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A Strong Carbon-Coated Silica Fibre

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Freshly drawn silica fibre was coated with carbon by passing the still-hot filament through a chamber containing heated acetylene. As the coating thickness was increased, by increasing the temperature of the fibre or acetylene, the tensile strength of the fibre first increased and then decreased. This decrease in strength was concluded to be caused by reaction between the coating and the silica fibre. Optimum conditions were found which gave fibres with a mean strength of 500 000 lb/in.^{2} (1 lb/in.^{2} = 7 × 10^{-2} kg/ cm^2).

1. Introduction

Silica has been known for many years as a material which may show a very high strength. Although early reports [1] of strengths in excess of 3 × 10^6 lb/in.^{2} have not been substantiated, subsequent observations by Proctor [2, 3] and by Morley *et al* [4] have confirmed that strengths of 5 × 10^5 to 10 × 10^5 lb/in.^{2} are obtainable in a variety of glasses, even in large pieces, provided that sufficient care is taken in the preparation of the surface. This high nascent strength may, however, be easily lost as a consequence of mechanical damage or attack by various chemical agents, including water [5, 6].

Various methods have been used to apply protective coatings to the surface of the fibre, and have met with variable success.

This paper describes some observations on a method for making a carbon-coated silica fibre. The method, described elsewhere [7], has several notable advantages. It is quick and simple in execution, and requires the minimum of equipment for successful operation. It is a continuous, rather than batch, process, and does not involve long furnace treatments such as are needed for whiskers or fibres produced by pyrolytic means.

Previous workers had reported only relatively small gains in strength using this coating method, but it was felt that, in view of the advantages of the method, it merited further investigation.

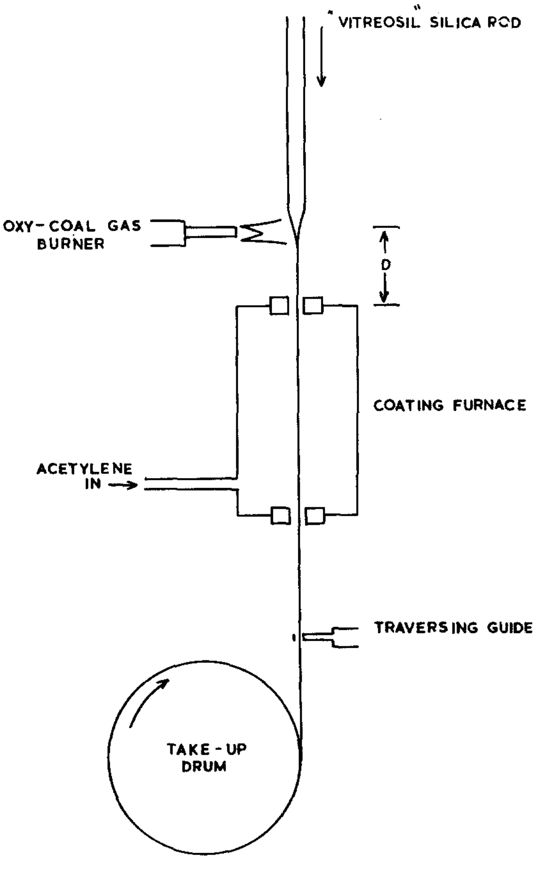

Figure 1 Schematic elevation of the silica-fibre coating apparatus.

2. Apparatus

The apparatus is sketched in fig. 1. The silica fibre was drawn from a 3 mm rod of "Vitreosil", pure, fused silica. This rod was lowered at a rate of 2.3 mm/min into an oxy-coal gas flame. A fibre was drawn out from the softened rod at a rate of 1.5 to 2.5 m/sec. A rate of 2 m/sec gave a fibre of 41 μm diameter.

The conditions for successful drawing were not critical: with a drawing rate of 2 m/sec, it proved possible to draw a uniform fibre with the temperature of the drawing zone between 1440 and 1740° C (these being the approximate temperatures at which the glass became so viscous that the drawing tension caused it to snap, or at which the filament was liable to be completely melted). Generally, drawing was carried out at 1600 to 1650° C. The drawn fibre was passed through a guide-fork covered in "Teflon" and then wound onto a 12 cm diameter, polished drum. The guide was 80 cm below the drawing zone, and, by comparison with results obtained by Arridge and Prior on the cooling of drawn silica fibres [8], the drawn filament had probably cooled to below 200° C by that time.

The protective carbon coating was applied to the fibre immediately after drawing, by passing it through a heated chamber containing acetylene. The hot fibre cracked the acetylene, which deposited a thin, continuous film of carbon on the surface of the fibre.

The chamber, 19 cm long and 1.5 cm wide, was constricted at each end to minimise loss of acetylene, but at no point did the silica filament make physical contact with the furnace, it being considered of paramount importance to avoid mechanical abrasion of the uncoated fibre. The acetylene was led into this furnace at the bottom, and the whole assembly was heated electrically.

Electron microscope studies of the carbon film showed it to be continuous and of thicknesses up to 2000 Å. Diffraction images showed diffuse rings corresponding to a microcrystalline graphite structure, but individual crystallites could not be resolved.

The carbon coating produced by this process is electrically conducting, which enables the fibre to be used directly in the manufacture of composites by electroplating [9]. The fibre may also, by virtue of its electrical conductivity, cheapness, and ease of manufacture, form a satisfactory substrate for the production of fibres by pyrolytic deposition of other materials (e.g. boron, silicon carbide) onto the silica fibre.

3. Testing of the Drawn Fibre

The tensile strength of the fibres was measured in the "Instron" testing machine at a strain rate of 0.05 cm/min. Various methods of gripping were tried – the most successful was to glue individual fibres across a piece of cardboard cut so as to leave a 5 cm wide hole in the centre. When the glue had dried, the cardboard was cut away leaving the fibre attached at each end to a small rectangle of card. Better results were obtained with a cellulose glue than with epoxy resins, because the former proved to be more flexible: a fibre which had been accidentally misaligned in the testing machine would deform the glue and bend in a smooth curve, whereas a fibre embedded in the rigid epoxy compound tended to break at the point where it entered the gripping medium.

At no time during the preparation or testing of these fibres were they handled. The only mechanical damage to which they were subjected occurred as the fibre was passed over the guide, or was being wound onto the take-up drum, both of which were provided with smooth, soft surfaces ("Teflon" and colloidal graphite respectively).

The diameter of each fibre was measured after the test, by means of a microscope with measuring ocular. In no case was it possible to observe the fracture surface, as the fibres tend to disintegrate at the moment of breaking leaving only a millimetre or so of fibre end projecting out of the glue.

Approximately eighty tests were made on each run of fibre, specimens of which were cut at intervals of about 2 m.

4. Results

The first series of experiments was conducted to investigate the dependence of fibre strength upon the coating temperature.

A control experiment with no acetylene in the coating furnace was followed by coating runs at 20, 200, 400, 600, and 800° C, respectively. Histograms were plotted to show the distribution of fibre strength, and means and coefficients of variation were calculated by computer. The distance between the centre of the drawing zone and the top of the coating furnace was 1.5 cm for all these experiments.

Representative histograms are shown in figs. 2, 3, and 4, and show the strength distributions for the uncoated fibre, and for coating temperatures of 20 and 800° C.

The "uncoated" series shows, as might be expected, many results in the range 100 000 to

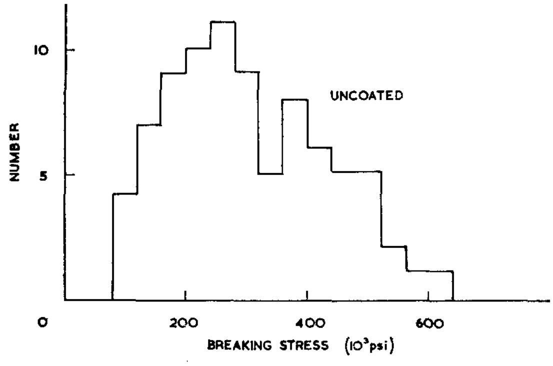

Figure 2 Histogram of fibre strengths – uncoated fibre. (In the figures, psi is used for lb/in.^{2} – 1 lb/in.$^2 = 7 \times 10^{-2}$ kg/cm^2.)

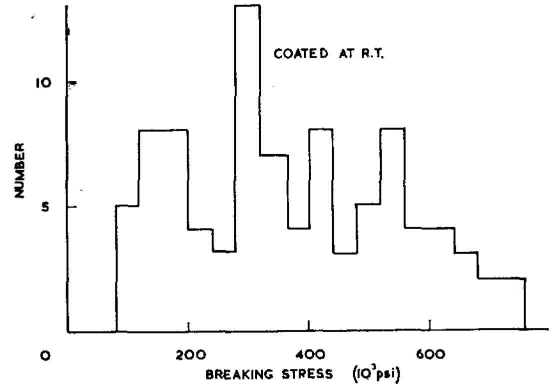

Figure 3 Histogram of fibre strengths – coating furnace at 20° C.

300000 lb/in.^{2} (1 lb/in.$^2 = 7 \times 10^{-2}$ kg/cm^2). This is thought to correspond to the mechanical damage caused during manufacture. It is not very severe, as shown by the mean strength of 300000 lb/in.^{2}, and the presence of several results greater than 500000 lb/in.^{2}; neither of these features is found in commercial filament.

The fibre coated at room temperature is significantly different from the uncoated material. Although there is still a large number of mechanically damaged fibres, there exist many very strong fibres, up to nearly 800000 lb/in.^{2}, and it was under these conditions that the strongest individual fibres were found in any experiment.

As the coating temperature was increased from 200° C up to 800° C, the protection of the carbon coating became increasingly effective. However, not only were the mechanically damaged fibres eliminated, but so were the very high-strength ones.

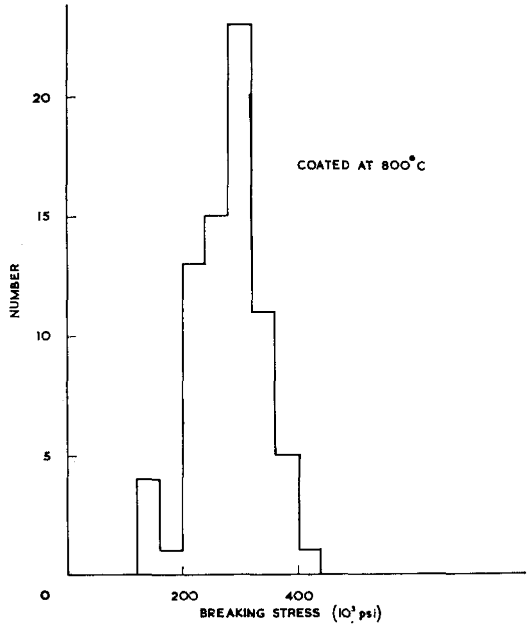

Figure 4 Histogram of fibre strengths – coating furnace at 800° C.

Under none of these conditions, with the coating furnace 1.5 cm from the drawing zone, was it possible to obtain fibres with mean strengths significantly greater than 300000 lb/in.^{2}, the figure quoted in previous work [7].

However, the disappearance of the few very strong fibres as the coating temperature was increased suggested the hypothesis that the coating process itself caused some form of damage.

The temperature at which carbon will begin to reduce silica is about 1450° C [10], and the fibre, which is drawn at 1600° C, may well have been above 1450° C as it entered the stream of acetylene gas. At the usual drawing speed, the time taken by the fibre to travel from the drawing zone to the coating furnace is about 7.5 msec, which seems sufficiently small, but published data on the cooling of drawn filament do not extend to this range [8].

At this stage, it seemed possible that some such reaction as $SiO_2 + 2C = 2CO + Si$, or $3SiO_2 + 2C_2H_2 = 3Si + 4CO + 2H_2O$ (which would be favoured at lower temperatures) was responsible for causing surface damage to the drawn fibre, although microscopic examination of the coated fibre did not reveal any surface irregularity.

A second series of experiments was carried out therefore in which the coating temperature was maintained at 600° C, but the coating furnace was moved progressively further away from the hot zone. Two representative histograms from this series are shown in figs. 5 and 6, while the complete results are summarised in fig. 7. It is seen that, as predicted, the number of high-strength fibres increases as the coating is applied to cooler fibres. Unfortunately, however, after a certain improvement, the number of damaged fibres begins to increase, probably because the coating process relies upon the temperature of the fibre finally to crack the heated acetylene, and cooler fibres produce thinner coatings. Under these conditions, the best compromise was found to be for a coating temperature of 600° C and a distance between hot zone and coating furnace of 2.5 cm, corresponding to a cooling time of about 12 msec.

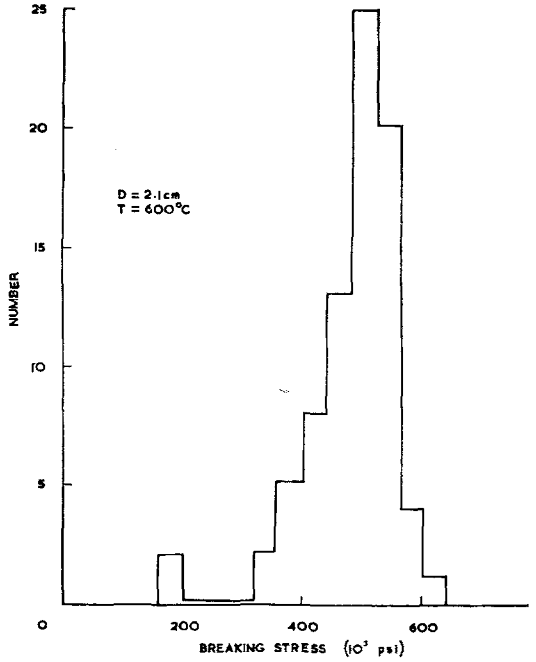

Figure 5 Histogram of fibre strengths – coating furnace at 600° C, distance between drawing zone and coating furnace $D = 2.1$ cm.

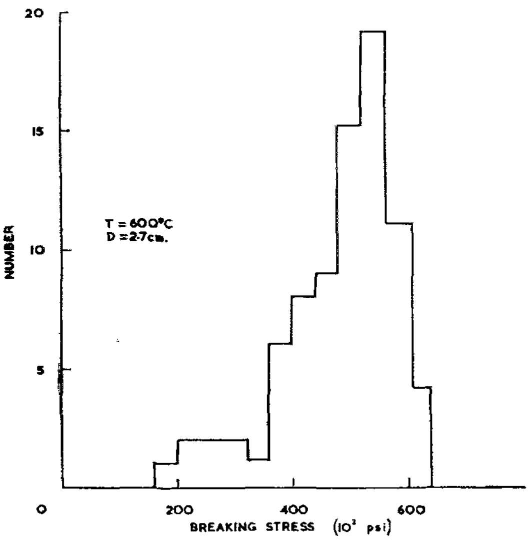

Figure 6 As fig. 4, $D = 2.7$ cm.

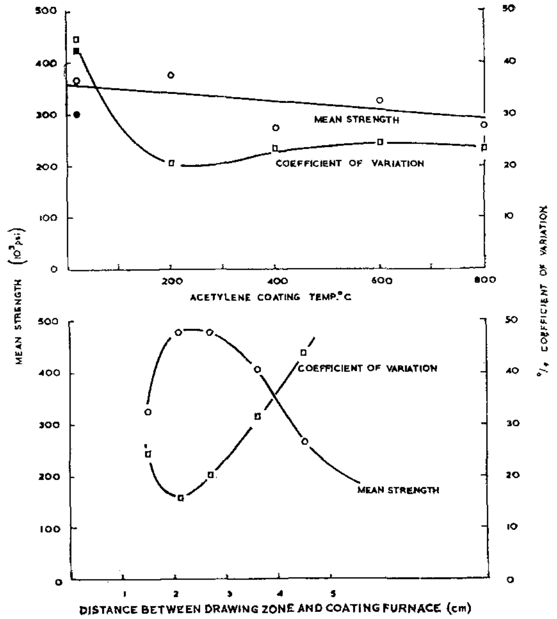

Figure 7 Variation of properties of silica fibre with manufacturing conditions.

The apparatus in which the original coating process was developed, and from which the apparatus described above was derived, had the coating furnace situated immediately below the drawing zone [11]. It is suggested that the above observations may explain why only moderate improvements in strength were made in the original process.

The fibre produced with a coating temperature of 600° C and a drawing-zone/coating-furnace distance of 2.4 cm had a mean strength of just less than 500 000 lb/in.^{2}, with a coefficient of variation of 15 to 20%.

5. Strength of Silica-Reinforced Composites

Short experiments were undertaken to determine the greatest composite strength obtainable with this fibre as reinforcement. Composites were made without removing the fibre from the drum, either by electroplating, or by infiltration with an epoxy resin. The making of a composite by electroplating is described in detail elsewhere [9]. The winding drum was first coated with a layer of graphite. It was then made the cathode in an acid copper sulphate plating bath, and a flash of copper was struck onto its surface. The drum was then removed and transferred to the fibre-drawing apparatus, where a layer of carbon-coated silica fibre was applied. Subsequent electroplating followed by further applications of fibre eventually built up a composite of the desired thickness. This was stripped from the drum at the original graphite coating by making an axial cut in the surface of the composite. The method for making composites with a resin matrix followed parallel lines, with the exception that the composite was built up on a sheet of tin foil wrapped around the drum. This was subsequently removed from the back of the composite by solution in dilute hydrochloric acid.

The highest strength obtained from a composite with a copper electroplate matrix was 94 000 lb/in.^{2}, at a volume fraction of 25%; while the best result using an epoxy resin matrix was 140 000 lb/in.^{2} at 41% volume fraction. These results give average fibre stresses at breaking of 370 000 and 345 000 lb/in.^{2} respectively, or, more probably, nearer 350 000 lb/in.^{2} in the former case if the contribution of the matrix is allowed for. This is obviously at variance with the observed mean strength of the fibre, but allowance must be made for the variation in fibre strength. Using the measured value of the coefficient of variation of 15 to 20%, and the data published by Coleman [12], one would expect the measured values to be 65 to 75% of the statistical mean strength, giving corrected values of 540 000 and 530 000 or 470 000 and 460 000 lb/in.^{2} respectively.

The agreement of these values with the measured statistical mean of just less than 500 000 lb/in.^{2} seems surprisingly good, and implies that very little damage was done to the fibre, once drawn, during the subsequent manufacturing processes. (Coleman's analysis is strictly applicable to fibres which are end-loaded only, but if the initial load transfer length is long in comparison with the flaw separation, his results may apply to a first approximation.)

6. Conclusions

In this paper, we have investigated the effect of manufacturing conditions upon the properties of a carbon-coated silica filament. We have noted that the strength appears to depend upon the coating being of sufficient thickness to protect the fibre from adventitious damage, but that the coating process itself appears to have a deleterious effect upon the fibre. Under the best conditions, a fibre with a strength of up to 500 000 lb/in.^{2} may be made. Fibres coated in this way are sufficiently well protected to retain their high strengths in subsequent composite manufacturing processes.

The electrical conductivity of the carbon coating enables it to be used directly in electroforming processes, and the fibre may be useful as a substrate in making filaments by pyrolytic means.

Finally, it should be emphasised that the process, although not producing a fibre of the very greatest strength, does have the virtues of cheapness, simplicity, and speed.

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