JOURNAL OF MATERIALS SCIENCE 32 (1997) 135–139

Effect of sintering temperature on the characteristics of carbons based on mesocarbon microbeads

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A study was conducted to determine the effect of sintering temperature, ranging between 350 and 2700 °C, on the characteristics of carbons made from mesocarbon microbeads (MCMB) of size 4–16 μm, formed in a coal tar pitch by heat treatment at 420 °C for 2.5 h, and separated by solvent extraction using a tar oil. It was found that the MCMB-based carbon plates heat treated to 1000 and 2700 °C possess, respectively, an apparent density of 1.64 and 1.78 g cm^{-3}, a weight loss of 11.5% and 15.3%, a volume shrinkage of 32.4% and 45.0%, an open porosity of 7.6% and 14.0%, a bending strength of 72 and 50 MPa, and an atomic C/H ratio of 30 and 417. The 2700 °C heat-treated plates revealed homogeneity and fine isotropic structure.

1. Introduction

Mesocarbon microbeads (MCMB) have recently increased in importance as a raw material, requiring no external binder, for the production of fine-grained isotropic graphite which finds potential applications as Electric Discharge Machine (EDM) electrodes, electrical brushes and contacts, heaters, crucibles, packings, jigs, hot-pressing dies, nuclear graphite, rocket nozzles, lining for continuous casting of metals and alloys, primary walls in nuclear fusion reactors and other high-technology products [1–4]. Although considerable interest [4–11] is being taken in the above-mentioned MCMB-based fine-textured isotropic graphite because of its excellent performance in the practical tests [3], little has been reported in the literature regarding its developmental aspects. The present authors have reported work [9, 12–14] on the formation of mesophase spherules in low-Quinoline Insolubles (QI) coal tar pitches and their use in the production of high-density monolithic graphite. This work was extended to study the effect of heat-treatment (sintering) temperature on the changes in the physical properties of the carbon plates made from the MCMB (mesophase spherules) generated in a low-QI precursor coal tar pitch by a suitable heat-treatment and separated out of the heat-treated pitch using a suitable tar oil. The present paper gives a detailed account of this study and the results obtained therein.

2. Experimental procedure

A coal tar pitch having 2.5% primary-QI with its characteristics shown in Table I, was heat-treated at 420 °C for 2.5 h to generate mesophase spherules in the pitch. The primary-QI of the precursor pitch was observed under a scanning electron microscope, the photograph of which is shown in Fig. 1. A specimen of the heat-treated (mesophase) pitch was examined on an optical microscope using cross-polarized light and the micrograph obtained is shown in Fig. 2. The heat-treated pitch was extracted with a suitable tar oil to obtain the anisotropic mesophase spherules. These mesophase spherules, also called the "mesocarbon microbeads" (MCMB), were also examined on the scanning electron microscope and the resulting micrograph is shown in Fig. 3. The size-distribution curves of the mesophase spherules were plotted in terms of their differential frequency versus size (histogram) and cumulative frequency versus size, and the same are shown in Fig. 4. The mesophase pitch and the mesocarbon microbeads, were both tested with respect to

TABLE I Characteristics of precursor coal tar pitch, mesophase pitch and mesocarbon microbeads

Characteristics	Precursor coal tar pitch	Mesophase pitch	Mesocarbon microbeads
1. Softening point (°C)	86	–	–
2. Quinoline insolubles (%)	2.5	31.0	92.6
3. Toluene insolubles (%)	21.5	58.0	99.7
4. Coking yield (%)	46.8	67.0	89.2
5. Heat-treatment/ extraction yield (%)	–	80	39
6. Atomic C/H ratio	–	2.06	2.38
7. Mesophase size (μm)			
(a) Predominant range	–	5–15	5–15
(b) Average	–	9.0	9.0

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a number of parameters, and the characteristics obtained are also shown in Table I along with those of the precursor coal tar pitch and the heat-treated pitch.

The mesocarbon microbeads were calcined at a temperature of 275 °C and then hot-moulded into rectangular plates of size 60 mm × 20 mm × 4 mm

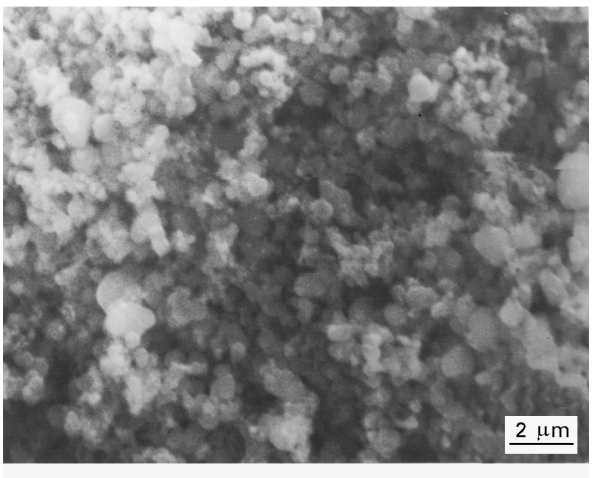

Figure 1 Scanning electron micrograph of the primary-QI separated from the precursor coal tar pitch.

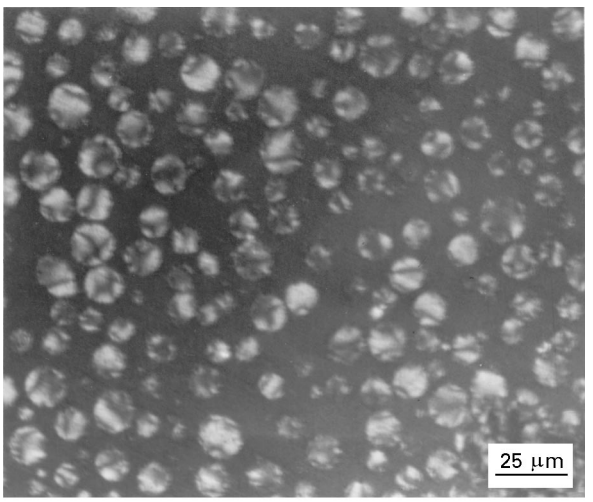

Figure 2 Optical micrograph of the heat-treated (mesophase) pitch.

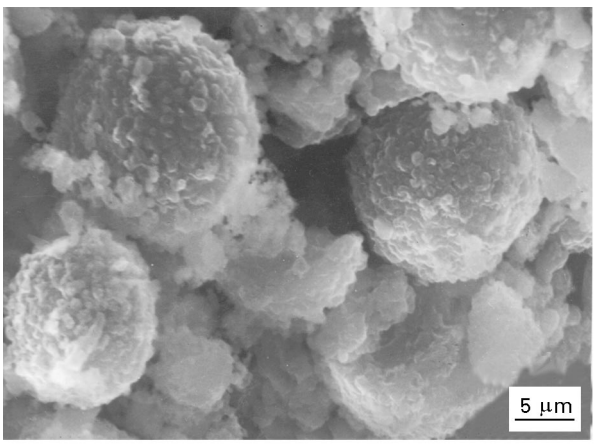

Figure 3 Scanning electron micrograph of the mesocarbon microbeads separated out of the mesophase pitch.

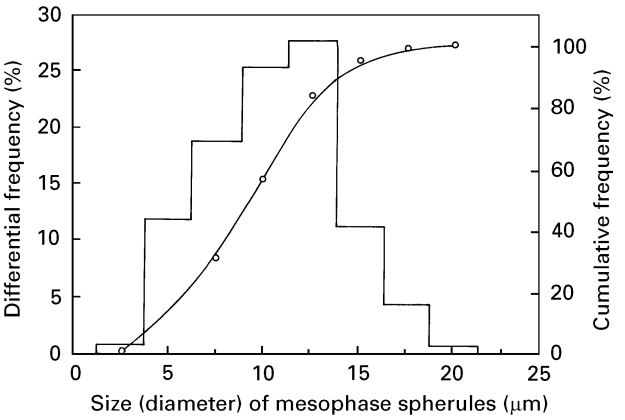

Figure 4 Differential (histogram) and cumulative frequencies of mesocarbon microbeads as a function of their size.

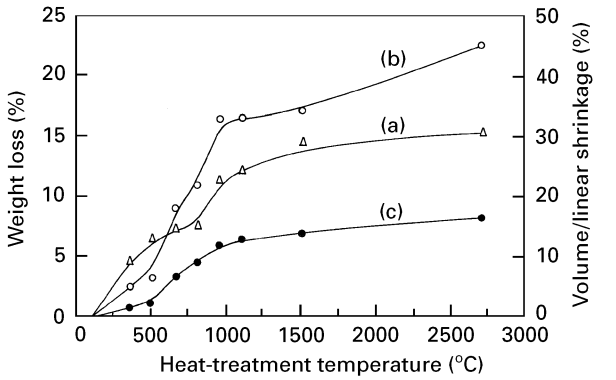

Figure 5 Variation of (a) weight loss (b) volume shrinkage and (c) linear shrinkage of MCMB-based plates with heat-treatment temperature.

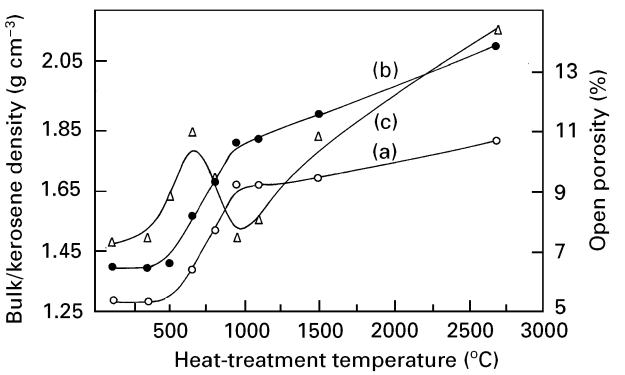

Figure 6 Variation of (a) bulk density (b) kerosene density and (c) open porosity of MCMB-based plates with heat-treatment temperature.

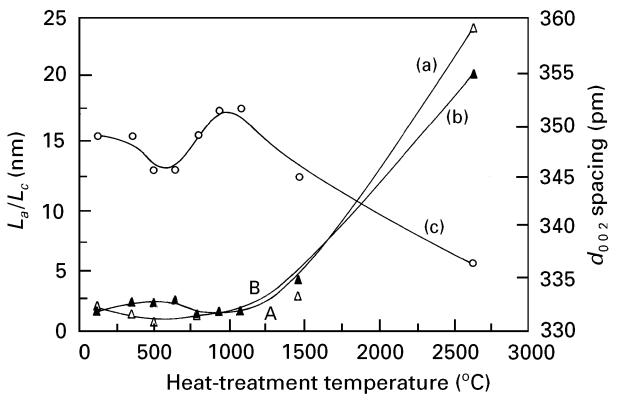

Figure 7 Variation of (a) L_a, (b) L_c and (c) d_{002} spacing of crystallites in materials of MCMB-based plates with heat-treatment temperature.

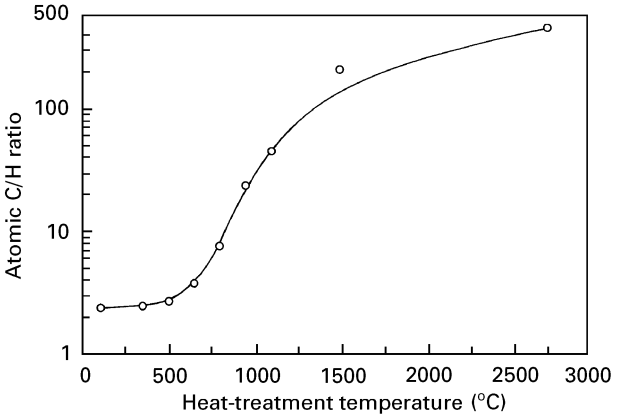

Figure 8 Variation of atomic C/H ratio in materials of MCMB-based plates with heat-treatment temperature.

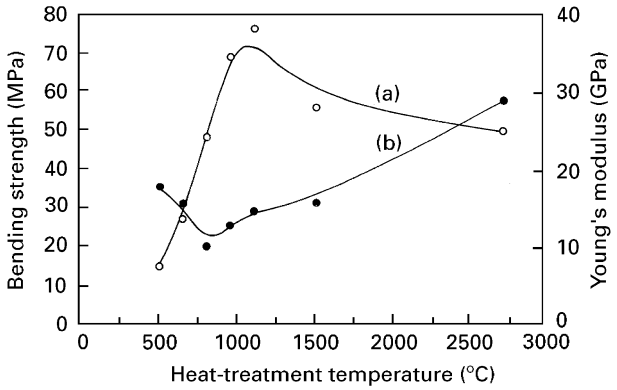

Figure 9 Variation of (a) bending strength and (b) Young's modulus of MCMB-based plates with heat-treatment temperature.

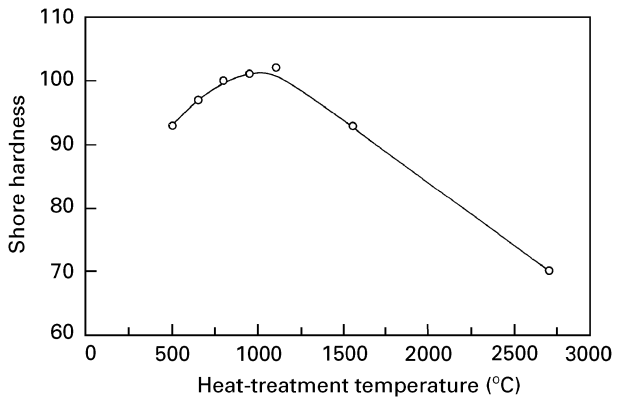

Figure 10 Variation of Shore hardness of MCMB-based plates with heat-treatment temperature.

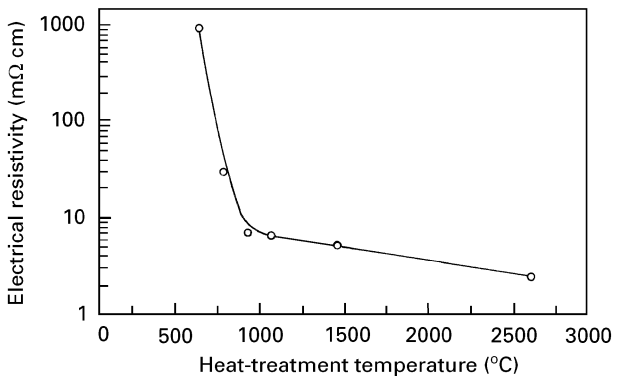

Figure 11 Variation of electrical resistivity of MCMB-based plates with heat-treatment temperature.

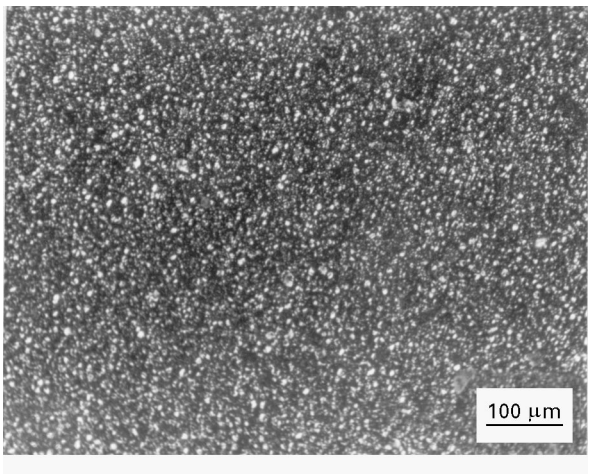

Figure 12 Optical micrograph of the MCMB-based plates heat treated to 2700 °C.

under a pressure of 120 MPa using a conventional hydraulic press. The resulting green plates were carbonized in an inert atmosphere to temperatures ranging between 350 and 2700 °C. The plates, so obtained, were subjected to determinations of weight loss, volume and linear shrinkages, apparent density, bending strength, Young's modulus, Shore hardness, electrical resistivity, open porosity, atomic C/H ratio and crystallite parameters (L_a, L_c and d_{002}). The values of the various characteristics were plotted as a function of the heat-treatment temperature (HTT) and the graphs obtained are shown in Figs 5–11. Besides this, the 2700 °C heat-treated plates were examined on an optical microscope and the micrograph obtained is shown in Fig. 12.

3. Results and discussion

It is seen from Table I that the quinoline and toluene insolubles contents and the coking value of the mesocarbon microbeads are considerably higher than those of the mesophase pitch. This is quite obvious, because the microbeads represent the condensed (denser) component of the mesophase pitch. In addition, it is in agreement with the higher atomic C/H ratio (degree of aromaticity) of 2.38 of the mesocarbon microbeads compared to 2.06 of the mesophase pitch.

The scanning electron micrograph of the primary quinoline insolubles (Fig. 1) clearly shows that these particles have essentially a spherical shape, with a size predominantly below 1 μm. The optical micrograph of the heat-treated pitch (Fig. 2) reveals the mesophase to be in the form of spherules, having a size of 1.3–21.3 μm. The mesocarbon microbeads are observed to be essentially spherical in shape as seen in the scanning electron micrograph (Fig. 3). The differential (histogram) and the cumulative frequency curves of the size distribution of the mesophase spherules (Fig. 4) shows them to have a size lying in the predominant range of 3.8–16.4 μm with an average of 9.0 μm.

The variations of weight loss and volume and linear shrinkages of the monolithic plates with the HTT are shown in Fig. 5. It is seen that the weight loss increases

sharply from a value of 6.2% at 500 °C to 11.8% at 1000 °C, which corresponds to the evolution of various pyrolysis products. Above 1000 °C, however, the rate of weight loss with the HTT decreases gradually and the weight loss reaches a value of 15.3% at 2700 °C. The volume shrinkage, in turn, shows a rapid increase from a value of 6.4% at 500 °C to a value of about 32.4% as the HTT increases to 1000 °C, beyond which, however, the increase is comparatively slow until the highest HTT of 2700 °C, when the volume shrinkage attains a value of 45.0%. The linear shrinkage, as expected, shows an essentially parallel behaviour with the volume shrinkage, with a value of 16.3% at 2700 °C.

Fig. 6 shows the variations of apparent and kerosene densities, and open porosity of the plates with the HTT. It is found that up to an HTT of 500 °C, the apparent density remains almost the same as in the green stage (1.29 g cm^{-3}), above which it increases and attains a value of about 1.64 g cm^{-3} at 1000 °C and finally a value of 1.78 g cm^{-3} at 2700 °C. Up to 500 °C, the effects of weight loss and volume shrinkage nullify each other and result in the constancy of the value of apparent density, as seen from Fig. 5. Above 500 °C, the volume shrinkage dominates the weight loss, and thus increases the density of the plates until the highest HTT of 2700 °C. Further, the kerosene density is found to be always higher than the apparent density, which reflects the presence of some porosity in the plates at all stages of the heat-treatment.

It is furthermore observed from Fig. 6 that the open porosity increases from 7.2% in the green stage to 10.1% at an HTT of 650 °C, beyond which it rapidly decreases to a value of 7.6% at 1000 °C. Above 1000 °C, however, once again the porosity starts increasing continuously, and attains a maximum value of 14.0% at 2700 °C. The increase in the open porosity up to 650 °C corresponds to the evolution of pyrolysis products resulting in the creation of pores, and the decrease (during 650–1000 °C) may be due to the narrowing of these pores as a result of the dominating effect of the volume shrinkage over the weight loss. Finally, the continuous increase in the open porosity during the HTT range of 1000–2700 °C may be attributed to an improvement in the alignment of crystallites, i.e. groups of graphite-like layers (which already exist in carbons based on coal tar pitch), which takes place because of the growth (increase in size) of the crystallites at the cost of disorganized matter between them followed by their rearrangement and fusion. This growth of crystallites is clearly revealed from the results of XRD plots shown in Fig.7, where L_a and L_c are seen to increase from 1.57 and 1.59nm at about 1000 °C to 24.1 and 20.5nm at 2700 °C, respectively. This increase in the size of L_a and L_c results in a corresponding decrease in the d_{002} interlayer spacing from a value of about 351pm at 1000 °C to 337pm at 2700 °C.

Fig. 8 shows the atomic C/H ratio of the plate materials as a function of the HTT on a log centimetre scale. It is seen that this ratio is 2.38 for the green plates which increases slowly to 2.45 and 2.63 at temperatures of 350 and 500 °C, respectively. This may be attributed mainly to the loss of volatile hydrocarbons. Beyond 550 °C, however, this ratio increases rapidly and attains a value of about 3.7 at 650 °C, and 7.6 at 800 °C, which may be due to the removal of relatively lower molecular weight components as well as to the dehydrogenative condensation reactions. Further, above 800 °C, the carbonization proceeds more and more by dehydrogenative reactions leading to a sharp increase in the atomic C/H ratio, which attains a value of about 30 at 1000 °C, and finally a value of 417 at 2700 °C.

The variations of bending strength and Young's modulus with the HTT are shown in Fig. 9. During the heat-treatment from 500–1000 °C, the bending strength of the plates continues to increase almost linearly and reaches a maximum value of 72 MPa at about 1000 °C. This may be attributed to both, a continuous increase in the apparent density of the plates, resulting from an improvement in the densification and bonding between the mesocarbon microbeads, and, in general, to a continuous decrease in the open porosity. Beyond 1000 °C, however, the bending strength shows a gradual fall, right up to 2700 °C, at which point it attains a value of 50 MPa. This may be due to the corresponding increase in the open porosity during this HTT range. The Young's modulus, on the other hand, first decreases from a value of 18 GPa at 500 °C to 10 GPa at 800 °C, after which it increases continuously and attains a value of 29 GPa at 2700 °C.

It may be mentioned here that the values of bending strength of 72 MPa at the HTT of 1000 °C or 50 MPa at 2700 °C obtained in the present study are on the lower side of the values of 90–140 MPa at around 1000 °C [5, 7] or around 100 MPa at 2500 °C [6] and 86 MPa at 2100 °C [7], as observed by the various researchers. This discrepancy may be attributed to two main factors, namely (i) the use of uni-directional moulding employing a relatively lower pressure of 120 MPa by the present authors, compared to isostatic moulding at 200–400 MPa used by the above-quoted researchers [5–7], and (ii) the use of MCMB of higher size (predominant size 4–16 μm, average 9.0 μm) by the present authors as against MCMB of lower size used by other authors [5]. All these factors are of paramount importance in controlling the strength of the MCMB-based products.

Fig. 10 shows the variation of Shore hardness with the HTT. It is seen that starting from an already high value of 93 at 500 °C, it gradually increases further and attains a maximum value of 102 at 1000 °C, beyond which, however, it decreases almost linearly, attaining a value of about 70 at the final HTT of 2700 °C. It is interesting to note here that the variation of the hardness follows a pattern similar to that of the bending strength.

Fig. 11 shows the variation of electrical resistivity with the heat-treatment temperature. It is seen that the electrical resistivity of the plates undergoes a steep fall from 933 mΩ cm to 30.6 mΩ cm as the HTT increases from 650 °C to 800 °C. Beyond 800 °C, however, it decreases gradually to 7.1, 4.9 and 2.4 mΩ cm at the temperatures of 950, 1550 and 2700 °C, respectively.

This is what is expected, because the material is gradually becoming converted from a molecular solid to graphite.

Finally, Fig. 12 shows that there is homogeneity and fine isotropic texture in the MCMB-based plates heat-treated to 2700 °C. It is expected that all the characteristics of the carbons, including homogeneity and fine isotropic texture, would be improved considerably if the compaction of the mesocarbon microbeads was done using an isostatic press in place of the conventional (uni-directional) press employed in the present study.

4. Conclusions

1. The carbon plates heat-treated to 1000 and 2700 °C exhibit apparent density of 1.64 and 1.78 $g\,cm^{-3}$, with weight loss of only 11.5% and 15.3%, and enormous volume shrinkage of 32.4% and 45.0%, respectively.

2. The open porosity has a value of 7.6% at an HTT of 1000 °C which is close to its minimum value of 7.2% in the green stage, and a maximum value of 14.0% at an HTT of 2700 °C.

3. The atomic C/H ratio of the plates increases from an initial value of 2.4 in the green stage to 30 and 417 at the HTT of 1000 and 2700 °C, respectively.

4. The bending strength is found to have a maximum value of 72 MPa at an HTT of about 1000 °C, above which it decreases gradually to attain a value of 50 MPa at 2700 °C.

5. The plates heat-treated to 2700 °C reveal homogeneity and fine isotropic texture.

Acknowledgements

The authors thank Professor E. S. R. Gopal, Director, National Physical Laboratory, New Delhi, for his keen interest in the work and the permission to publish this paper. Thanks are due to Dr D. K. Suri and Mr K. Rawat for their help in the X-ray diffraction and SEM examinations of the samples, respectively. One of the authors (NP) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship.

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Received 31 May 1995
and accepted 2 July 1996