scanning electron microscopy was provided by M. Lortholary. Analyses of the silicon nitride starting powder were carried out by F. Chukukere and hot-pressed sialon materials were prepared by M. N. A. Rahaman.

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ESR linewidths of some iron group ions in MgO

In a recent paper [1] the authors reported a study of intensity and linewidth measurements on the ESR spectrum of Fe^{3+} in MgO. It was shown that very little of the iron contributed to the Fe^{3+} cubic site spectrum, and that taking this into account and analysing the results by means of the Kittel and Abrahams' [2] dipolar theory the experimental linewidths were broadened, rather than narrowed as had been suggested previously [3]. Without more information regarding the bulk of the iron, which does not contribute to the cubic site spectra, it is difficult to say whether this line broadening is a result of interactions with the Fe^{2+} and the clusters, or whether there is some fault inherent in the model used.

In this context it is of interest to look at the linewidths of Co^{2+} in MgO, which were reported by Thorp *et al.* [4]. It would be a difficult proposition to count spins for Co^{2+}/MgO as this would require a dual low temperature cavity arrangement since the Co^{2+} signal only appears at temperatures less than 60 K. However, although Co^{+} can be produced by X-irradiation [5] it is likely that under normal circumstances the cobalt will all be in the Co^{2+} state. We also expect that being divalent it will substitute directly for the Mg^{2+} ions, no vacancy compensation being required; furthermore, there is little likelihood of pairs forming or non-random clustering occurring, as may happen with Ti^{3+}, Cr^{3+} and Fe^{3+}. Consequently, it should be possible in the case of cobalt-doped magnesia to take the manufacturer's concentration, fit this directly into the appropriate calculation, and derive a reasonable comparison between theoretical and experimental linewidths.

Taking account of the Co^{2+} spin = 3/2 and the experimental value of $g = 4.2785$ [6] we obtain from the Kittel and Abrahams equations for second and fourth moments [2] the relationship between the peak-to-peak linewidths ΔH_{ms} and concentrations

$$\Delta H_{ms} = 0.6671 f \text{ (Tesla)} \qquad (1)$$

where f is the cation site fraction i.e. the fraction of magnesium sites occupied by Co^{2+} ions. Conver-

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TABLE I Comparison of predicted and measured linewidths for Co^{2+} in MgO, $\theta_H = 0$.

Dopant concentration (wt ppm)	Cation site fraction (f)	ΔH_{ms} calculated previously (mT)	ΔH_{ms} calculated using KA [2] model (mT)	ΔH_{ms} experimental, measured at 20 K (mT)
310	2.11×10^{-4}	25	0.14	0.8
1250	8.49×10^{-4}	48	0.57	2.1
1900	1.29×10^{-3}	62	0.86	–
2500	1.70×10^{-3}	71	1.13	2.1
3300	2.25×10^{-3}	81	1.50	2.0
4800	3.27×10^{-3}	98	2.18	2.4
8200	5.59×10^{-3}	128	3.73	4.4
9900	6.75×10^{-3}	142	4.5	4.0

sion of the manufacturer's concentration (given as weight ppm) for the samples reported by Thorp *et al.* [4] to cation site fractions, and substition of these values in Equation 1 leads to the calculated linewidths listed in column 4 of Table I. In column 5 of the table, we show the experimental linewidths measured previously at 20 K, and in column 3 the linewidth values calculated using the Van Vleck gaussian model as given by Thorp *et al.* [4].

The Kittel and Abrahams' model gives a good fit with experiment, especially for the higher concentrations (cation site fraction $> 2 \times 10^{-3}$) where it is not merely an order of magnitude fit but also mirrors the change of linewidths with concentration. This is illustrated by Fig. 1, where the points are the experimental values reported by Thorp *et al.* [4] and the line shows the expected behaviour. There is no evidence here for exchange narrowing; the largest departures from theory are in the opposite sense in that for low concentrations the measured linewidths are relatively independent of concentration, and somewhat broader than predicted. It is not clear at present why the lowest concentrations alone should tend to be independent of linewidth, but one might conjecture that once the concentration drops below a certain value direct interactions between the cobalt ions become negligible compared with their interactions with other defects.

On the basis of this result and taking into account our recent conclusions regarding clustering and ESR linewidths in Fe/MgO [1] it would appear that the proposition [7] that the linewidths of some iron group transition metal ions in MgO are dominated by exchange narrowing mechanisms is probably erroneous; it is a curious coincidence

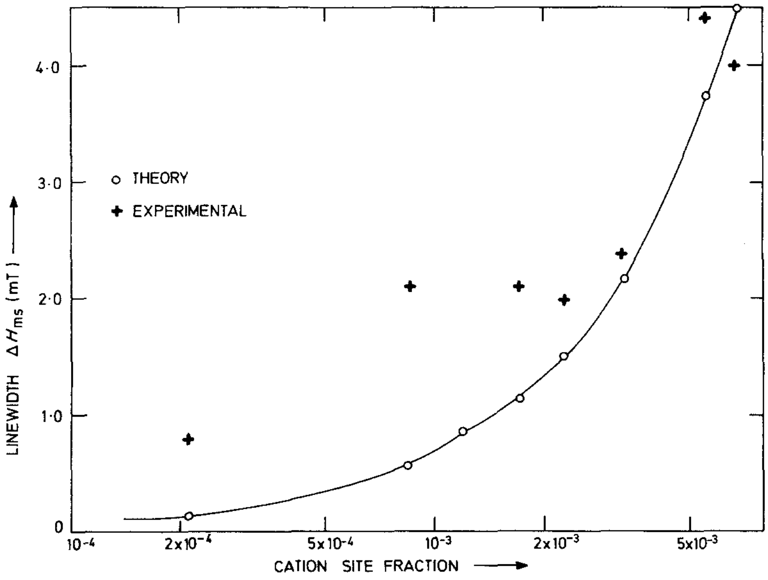

Figure 1 Variation of ESR linewidth with concentration (Co^{2+}/MgO; 20 K, $\theta_H = 0$).

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

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

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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