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Electron spin resonance studies of amorphous and crystallized residues derived from pyrolysis of pre-ceramic polymers

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ESR spectra are presented for pyrolysis residues derived from 5 pre-ceramic polymers: polycarbosilane (PCS), hydridomethylcyclosilazane (HMCS), hydridomethylcyclopolysilazane (HMCPS), polydiphenylsilazane (PDPS) and polymethylsilylethylenediamine (PMSED). The amorphous black and white residues derived from 1100 °C pyrolysis in N_2 and NH_3, respectively, exhibit symmetric peaks with *g* values of 2.003. This is compatible with values obtained for unpaired spins existing in carbon impurities that remain in the ceramic residues after pyrolysis of the organosilicon precursor polymers. The spin concentrations of black residues obtained from pyrolysis of pre-ceramic polymers at 1100 °C in N_2 are invariably higher in magnitude than those measured for white-grey residues generated by initial 1100 °C-NH_3 pyrolysis of pre-ceramic polymers showing that the NH_3 pyrolysis removes polymer-associated carbon more efficiently from ceramic residues than 1100 °C-N_2 pyrolysis. The Si_2N_2O/Si_3N_4 powders produced are purer and have lower ESR activity than commercial Si_3N_4. When the black residues are crystallized at 1550 °C under Ar, carbon is removed and the ESR activity reduced. The ESR signal becomes asymmetric and exhibits some partially resolved structure. Crystallization of white-grey residues is accompanied by an overall increase in ESR activity caused in part by the uptake of carbon from the graphite resistance furnace. For the PCS- and PDPS-derived white-grey residues, additional ESR activity probably arises from the creation of defects in the crystalline Si_2N_2O formed as a result of the 1550 °C firing. In general, ESR properties of the pyrolytic residues correlate well with the relative conducting properties of the corresponding ceramic coatings.

1. Introduction

Electron spin resonance (ESR) studies on amorphous SiC obtained from the pyrolysis of polycarbosilane (PCS) in Ar have been previously carried out by McKenzie and co-workers [1, 2] with the aim of better understanding defect structures in such materials which are of potential use in optoelectronic devices. Spectra were reported to consist of single isotropic signals centred at $g = 2.0030$, which were attributed to carbon-dangling bonds with spin densities in the order of 10^{19} cm^{-3} calculated from the spectra. Spin density was found to increase with firing temperature, reaching a maximum at 1200 °C. Significantly lower spin densities were calculated for samples fired under H_2. The source of the carbon-dangling bonds in the amorphous SiC is excess carbon remaining after pyrolysis of the PCS. In structural and nanotextural studies on Nicalon SiC fibres derived from PCS, Le Coustumer *et al.* [3] reported that the fibres are a microcomposite, 5% by weight which is free carbon composed of isolated aromatic entities less than 1 nm in diameter.

The presence of carbon-dangling bond defects in amorphous SiC can degrade any potentially useful electronic properties such as photoconductivity, for instance, by acting as trapping or recombination centres [4]. Carbon dangling bonds are not the only defects to be detected. ESR studies [4] of hydrogenated amorphous silicon carbide ($Si_{1-x}C_x$:H) films produced by glow-discharge show *g* values of 2.0055 typical of silicon dangling bonds for values of x up to 0.4 At $x = 0.6$, *g* is observed to decrease to 2.003 which is more compatible with carbon dangling bonds.

The purpose of this work is to study the ESR characteristics of various amorphous and crystallized

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residues obtained from pyrolysis of pre-ceramic polymers and to compare the ESR behaviour observed with information gained in allied studies [5–7] on the chemical and physical properties of bulk residues and ceramic coatings formed on various substrates from the pre-ceramic polymers

2. Experimental details

The preparation and spectroscopic characterization of polycarbosilane (PCS), polymethylethylsilylenediamine (PMSED), hydridomethylcyclosilazane (HMCS), hydridomethylcyclopolysilazane (HMCPS) and polydiphenylsilazane (PDPS) have all been described [5]. Amorphous and crystallized residues derived from the pre-ceramic polymers were generated via pyrolysis which is also described in [5]. Polymers pyrolysed initially in N_2 at 1100 °C gave amorphous black residues while polymers subjected to 1100 °C pyrolysis in NH_3 gave white/grey amorphous residues. Additional residue samples were obtained by pyrolysis of the PCS polymer at 700 and 800 °C which gave brown-black and black residues, respectively. Amorphous residues were partially or fully crystallized by heating at 1550 °C for 3.5 to 4 h in a graphite resistance furnace under an atmosphere of flowing Ar gas [5]. After crystallization, black residues turned grey-green in instances, while the white-grey residues occasionally took on a more definitively grey hue. In addition to pre-ceramic polymer residues, commercial samples of Si_3N_4 (Starck LC-10) and SiC (carborundum, British Patent Application 44152/60 were examined by ESR for comparison. The chemical composition of Starck LC-10 Si_3N_4 powder supplied by the manufacturer was by weight Si(59.207%), N(38.6%), Fe(0.012%), Al(0.045%), Ca(0.007%), C(0.18%) and O(1.85%).

All spectra were recorded on a Varian V4502 X-band ESR spectrometer. Samples were examined in tubes in a cavity providing an effective sample length of 1.0 cm. Spectra were acquired in first derivative mode with g values and spin concentrations (in spins g^{1}) measured relative to a "strong" pitch sample as supplied by the spectrometer manufacturer. The "strong" pitch consisted of 0.1% pitch in KCl with a g value of 2.0028, line width of 1.7 G, and a spin concentration of $3 \times 10^{15} \pm 25\%$ spins per centimetre of sample length. Spin concentrations are calculated on the assumption that the number of spins is proportional to product of (peak-to-peak width)^2 × (peak-to-peak height). In the absence of peak fitting, these values of spin concentration are only approximate and are intended to illustrate the relatively significant differences in ESR activity between the black and white/grey residues as well as crystallized and amorphous residues.

X-ray diffraction (XRD) patterns were acquired of powdered ceramic residues using a Philips PD1700 APD system employing a diffracted beam graphite monochromator, automatic divergence slit and CoK_α radiation.

3. Results and discussion

3.1. Black residues obtained from initial pyrolysis in N_2

Table I summarizes ESR data obtained for black amorphous residues. Residues from pyrolysis of PCS in N_2, showed a steady decrease in spin concentration for samples pyrolysed from 700 through to 1550 °C. ESR peaks were usually symmetrical with peak widths decreasing as a function of pyrolysis temperature (see Table I). However, the 1550 °C sample indicated a small increase in peak width due not to broadening but to the appearance of a partially resolved structure. Soraru *et al.* [1] reported that residues from PCS pyrolysis in Ar at 840 °C gave spin densities of 2.5×10^{19} cm^{-3} (or spin concentrations of 1.1×10^{19} spins g^{-1} assuming a density of 2.2 g cm^{-3}) with an ESR peak width of 3.9 G. This is in excellent agreement with the results in the present study although spin concentrations were not maximized at 1200 °C as reported by Soraru *et al.* [1] (see Introduction).

The g values from all ESR spectra summarized in Table I fell in the range 2.0024–2.0037 which are compatible with unpaired spins or dangling bonds on

TABLE I ESR data for black residues derived from pre-ceramic polymer pyrolysis

Sample	Pyrolysis history[a]	Composition (from XRD analysis)	Peak width (Gauss)	g value	Spin concentration (spins g^{-1} × 10^{19})[b]
PCS	700 °C, N_2	Amorphous	5.7	2.0030	4
PCS	800 °C, N_2	Amorphous	4.0	2.0030	3
PCS	1100 °C, N_2	Amorphous	2.4	2.0024	0.3
PCS	1. 1100 °C, N_2 2. 1550 °C, Ar	SiC phase mixture[d]	3.0	2.0037	0.02
PMSED	1100 °C, N_2	Amorphous	3.0	2.0030	4
PMSED	1. 1100 °C, N_2 2. 1550 °C, Ar	SiC phase mixture[d]	2.9	2.0033	0.02
HMCS	1100 °C, N_2	Amorphous	2.95	2.0030	1.3
HMCS	1. 1100 °C, N_2 2. 1550 °C, Ar	SiC phase mixture[d]	2.3	2.0029	0.006
SiC[c]	As-received	α-SiC	6.0	2.0039	0.0002

[a] 1500 °C pyrolyses carried out in alumina crucibles.
[b] Approximate spin concentration values.
[c] Carborundum Co. Ltd commercial SiC powder.
[d] XRD analysis of residue crystallized at 1550 °C.

carbon species. Previous X-ray photoelectron spectroscopy (XPS) studies on amorphous coatings on stainless steel comprising PCS pyrolysed at 700 °C have detected the excess carbon directly as a graphitic-type species, which did not diminish with prolonged Ar ion sputtering of the coating surface [7]. It is strongly believed that the principal mechanism responsible for the reduction in spin concentrations with increasing pyrolysis temperature is removal of the excess carbon as CO. Indeed, allied studies [7] of PCS-derived SiC coatings on stainless steel substrates indicated that such PCS-derived SiC residues generated at 700 °C in N_2 contain a small amount of SiO_2 as indicated by ^{29}Si Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. NMR spectra showed no such SiO_2 peak in bulk SiC residues generated by pyrolysis at 1100 °C in N_2 [5] thus showing that any remaining free carbon is consumed when carbothermal reduction of the SiO_2 in the bulk of the pyrolytic residues occurs (generating SiC and CO) over the temperature range 700–1100 °C. Indeed, XPS studies of SiC-coated stainless steel plates [7], showed a *c.* 50% reduction in coating-associated graphitic carbon between spectra of coatings formed at 700 and 800 °C. SiC coatings formed at 1100 °C on alumina plates showed no evidence of incorporated graphitic carbon in the XPS. This is reflected in the ESR spectrum of bulk amorphous SiC residue formed at 1100 °C which exhibits a significantly lower spin concentration (by a factor of 10). A further ten-fold reduction in ESR activity is detected when the amorphous SiC residue is partially crystallized at 1550 °C in Ar. In this sense, the ESR spectra of the residues serves as an indicator of the level of free carbon in the residues.

Given that the carbon remaining in the PCS-derived residues is the source of ESR activity, it is likely to confer conductive properties on the residues. Thus, the electrical conductivity of coatings formed from the amorphous PCS-derived SiC over the temperature range 700–1100 °C would decrease as pyrolysis temperature is increased and carbon is removed.

Residues derived from 1100 °C pyrolysis of PMSED and HMCS in N_2 which have not been previously characterized by ESR in the literature, exhibit similar trends to PCS-derived residues. Fig. 1 shows ESR spectra for PMSED heated (a) to 1100 °C in N_2 and (b) to 1550 °C in Ar. The spectrum of the residue obtained after 1100 °C pyrolysis is similar in appearance to the isotropic bands observed for PCS in this study and earlier work [1, 2]. Spin concentrations for PMSED and HMCS-derived residues generated at 1100 °C, are, however, an order of magnitude higher than for the equivalent PCS-derived residue. It is evident that the pyrolysis of PMSED and HMCS leaves a larger amount of excess carbon in the residues than does PCS.

When PMSED and HMCS-derived black residues are crystallized at 1550 °C, the ESR peak becomes asymmetric and partially resolved smaller peaks appear to both sides (see Fig 1b). An identical trend was observed for the crystallized PCS-derived residues. This asymmetry in the main peak could be either caused by: (i) anisotropy in the *g*-tensor for the unpaired spins, or (ii) the presence of spins of two or three types with slightly different *g*-values and linewidths. It is difficult to confirm whether the species causing the asymmetry in the main peak were originally present but "swamped" by the predominant ESR-active species present in the amorphous residues or whether the ESR-active species were produced possibly by breakdown of the graphitic carbon during 1550 °C pyrolysis. The partially resolved peaks either side of the main peak (see Fig. 1b) may reflect hyperfine structure caused by the interaction of the unpaired spin with a nearby spin-$\frac{1}{2}$ nucleus. This is supported by the observation that the partially resolved lines observed for the crystallized PCS, HMCS and PMSED residues are approximately equidistant from the main peak. The ESR spectra for amorphous black residues generated at 1100 °C are dominated by unpaired spins on graphitic carbon residues. By 1550 °C, most of this graphitic residue has been removed and many of the remaining spins are probably localized on carbon atoms bonded to one or more spin-$\frac{1}{2}$ hydrogen atoms thus giving rise to the partially resolved peaks on either side of the main peak. Support for this hypothesis can be found from time-dependent mass spectrometric studies reported earlier [5] which showed (for the HMCPS-derived residue) that a detectable level of hydrogen was still being evolved from the residues after 4 h of heating at 1550 °C. Thus the small amount of hydrogen responsible for the hyperfine interactions may represent tenaciously bound hydrogen present in the crystallized residue.

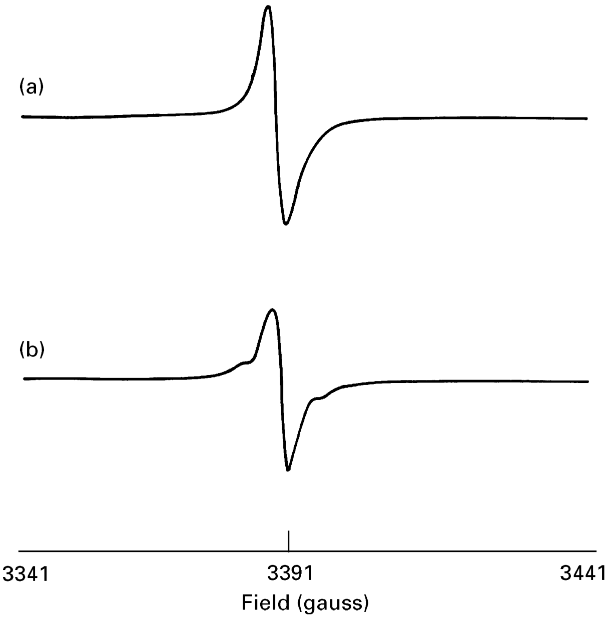

Figure 1 ESR spectra of (a) the amorphous black residue obtained from pyrolysis of PMSED to 1100 °C in N_2 and (b) crystallized black PMSED-derived residue obtained by further heating to 1550 °C in Ar.

For comparison, the ESR spectrum of a commercial sample of crystalline SiC (Carborundum Co. Ltd) was recorded. The sample had extremely low ESR activity with the weak peak exhibiting no asymmetry or hyperfine structure. The calculated spin concentration for the commercial sample of SiC was in fact 30–100 times lower than that found for the crystallized black

TABLE II ESR data for white-grey pyrolysis residues derived from pre-ceramic polymer pyrolysis

Sample	Pyrolysis history[a]	Composition (from XRD analysis)	Peak width (Gauss)	*g* value	Spin concentration (spins $g^{-1} \times 10^{19}$)[b]
PCS	1100 °C, NH_3	Amorphous	3.25	2.0030	0.0017
PCS	1. 1100 °C, NH_3 2. 1550 °C, Ar	Si_2N_2O and Si_3N_4 (major) β-Si_3N_4 (minor-medium)[c]	6.85	2.0033	0.02
HMCPS	1100 °C, NH_3	Amorphous	6.5	2.0029	0.003
HMCPS	1. 1100 °C, NH_3 2. 1550 °C, Ar	Si_2N_2O (major), α + β-Si_3N_4 (trace)[c]	7.0	2.0036	0.009
PDPS	1100 °C, NH_3	Amorphous	1.0	2.0030	0.00004
PDPS	1. 1100 °C, NH_3 2. 1550 °C, Ar	Si_2N_2O (+ amorphous component)[c]	5.0	2.0032	0.009
Starck LC-10 Si_3N_4	As-received	95% α-Si_3N_4, 5% β-Si_3N_4	7.75	2.0030	0.14

[a,b] See corresponding footnotes for Table I.

[c] XRD analysis of residue crystallized at 1550 °C.

pyrolytic residues. Thus, graphitic contamination in the black pyrolytic residues presents an obstacle for preparing SiC residues of higher purity than commercial samples produced by other processes.

3.2. White-grey residues obtained from initial pyrolysis in NH_3

Table II summarizes the ESR data obtained for white-grey residues generated by initial 1100 °C-NH_3 pyrolysis as well as for a sample of commercial LC-10 Si_3N_4 powder (Starck LC-10). Figs 2–4 show the ESR spectra of amorphous and crystalline samples. In general, the white pyrolytic residues exhibited very much lower ESR activity than the black pyrolytic residues. Spectra from the residues each exhibited a single symmetric peak (see Fig. 2). All peaks observed for the white-grey residues had *g* values close to 2.0030 which indicates that ESR activity is compatible with carbon-dangling bonds from small traces of carbon remaining in the residues. Indeed, allied XRD and XPS studies of the bulk residues and coatings composed of the white material [5–7] demonstrated that the white residues contained a small amount of carbon probably in the form of graphite.

These ESR results indicate that the 1100 °C-NH_3 pyrolysis very efficiently removes carbon from such residues resulting in an extremely low ESR activity. As a consequence, coatings composed of such materials have low conductivity effectively behaving as insulators. In the previous studies of coatings composed of white residue material on alumina plates (i.e. "Si_2N_2O/Si_3N_4" coatings from 1100 °C-NH_3 pyrolysis of PDPS layers) the insulating properties of the coatings were encountered in their examination by scanning electron microscopy (SEM) which can induce charge build-up on insulator-type specimens. Indeed, an additional Au–Pd overlayer on top of a deposited carbon coating was required for non-distorted micrographs [6]. For coatings of PDPS-derived residue, the insulating properties are particularly extreme since the PDPS-derived residue exhibited one of the lowest spin concentration values calculated in this study (see Table II).

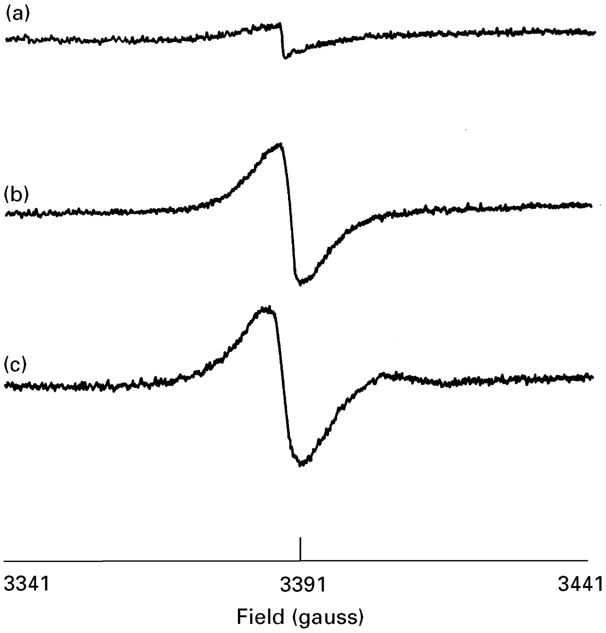

Figure 2 ESR spectra of white-grey amorphous residues generated by 1100 °C–NH_3 pyrolysis of (a) PDPS, (b) PCS and (c) HMCPS.

HMCPS was not found suitable for forming Si_3N_4-type coatings while PCS-derived "Si_2N_2O/Si_3N_4" coatings although less thoroughly studied, exhibited similar insulator behaviour.

Crystallization of the white amorphous residues by 1550 °C pyrolysis in Ar led to an increase in spin concentrations (see Table II). It is probable that the carbon contamination is picked up from the 1550 °C firing which is carried out in a graphite resistance furnace. The level of carbon contamination arising from the 1550 °C firing and giving rise to the ESR activity is small and not detectable as crystalline products such as SiC since XRD analysis reveals only Si_3N_4 and/or Si_2N_2O (see Table II).

The ESR peaks given by the white-grey solids change markedly upon crystallization, giving overall increased peak widths which contribute to the higher spin concentrations calculated for these samples (see Fig. 3). In all cases, the main ESR peak, which was initially symmetric for the amorphous residues, develops

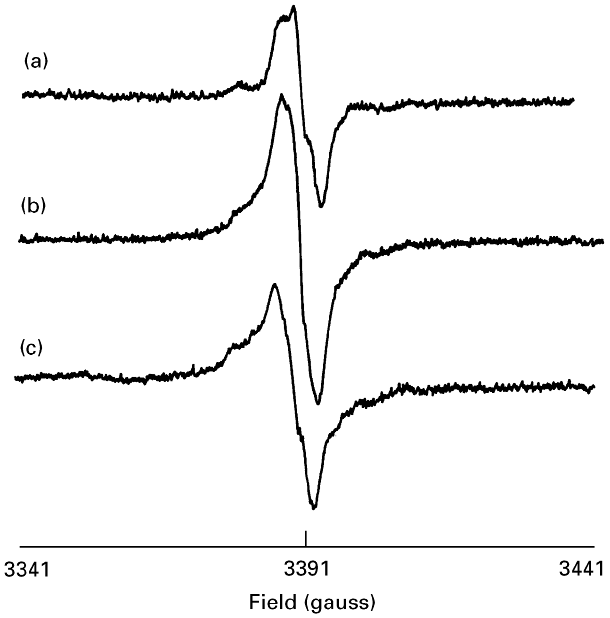

Figure 3 ESR spectra of white-grey amorphous residues crystallized by 1550 °C-Ar pyrolysis in a graphite resistance furnace: (a) PDPS-derived residue, (b) PCS-derived residue and (c) HMCPS-derived residue.

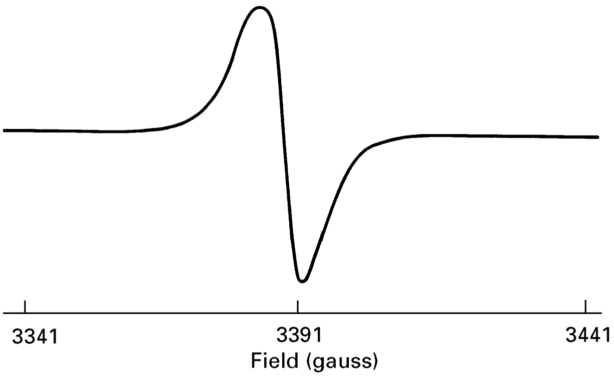

Figure 4 ESR spectrum of a commercial sample of Si_3N_4 powder (Starck LC-10).

asymmetries for the crystallized residues with some partially resolved structure. The asymmetry in the peaks appears to result from two different species with slightly different g values centred at c 2.001 and 2.003. The relative concentration of the different species varies noticeably between the three crystallized white samples. The component centred at $g = 2.003$ is most likely due to unpaired spins resident on carbon impurities picked up by the 1550 °C firing in the graphite resistance furnace while the component with $g = 2.001$ is probably associated with the Si_2N_2O product. Pfeffer *et al.* [8] reported a relatively narrow ESR peak with $g = 2.001$ for an oxidized Si (1 1 1) standard sample used in their ESR study of Si_3N_4 coatings. They also reported an ESR spectrum of a plasma-enhanced chemical vapour deposited Si_3N_4 film on silicon which appeared to consist of overlapping $g = 2.003$ and $g = 2.001$ components and they attributed the $g = 2.001$ component to paramagnetic centres at or near the silicon substrate surface.

Thus in the present study, the $g = 2.001$ component observed in spectra of the crystallized white-grey residues is due to paramagnetic centres existing within the Si_2N_2O. The ESR peak components were only observed after crystallization of the ceramic residues and so are likely to reflect unsatisfied valencies in the Si_2N_2O crystal structure. The weak intensity features observed out from the main peak (see Fig. 3) are similar in appearance and intensity to those observed for the crystallized black SiC residues and so are expected to be due to hyperfine interactions involving hydrogens attached to the small amount of carbon residue in the crystalline material. These features are too intense relative to the main ESR peak to be explained by hyperfine splittings arising from interaction of unpaired spins on Si_2N_2O with the spin-$\frac{1}{2}$ ^{29}Si nucleus.

Fig. 4 shows an ESR spectrum of commercially sourced Si_3N_4 which exhibits a slightly asymmetric peak with no hint of structure. The calculated spin concentration is the highest of all the values calculated for the white-grey residues examined in this study. The source of the ESR activity of the commercial Si_3N_4 is probably the impurities present in the powder, (see Section 2). Given that g is centred at 2.003, it is likely that the ESR signal arises in large part from unpaired spins centred on carbon impurities remaining after the synthesis of the powder. Unlike the crystallized SiC residues from initial N_2 pyrolysis of pre-ceramic polymers, the synthesis of Si_3N_4/Si_2N_2O powders via the NH_3 pyrolysis pathway appears a favourable route to purer powders with significantly lower ESR activity than commercially available powders made by conventional means.

4. Conclusions

ESR has been used to probe paramagnetic species in black and white ceramic residues from initial pyrolysis of pre-ceramic polymers in N_2 and NH_3. For the black residues, excess carbon remaining gives rise to a relatively intense isotropic ESR signal which reduces in intensity as the residue is heated further or is crystallized at 1550 °C. Consequently, coatings of these black residues (e.g. PCS-derived SiC coatings) are more conductive because of the ESR-active carbon incorporated in the coating material. In contrast, initial 1100 °C-NH_3 pyrolysis of pre-ceramic polymers effectively removes polymer-associated excess carbon to give white powders which exhibit low ESR activity but which pick up carbon contamination after crystallization in a graphite resistance furnace at 1550 °C. It is not unreasonable to assume that carbon contamination also occurs for the crystallized black residues during 1550 °C-Ar pyrolysis although it is less evident given that the black residues contain more graphitic carbon impurities than white residues.

It appears that crystal-associated defects lead to additional peak components in the ESR spectra of the crystallized white residues. Comparisons of ESR data for the amorphous white residues with the charging tendencies of coatings during examination by scanning electron microscopy explain why the coatings behave typically as insulators. Comparison of spin concentration data for the crystallized white residues with that of commercial Si_3N_4 reveals that crystallized residues derived from initial NH_3 pyrolysis of preceramic polymers are potentially a favourable route to purer Si_3N_4/Si_2N_2O powders.

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