that the exchange energies and Weiss constants calculated on the assumption of exchange narrowing agree so well with values directly obtained in other ways [8–11].

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Chemical vapour deposition of titanium carbide on glass-like carbon

Many thermosetting polymers pyrolyse to form disordered non-graphitizing carbons with glass-like properties [1, 2]. Glass-like carbon with low porosity can be obtained by slow carbonization of the precursor resin under carefully controlled conditions in the solid state. However, it is impossible to make non-porous glassy carbon artefacts thicker than 3 mm because of fissuring at temperatures at which the greatest evolution of gaseous products occurs [2]. If bulky artefacts of glass-like carbon are required, the preparation conditions must be regulated in such a way that a microporous structure is allowed to be formed [3, 4].

The porosity may be advantageous in some applications (e.g. in filters, in lubricant-impregnated bearings and in human implants) but in many cases it is disadvantageous. It is evident that the disadvantageous effects of porosity can be eliminated in many cases by coating the porous carbon surface with some non-porous material. The glass-like carbon can be coated e.g. by titanium carbide (TiC) using chemical vapour deposition (CVD) as will be reported here.

The use of TiC is mainly based on its high hardness, good wear resistance and to some extent on its corrosion resistance. The hardness of TiC varies between 2900 and 5000 HV depending on its purity, stoichiometry and method of production. The melting point of TiC is rather high $T_m = 3067°$ C. Brittleness at room temperature is a typical feature for TiC, as for all the carbides of transition metals. The brittleness is caused by the sensitivity of TiC to crack initiation and crack propagation. Defects at the surface and internal pores easily lead to crack initiation. This is a consequence of the low mobility of dislocations and of the high Peierls stress in TiC at room temperature. At higher temperatures, above 800° C, however, several slip systems are activated in TiC. This improves the toughness of TiC [5].

These limitations in the plastic properties of TiC do not greatly effect the use of TiC coated glass-like carbon, because TiC and glass-like carbon are rather similar in this respect. Furthermore, thin layers of brittle materials behave in a more ductile manner than bulky materials.

The deposition of the TiC coating is based on the overall equation

$$TiCl_4(g) + CH_4(g) + H_2(g) \xrightarrow{T,P} TiC(s) + 4\,HCl(g) + H_2(g). \quad (1)$$

The most important variables in the CVD process are the total and partial pressures of the reactants, the flow rate, the temperature of the substrate and the reaction time. The CVD process is presented schematically in Fig. 1.

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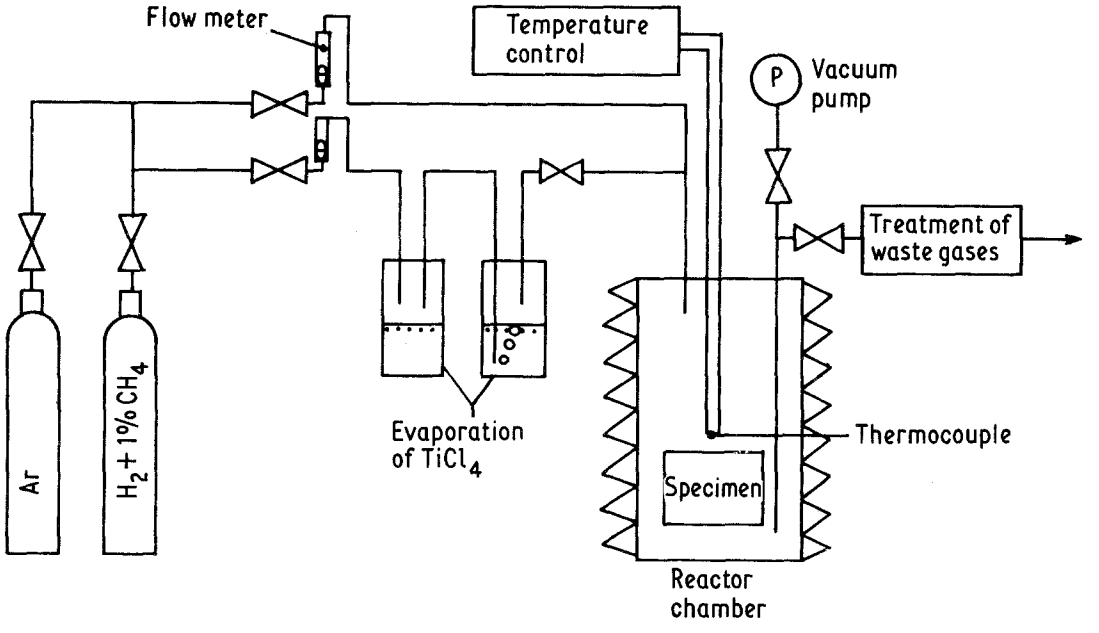

Figure 1 CVD process.

The advantages of the CVD method are its suitability for many different coatings and substrate materials and also for the formation of thin layers on surfaces of complicated shape.

TiC was deposited onto the glass-like carbon by using the CVD method. The deposition was carried out in a hot-wall reactor. According to this method a coating layer is deposited onto heated substrate from gaseous reactants by means of chemical reactions.

The specimens were cleaned and sealed in the reactor. Then the reactor was purified by repeated vacuum evacuation and filling with inert gas. At first, the specimens were annealed in a flowing gas mixture of $H_2 + 1\% CH_4$ before the evaporated $TiCl_4$ was allowed to flow with the gas mixture into the reactor. The deposition conditions are given in Table I.

In the CVD process, a metallic grey TiC coating was deposited onto the glass-like carbon substrates.

TABLE I Deposition conditions used

Parameter	Value
Temperature	990° C
Total pressure	1 bar
Flow rate of gas mixture	150 ml min^{-1}
Deposition time	50 to 150 min
Thickness of deposition	3 to 10 μm

This coating forms a uniform, even and adherent layer protecting the glass-like carbon.

The qualitative analysis of the TiC coating was carried out by using a scanning electron microscope and an X-ray diffractometer. Fig. 2 gives an example of the TiC coating. The thickness of the TiC layer is 9 μm. This thickness is quite even also at the sharp edge shown in Fig. 2. The relative intensities of the X-ray diffraction peaks from the TiC layer are shown in Fig. 3 together with the

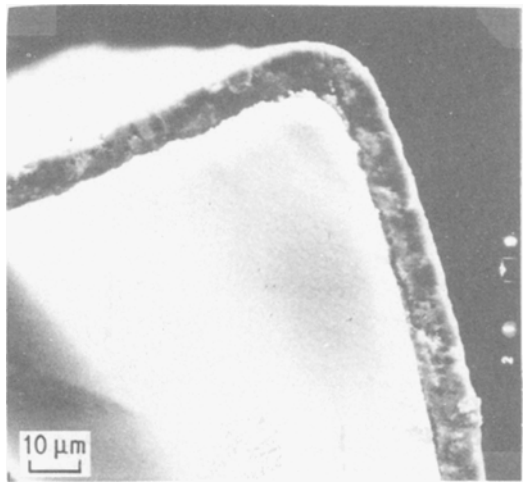

Figure 2 TiC coating on the glass-like carbon. Thickness of the coating is 9 μm, × 660.

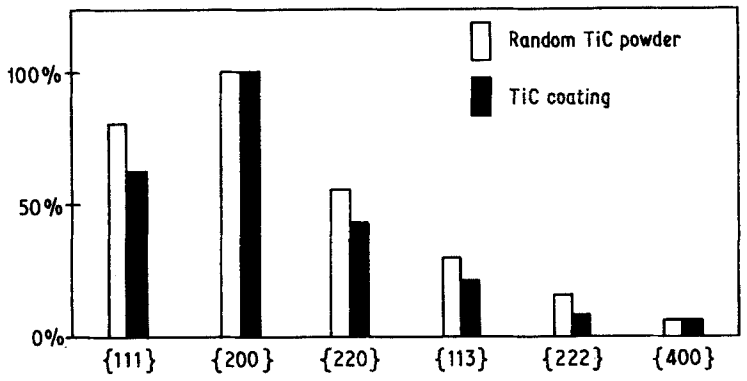

Figure 3 Relative X-ray line intensities from the TiC coating compared with the random X-ray intensities from a TiC powder.

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.

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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 x 4 mm x 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.

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