JOURNAL OF MATERIALS SCIENCE 14 (1979) 2726–2732

The morphologies of boron fibres in the temperature range 1000 to 1500° C and the relationship between mechanical properties and morphology

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The main surface morphologies of boron fibres in the temperature range 1000 to 1500° C and the relevant experimental conditions for obtaining them have been investigated. After tensile testing of boron fibres with the various main morphologies, an approximate value for the tensile fracture stress could be assigned to each morphology. A method for identifying *in situ* the morphologies formed during the deposition process is described. Finally, the maximum preparation times for obtaining high-strength boron fibres at various temperatures have been calculated.

1. Introduction

Boron fibres are usually prepared by a chemical vapour deposition (CVD) process. It is well known that the properties of CVD materials are strongly affected by the experimental conditions in the preparation process. The fracture stress of boron fibres is consequently dependent on the deposition conditions maintained in the CVD system used. The various techniques for the preparation of boron fibres as well as the average fracture stress attributed to each technique have recently been reviewed [1].

High-strength boron fibres can be prepared by hydrogen reduction of boron trichloride or boron tribromide on heated tungsten filaments. The average tensile fracture stress of tungsten-based boron fibres produced in a halide process without any after-treatment is about 3.5 GN m^{-2} [1]. The standard deviation of the fracture stress is normally of the order of 0.5 GN m^{-2}. Wawner [2], Line and Hendersson [3], Layden [4] and Vega-Boggio and Vingsbo [5] related the crack-nucleation mechanism of boron fibres to stress intervals. At high fracture stresses the fracture nucleates in the tungsten boride core, while low fracture stresses are caused by crystal growth, radial cracks, inclusions and surface defects. Carlsson and Lundström [6] identified various surface defects and classified them as fracture-stress depressive and non-fracture-stress depressive defects.

The growth of boron fibres with amorphous nodule morphology is a prerequisite for the fibres to have high strength. Three different amorphous nodule morphologies with different mechanical properties have been identified in the present investigation. The growth conditions for obtaining the amorphous as well as the crystalline morphology have been determined. From the preparation data of the various morphologies, the maximum preparation times for obtaining high-strength boron fibres at various temperatures were calculated.

2. Experimental details

2.1. Preparations

Boron fibres, 16 cm long, were prepared in a closed CVD system. Details of the CVD system are given elsewhere [7]. The gas mixtures used in the preparation (total pressure 66.5 kPa) contained hydrogen (claimed purity 99.99%) and boron trichloride (purity >99.8%). The molar ratio of the reactants hydrogen and boron trichloride was in the range 3/2 to 20/1. The temperature was

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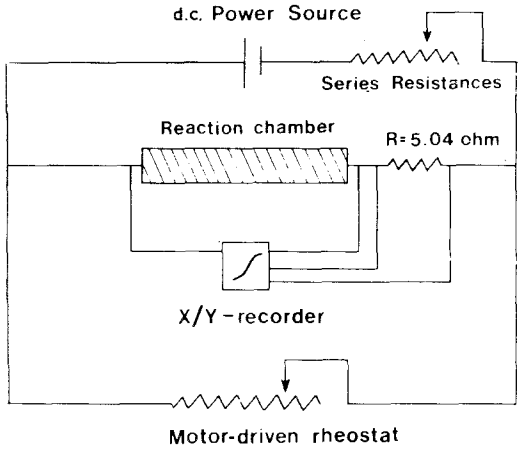

Figure 1 Circuit diagram for recording current/potential curves during boron fibre growth.

measured with a visual micro-optical pyrometer. Corrections for absorption in glass and for the emissivity of boron were made [7].

Information on the progress of the deposition process and on the nucleation time and fibre morphology can be obtained by recording current and potential during the deposition process (circuit diagram in Fig. 1). Since the relationship between current and potential changes rapidly, particularly at the beginning of the process, a high-speed recorder was used (maximum speed in the X and Y directions is 88 and 125 cm sec^{-1}, respectively).

By interrupting the process at different stages, the various sequences of fibre growth in relation to the current/potential curve could be established. After interruption, measurements of the room temperature resistances of the fibres, as well as microscopic examinations of the fibre surfaces were performed.

2.2. Tensile testing

The fibres were examined at 22° C in a micro-tensile testing machine (Alwetron TCS-100). The gauge length and the strain rate were 30 mm and 2.8×10^{-3} sec^{-1}, respectively. The fibre diameters were measured in an optical microscope to an accuracy of $\pm 0.5\,\mu m$.

2.3. X-ray work and electron microscopy

X-ray photographs of the boron fibres were taken with a Debye–Scherrer camera ($R = 57.3$ mm) using Cu$K\alpha$-radiation ($\lambda = 1.5478$ Å). The morphologies of the fibres were examined in a scanning electron microscope (JSM-U3), operated at 15 to 25 kV. All the specimens were cleaned in alcohol in an ultrasonic cleaner for 10 min and then coated with gold.

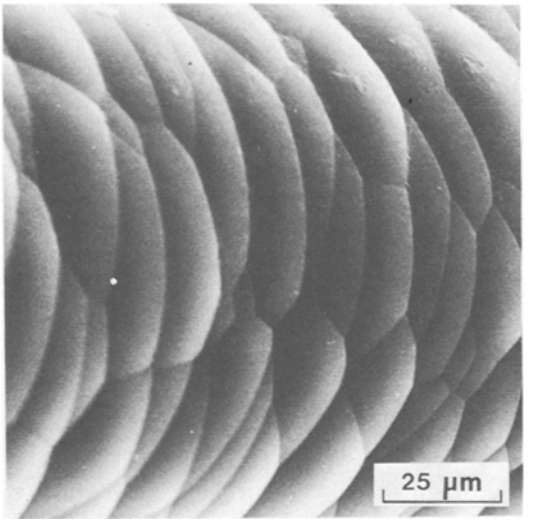

Figure 2 Well-oriented amorphous boron nodules.

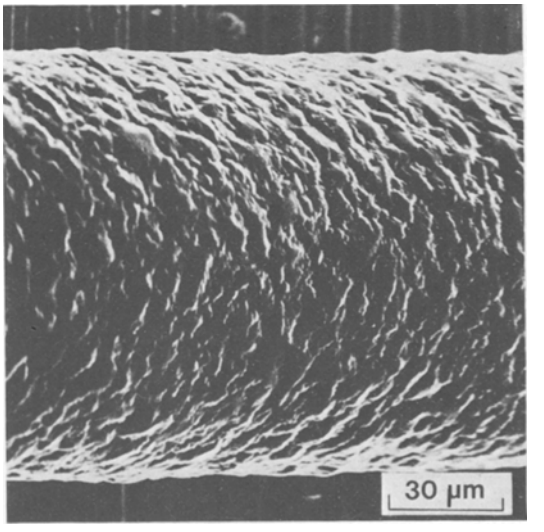

Figure 3 Crystalline boron fibre.

3. Results and discussion

3.1. Main surface morphologies of boron fibres in the temperature range 900 to 1500° C

The surface morphologies of the boron fibres can be divided into two main categories, namely amorphous fibres and crystalline fibres. The amorphous morphology is characterized by well-defined rounded nodules. The smooth nodule boundaries can easily be seen (see Fig. 2). Fibres with crystalline morphology (Fig. 3) display a

rougher surface than fibres with amorphous morphology. The edged crystallite boundaries can rarely be distinguished.

3.1.1. Amorphous fibre morphology

Three types of morphologies for amorphous fibres could be distinguished: (i) a well-oriented nodule morphology (Fig. 2); (ii) a randomly oriented nodule morphology (Fig. 4); and (iii) a morphology with uneven nodule surfaces (Fig. 5).

(i) In the well-oriented nodule morphology, the nodules are aligned radially. The radial orientation (Fig. 2) is caused by a preferential nucleation process on the original tungsten filament (Fig. 6). The axially oriented ridges of the tungsten filament, originating in the filament drawing process, serve as preferential nucleation sites [8]. Since the distance between the original ridges is larger than the distance between the nucleation sites on the ridges, radially well-oriented nodules are obtained after growth. This morphology type, yielding the highest fibre strength, is predominantly obtained at high temperatures ($> 1100^\circ$ C) and high deposition rates ($> 89\,g\,cm^{-2}\,sec^{-1}$).

(ii) In the formation of randomly oriented nodules (Fig. 4), the effect of the ridges on the nucleation process has been suppressed. Boron fibres with randomly oriented nodules have low fracture stresses ($< 1.5\,GN\,m^{-2}$). The latter are caused by the presence of crystalline boron underneath the amorphous surface layer and not by the orientation of the nodules. An X-ray investigation showed that the crystalline phase consisted of β-rhombohedral boron.

The deposition conditions for obtaining amorphous and crystalline boron, respectively, are illustrated in Fig. 7 [9]. At high temperatures, amorphous boron can only be formed if the deposition rate is very high. Lower deposition rates allow the formation of crystalline boron. The reaction path for obtaining random orientation of the nodules is shown schematically in Fig. 7. The deposition process starts in the stability range of amorphous boron, passes the crystalline range and finally returns to the amorphous region. The

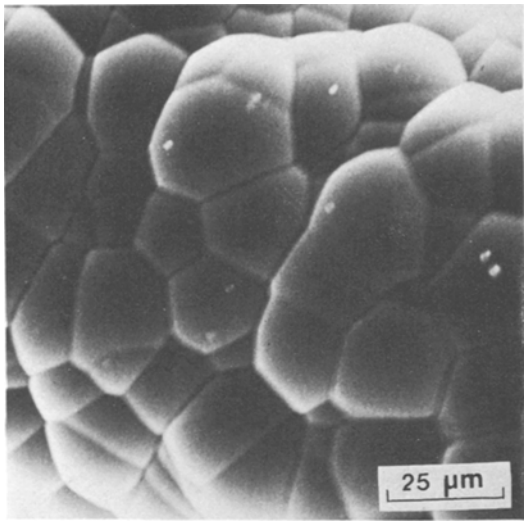

Figure 4 Randomly oriented amorphous boron nodules.

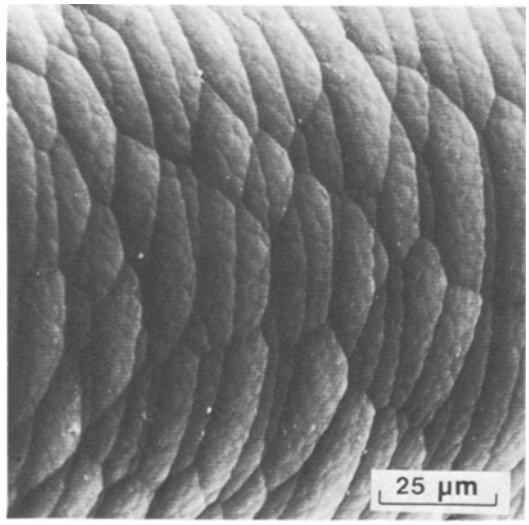

Figure 5 Uneven amorphous well-oriented boron nodules.

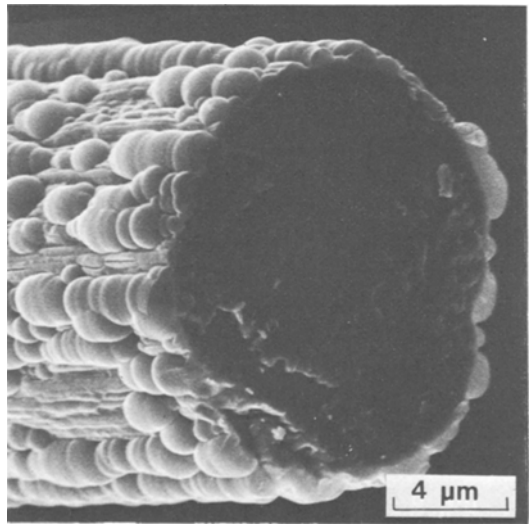

Figure 6 Preferential nucleation of boron on the ridges of the tungsten filament.

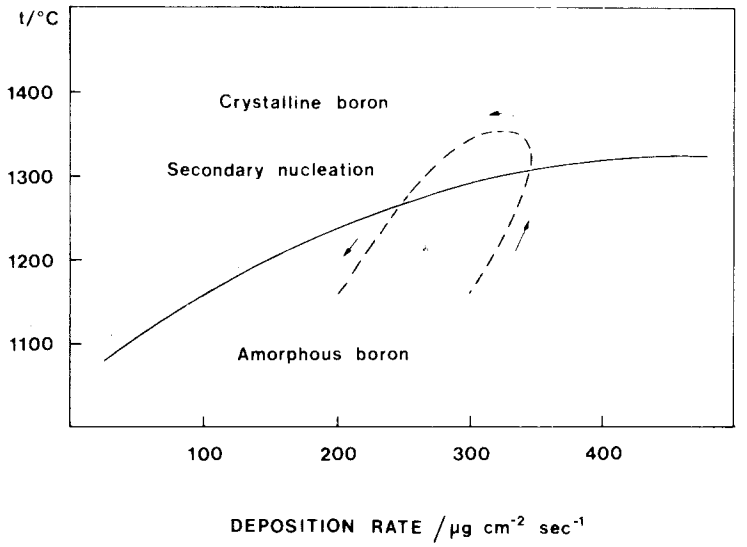

Figure 7 Experimental conditions for obtaining random orientation of amorphous boron nodules. The reaction path (— — —) is shown schematically. The line separating the two morphologies is based on [9].

thicknesses of the crystalline deposit and of the outer amorphous deposit are given by the time and deposition rates in the different ranges.

The random orientation of the amorphous nodules can be explained by secondary nucleation in the following manner. Primarily, the axially oriented nuclei, according to (i), are formed. After increasing the temperature, a crystalline morphology replaces the amorphous radially oriented nodule morphology. Since the crystalline surface does not exhibit any preferred orientation of nucleation sites, a random orientation of the boron nuclei is obtained, on returning to the stability range of amorphous boron.

According to the nucleation and growth sequence given above, amorphous boron is obtained at the beginning and end of the deposition process, while crystalline boron is formed at intermediate stages. However, no amorphous boron near the boride core could be observed in microscopic examinations of cross-sections of the fibres. The initially formed amorphous boron layer is only a few microns thick. During subsequent fibre growth the boron atoms near the core diffuse into the core and tungsten borides are formed. The boride formation, which causes an expansion of the core, preculudes observation of the initially formed amorphous boron.

The experimental conditions for obtaining random orientation of amorphous boron nodules, prepared on conventional tungsten substrates, are summarized in Fig. 7. The dotted line shows how the experimental conditions initially give rise to amorphous nucleation, then move into the region of crystalline nucleation, before subsequently returning to the region of amorphous nucleation. At constant temperature or at a constant deposition rate this type of morphology can only be formed after passing a minimum in the deposition rate or a maximum in temperature, respectively. In the normal boron fibre preparation process the deposition rate decreases continuously, when the temperature passes through a maximum [6]. Consequently, the random nodule morphology can be avoided in the normal preparation process by minimizing the temperature decrease after passing the maximum in the temperature/time curve and by using high deposition rates so that the whole preparation takes place in the stability range of amorphous boron.

(iii) The morphology of the uneven amorphous boron nodules (Fig. 5) is characterized by a superposition of small nodules on the radially oriented large nodules. The observations indicate that primary nucleation takes place in the usual manner on the ridges of the tungsten filament. At a later stage of fibre growth, more than twenty small boron nodules are frequently observed within one former nodule (Fig. 5). The most probable explanation of this is a secondary nucleation process although other, less probable, explanations such as surface etching during the preparation process or shrinkage due to sintering, cannot be completely excluded. The uneven nodule morphology type, yielding fibres of intermediate strength, is obtained at low temperatures and low deposition rates.

Secondary nucleation is not caused by drastic

changes in the deposition conditions but rather a change in the deposition mechanism indicated by a change in the activation energy of the deposition reaction [9]. This mechanism change occurs in the normal fibre preparation process at approximately 1100° C. The uneven surface morphology was observed on fibres for which the preparation time was terminated at temperatures lower than 1050° C, and it seems probable that the secondary nuclei start to grow at approximately 1100° C, i.e. close to the temperature for secondary nucleation observed earlier [9]. In a previous paper [6] it was concluded that the minimum in the fracture stress deposition temperature curve at approximately 1150° C was caused by this secondary nucleation (secondary boron nuclei reduce the strength of the fibres by a notch effect). Since the deposition temperature given was the maximum temperature during the preparation process and the temperature decrease after passing the maximum is at least 100° C for preparing 100 μm thick boron fibres, there is good agreement between the observations.

3.1.2. Crystalline fibre morphology

The crystalline morphologies of the boron fibres are of less interest since they imply low tensile fracture stresses ($<1\,GN\,m^{-2}$). Generally, the crystalline morphologies are formed at lower deposition rates than the amorphous morphologies (see Fig. 7). No correlation between the morphology and the boron polymorph formed has been observed. The crystalline morphologies reveal only a variation in granular size, which is dependent on the deposition conditions rather than on the boron polymorph formed.

The crystalline boron polymorphs identified in the present investigation confirm the earlier results [10]. At high temperatures (>1450° C) β-rhombohedral boron is formed rapidly (Fig. 3). At lower temperatures and relatively low deposition rates (see Fig. 7) the formation of α-rhombohedral boron and β-tetragonal boron occurs. The crystalline boron polymorphs and the amorphous boron can exist together during certain deposition conditions. For instance, all three crystalline boron polymorphs and the amorphous boron were formed at 1150° C with a deposition rate of about $100\,\mu g\,cm^{-2}\,sec^{-1}$ and a preparation time of 2 min (total pressure 66.5 kPa and molar ratio 20/1 between the reactants hydrogen and boron trichloride).

3.2. Current/potential curves during boron fibre preparation in a closed CVD system

On recording current/potential curves during the fibre preparation process, approximate information on the progress of the process as well as the surface morphology of the fibres prepared can be obtained. Fig. 8 shows a schematic current/potential curve. After passing approximately 800° C (depending on the molar ratio between the reactants, total pressure, rate of power supply, etc.), boron starts to deposit. At the beginning of the deposition process, the formation rate of the tungsten borides is higher than the deposition rate of boron. When the first discontinuity of the curve (see Fig. 8) is approximately reached the nucleation process starts. At the second discontinuity of the curve, the boron nuclei can easily be observed. The first discontinuity is mainly due to a heating effect and can be induced by heating the tungsten substrate in a non-reactive gas or gas mixture. Its position and appearance are dependent on the total pressure, the composition of the gas mixture and the rate of the power supply. Low total

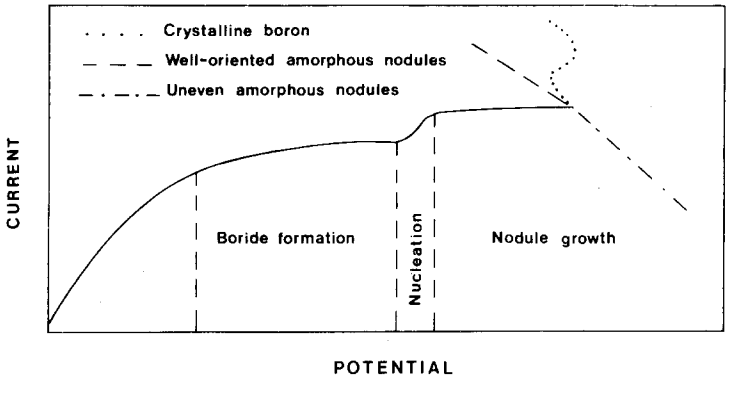

Figure 8 A schematic current/potential curve illustrating the different stages of the fibre growth process.

pressures, a high thermal conductivity of the gas mixture and a low rate of power supply cause an enhanced discontinuity. On observation of the heating of the substrate and the recorder simultaneously it was found that the first discontinuity was obtained when the glowing zone of the substrate, propagating from the centre of the substrate, reached the electrical contacts. At this stage no temperature variations were observed along the substrate except near the contacts. The second discontinuity of the curve is obtained when the substrate is completely coated by boron. The third discontinuity is formed when the power increase is stopped and the process is allowed to continue spontaneously.

By examining the shape of the current/potential curve after the third discontinuity an indication of the surface morphology of the fibre prepared is obtained. The combinations: increasing potential/decreasing current, decreasing potential/increasing current and fluctuating potential around a constant value/increasing current, indicate, respectively, the uneven nodule morphology, the well-oriented nodule morphology and the crystalline morphology (see Fig. 8). The shape of the actual part of the curve evidently roughly reflects the temperature range within which the various morphologies are expected. At high resistances, i.e. low temperatures, the amorphous uneven nodules are expected. At somewhat lower resistances, the radially oriented nodules are formed. The crystalline morphology is finally obtained at the highest temperatures implying the lowest resistances.

3.3. An estimation of the maximum preparation time for preparing high-strength boron fibres

A necessary condition required for high-strength boron fibres is that the whole boron mantle consists of amorphous boron. From the data given in Fig. 7, the maximum preparation times for obtaining 100 μm thick amorphous boron fibres at various temperatures have been calculated. Assuming constant density of the boron deposited ($\rho = 2.30\,\mathrm{g\,cm^{-3}}$ [9]) the deposition rate k, normalized for surface area, is given by

$$k = \frac{\rho}{2} \cdot \frac{\mathrm{d}D}{\mathrm{d}t}$$

where D is the diameter of the fibre and t is time. Neglecting the reaction between the substrate (thickness 14 μm) and the deposited boron, the preparation time t_{prep}, assuming constant deposition rate during the whole process, was calculated from

$$t_{\mathrm{prep}} = 43 \cdot \rho/k.$$

The calculations were repeated for different temperatures. The results of the calculations are summarized in Fig. 9. A preparation time longer than 30 sec at 1300° C causes growth of crystalline boron fibres since the deposition rate is then too low for the formation of amorphous boron (see Fig. 7). At lower temperatures longer preparation times can be utilized. For instance, at 1100° C a preparation time of 210 sec can be employed for obtaining high-strength 100 μm thick boron fibres.

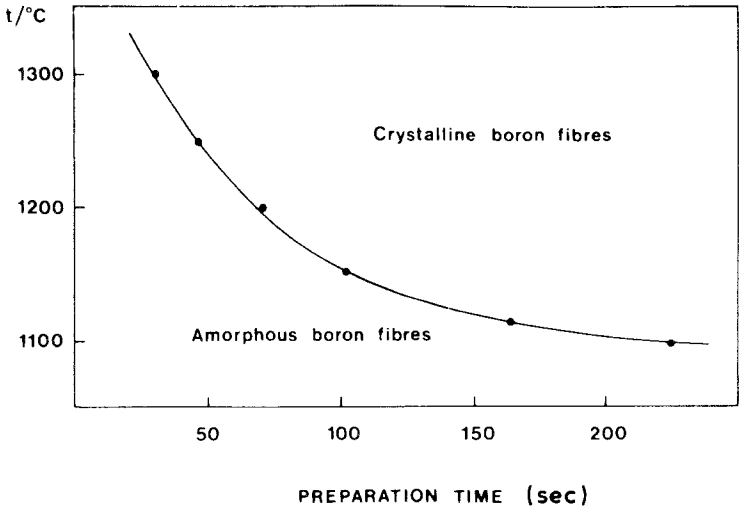

Figure 9 Calculated maximum preparation times for preparing high strength boron fibres at various temperatures (constant deposition rate assumed).

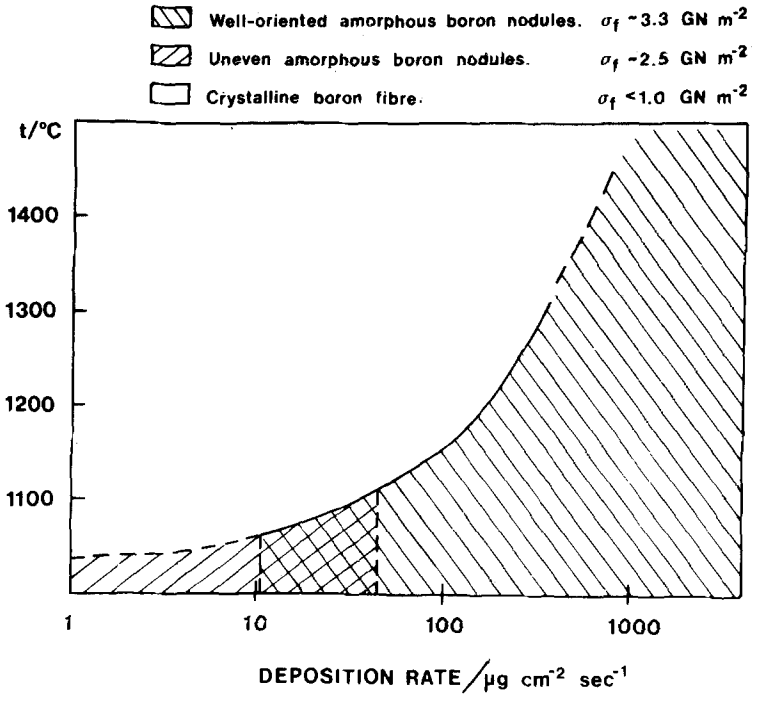

Figure 10 Diagram showing the relation between the average tensile fracture stress (σ_f) and the experimental conditions.

4. Conclusions

The experimental conditions for preparing high-strength boron fibres have been outlined. The correlation between average tensile fracture stress of the fibres and the deposition conditions is evident (see Fig. 10). The strongest fibres ($\sigma_f = 3.3\,GN\,m^{-2}$) are those with a radial orientation of the amorphous nodules. Formation of uneven amorphous nodules causes a reduction of the average tensile fracture stress to approximately $2.5\,GN\,m^{-2}$ [6]. Random nodule orientation (obtained on crystalline boron) as well as crystalline surface morphologies, reduce the strength of the fibres considerably ($\sigma_f < 1.5\,GN\,m^{-2}$ and $\sigma_f < 1.0\,GN\,m^{-2}$, respectively). The standard deviations of the fracture stresses given are approximately $0.6\,GN\,m^{-2}$.

A recording of the current/potential curves during the preparation process yields reliable information on the morphology of the fibres grown and thus on their mechanical properties. Finally, calculations of the maximum deposition time for producing high-strength 100 μm thick boron fibres at a specific temperature allow the choice of suitable experimental conditions.

Acknowledgements

The author wishes to express his gratitude to Professor S. Rundquist and Dr T. Lundström for valuable comments on the manuscript.

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Received 28 March and accepted 11 May 1979.