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Review

Techniques for the preparation of boron fibres

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The techniques for the preparation of boron fibres have been reviewed. The review contains a brief description of the following techniques: direct spinning, thermal decomposition of boranes, hydrogen reduction of boron halides and utilization of electrical discharges. In connection with the description of the dominating halide process various substrates are discussed, together with methods for increasing the deposition rate and methods for improving the tensile strength of the fibres after production. Finally, the tensile strengths of boron fibres produced by different techniques are compared.

1. Introduction

In man-made composites brittle materials with high specific strength and modulus are occasionally used in the form of fibres to provide strength and stiffness. Since whiskers are discontinuous and hard to handle, continuous thin filaments or fibres are preferred.

One of the most important fibres today is the boron fibre. Usually the boron fibre consists of a tungsten boride core surrounded by a mantle of amorphous boron (Fig. 1). Fig. 2 shows the characteristic morphology of the fibre. The modulus of elasticity of the boron fibres is almost independent of the production conditions and is in the range 390 to 440 kN mm^{-2}. Talley [1] reported 440 kN mm^{-2} for a 1 mm thick boron fibre. However the tensile strength of the fibres, which depends not only on the deposition conditions but also on the substrate used, is often in the range 3 to 5 kN mm^{-2}.

2. The technique of direct spinning

Molten boron is passed through an orifice so arranged that molten material flows downward in the form of a jet, which is rapidly cooled [2]. The jet is cooled by an impinging gas stream and occasionally by a particle flow. An increased cooling rate is achieved by using an electrostatic field between the filament formed and the gas nozzles. Boron fibres with a diameter of 76.2 μm have been produced. The fibres were coated with boron carbide by admitting a gas mixture containing propane and boron trichloride just below the orifice of the crucible. Finally the fibres were coated with silica at a distance of about 30 cm from the orifice by admitting an aerosol containing silica, helium and boron trichloride. The applied voltage between filament and counter electrode was 6 kV. The tensile strength of the fibres produced with direct spinning has not been reported.

3. Thermal decompostion of boranes

Resistive heating of a metal filament in an atmosphere containing a borane, such as B_2H_6, can be used for preparing boron fibres according to the reaction

$$B_2H_6(g) \rightleftharpoons 2B(s) + 3H_2(g)$$

The boranes are either admitted directly into the deposition chamber or by pressure atomization, which means that the borane is dissolved in an appropriate solvent and introduced into the deposition chamber as finely divided droplets with a size of 1 to 1000 μm. The droplets are projected directly against the heated filament. Withers [3] used a 1% solution of diborane in tetrahydrofuran for preparing a boron fibre with a diameter of

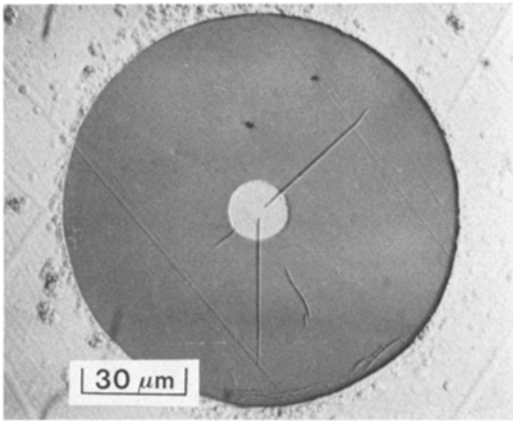

Figure 1 Cross-section of a boron fibre.

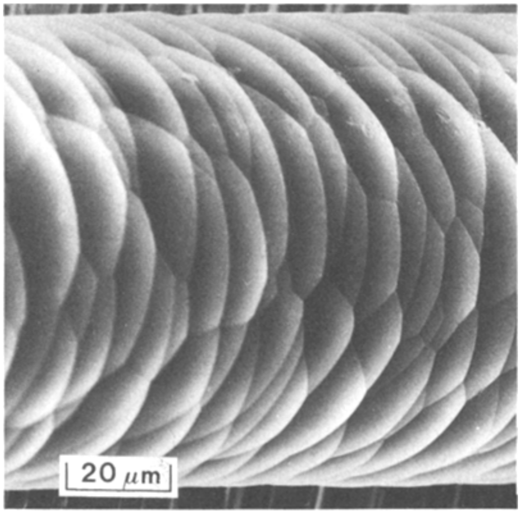

Figure 2 Morphology of a boron fibre

50 μm. The deposition process is always performed at reduced pressure (0.3 to 3 kPa) in the temperature range 450 to 650° C. Since the deposition temperature is low, substrates of low melting point can be employed. Schrägle and Dietz used filaments of tungsten, molybdenum, tantalum, platinum, titanium, silver and gold [4].

Generally boron fibres produced in a borane process seem to be weaker than the fibres produced in the halide process described below. Wawner and Satterfield [5] compared the average tensile strength of filaments with removed tungsten boride cores from the borane and halide processes, respectively. The boron filaments from the borane process had an average tensile strength of 5.5 kN mm^{-2} while those from the halide process had an average tensile strength of 6.2 kN mm^{-2}. Filaments tested with the core intact gave values in the range 3 to 4 kN mm^{-2}.

4. The preparation of boron fibres in electrical discharges

Elementary boron has been prepared in electrical discharges for many years. In 1909, Weintraub [6] used a high-potential alternating current arc maintained between water-cooled copper electrodes in an atmosphere containing hydrogen and boron trichloride. Depending on the experimental conditions, various polymorphs of boron were formed.

Attempts have been made to prepare boron fibres in electrical discharges, namely in glow, corona and arc discharges. In a glow discharge the ionized gas molecules are relatively uniformly distributed in the system, while in an arc the ions generate a narrow, low resistance path between the electrodes. Generally the glow discharges take place at lower pressures than the arc discharges. A corona discharge is intermediate between a glow and an arc discharge and is sustained between a small and a large electrode.

4.1. Glow discharge

Hultquist and Siebert [7, 8] used a high-voltage, low current, high frequency, electrodeless glow discharge in a gas mixture of hydrogen and boron trichloride. Boron was deposited on all surfaces within the glow discharge. Introducing a filament into the discharge made it possible to prepare boron fibres. The deposition temperature could be varied from room temperature to about 1000° C.

Hultquist and Siebert demonstrated that particularly insulating, static substrates could be coated with boron in a glow discharge at total pressures of 0.6 to 13 kPa. The deposition rate was about 5×10^{-5} g sec^{-1} and the deposit, which could be obtained to the desired thickness, was mainly amorphous. However, measurement of the physical and mechanical properties of the deposits were not made because only small samples could be prepared in the static system used.

4.2. Corona discharge

Wales [9] prepared boron-coated tungsten filaments in a corona discharge in a static as well as in a continuous production process. In order to obtain a uniform corona around the filament, the counter electrode was concentric around the filament. The reaction gas mixture contained hydrogen and boron tribromide or boron trichloride with the total pressure at or below atmospheric pressure. The temperature of the filament could be regulated by the power supply. Alternating current as well as half-wave rectified alternating current was used with the tungsten wire as a cathode.

In the static system boron tribromide and tungsten wires with diameters in the range 6 to 25 μm were employed. Good coatings with a thickness of about 15 μm were obtained at relatively low currents, moderate gas flows and a high molar ratio of boron tribromide to hydrogen.

In the continuous process boron was deposited on 12.5 μm- and 3.8 μm-thick tungsten filaments, which were moved in a hydrogen–boron trichloride atmosphere. In addition to a cleaning reactor, the system had deposition reactors arranged after each other. However, there were some difficulties in maintaining the discharge when the subtrate was pre-coated with boron. Consequently problems arose in the second deposition reactor, particularly when using the thinner filaments. The final diameter of the fibres produced on 12.5 μm and 3.8 μm-thick tungsten filaments were 48 μm and 15 μm, respectively. The deposition time ranged from a few minutes to about 20 minutes.

X-ray investigations of the fibres indicated that amorphous boron was obtained. Moreover, no tungsten borides were observed owing to the low deposition temperature. The mechanical properties of the fibres were not tested. However, from the morphology of the fibres it is concluded that the fibres produced should have relatively good mechanical properties even if they have only half the diameter of the normally used boron fibres.

4.3. Arc discharge

The crack nucleation mechanisms in boron fibres could be grouped and related to stress intervals as shown by Wawner [10], Line and Hendersson [11], Layden [12] and recently by Vega-Boggio and Vingsbo [13]. In the best fibres fracture nucleates in the tungsten boride core. Consequently the presence of the core in boron fibres determines an upper limit of the fracture stress. By producing a coreless boron fibre, that is, without any substrate, it should be possible to make a stronger fibre.

Juhola and Pferdehirt [14] used a d.c. thermionic arc discharge to prepare boron fibres without any substrate (see Fig. 3). The arc discharge is maintained between two refractory electrodes in a gas mixture containing 55 to 80 mol % hydrogen and 20 to 45 mol % boron trichloride preferably at atmospheric pressure. The boron fibre is formed on the positive electrode, which is moved away from the negative electrode at a rate equal to the growing rate of the fibre, maintaining a constant discharge gap. The boron deposits on the negative electrode are removed with a scraper between the runs.

The dimensions of the electrodes, particularly that of the positive one, are of importance in defining the diameter of the final fibre. The positive electrode should not have an end diameter exceeding the desired diameter of the final fibre. The negative electrode could be larger than the positive one. Fibres with diameter from 37 to 100 μm have been produced in the system.

Since the boron fibre formed has a higher electrical resistance than the initial tungsten substrate, the potential must be increased during the preparation in order to maintain the desired current (5 to 6 mA). However, Juhola and Pferdehirt have also developed a construction for producing boron fibres of infinite length without excessively increasing the potential (from 500 V to estimated 2000 V).

Although boron fibres could be produced using any d.c. power source, the strongest fibres were prepared by using a rectified 50 to 60 c.p.s. alternating current. The tensile strength of fibres of 42 μm diameter was 2.3 kN mm^{-2}.

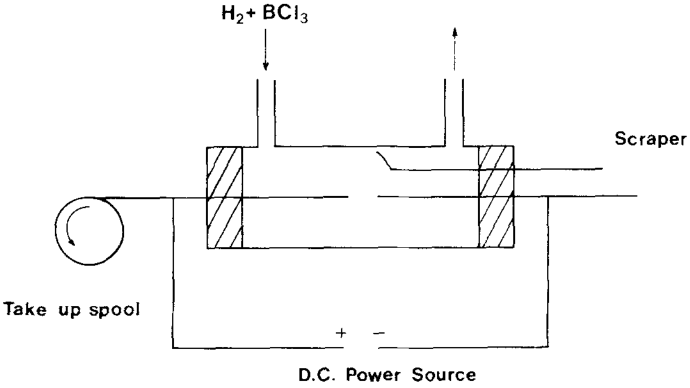

Figure 3 A schematic drawing of an apparatus for preparing boron fibres without any substrate. From [14].

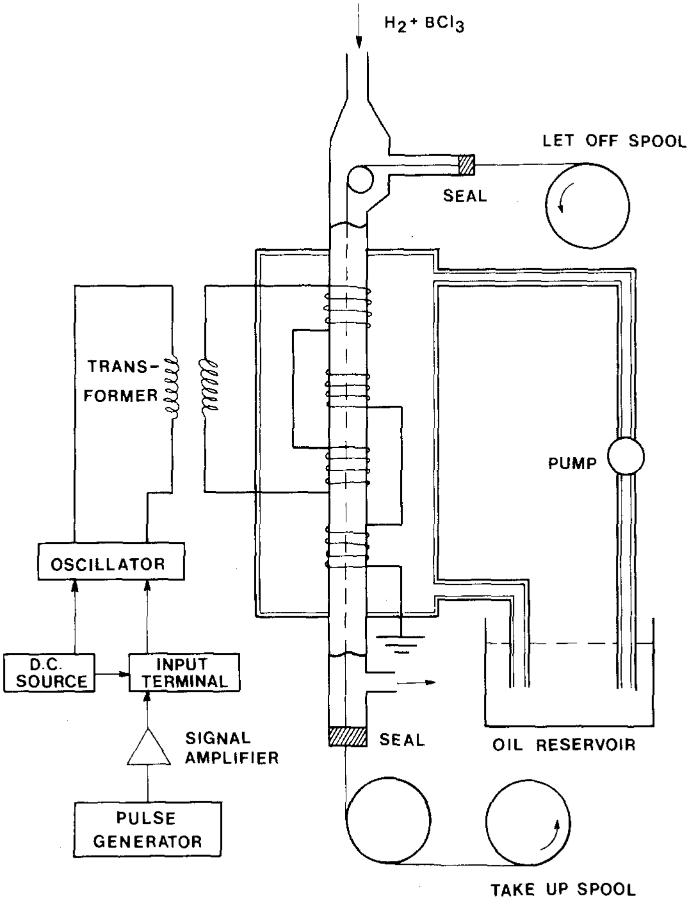

Figure 4 Capacitive coupling of pulsed high electric power for production of boron fibres [15]. The reactor is immersed in silicone oil for cooling.

4.4. Pulse discharge

Pulse discharges have been used by Hou [15] for boron coating of filaments. The excited gas species are formed by inductive or capacitive coupling of pulsed high electric power to a boron-containing gas mixture at a pressure of 1 to 3 atm. (see Fig. 4). Pressures lower than about 1 atm. imply a low deposition rate, while pressures higher than 3 atm. result in a non-uniform coating. The gases admitted to the deposition zone are hydrogen mixed with boron halides, boranes or alkyl borates. The deposition process is performed in the temperature range 20 to 350° C on electrically conductive or non-conductive filaments suspended in the deposition zone. Tungsten filaments, graphite yarns and polyacrylonitrile homopolymer yarns were coated with boron to a thickness of about 50 μm. The temperature in the deposition zone was 60° C except for the graphite yarns, where the temperature was 300° C. The residence time of the substrate within the deposition zone was about 5 min. The fibres produced were not tested mechanically.

5. Hydrogen reduction of boron halides

The various methods for preparation of elementary boron have been reviewed by Newkirk [16] and recently by Naslain [17]. One of the most important of these is the hydrogen reduction of boron halides according to the reaction

$$3H_2(g) + 2BX_3(g) \rightleftharpoons 2B(s) + 6HX(g)\ (X{=}Cl, Br)$$

When using the "hot-wire" technique a filament of a refractory metal is heated in an atmosphere containing hydrogen and boron tribromide or boron trichloride. At 700 and 1000° C, respectively, boron is deposited at an appreciable rate on the metal filament.

The principles of the "hot-wire" technique have been applied in industrial boron fibre production. A filament is heated to between 1000 and 1300° C in a gas mixture with boron halides and hydrogen in excess. The total pressure of the gas mixture is normally about 1 atm.

5.1. Techniques for heating the substrate

Morin and Leclercq [18] used a CO_2 laser beam for heating the filament. The laser beam was directed perpendicular to the filament, which was moved in a hydrogen–boron trichloride gas mixture. Tungsten, quartz and carbon monofilaments of 50, 62 and 52 μm in diameter, respectively, were used. Since the thickness of the deposit was about 1 μm, the technique described above has hitherto been of minor importance in the preparation of boron fibres.

However, the conventional method for preparing the high-modulus, high-strength boron fibres is resistive heating of the filament, normally a 12 μm tungsten filament, with direct current. Fig. 5 shows a typical chemical vapour deposition system for continuous production of boron fibres. The tungsten filament is drawn off the spool and transported via a mercury seal, which is also an electrical contact, into the cleaning chamber. The filament is heated to about 1200° C in a hydrogen atmosphere in order to reduce the tungsten oxides on the filament surface and to remove surface contaminants such as die lubricant from the drawing of the filament. After the cleaning procedure, boron is deposited on the filament in the deposition chamber. The deposition temperature generally lies in the range 1100 to 1200° C. The residence time of the fibre in the deposition chamber is about half a minute. Finally the fibre is wound on a take-up spool. In order to increase the production rate of boron fibres, several reactors are arranged one after the other in a so-called multi-stage system. Horizontal as well as vertical multi-stage systems have been used. Representative horizontal and vertical reactors for use in multi-stage systems are described in [19] and [20], respectively.

5.2. Reduction of the temperature gradient along the fibre

In the continuous production of boron fibres a temperature gradient along the fibre arises because of the non-uniform thickness of the boron coating and changes in the resistivity of the substrate [21]. By arranging several reactors one after the other, as in the multi-stage system, the temperature gradient in each reactor can be reduced. Another method for reducing the undesired temperature gradient is to manipulate the gas flows in the reactors. Kuntz [22] admitted a gas with a high coefficient of thermal conductivity, for example H_2, at the hot part of the filament. In that way the temperature gradient was reduced considerably. Fanti and Kuntz [23] used a counterflow principle for reducing the temperature gradient. Two gas mixtures of different compositions were added into the reactor near the filament entrances. At the colder end of the filament a more boron trichloride-rich gas mixture was admitted. The gases leave the reactor at its centre. By the regulation of the two gas flows it is feasible to produce the fibres at a temperature of 1300° C. Rice [24] used the counterflow principle in a vertical multi-stage system. A downward gas flow is introduced in the upper part of the first reactor and an upward flow in the lower part of the first reactor. The downward flow contains more hydrogen than the upward flow. The gases leave the reactor at the centre and enter the upper part of the second reactor with a downward flow to a bottom exit.

In the conventional reactor shown in Fig. 5, boron fibres with an average tensile strength of about 3.5 kN mm^{-2} and maximum strength values of 4.5 kN mm^{-2} can be produced on tungsten filaments. However, when using mercury seals hot spots on the filament often occur in the neigh-

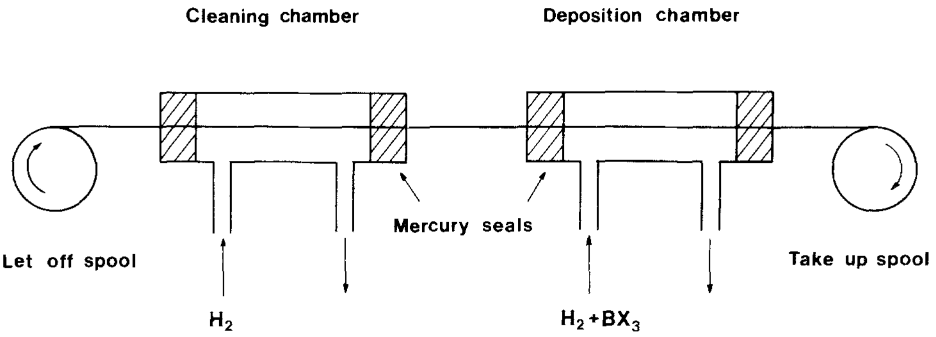

Figure 5 A schematic drawing of a typical chemical vapour deposition system for continuous production of boron fibres.

bourhood of the seals. Crystalline boron is formed in the hot spots, weakening the fibre considerably. Jacob *et al.* [25] constructed a r.f. heated reactor, which makes it possible to substitute the mercury seals for ordinary gas seals. In this type of reactor a uniform temperature along the fibre was obtained. The average tensile strength of 100 μm fibres produced on tungten filaments was 4.6 kN mm^{-2} with a maximum value of 8.4 kN mm^{-2}.

5.3. Substrate materials

Refractory metals, particularly tungsten, have been used as substrate material from the very beginning of boron fibre preparation. However, the utilization of metal filaments as substrates causes residual stresses in the fibres because of the formation of an expanding boride core during the fibre growth and the mismatch of the thermal expansion coefficients of the core and the mantle. The residual stresses caused by the boride formation can be eliminated by pre-coating the metal filament with a substance acting as a diffusion barrier, for example, boron nitride on tungsten [26, 27].

The tungsten filaments used as substrate exhibit a rough surface. The surface irregularities consist of die marks from the drawing process in the form of axial grooves and ridges (Fig. 6). Vega-Boggio *et al.* [28] proved experimentally that the nucleation of boron occurred preferentially on the ridges. The boron nodules formed are oriented axially, which is shown in Fig. 7. Depending on the preferential nucleation of boron nodules, relatively large distances between the nodules are obtained, giving rise to the final rough nodule surface of the fibres (Fig. 2). The nodule boundaries serve as stress concentrators under external load, which implies a notch effect and an increased probability of crack nucleation. A boron fibre with a smooth surface should be stronger and is anticipated to be obtained on a filament allowing denser nucleation sites than tungsten.

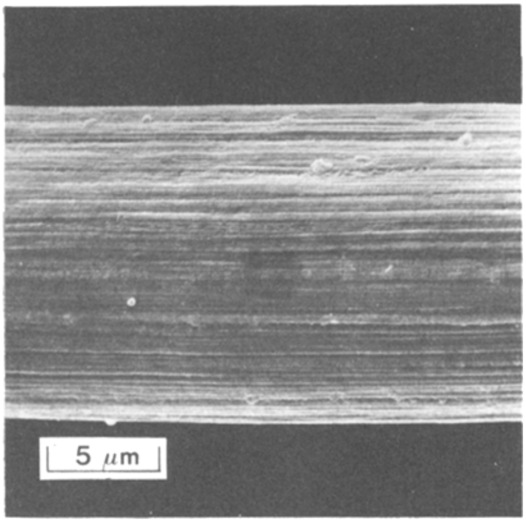

Figure 6 Photograph showing the rough texture of the tungsten filament.

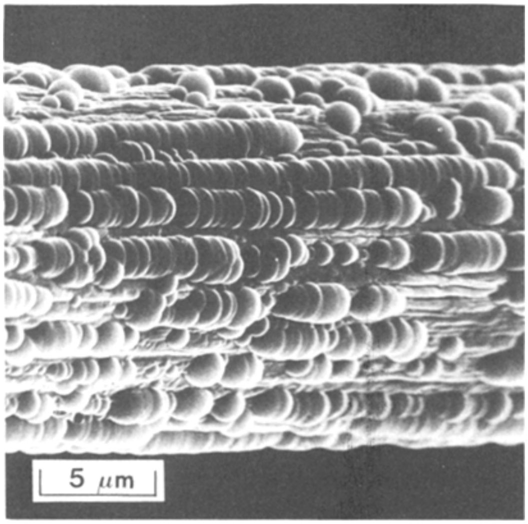

Figure 7 Photograph showing the axial orientation of the nodules.

Boron fibres with smooth surface can be obtained by using carbon monofilaments as the substrate [29]. The tensile strength of the fibres produced was 5 kN mm^{-2}. The carbon monofilament possess not only the required electrical conductivity and hot strength but also an attractive cost and density compared to tungsten. The density of the boron fibres based on tungsten filaments and carbon monofilaments is about 2.6 g cm^{-3} and 2.3 g cm^{-3}, respectively.

However, when using carbon monofilaments hot spots are formed after a short deposition time. The hot spots are caused by fractures in the carbon core, induced by the elongation of the boron sheath during the deposition reaction. At the fracture sites the current is no longer shared between the core and the boron sheath. Weakening abnormal nodules and crystalline boron are obtained at the hot spots.

By utilizing a short deposition time (5 sec) Bourdeau [30] succeeded in preparing a 55.9 μm-thick boron fibre on 25.4 μm-thick carbon monofilament. The tensile strength of the fibres produced was 3.1 kN mm^{-2}, while the modulus of elasticity of a 53.3 μm-thick boron fibre was 330 kN mm^{-2}. Mehalso and Diefendorf [29] investigated the boron elongation and the creep of the carbon core. By matching the creep and the elongation it was feasible to prepare boron fibres with a tensile strength of 5.0 kN mm^{-2}. Basche *et al.* [31] avoided the fracture of the carbon core by coating the carbon monofilament with a thin slip layer of pyrolytic graphite prior to the boron deposition. The graphite layers were prepared from a hydrogen/methane gas mixture at 1900° C. Boron fibres with a diameter of 94 μm were produced on 26.5 μm-thick carbon monofilaments with a 3.1 μm-thick graphite layer.

By pre-coating the carbon monofilament with an electrically conductive layer (1 μm-thick) of titanium carbide in a conventional CVD process, Galasso *et al.* [32] obtained a continuous unbroken path for the electrical current even if the carbon core fractured during the boron deposition process. The hot spots of the filament were completely eliminated by using this technique.

Hitherto, only electrically conductive substrates have been used in the halide process. However, Morelock added a pyrolytic carbon [33] and a boron coating [34] on the surface of a pre-carbon-coated silica filament. No data on the mechanical properties of the boron fibres produced were given.

5.4. Methods for increasing the deposition rate

Maximum production rate can be achieved after optimization of the depostion parameters, temperature, gas flow, gas composition, and total pressure. Utilization of a uniform temperature along the filament, which was described above, results in a higher production rate, as the whole filament is thus allowed to be heated to the maximum temperature for obtaining amorphous boron. Fenninger *et al.* [35] observed that the production rate of boron fibres could be increased five times by pre-heating the reaction gas mixture and by heating the reaction chamber. Finally the deposition rate can be increased by adding 0.5 to 3 mol % halide, such as the chlorides of zirconium and tantalum or the fluorides of molybdenum and tungsten [36]. The halides act as catalysts. An addition of tungsten hexafluoride to the reaction gas mixture increases the deposition rate more than four times.

5.5. Methods for improving the fracture strength of boron fibres after production

The tensile fracture strength of a boron fibre depends on the size and distribution of flaws (defects) and the residual stresses in the fibre. According to Witucki [37], the residual stresses arise from:

(1) The CVD process itself, where boron is deposited with a deposition stress.

(2) The volume increase of the core during the deposition process depending on the formation of tungsten borides in the core.

(3) The difference in thermal expansion between the tungsten boride core and the boron mantle.

The residual stresses, which change from compressive at the surface to tensile in the boron mantle and to compressive again near and in the core [10, 11, 37–40], are also influenced by the creep and the anelastic deformation in the boron mantle.

Wawner [10], Line and Henderson [11], Layden [12], and Vega-Boggio and Vingsbo [13] have shown that the crack nucleation mechanisms of the tungsten-based boron fibres are related to the fracture stress. Low fracture stresses are caused by crystal growth, radial cracks, inclusions and surface flaws. However, after improvement of the deposition process, the surface flaws are the major low fracture stress initiators. Wawner [41] removed the surface flaws by chemical etching of the boron fibres with nitric acid. After etching, the fibres displayed a smooth surface. The etching procedure increased the average fracture stress by about 1 kN mm^{-2} and decreased the standard deviation for fibres with low as-produced strength (2 to 3 kN mm^{-2}). Fibres with high as-produced strength showed only a slight improvement. Smith [42] also etched boron fibres with nitric acid and observed that for the etched fibres, fracture was almost always nucleated in the core. Ducrot *et al.* [43] increased the fracture stresses of the fibres by etching with an alkaline potassium ferricyanide solution. The fibres could also be pre-treated electrolytically with the fibre as anode in a hydrogen peroxide solution. Finally, Vrieze and Schob [44] etched the fibres with a solution containing nitric and phosphoric acids, which increased the average fracture stress from 2.2 kN mm^{-2} to 2.9 kN mm^{-2}.

Normally only a few microns of boron are removed by etching. However, Smith [42] etched a 203 μm-thick boron fibre down to about 100 μm and observed that the fracture stress gradually increased with the successive removal of boron. Behrendt [40] has explained this increase on the basis of the longitudinal residual stress pattern in the fibre. Etching of fibres implies both removal of the surface flaws and the compressive stresses in the surface layers. Removal of the layers in compression causes a contraction of the fibre, which increases the initial compressive stresses in the core. If the fracture of the fibres depends on the core flaws and if the fibres deform elastically, the axial contractive strain developed on etching can be added to the initial strain. DiCarlo [45] converted Smith's fracture stress data to fracture strain data and obtained an increase in fracture strain from 1.11% (surface flaws removed) to 1.3% after etching the fibre to 100 μm.

All nonelastic axial behaviour of boron fibres up to at least 800° C can be explained in terms of an elastic tungsten boride core and an anelastic boron mantle [46]. The anelasticity of the boron mantle allows creep recovery of the boron mantle after stress removal. The creep recovery depends on temperature and time.

DiCarlo has used two techniques for increasing the fracture stress of boron fibres [45]. In the etch–heat technique the boron fibres are etched prior to the heat-treatment. Only etching of the fibres from 203 to 102 μm increased the fracture stress from 3.59 kN mm^{-2} to 5.08 kN mm^{-2}, while a combination of etching and heat-treatment at 1100° C for 0.5 min increased the fracture stress to 5.59 kN mm^{-2} (fibre diameter 107 μm). These results are explained by a model, where the layers within the surface have undergone axial anelastic tensile creep during the boron fibre production. Removal of outer boron layers will reduce the elastic and anelastic strain components and allow the fibre to contract. Fibre contraction will increase the core flaw fracture strain. However, at room temperature, anelastic recovery is very slow. Thus, etching of the fibres close to room temperature, will cause reduction of the elastic strain component, while reduction of the anelastic component is obtained at high temperatures (500 to 1100° C). DiCarlo has also heat-treated the fibres prior to the chemical etching procedure. By using this heat–etch technique, the fracture stress of the fibres increased to 5.57 kN mm^{-2} (diameter 117 μm) after heat-treatment for 6 min. at 1100° C.

Waterman *et al.* [47] used another method for increasing the fracture stress. The boron fibres were suspended horizontally or vertically under tension to keep them straight. The fibres were then heated with strip heaters to about 150° C for 5 min. The average fracture stress was increased from 3.3 kN mm^{-2} to 4.2 kN mm^{-2} while the standard deviations of the tests decreased from 15.6% to 8.9%. The treatment of the fibres as described above is assumed to stress-relieve the fibres and to reduce the effect of surface discontinuities of the fibres.

6. Concluding remarks

From the data presented in this review it is possible to rank the various production techniques employed with respect to the fracture stress exhi-

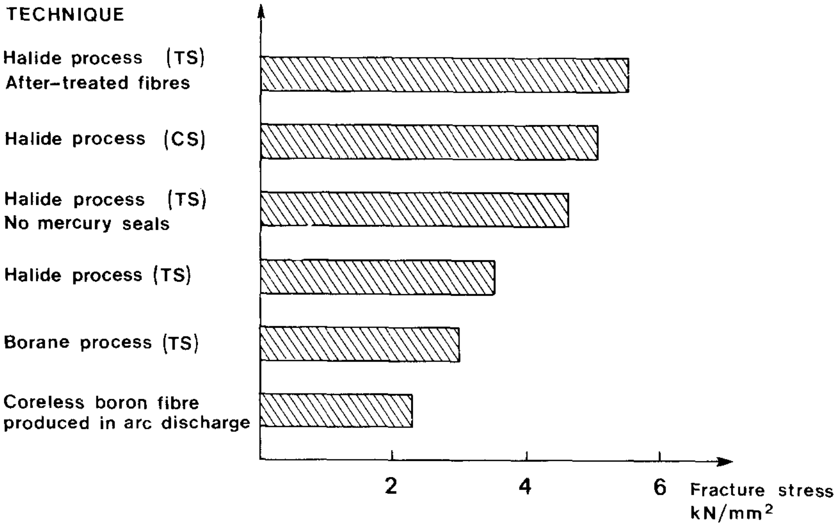

Figure 8 Approximative achievable fracture stresses of boron fibres produced with different techniques. TS and CS refer to tungsten substrate and carbon substrate, respectively.

bited by the boron fibres. The average fracture stress attributed to each technique in Fig. 8 can vary within relatively wide limits (the standard deviations are often about 10 to 15% of the fracture stresses). Moreover, it is difficult to compare fracture stresses given in the literature as the testing conditions are often not described. Thus it is of great importance to know the gauge length used. However, the values given in Fig. 8 constitute a summing up of values, which have often appeared in several papers. Fig. 8 can be used for a rough survey of the fracture stresses of boron fibres produced and treated in different ways. From the review it is concluded that coreless boron fibres of high strength cannot yet be produced. The boron fibres prepared in the halide process on tungsten substrates can be expected to be stronger than fibres from the borane process. Finally, tungsten substrate-based boron fibres, which are after-treated or produced in a reactor without any mercury seals, have fracture stresses comparable with carbon substrate based on boron fibres.

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