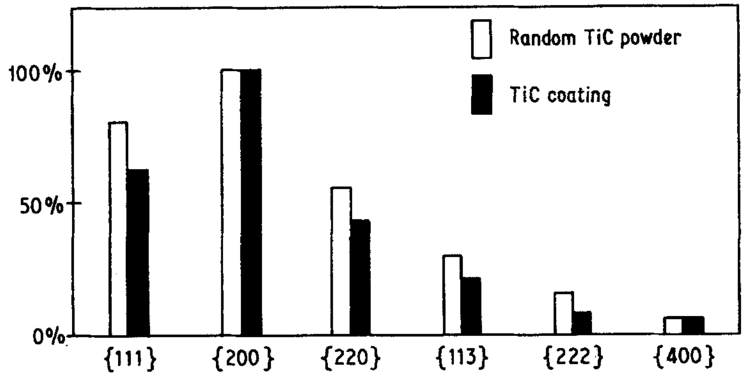

Figure 3 Relative X-ray line intensities from the TiC coating compared with the random X-ray intensities from a TiC powder.

intensities measured from fine grained TiC powder. The figure shows that the reflections from the TiC layer have rather a similar distribution to those from the random TiC powder, except those from the {2 0 0} crystal planes, which are slightly preferred in the layer.

A thin layer of TiC can be successfully deposited onto the surface of glass-like carbon by means of CVD. TiC forms a thin, adherent and wear resistant coating on the substrate. Furthermore, this continuous and even coating eliminates the disadvantageous effect of porosity on the surface of the glass-like carbon.

Acknowledgements

One of the authors (RA) is indebted to the Emil Aaltonen Foundation and the other (JR) to the Foundation of Finnish Inventions for financial support.

References

1. D. W. McKEE, *Ann. Rev. Mater. Sci.* 3 (1973) 195.
2. G. M. JENKINS and K. KAWAMURA, "Polymeric Carbons – Carbon Fibre, Glass and Char" (Cambridge University Press, Cambridge, 1976).
3. J. RAUTAVUORI and P. TÖRMÄLÄ, *J. Mater. Sci.* 14 (1979) 2020.
4. *Idem,* US Patent 4188369 (1980).
5. B. L. MORDIKE, *Wear* 3 (1960) 374.

Received 2 December 1980
and accepted 5 February 1981

R. AHLROTH
J. RAUTAVUORI
P. TÖRMÄLÄ
P. KETTUNEN
Institute of Materials Science,
Tampere University of Technology,
PO Box 527, SF-33101 Tampere 10,
Finland

Ageing of sintered $Bi_2Te_{2.7}Se_{0.3}$ thermoelements containing AgI

Thermoelements, consisting of alloys of Bi_2Te_3 have been prepared by a low-cost sintering process. Samples of dimensions 4 mm × 4 mm × 20 mm have been produced by cold-pressing powders of the alloys having particle sizes in the range 100 to 250 μm at a pressure of 1.6×10^6 kPa. The samples have then been sintered at temperatures of 420° C or higher in argon or nitrogen for 6 h. The final density was about 95% that of the cast material. The thermoelectric figure-of-merit*, when the carrier concentration was optimized, was not as high as for single-crystal material, but this is due to the random orientation of the grains rather than to the porosity which affects the electrical and thermal conductivity in the same way.

No difficulties were experienced for the p-type alloy $Bi_{0.5}Sb_{1.5}Te_3$ but ageing effects were observed for the n-type alloy $Bi_2Te_{2.7}Se_{0.3}$ when doped with AgI. These effects were unexpected

---

*Thermoelectric figure-of-merit = $\alpha^2\sigma/\lambda$, where α is the Seebeck coefficient, σ is the electrical conductivity and λ is the thermal conductivity.

0022–2461/81/092632–03$02.30/0

since AgI and similar compounds (e.g. CuBr) have been successfully used as donor impurities in the past [1,2].

It was found that about 0.15 at % of AgI was needed to produce the optimum carrier concentration for thermoelements intended for use in generators working up to about 150° C but a rather wide variation in electrical conductivities and Seebeck coefficients was observed and these properties were subsequently found to vary with time after storage of the samples at room temperature. Fig. 1 shows the time dependence of the electrical conductivity at 300 K for two samples, Samples A and B, that had been sintered at 420° C and 522° C, respectively. The electrical conductivity of another sample, Sample C, that had been accidentally heated to close to the melting temperature so that it developed a smooth surface is also shown in Fig. 1. No significant variation of electrical conductivity with time was noticed for this sample.

The ageing effects observed for Samples A and B are undoubtedly associated with the fact that silver (like copper) diffuses rapidly through crystals of Bi_2Te_3 and its alloys at relatively low temperatures [3, 4]. Indeed, the use of Cu or Ag dopants in single-crystal or cast polycrystalline thermoelements has been avoided by manufacturers because of these diffusion effects. However, it has been assumed that diffusion of Cu and Ag in sintered thermoelements is prevented by the randomness of the orientation of the crystals on either side of the grain boundaries. Our results show that this assumption is not always justified.

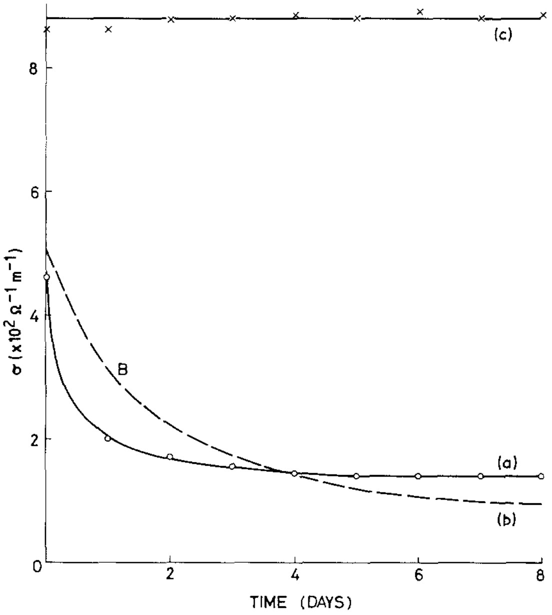

Figure 1 Variation of electrical conductivity measured with time at 300 K for AgI-doped samples. (a) Sample A sintered at 420° C, (b) Sample B sintered at 522° C and (c) Sample C accidentally overheated.

Immersion of samples such as Samples A and B in water showed clearly that, in spite of the relatively high density, the pores are interconnected. Scanning electron micrographs indicate that the pores are sheet-like rather than spherical and this, of course, allows connections between them to occur more readily. Overheated samples, such as Sample C, probably also have interconnected pores but these are isolated from the surrounding atmosphere by the smooth skin, since such samples do not take up water on immersion.

The behaviour can therefore be explained as follows. When AgI is added to $Bi_2Te_{2.7}Se_{0.3}$, the elements dissociate so that both Ag and I can act independently as donors. We think that the Ag ions diffuse to the pores where they react with oxygen to become neutralized. The stable electrical conductivity that is reached after several days corresponds to the oxidation of all of the Ag. This is particularly catastrophic from the thermoelectric device view-point since some of the I also seems to have been lost by evaporation during the initial casting of the alloys. The slower decay of the electrical conductivity of Sample B compared with Sample A is probably due to the partial seal-

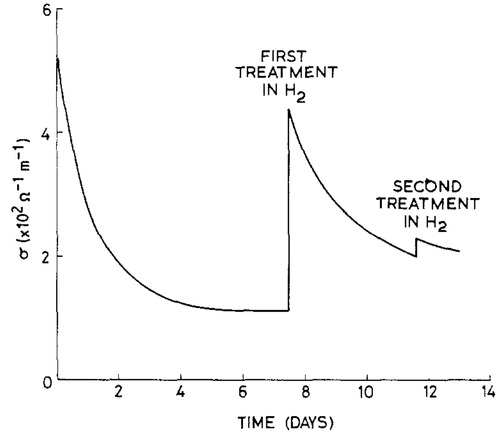

Figure 2 Recovery of electrical conductivity at 300 K on heating in hydrogen.

ing of the pores of the former at its high sintering temperature.

Strong support for our explanation is provided by the recovery of the electrical conductivity on heating an aged sample in hydrogen gas at 150 to 250° C for 0.5 h, as shown in Fig. 2. Presumably the hydrogen reduces the silver oxide content so that Ag ions can again be formed. On removal from a hydrogen atmosphere the conductivity decays once more. It should be noted that recovery of the conductivity in hydrogen is not complete and, as shown in Fig. 2, the hydrogen treatment is less effective when repeated.

In view of the above observations, we have abandoned the use of AgI as a doping agent and have instead employed 0.2 at % of S. There have been no further ageing problems and the resultant figure-of-merit of $2.5 \times 10^{-3}\ \mathrm{K}^{-1}$ at 300 K compares well with the best results that can be achieved using hot-pressed sintered n-type materials [5].

References

1. R. G. COPE and A. W. PENN, *J. Mater. Sci.* **3** (1968) 103.
2. U. BIRKHOLZ, *Z. Naturforsch.* **13a** (1958) 780.
3. R. O. CARLSON, *J. Phys. Chem. Sol.* **13** (1960) 65.
4. T. A. McCARTHY and H. J. GOLDSMID, *Energy Conversion* **10** (1970) 125.
5. H. J. GOLDSMID, "Thermoelectric Refrigeration" (Plenum Press, New York, 1964) p. 200.

Received 6 January
and accepted 26 February 1981

T. DURST
H. J. GOLDSMID
L. B. HARRIS
Department of Applied Physics,
University of New South Wales,
P.O. Box 1, Kensington 2033,
Australia