molecules which go through to other crystalline domains. These connections can be fixed by irradiation with Co^{60}, to relatively small doses, in our case 12 or 30 Mrad. Non-irradiated material molten in glycerine shows the same affine transformation but after a longer annealing time it progressively loses its original shape (Fig. 1e, annealing time 1000 min at 135°C). If molten immediately above the melting point only partial transformation takes place. In Fig. 1c the rod is oriented orthogonal to the drawing plane and only its right hand part has returned towards the platelet-like shape.

The observed phenomenon proves that in nature there exist polymers which in the liquid state do not lose their macroscopic shape and have a "memory" which allows them to re-obtain it if affinely deformed. By small-angle X-ray scattering it has been made evident that this transformation takes place down to colloidal dimensions, whilst on the atomic scale much more complicated transformations are observed [2, 3]. With no regard to this, the small crystalline regions act as the nodes in rubber-like networks and cause rubber-like elastic behaviour of the colloidal superstructure.

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References

1. I. L. HAY, and A. KELLER, *Kolloid-Z.&.Z. Polymere* **204** (1965) 43.
2. N. KASAI and M. KAKUDO, *J. Polymer Sci.* **A2** (1964) 1955.
3. R. CORNELIUSSEN and A. PETERLIN, *Makromol. Chem.* **105** (1967) 192.

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R. HOSEMANN
J. LOBODA-ČAČKOVIĆ
H. ČAČKOVIĆ

Fritz-Haber-Institut der Max-Planck-Gesellschaft Berlin, Germany

An interpretation of radiation effects on mechanical properties of carbon fibres based on a "sheath" and "core" model of fibre structure

The effects of diameter on tensile strengths and Young's moduli of carbon fibres have recently been explained [1-3] on the basis of a "sheath" and "core" structure previously proposed for such fibres [4]. It appears that radiation effects on these mechanical properties of carbon fibres are also explainable on the basis of such a fibre structure, as will be outlined in this letter. The tensile strengths [5] and Young's moduli [6] of high strength (HTS) and high modulus (HMS) PAN-based fibres from Courtaulds Ltd are plotted against fast-neutron exposure in Figs. 1 and 2, and percentage strains to failure are plotted in Fig. 3. Previously reported data [7-9] on neutron-irradiated carbon fibres are also shown, where these data have been normalized by factors necessary to make their control values agree with those of the figures.

It is observed that radiation exposure in air has a considerable effect on the strength of the HTS fibre and on the modulus for both fibre types, but it has very little effect on the strength of the HMS fibre. The mechanical properties that are significantly affected by radiation all behave in similar manners, first increasing with exposure above a fast-neutron fluence of about 6×10^{17} n/cm^2 ($E > 1$ MeV) and then decreasing at fluences somewhere above 1×10^{18} n/cm^2 for

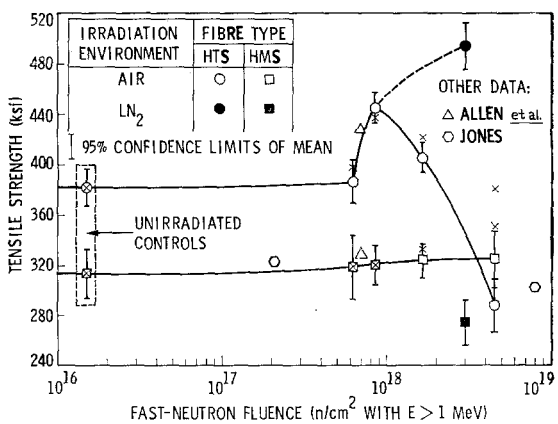

Figure 1 Tensile strengths of carbon fibres for various radiation exposures.

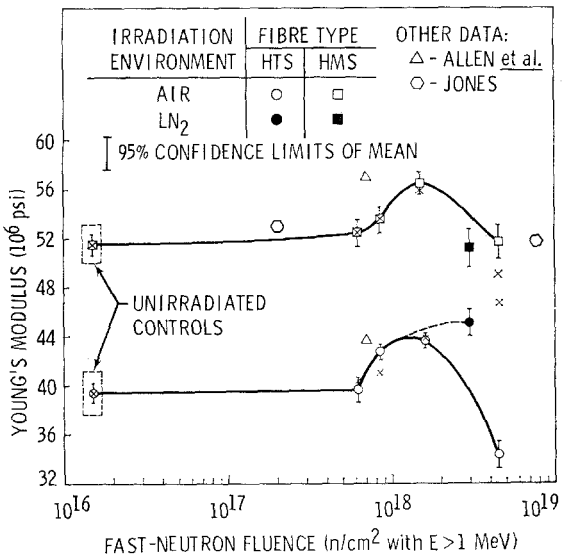

Figure 2 Young's moduli of carbon fibres for various radiation exposures.

air irradiations at ambient temperatures below 80° C. This rise and fall of mechanical properties of fibres with radiation exposure in air is thought to be caused by two competing processes: (1) properties increase initially as carbon atoms are displaced from their lattice sites in basal planes of tightly bound atoms and come to rest in inter-layer spaces between weakly bound planes of turbostratic graphite crystallites, but (2) properties eventually decrease as radiation-enhanced oxidation at resulting vacant lattice sites on fibre surfaces begins to dominate over displaced-atom effects.

Additional support for displacement-oxidation competition in air irradiations is provided by data for fibres irradiated in liquid nitrogen (LN_2) where oxidation does not take place, for room-temperature mechanical properties of HTS fibres irradiated in LN_2 continue to increase smoothly beyond maximum values reached for irradiations in air (dashed sections of curves). In particular, for a fluence of 3×10^{18} n/cm^2, the strength increases over that for unirradiated controls by 30 %, the modulus by 14 %, and the strain to failure by 12 %. More directly still, microscopic observations show that certain sites on surfaces of highly irradiated fibres of both types are preferentially attacked in air to form "pits" as carbon atoms are lost through oxidation degassification, and this surface pitting is not found for fibres irradiated in LN_2.

Thus, there is considerable evidence that mechanical properties of air-irradiated carbon fibres are controlled by displacement-oxidation competition [5, 6], but some of the property changes of the HMS fibre do not seem to have the proper behaviour for such a mechanism. The strength of this fibre changes very little with radiation exposure, neither rising in the displaced-atom regime nor falling in the oxidation regime, the latter finding being in agreement with Johnson's etching studies [10]. Moreover, both the room-temperature strength and modulus of HMS fibres irradiated in LN_2 show a decrease rather than an increase, as for HTS fibres, but it is believed that all of these radiation effects can be explained on the basis of displacement-oxidation competition if the HMS fibre is assumed to have a flawed core whose fracture always causes fibre failure.

According to the sheath and core model [4], graphite crystallites within outer sheaths of

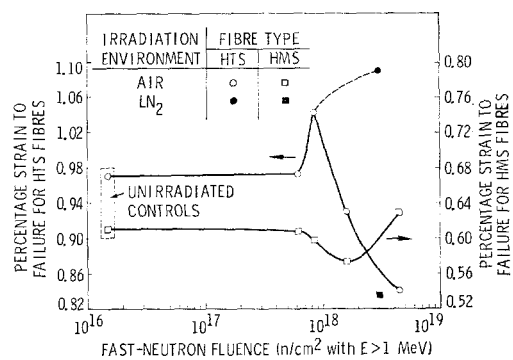

Figure 3 Strains to failure for irradiated carbon fibres.

fibres tend to be larger and better aligned along fibre axes than are crystallites within inner cores of fibres, and this duplex structure becomes more pronounced as the heat-treatment temperature (HTT) of the fibre increases. It has been suggested that thermal stresses during cooling of circular PAN-based fibres cause microcracks in these misaligned cores when the HTT exceeds ~1200° C, and that this is the reason that the strength of such fibres begins to decrease steadily with HTT above that temperature [11]. The HMS fibre (HTT > 2000° C) is known to have a sheath and core structure [12], and the misaligned core of the fibre will be assumed herein to be

TABLE I Mechanical properties for HMS fibres irradiated in air

Fast-neutron fluence $E > 1$ MeV (10^{18} n/cm^2)	Mechanical properties								
	Measured*			Assigned					
	Fibre			Core			Sheath		
	σ(ksi)†	$Y(10^3$ksi)	ϵ(%)	σ(ksi)	$Y(10^3$ksi)	ϵ(%)	σ(ksi)	$Y(10^3$ksi)	ϵ(%)
0	314	51.5	0.610	210	34.5	0.610	400	60.0	0.667
0.62	319	52.4	0.609	213	35.1	0.609	410	61.0	0.672
0.85	320	53.5	0.598	214	35.8	0.598	460	62.3	0.738
1.60	324	56.5	0.573	222	38.7	0.573	440	65.4	0.673
4.50	325	51.7	0.629	255	40.6	0.629	365	57.2	0.638

*These measured values for the core failure of a perfectly elastic fibre which is one-third core and two-thirds sheath are given in terms of assigned values by the formulas:
$Y = (Y_{core} + 2Y_{sheath})/3$ and $\sigma = \epsilon_{core} Y$.
†1 ksi = 10^3psi = 70.3 kg/cm^2 = 6.89 MN/m^2.

flawed to such an extent that its strain capability always determines the fibre failure strain. On the basis of such a model, it is understandable that radiation exposure could first improve and then degrade measured moduli of HMS fibres through sheath changes, without significantly altering their measured strengths which are independent of sheath strengths as long as core fracture always initiates fibre failure.

The data of Table I are supplied as an example to show in more detail how measured mechanical properties of HMS fibres irradiated in air can be satisfied by a flawed-core model. The measured fibre properties are listed first, and then sheath and core properties are assigned in such a way that measured values are satisfied within the framework of the model, where the HMS fibre is arbitrarily assumed to consist of one-third core and two-thirds sheath. The measured modulus should be largely determined by the modulus of the larger, stiffer sheath of the fibre. Therefore, the assigned values of Table I were obtained by assuming the modulus of the sheath to have essentially the same type of dependence on radiation exposure as does the measured modulus of the fibre, with the modulus of the unirradiated sheath being arbitrarily set equal to 60×10^6 psi. In particular, the modulus of the sheath and the modulus of the HMS fibre (Fig. 2) are assumed to have exactly the same shapes until the latter begins to be degraded by oxidation. When oxidation begins, the sheath modulus should fall off more rapidly than the measured modulus does, since the latter includes a contribution from the increasing modulus of the unoxidized core of the fibre. The value of the sheath modulus obtained from normalized HMS data was reduced by 5% for the highest radiation exposure and by 0·5% for the next highest exposure in an attempt to account for this overestimation.

The above assignment of sheath modulus then fixes the less well-known strengths and moduli of the flawed cores of fibres, and these values appear to be perfectly acceptable in all respects. Not being subject to oxidation degradation, these core properties increase steadily with radiation exposure. The resulting core strengths have the same dependence on radiation exposure as do measured strengths of HMS fibres before oxidation begins, as they must have if weak cores are causing fibre failures and if sheath and core moduli are increasing at roughly the same rates, but after oxidation starts the core strengths begin to increase more rapidly than do strengths of HMS fibres because of the decreasing ratios of sheath modulus to core modulus. The core moduli have a dependence on radiation exposure very similar to the measured modulus curve for HTS fibres, taking the appropriate unoxidized branch of the curve (Fig. 2).

Sheath strengths of Table I are completely arbitrary as long as the sheath strain capabilities exceed the core failure strains, and these strengths were assigned roughly the same dependence on radiation exposure that was demonstrated by strengths of HTS fibres (Fig. 1). Thus, one can satisfy the measured strengths and moduli of two-component HMS fibres with four assigned property curves which are very similar

to the four measured curves for HMS and HTS fibres, where the assigned property values of Table I normalized to measured control values are shown by the X's in Figs. 1 and 2. It is interesting to note that with higher levels of radiation exposure in air than have been obtained at present, the sheaths of HMS fibres should eventually be so weakened by oxidation that the fibres would begin to undergo sheath-initiated failure, and according to the assigned values of Table I this failure regime was almost reached. When this occurs, the HMS strength of Fig. 1 should then begin to decrease rapidly with additional radiation exposure, and the strain curve of Fig. 3 after reaching a maximum should then begin to fall off once again.

Based on what has been said to this point, one should expect the strength of HMS fibres irradiated in LN_2 to remain fairly constant and the modulus to continue increasing beyond the maximum value for an air irradiation, but instead they decrease. The lower-than-expected values here are also thought to be caused by the sheath and core structure of the HMS fibre, however, but this is thought to be the result of a radiation-enhanced temperature effect rather than a radiation effect alone. Radiation energy is stored in graphite crystallites of fibres as a result of displaced lattice atoms [13], and this "Wigner energy" [14] begins to be released in the form of heat when the temperature is raised to the point where displaced carbon atoms become mobile and re-enter vacant lattice sites. When carbon fibres irradiated to a fast-neutron fluence of 3×10^{18} n/cm^2 were lifted out of LN_2 into the dense nitrogen vapour ($\sim -140°C$) immediately above the liquid level, this release of stored energy was sufficient to very rapidly raise the temperature of the fibres to more than 175° C. The fibres, which before warming had been stiffened by radiation exposure in LN_2, it is supposed, then cooled off very rapidly in the gaseous nitrogen; it is felt that the resulting thermal shock on the HMS fibre, with its widely different coefficients of thermal expansion for the sheath and core of the fibre, caused additional damage to the already-flawed fibre which resulted in reduced strength and modulus. The more uniform HTS fibre was evidently able to withstand this thermal shock without being damaged. All reported radiation-effects data, then, seem to be explainable by displacement-oxidation competition in conjunction with a flawed-core model for HMS fibres.

References

1. B. F. JONES, 10th Biennial Conf. on Carbon (June 1971). Summary of Papers p. 190.
2. B. F. JONES and R. G. DUNCAN, *J. Mater. Sci.* **6** (1971) 289.
3. B. F. JONES, *ibid.* **6** (1971) 1225.
4. B. L. BUTLER and R. J. DIEFENDORF, 9th Biennial Conf. on Carbon (June 1969). Summary of Papers p. 161.
5. R. E. BULLOCK, *Rad. Effects* **11** (1971) 107.
6. *Idem, ibid*, in press.
7. S. ALLEN, G. A. COOPER, and R. M. MAYER, *Nature* **224** (1969) 684.
8. G. A. COOPER and R. M. MAYER, *J. Mater. Sci.* **6** (1971) 60.
9. B. F. JONES and I. D. PEGGS, *J. Nucl. Mater.* **40** (1971) 141.
10. J. W. JOHNSON, Applied Polymer Symposia No. 9 (1969) 229.
11. C. W. LeMAISTRE and R. J. DIEFENDORF, 10th Biennial Conf. on Carbon (June 1971). Summary of Papers p. 163.
12. L. E. MURR and O. T. INAL, *J. Appl. Phys.* **42** (1971) 3487.
13. R. W. CAHN and B. HARRIS, *Nature* **221** (1969) 132.
14. M. BURTON and T. J. NEUBERT, *J. Appl. Phys.* **27** (1956) 557.

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R. E. BULLOCK
General Dynamics, Convair Aerospace Division Fort Worth, Texas 76101, USA

A new contribution to the equilibrium diagram of the Cu-Se system

The latest systematic examination of the copper-selenium equilibrium diagram has been reported by Heyding [1]. In the range where non-stoichiometric cuprous selenide $Cu_{2-x}Se$ is stable, measurements have been carried out above 80° C only and so the phase relations at lower temperatures are as yet unknown. In this work we used some of the results which we obtained in our general investigations of the semiconducting properties of non-stoichiometric cuprous selenide, i.e. those which are suitable for construction of the unknown part of the equilibrium diagram. In fact, this work is a logical extension of our recent paper about the relation between the electrical conductivity and