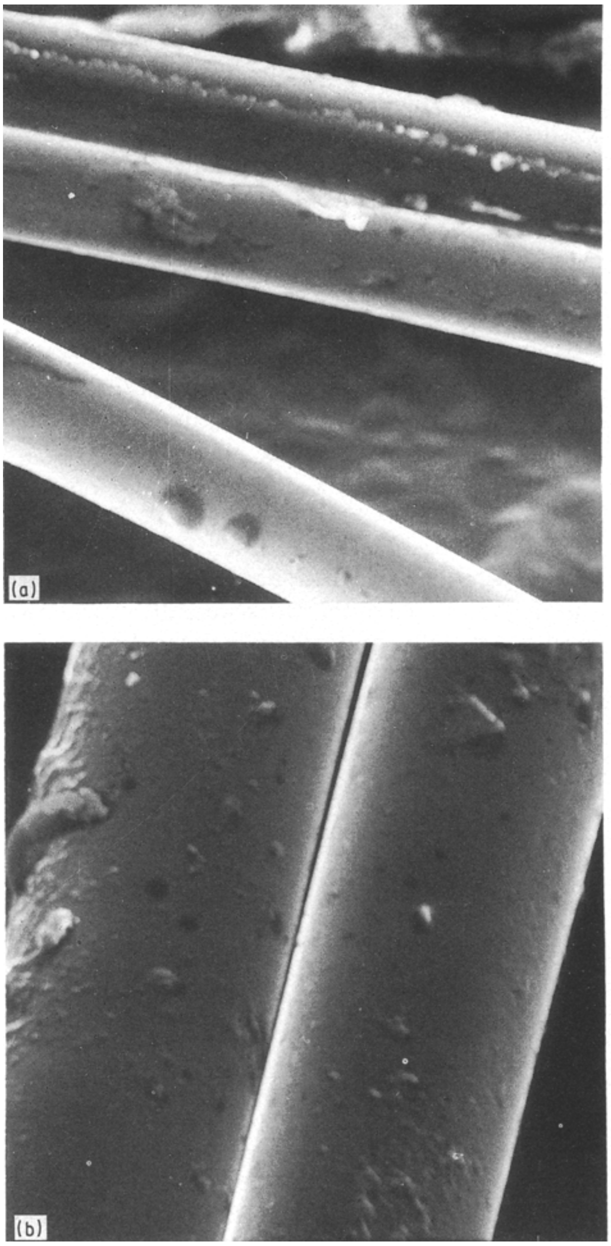

Figure 1 SEM of original SiC fibres: (a) × 1500, (b) × 3250.

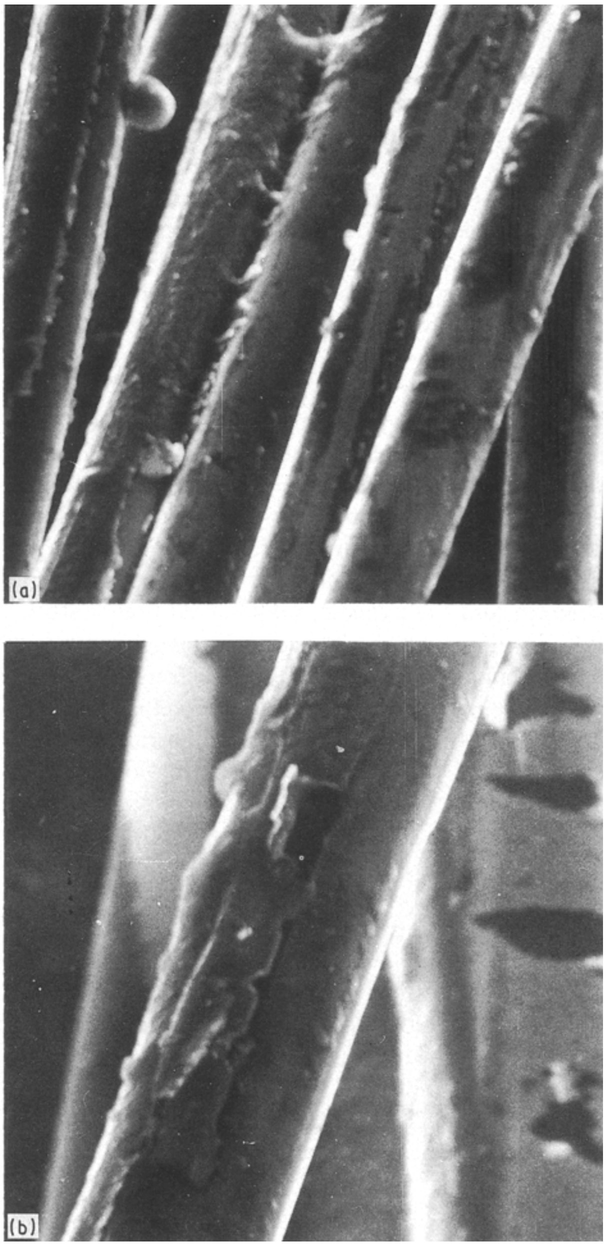

Figure 2 SEM of corroded SiC fibres: (a) × 1250, (b) × 3050.

4.2. Specific surface area

The surface areas determined by low-temperature adsorption of nitrogen are 0.137 and 0.229 $m^2 g^{-1}$ for the original and corroded Nicalon fibres, respectively. The area of a nitrogen molecule was taken as 0.162 nm^2. The quantities were obtained with 9 and 7 independent runs, respectively.

The surface areas are consistent with what was expected from observation of the electron micrographs of the fibre surface. The original fibres with a low specific area showed very little surface roughness. In contrast, the specific surface area of the corroded fibres is much greater, which is consistent with the surface roughness revealed by electron micrographs. The increase in the specific surface area of the corroded fibres is about 67% of the original value.

4.3. Infrared spectroscopy

Fig. 3 shows the IR spectra of SiC fibres, both original and corroded. The spectra for both fibres consist of broad overlapping bands which we have deconvoluted into several bands by curve fitting. In Fig. 3 the solid lines show the measured spectra, and dotted lines represent the bands and the deconvoluted spectra. In both cases (original and corroded fibres) we assume Gaussian bands and a constant background. No sharp lines have been observed in the spectra. Eight bands have been found between 1300 and 400 cm^{-1}. Some bands are clearly seen in the spectra, while others have been introduced with the aid of the second derivative of the spectra. A good curve fit is obtained for the deconvoluted spectra as shown in Fig. 3. Both spectra are very similar to those reported by Hasegawa *et al.* [12] for the conversion of polycarbosilane into the inorganic state. Obviously no bands of hydrocarbons appeared.

Table I gives the positions and integrated intensities of the different IR bands (1300 to 400 cm^{-1}) which appeared in the spectra of original and corroded SiC fibres. Both original and corroded Nicalon fibres show adsorption bands at 1182, 983, 893, 809, 593, 540 and 463 cm^{-1}. The characteristic silica peaks detected and resolved by the instrument are at about 1182, 1089, 983, 809, 540 and 463 cm^{-1}. There are two peaks not due to Si–O, situated at 893 and 596 cm^{-1}. The 890 and 690 cm^{-1} region corresponds to the stretching vibrations of Si–C [13], so the 893 cm^{-1} adsorption band may be due to the Si–C vibration. The 809 cm^{-1} band may correspond to crystalline or amorphous silica [14]. The 983 and 540 cm^{-1} bands correspond to Si–O stretching in SiOH groups of silica gels or amorphous silica, in agreement with Raman studies [15]. The 1182 and 1089 cm^{-1} bands correspond to the stretching of Si–O in Si–O–Si or Si–O–C.

TABLE 1 Integrated intensities for SiC fibres

Band position (cm^{-1})	Integrated intensity	
	Original	Corroded
1182	0.088	0.124
1089	0.293	0.422
983	0.038	0.051
893	0.176	0.209
809	0.172	0.201
596	0.043	0.052
540	0.032	0.034
463	0.111	0.131

After corrosion the IR bands do not change in position nor integrated intensity as compared with the original fibres. Therefore the microstructure and the different phases, such as microcrystalline SiC, carbon microcrystals and silicon oxide, crystalline or amorphous [15], do not change with the corrosion process.

4.4. Benzene adsorption

Adsorption isotherms of benzene (Merck, spectroscopy grade) on original and corroded SiC fibres were determined at 30 °C by the method of frontal analysis by characteristic points [9], using a commercial chromatograph previously modified for this application [16]. Samples were degassed at 170 °C for 17 h in a dry helium flow. The acquisition and analysis of the data supplied by the flame ionization detector of the chromatograph was carried out by a computer system which enables the analysis of 300 points of each

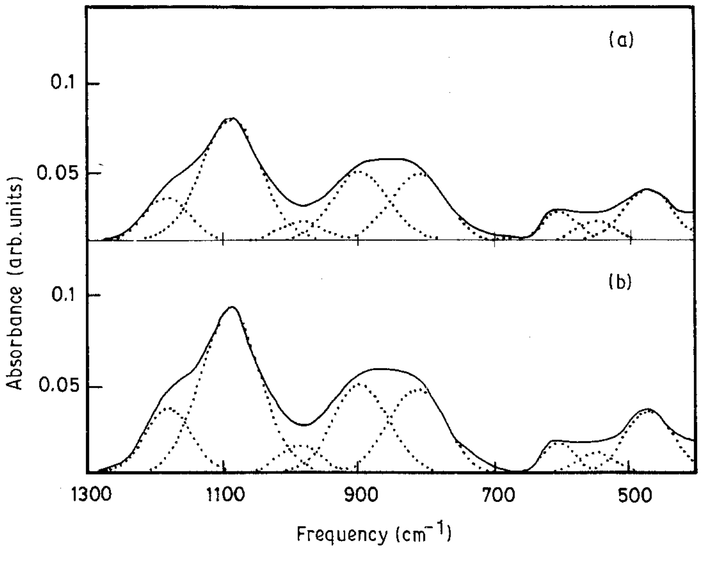

Figure 3 Curve fit to the IR spectra of (a) original and (b) corroded SiC fibres.

isotherm. This high quantity of experimental points makes it possible to determine the smaller changes which may occur in the adsorption of benzene on the fibres in a very small interval of pressure of the adsorbate.

Fig. 4 shows the adsorption isotherms of benzene on original and corroded SiC fibres. The isotherms are approximately of Type II in Brunauer's classification [17]. The isotherms in the sub-monolayer region display curvature over the entire coverage range which is concave to the pressure axis; this is typical for a heterogeneous surface. The adsorption of benzene on the original fibres, 3.66×10^{-3} mol m^{-2} (0.457 mol g^{-1}) is greater than in the corroded ones, 1.04×10^{-3} mol m^{-2} (0.230 mol g^{-1}). This fact implies a decrease in the sorption properties on the surface of the corroded fibres caused by the HNO_3 attack. This change in the sorption properties of SiC surface is related to the sorption sites (active sites) that exist on that surface. Therefore a knowledge of the energy distribution function of both surfaces gives us important information about the heterogeneous nature of the fibre surface.

The chemical composition and structural features of fibre surfaces determine the magnitude of the surface free energy. This latter property governs the fibre wettability and chemical reactivity, which are relevant to surface treatments, formation of chemical bonds between fibre and matrix materials, and vulnerability to reaction with the environment (O_2, H_2O, etc.). The possibility of formation of strong bonds in composite materials is related to the active sites on the fibre surface. The distribution of active sites may be determined by means of the energy distribution functions.

Determinations of surface energy distribution functions were carried out from chromatographic data obtained from the adsorption isotherms in accordance with the method developed by Rudzinski *et al.* [17], based on the method of Hobson [18, 19]. This method is known as the "asymptotically corrected approximation" [20] in which the true local isotherm is replaced by a combination of a Henry's law isotherm and a "step approximation" one.

Fig. 5a and b show the energy distribution functions for the adsorption of benzene on original and corroded SiC fibres, respectively. Both distributions correspond to a clearly heterogeneous surface, and various peaks associated with active sites can be distinguished.

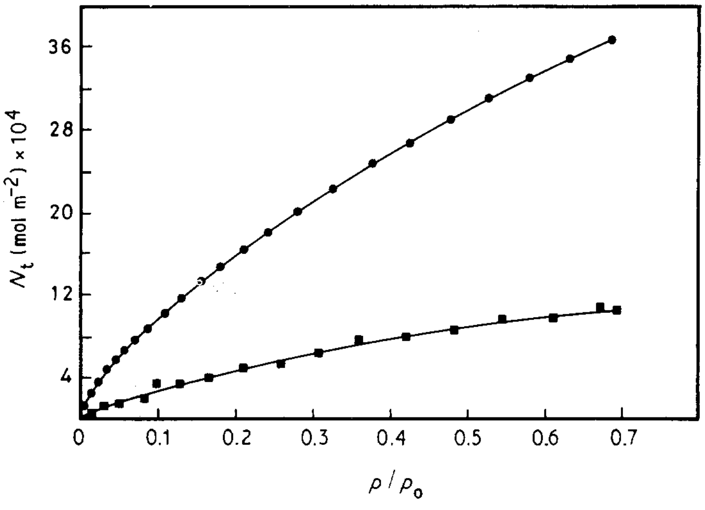

Figure 4 Adsorption isotherms of benzene on (●) original and (■) corroded SiC fibres.

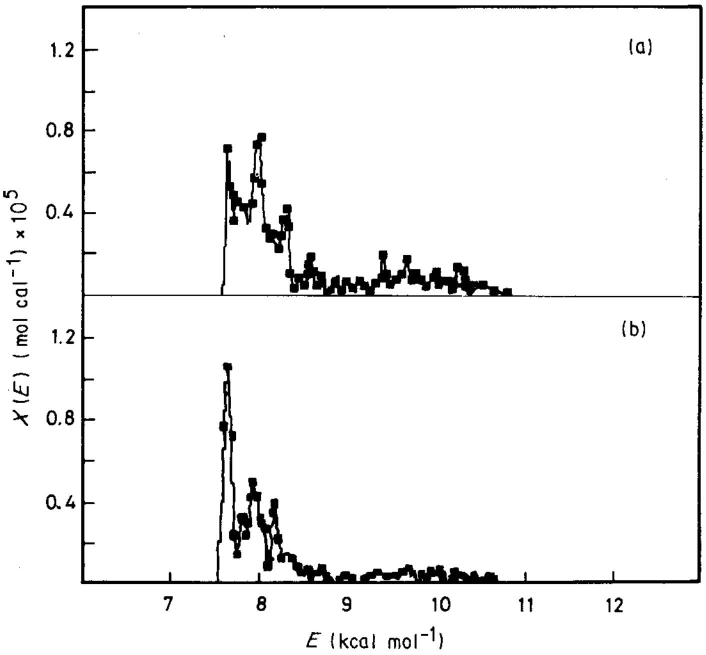

Figure 5 Surface energy distribution functions for the adsorption of benzene on (a) original and (b) corroded SiC fibres 1 cal = 4.19 J.

The interpretation of the different peaks is rather difficult and would require quantum-mechanical calculations in order to know the interaction energy of benzene with the different groups (active sites) existing on the surface of the SiC fibres, and would also necessitate the use of modern techniques such as X-ray photoelectron spectroscopy and Auger electron spectroscopy for studying the physicochemical nature of the fibre surface. We shall only give a qualitative interpretation of both energy distribution functions.

Both surface energy distributions have a lot of peaks which we assume to be associated with active sites on the surface of the SiC fibres. In both distributions the Savitzky–Golay method of smoothing experimental data has been applied [21]. The energy distribution function of the original fibres has in the low-energy region, 7.5 to 8.5 $\mathrm{kcal\,mol^{-1}}$ (31 to 36 $\mathrm{kJ\,mol^{-1}}$), the same peaks as that of the corroded fibres. In the medium and high energy regions, 8.5 to 11 $\mathrm{kcal\,mol^{-1}}$ (36 to 46 $\mathrm{kJ\,mol^{-1}}$), the distribution for the original fibres has more peaks than that of the corroded ones. Therefore we can suppose that corrosion attack has reduced the number of adsorption sites of the SiC fibres. This is in agreement with the above-mentioned adsorption isotherms.

Peaks in the surface energy distribution of the original fibres have higher frequencies of occurrence than those of the corroded fibres, except for the peak appearing in the lower region of adsorptive energy (at 7.8 $\mathrm{kcal\,mol^{-1}}$) (33 $\mathrm{kJ\,mol^{-1}}$). This indicates that the original SiC fibres have more adsorption sites and more sites of a given energy than the corroded fibres. Therefore we suppose that the possibility of formation of chemical bonds between SiC fibres and matrix materials is higher for the original fibres.

It is clear how the adsorption of organic vapours gives an important description of the energy surface heterogeneity of solid surfaces. This surface energy is of great importance in order to determine the surface reactivity, which must be known in order to determine which are optimum material combinations and which modifications can be made to develop strong bonds in composite materials.

5. Conclusions

SiC fibres (Nicalon type) are very resistant to the corrosion attack of HNO_3. The surface roughness of the fibres increases after the attack, and in the same way the specific surface area is increased.

The corrosion attack does not change to a great degree the microstructure of the fibres; the principal constituents such as amorphous or microcrystalline SiC, carbon microcrystals and silicon oxide, remain constant in the fibre.

The surface heterogeneity of the fibres changes with corrosion attack. The corroded SiC fibres have fewer adsorption sites than the original ones. The frequency of the active sites of the original fibres is greater than for the corroded ones. Therefore the decrease in adsorption sites in the corroded fibres decreases the number of chemical bonds between the SiC fibres and any matrix material.

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