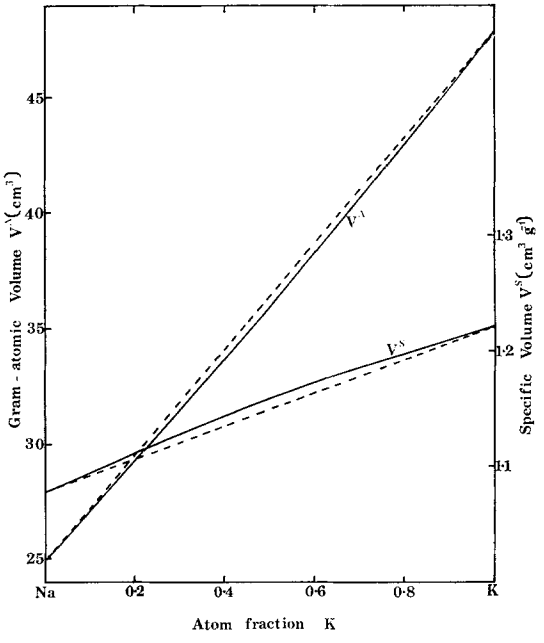


*Figure 1* Plots of gram-atomic volume $V^A$ and specific volume $V^S$ against atom fraction for the liquid alloy system Na-K at 100°C. The dashed lines represent the linear interpolations between the values for the pure components.

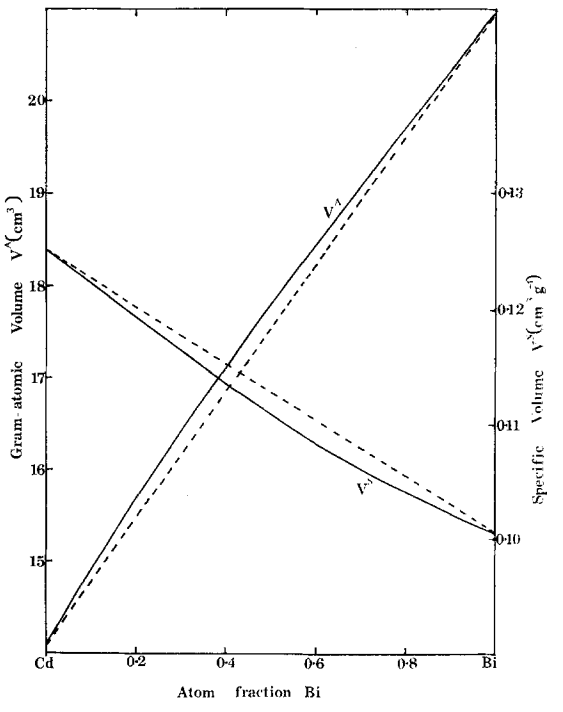


*Figure 2* Plots of gram-atomic volume $V^A$ and specific volume $V^S$ against atom fraction for the liquid alloy system Cd-Bi at 350°C. The dashed lines have the same significance as those in Fig. 1.

misinterpretation when plotted as specific volume against atomic concentration and serve to emphasize that this method of plotting should be avoided.

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*Received 3 July*
*and accepted 30 July 1973*

H. A. DAVIES
*Department of Metallurgy,*
*University of Sheffield,*
*Sheffield, UK*

## *The effect of cooling rate on the mechanical properties of PAN-based carbon fibres*

It has been postulated that the decrease in fracture strength exhibited by polyacrylonitrile (PAN) precursor carbon fibres on heat-treatment above 1500°C is related to the formation of cracks, particularly in the less well-ordered core regions of the fibres, during cooling from the final heat-treatment temperature [1-3]. More recently, transmission electron microscopy was used to indicate that a high proportion of voids associated with the core regions of the fibre might represent the primary factor in relation to fibre strength [4]. The origin of such voids is obscure, but it seems unlikely that their formation is associated with cooling [5].

The present experiment was designed to examine whether the cooling cycle has any significance in relation to fibre strength. If flaws occur during cooling owing to the anisotropic

TABLE I Influence of cooling rate from 2000°C on the fracture strength and Young's modulus of carbon fibres (standard deviations shown in brackets)

| Maximum heat-treatment temperature (°C) | Cooling rate (°C $min^{-1}$) | No. of fibres tested | Mean diameter (μm) | Mean fracture strength (GN $m^{-2}$) | Mean Young's modulus (GN $m^{-2}$) |
|---|---|---|---|---|---|
| As received | Unknown | 80 | 8.5 (0.9) | 2.86 (0.67) | 215 (19) |
| 2000 | 2 | 90 | 8.4 (0.7) | 2.78 (0.51) | 315 (21) |
| 2000 | 27 | 140 | 8.2 (0.9) | 2.30 (0.71) | 304 (28) |
| 2500 | Unknown | 76 | 7.7 (0.6) | 2.05 (0.66) | 389 (46) |

TABLE II Comparison of mechanical properties of carbon fibres cooled at 2 and 27°C $min^{-1}$ from 2000°C ($P$ is the probability of equivalent sets of data yielding the determined mean values)

| Comparison between fibres cooled at 2 and 27°C $min^{-1}$ | Degrees of freedom | Student's $t$ | $P$ | Significance of difference |
|---|---|---|---|---|
| Fracture strength | 228 | 5.53 | $\ll 0.1\%$ | Very high |
| Young's modulus | 228 | 3.15 | $\ll 1\%$ | High |

thermal contraction of crystallites, then a reduction of the time during which such stresses can be accommodated should result in a decrease in the fracture strength of the fibres. Stresses must be accommodated to some degree by plastic flow at the higher temperatures ($\gg 1500$°C so that an increase in cooling rate should prevent such accommodation. Fibres were, therefore, heated to the maximum temperature which we could obtain with good control (2000°C), cooled at various rates, and their fracture strengths compared.

A PAN-based carbon fibre produced by Rolls Royce Ltd and heat-treated to about 1060°C was used as the starting material. This fibre has a mean fracture strength of 2.86 GN $m^{-2}$ and a Young's modulus of 215 GN $m^{-2}$. Small batches of fibre were heat-treated in a Brew furnace in an atmosphere of helium to a temperature of 2000°C, and held at temperature for 1 h. Some batches were then cooled at an average cooling rate of 27°C $min^{-1}$ by switching off the furnace power. Other fibres were cooled at a rate of 2°C $min^{-1}$ by controlled reduction of power to the furnace. Single fibres were tested in a Tecam microtensile testing machine [6] using a gauge length of 1 cm.

The results of tensile tests performed on the as-received fibres, on fibres heat-treated at 2000°C and cooled at 27°C $min^{-1}$, and on fibres known to have been heat-treated to 2500°C in a similar process to that used in commercial fibre production,* are shown in Table I. The significance of these data was examined by "Student's $t$-test", and is summarized in Table II.

These data clearly indicate that cooling rate has an important effect on the fracture strength of fibres heat-treated to 2000°C. Fibres cooled at 2°C $min^{-1}$ show superior fracture strength compared to those cooled at 27°C $min^{-1}$. Young's modulus was also found to be significantly lower in fibres cooled at the faster rate. This observation may be explicable in terms of the elastic opening of the flaws induced by the more rapid cool [1-3, 7], but could be owing to the fact that the more slowly cooled fibre had a longer residence time at temperatures where structural modification leads to improved Young's modulus In the case of fracture strength, however, longer residence time at these temperatures, i.e. slower cooling, might be expected to result in lower strengths (as Young's modulus increases, so strength is reduced), and this consideration provides further indication of the importance of cooling rate.

Whilst the significant effect of cooling rate on fracture strength is clearly established by these results, there is no clear evidence concerning the

*This fibre was obtained from the Royal Aircraft Establishment, Farnborough, UK, who developed the NRDC patent process [8] for the production of carbon fibres from PAN.

actual mechanism of flaw formation. The possibility that these results could be explained in terms of thermal shock (i.e. the production of internal stresses due to a temperature gradient within the fibre) cannot be dismissed, although the following factors cast some doubt on this possibility: (a) the fibres have a small diameter (~8 μm) and good thermal conductivity; (b) although little thermal shock can have occurred in the case of the fibre cooled from 2000°C at 2°C $min^{-1}$, its strength is reduced compared to the original fibre, indicating the likelihood of another mechanism for flaw formation; (c) recent work by Bullock [9] showed flaw formation to be associated with rapid temperature change, but his results give clear evidence [10, 11] that thermal shock effects did not cause the flaws. The results were, however, explicable in terms of the crystallite interaction model of Jones and Duncan [1-3].

We can be certain then, that the voids observed by electron microscopy [4] do not represent the sole factor governing fibre strength. It seems likely, however, that the flaws generated during cooling will often be associated with existing voids and, for this reason, the voids probably represent an important structural factor in relation to the influence of cooling rate on fibre strength.

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*Received 21 August*
*and accepted 1 September 1973*

B. F. JONES*
R. G. DUNCAN
*Atomic Energy of Canada Limited,*
*Whiteshell Nuclear Research Establishment,*
*Pinawa, Manitoba, Canada*

*Now at Admiralty Materials Laboratory, Poole, Dorset, England.

## *On a statistically-designed nickel-base alloy*

In a paper a few years ago, Collins *et al* [1] described the development of the alloy NASA TRW VI A through the application of statistically-designed experiments. By having recourse to such experiments they were able to screen the effects of fourteen elements in about a 2 year period, and so produce an alloy which is amongst the strongest nickel-base superalloys presently available [2, 3]. It is strengthened by two MC-type and one $M_{23}C_6$-type carbide together with $\gamma'$ [4].

The experiments which were used fell into five series and comprised two types: the preliminary studies (series I-III in their notation which we retain) were based on Latin Square designs and were followed by a detailed optimization (series IV and V) using the fractional factorial approach. The results of the latter were then incorporated into a regression analysis for the four most effective elements, namely Cr, W, Ta and Hf. The stationary point of the resulting equation was labelled alloy VI A, tested experimentally, and found to be better than all development alloys.

As part of a study on the use of statistical design in alloy development, we have re-examined the design and analysis of these experiments of Collins *et al* [1]. The object of the present note is to point out that the analysis of their Latin Square designs is incorrect and to remark on the consequences of a corrected analysis. It should be pointed out at this stage that the final alloy VI A is not affected by the revision.

In their study, Collins *et al* [1] cast-up each alloy melt as a tensile bar cluster. These preforms were then ground down into test samples, some of which were tested as follows:

(a) SRL: stress rupture life (three samples) at