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Morphological aspects of silicon carbide chemically vapour-deposited on graphite

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The morphological features of silicon carbide coatings, deposited on graphite from $SiCl_4$, C_3H_8 and H_2 mixtures, were investigated. Based on preliminary thermodynamic calculations, the experiments were performed at atmospheric pressure in a cold-wall reactor by varying the deposition temperature T_D in the 1473–1673 K range, and varying the deposition time between 10 and 120 min. Scanning electron microscopy examinations showed considerable differences in surface morphology depending on the process parameters. A transition from a nodular to a faceted structure was observed by moving towards higher T_D values. A double-layer structure was detected on the thickest coatings due to a sharp columnar–microcrystalline transition. The coatings prepared at $T_D = 1673$ K showed surface microhardness values as high as 4000 HK and an optimum capability to protect graphite substrates against oxidation at 1273 K.

1. Introduction

Silicon carbide prepared by chemical vapour deposition (CVD) has recently achieved increasing interest as a high-temperature engineering ceramic, particularly for its high strength and corrosion resistance. It is, therefore, extensively studied as a protective coating on a broad range of substrate materials [1–3]. The CVD silicon carbide–graphite system is particularly interesting, as its use in important industrial applications – such as heat exchangers, furnace resistors, nozzle materials, electrodes [4], and so on – is demonstrating. The protection of a graphite substrate in oxidizing environments is a very critical aspect when high temperatures are involved. It is evident that an important property of the coating material should be its impermeability to oxidizing agents. Free graphite in the coating must then be avoided, as a porous medium can be created when the graphite is released as oxides after oxidation. Furthermore, the presence of free carbon can produce internal stresses which determine microcracks [5]. Since a single silicon carbide phase can be passivated by an impermeable oxide layer only when operating at $T \geqslant 1473$ K [6], a small amount of free silicon could also assure the formation of a sealing oxide layer at intermediate temperatures.

With regard to the microstructure, it is clear that it influences both erosion and corrosion resistance properties of the coating. In particular, a columnar structure is to be avoided in any case, whereas a fine-grained microstructure has to be favoured to some extent in order to increase the microhardness, and therefore the erosion resistance, without affecting the corrosion resistance too much [7].

Among the methods used to prepare SiC coatings, the most widely employed involves the thermal decomposition of methyltrichlorosilane (MTS) [4], due to the presence of carbon and silicon atoms in a 1:1 ratio in the reactant gas. Extensive studies on the morphology of SiC deposited by this method under different experimental conditions have been carried out [8–10]. The main advantage of using alkylchlorosilanes as precursors of SiC is the low decomposition temperature [2] which allows the deposition of SiC on high temperature (> 1273 K) sensitive substrates. With high temperature-resistant substrates (like graphite), gaseous precursors carrying the carbon and silicon atoms separately can be used. The $SiCl_4/C_3H_8/H_2$ system is worthy of interest as it affords high SiC deposition rates on graphite in the high-temperature range ($T \geqslant 1573$ K) [11].

The aim of the present work is to identify the most suitable experimental conditions for the preparation of thick, slightly siliconized CVD–SiC coatings. For this purpose, the morphological and structural properties of the deposited material were investigated and correlated to mechanical (microhardness) and chemical (oxidation resistance) properties. For the surface morphology aspects, a comparison between our results and those reported by Chin [8] was also made.

2. Thermodynamic calculations

In order to find the most suitable experimental conditions, preliminary thermodynamic calculations for the $SiCl_4/C_3H_8/H_2$ system, considering a wide range of process parameters, were performed. For this purpose,

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the SOLGASMIX-PV computer program, firstly devised by Eriksson [12] and subsequently modified by Besmann [13], was used. The thermodynamic approach is based on the minimization of the Gibbs free energy of the total system which, in the present case, consists of the gaseous and condensed species reported in Table I.

Fig. 1 shows the CVD phase diagram obtained at $p_{tot} = 10^5$ Pa and at $H_2/(SiCl_4 + C_3H_8) = 50$ molar ratio in the input gas. The diagram shows the different phase fields which occur as a function of temperature and Si/(Si + C) atomic ratio in the input gas. It is evident that obtaining a slightly siliconized silicon carbide phase at $T \geqslant 1473$ K is critical, as it is restricted to Si/(Si + C) values close to 0.65. The deposition efficiency of the single silicon carbide phase, η_{SiC}, calculated for Si/(Si + C) = 0.65, is reported in Fig. 2, and reaches values of about 100% at $T > 1273$ K. Starting from η_{SiC}, and assuming excess of silicon with respect to carbon input, the thermodynamic growth rate is obtained by [16, 17]

$$\tau = \eta_{SiC}\phi_c M \frac{1}{dS} 6 \times 10^5 \, (\mu m \, h^{-1})$$

where:

ϕ_C = carbon atom molar flow in input (mol min^{-1}); M = SiC mol wt; d = SiC theoretical density (g cm^{-3}); and S = substrate surface area (cm^2).

TABLE I Gaseous and condensed species utilized in the thermodynamic calculations: sources of thermochemical data

Species	Reference
$H(g)$, $H_2(g)$, $CH_3(g)$, $CH_4(g)$, $C_2H(g)$, $C_2H_4(g)$, $C_2H_2(g)$, $Cl(g)$, $Cl_2(g)$, $HCl(g)$, $CH_3Cl(g)$, $CCl_4(g)$, $Si(g)$,	[14]
$Si_2(g)$, $Si_2C(g)$, $SiH(g)$, $SiCl(g)$, $SiCl_2(g)$, $SiCl_3(g)$, $SiCl_4(g)$, $SiHCl_3(g)$, $SiH_2Cl_2(g)$, $Si(s)$, $C(s)$, $-SiC(s)$, $-SiC(s)$ $C_3H_8(g)$	[15]

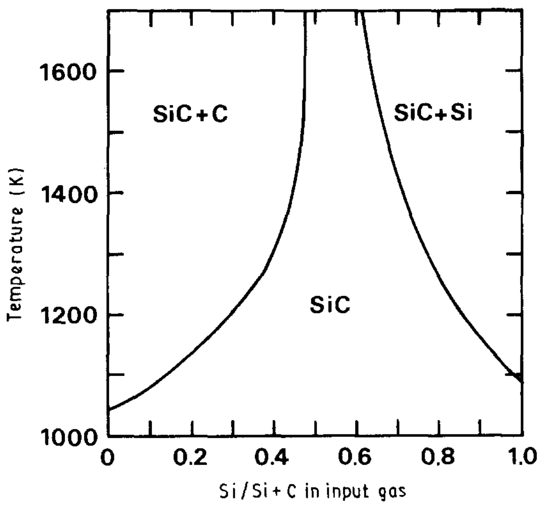

Figure 1 CVD phase diagram of the $SiCl_4/C_3H_8/H_2$ system at 10^5 Pa total pressure and at $H_2/(SiCl_4 + C_3H_8) = 50$ molar ratio in input gas. The phase fields are indicated as function of temperature and Si/(Si + C) molar ratio in input gas.

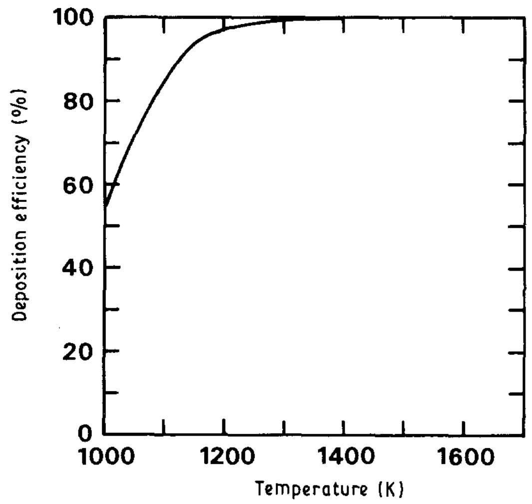

Figure 2 Calculated deposition efficiency of the single β_{SiC} phase as function of temperature at $P_{tot} = 10^5$ Pa and at $H_2/(SiCl_4 + C_3H_8) = 50$ and Si/(Si + C) = 0.65 molar ratios in input gas.

3. Experimental procedure

Refractory graphite type 2239 from Le Carbone, Lorraine, was used as substrate. Mechanically polished disc-shaped samples were 1 mm thick and 20 mm in diameter. The deposition experiments were carried out in a conventional horizontal cold-wall CVD reactor provided with a quartz reaction tube of rectangular section (10 × 5 cm^2). The substrates were placed on an SiC-coated graphite susceptor inductively heated at 450 KHz (RF). The depositions were carried out according to the overall reaction

$$3SiCl_4(g) + C_3H_8(g) + 2H_2(g) \rightleftharpoons 3SiC(s) + 12\,HCl(g)$$

The reactant gas-flow rates were fixed in such a way as to have the following molar ratios in the input gas: $H_2/(SiCl_4 + C_3H_8) = 50$ and Si/(Si + C) = 0.65. Deposition temperatures and times were varied as reported in Table II.

The reported temperatures, T_D, were measured on the samples using a two-colour optical pyrometer just before deposition. The samples prepared for oxidation tests were coated on the whole surface by two deposition runs. The spherical erosion method [18] was used in order to investigate bulk features of the coatings. A steel ball 30 mm in diameter, coated with 1 μm diamond paste, was utilized. Coating thicknesses and grain sizes were obtained from micrographs of cross sections and mechanically polished surfaces, respectively. The micrographs were taken with a scanning electron microscope operating at 6 to 40 kV. In order to detect grain structure of the SiC coating, an electron channelling contrast mode was used in the SEM:

TABLE II Preparation conditions

Total gas pressure	10^5 Pa
Deposition temperature	1473–1673 K
Deposition time	10–120 min
Gas flow rates (FR)	
FR(H_2)	4000 sccm^{-1}
FR($SiCl_4$)	68 sccm^{-1}
FR(C_3H_8)	12 sccm^{-1}

high brightness electron source, low accelerating voltages and backscattered electron detector of high resolution were necessary [19]. With these operating conditions, grain sizes down to about 0.5 μm can be imaged.

Analysis of phase composition and texture was carried out by X-ray powder diffraction (using a standard camera with CuK_α radiation) and morphological characterization by optical and scanning electron microscopy. Knoop microhardness measurements were made using a Zwick 3212 microdurometer. The load used (100 g) assured the absence of any substrate influence on the measurements for most of the examined samples.

The oxidation process was studied by thermogravimetry under isothermal conditions at 1273 K in a high-purity oxygen atmosphere. A 0.1-mg sensitivity thermobalance was used. The 1273 K oxidation temperature allows verification of the capability of the silicon phase to form a protective coating, as silicon carbide is not passivated at this temperature.

4. Results

4.1. Growth rates

Fig. 3 shows the experimental growth-rate curve. The small dependence on temperature of the growth mechanism is limited by mass diffusion in the gas phase [20]. By comparison, the calculated thermodynamic growth rate (see below) was quite constant and equal to 120 $\mu m\,h^{-1}$.

4.2. Morphological and crystallographic characterization

Coating surface morphology was dependent on both deposition temperature and time. At $T_D = 1473$ K, relatively smooth deposits with a needle-like structure [21] (Fig. 4), together with rounded features (Fig. 5), and greater in size at higher coating thicknesses, were observed. At $T_{dep} = 1573$ K, the morphology is essentially rounded columnar (Fig. 6), whereas at $T_D = 1673$ K, a faceted structure grew (Fig. 7). The surface morphology change with temperature (Table III) seems to follow that found by Chin *et al.* for the MTS/H_2 system [8].

All fractured surfaces of the samples prepared at different deposition temperatures and times were analysed by SEM. The thickest coatings prepared at 1573

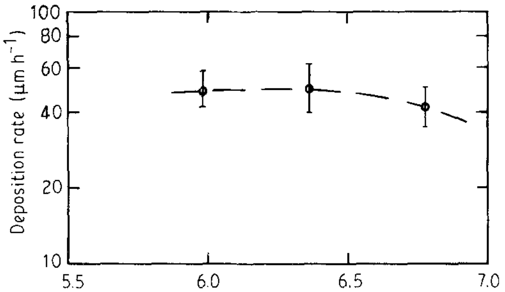

Figure 3 Arrhenius plot of the experimental deposition rate.

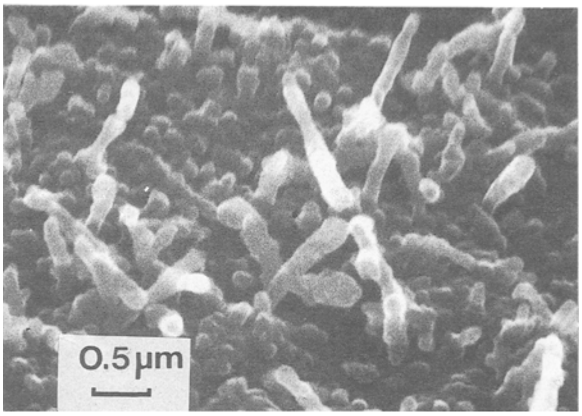

Figure 4 Surface morphology of a 52 μm thick SiC coating deposited at 1473 K.

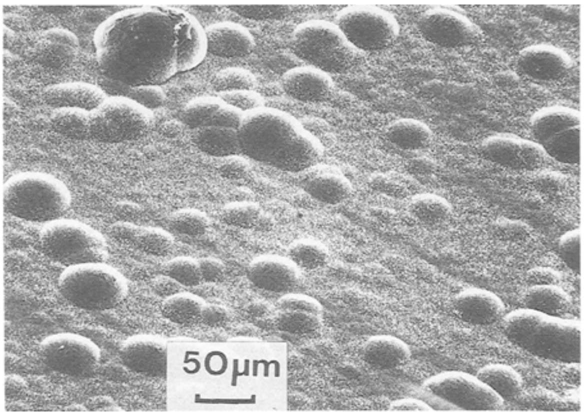

Figure 5 Surface morphology of a 52 μm thick SiC coating deposited at 1473 K.

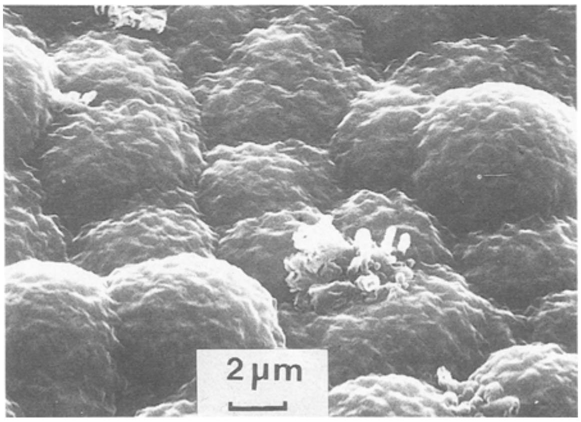

Figure 6 Surface morphology of a 10 μm thick SiC coating deposited at 1573 K.

TABLE III Surface morphology of SiC coatings as observed at different deposition temperatures

Morphological features	T_D(K)
Smooth/rounded columnar	1473
Rounded columnar	1573
Faceted	1673

and 1673 K clearly show a two-layer structure (see Figs 8 and 9), while this is less evident for the coatings prepared at 1473 K (Fig. 10). However, for the 1473 K sample a two-layer structure can also be identified, observing the craters produced after a spherical erosion test (Fig. 11: the inner circle is the graphite substrate and the two dark rings are thin porous interface layers). The first grown layer, adjacent to the substrate, generally shows a columnar morphology (see e.g. Fig. 12), whereas the upper layer always appears fine-grained.

The first layer thickness, measured when the two layers are present, depends on T_D. The following values were measured on thick coatings prepared at

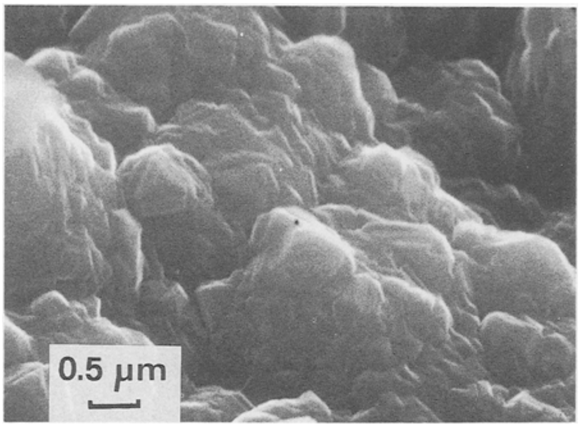

Figure 7 Surface morphology of a 9 μm thick SiC coating deposited at 1673 K.

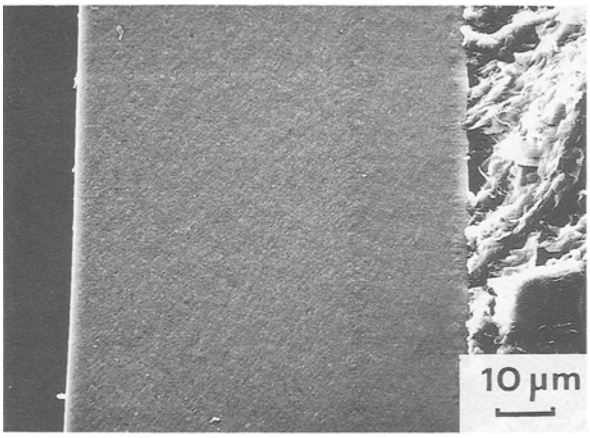

Figure 8 Fracture surface of a 75 μm thick SiC coating deposited at 1573 K.

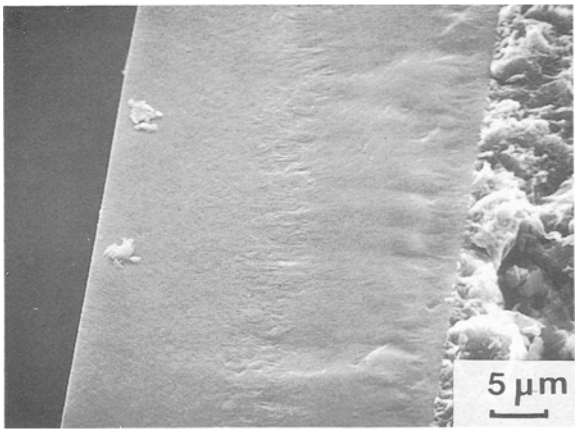

Figure 9 Fracture surface of a 32 μm thick SiC coating deposited at 1673 K.

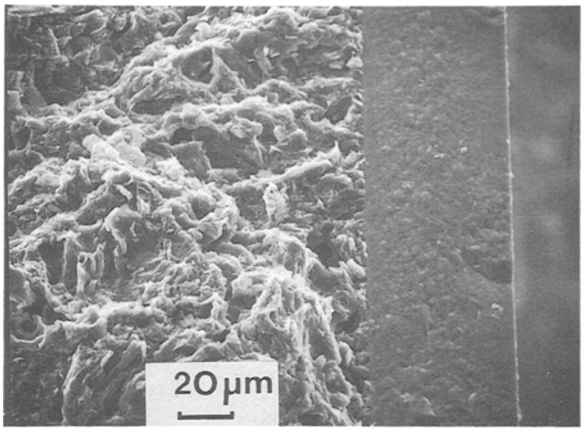

Figure 10 Fracture surface of a 52 μm thick SiC coating deposited at 1473 K.

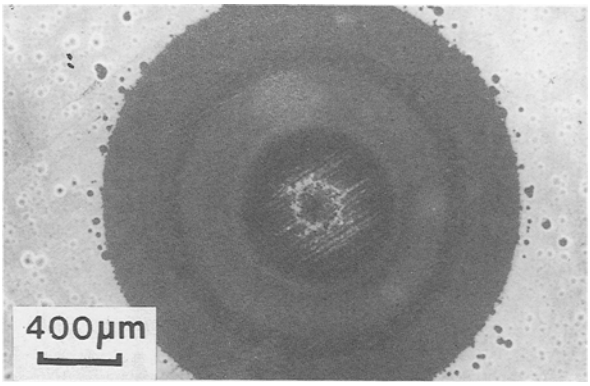

Figure 11 Spherically eroded crater on a sample prepared at 1473 K.

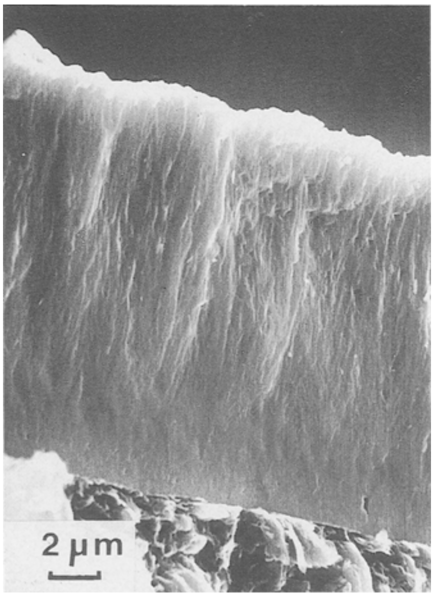

Figure 12 Fracture surface of a 15 μm thick SiC coating deposited at 1573 K.

1473, 1573, and 1673 K: 40, 20, 15 μm, respectively. As shown by X-ray diffraction, a β_{SiC} phase was always detected together with a small amount of silicon, the latter being more evident on the coatings grown at 1573 and 1673 K. Fig. 13 shows, as an example, the X-ray spectrum of the sample reported in Fig. 7. All the X-ray spectra show a preferential orientation towards the [1 1 1] direction, as generally reported [4]. The degree of such preferential orientation, as follows by applying the Harris method [22], undergoes a sharp decrease when going from a single- to a double-layer coating (prepared at the same T_D). Structures obtained at 1673 K generally show the smallest grain sizes (Figs 14 and 15).

4.3. Microhardness measurements

The surface Knoop microhardness of most samples is reported in Fig. 16 as function of coating thickness. All the reported data are unaffected by the substrate, as the ratio between film thickness and indentation depth was always greater than 10 [23]. The values obtained on the samples prepared at 1673 K refer only to the microcrystalline region.

4.4. Oxidation behaviour

The oxidation in flowing oxygen at 1273 K of the samples prepared at 1673 K followed a parabolic law. The average value of the oxidation rate constant was 3.8×10^{-9} g^2 cm^{-4} h^{-1}. This value is consistent with that reported for the oxidation of silicon [24].

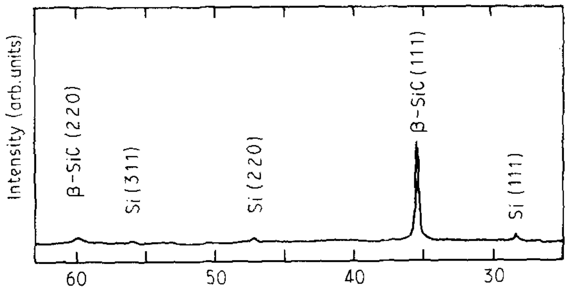

Figure 13 X-ray diffraction pattern (CuK_α) of a 75 μm thick SiC coating deposited at 1573 K.

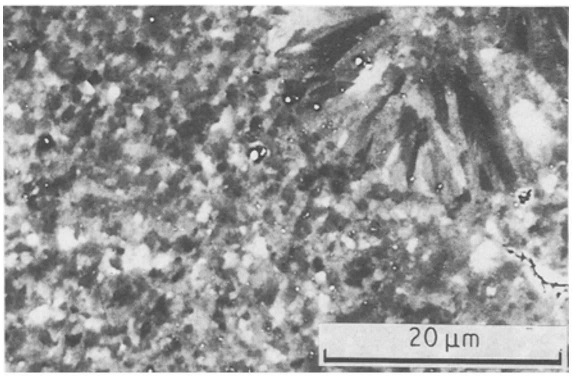

Figure 14 Typical grain structure of a SiC coating deposited at 1573 K.

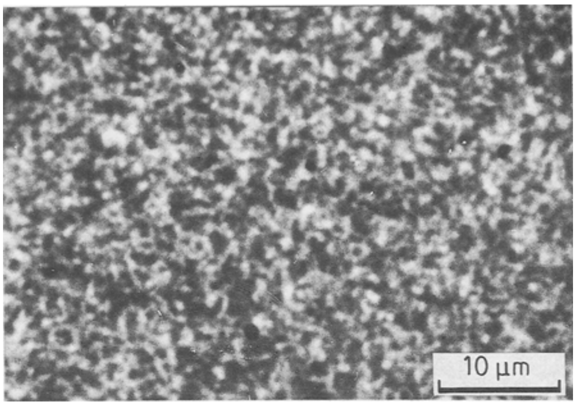

Figure 15 Typical grain structure of a SiC coating deposited at 1673 K.

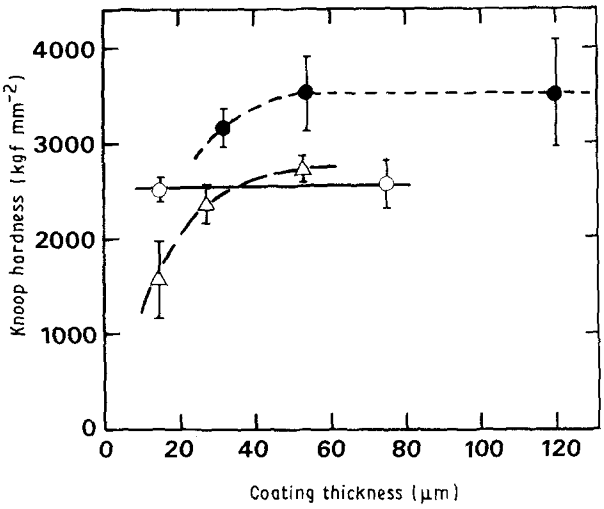

Figure 16 Knoop hardness (100 g load) as function of deposition temperature and coating thickness. T_D = ●, 1673; ○, 1573; △, 1473 K.

5. Discussion and conclusions

The morphological and crystallographic features of silicon carbide coatings, prepared by the $SiCl_4/C_3H_8/H_2$ CVD system at atmospheric pressure, were examined. The results indicate a strong dependence on deposition temperature, from 1473 to 1673 K, of the material characteristics (surface morphology, microstructure) and of its mechanical properties (microhardness). The most relevant aspect is the presence of a double-layer structure on the thickest coatings.

The first-grown layer is generally columnar, whereas the second shows a fine-grained microstructure and a lower degree of orientation towards the [1 1 1] direction. The morphological transition could be attributed to variations in deposition temperature during growth. The control of deposition temperature in growing thick silicon carbide deposits has also been recognized as critical by other authors [25], who demonstrated at some deposition conditions a banded structure inside the coating. Ths surface microhardness depends on deposition temperature, T_D, and coating thickness. The coatings with a single layer show the lowest microhardness values. The coatings with a double layer, on the contrary, show values as high as 2500–3500 HK. The highest values are obtained on samples prepared at $T_D = 1673$ K, in agreement with the very small grain sizes measured on them. The oxidation behaviour of these last coatings agrees well with a material containing a second phase of silicon, as expected from the thermodynamic calculations.

The coatings prepared at $T = 1673$ K and having a thickness $\geqslant 20$ μm could then be suitable for the protection of graphite substrates against erosion and oxidation. The erosion and oxidation resistance are assured by a hard (~ 3500 HK), fine-grained upper layer containing a little excess of silicon.

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