Journal of the European Ceramic Society 16 (1996) 1115–1120
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PII: S0955-2219(96)00025-8
0955-2219/96/$15.00

Polymer-Derived Ceramic Coatings on C/C–SiC Composites

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(Received 20 December 1994; revised version received 3 January 1996; accepted 8 January 1996).

Abstract

A protective coating has been developed to enhance the oxidation stability of C fibre reinforced SiC (C/C–SiC). The coating was prepared by pyrolysis of a polysilazane layer, which was obtained by dip-coating. Silicon powder was added to the polysilazane solution to prevent shrinkage during pyrolysis. The ceramic coating was characterized regarding layer thickness, adhesion, and oxidation protection for C-fibres. Under the prevailing conditions the thickness of the ceramic layer was determined to be up to 5 μm after one coating–pyrolysis cycle and could be increased by further coating. Additionally, the thickness could be varied by changing the viscosity of the polymer solution as well as the withdrawal speed. The highest values measured for the adhesion of the ceramic coating on the substrate were 14 MPa. The lifetime of the composite material at high temperatures in air could be increased by up to 120% with the coating, compared with the uncoated samples. © 1996 Elsevier Science Limited.

1 Introduction

Carbon-fibre reinforced composites are one of the most promising materials with which to realize light-weight structures at high temperatures, and find application in areas such as the aircraft and space industry as well as in automotive and energy technologies.[1]

The crucial drawback for C fibres is their low stability in an oxygen-containing atmosphere at elevated temperatures. While the C fibres inside a carbon-fibre reinforced SiC (C/C–SiC) composite are protected by the surrounding SiC matrix,[2] the top fibres are unprotected at the surface due to additional machining. These fibres can be oxidized easily and so carry the oxidation through the entire component. Thus it is necessary to develop an effective ceramic coating that prevents oxidation of the C fibres. Among other methods, such ceramic oxidation protective films can be made by chemical vapour deposition (CVD), sputter and spray processes.[3]

In this research work polymer pyrolysis, which is a suitable method for the manufacture of ceramic bodies, fibres, powders and thin layers,[4–6] has been used for the development of protective coatings. Metal organic polymers, and especially organosilicon polymers, are used as starting materials. Pyrolysis at temperatures around 1000°C leads to silicon-based amorphous ceramics. By raising the temperature up to 1400–1600°C, transformation into the corresponding crystalline modifications occurs.[7] Two points in favour for polymer pyrolysis are the low reaction temperatures (around 1000°C) as well as the ability to control the purity of the products easily.

2 Experimental

2.1 Dip-coating

C/C–SiC composite samples were coated by means of dip-coating (Fig. 1). This process, well known from the sol–gel technique to produce oxide ceramic layers, allows simple, rapid and economical coating.[8,9] The substrate is dipped into the precursor solution and withdrawn after a few minutes with a certain velocity, v.

The thickness of the adherent polymer layer can easily be varied in a wide range by changing the velocity v as well as the viscosity η of the solution and the concentration c of the polymer.[10] After coating the adherent polymer layer is pyrolyzed in an inert atmosphere forming an amorphous ceramic coating.

2.2 Materials

Commercially available polysilazane NCP 200 (Nichimen Corp., Japan), with a number-average molecular weight (M_n) of 1100–1300 g mol^{-1},[11] was used as starting material. Pyrolysis up to 1100°C in nitrogen or argon leads to an amorphous ceramic

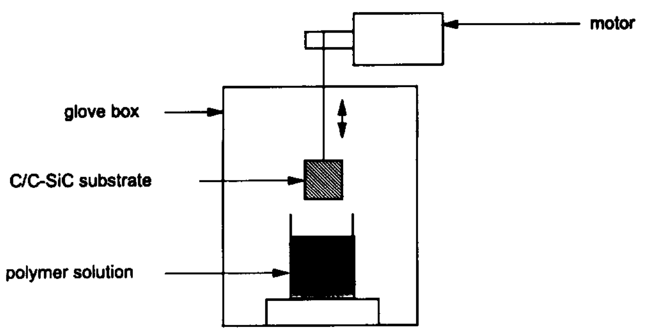

Fig. 1. Dip-coating facility.

with the composition $SiC_{0.7}N$ determined by chemical analysis. During the transformation of the polymer into Si/C/N ceramic several gaseous reaction products, such as hydrogen, ammonia and methane, are released. This is shown schematically in Fig. 2. The appropriate heating programme is illustrated in Fig. 3.

Solutions were prepared by dissolving NCP 200 in distilled toluene (Aldrich) which was dried over sodium. Silicon powder (Elcem) with $d_{90} < 3$ μm was added to the polymer solution and dispersed by ultrasonic mixing and intensive stirring. During the coating process no sedimentation could be observed.

Two-dimensional (0°/90°; C fibres: T300, Toray, Japan) C/C–SiC ($20 \times 10 \times 3$ mm^3) with a carbon content of 57–60 wt%, a silicon carbide content of 33–37 wt% and a free silicon content of 3–6 wt% was used as substrate. The material (ρ = 1·95 g cm^{-3}) was produced by infiltration of a C/C preform with fused silicon.[12] The substrates were ground using a 65 μm diamond emery paper, cleaned in toluene and finally heated in vacuum (10^{-2} mbar) up to 900°C for 5 h.

2.3 Layer thickness

The thickness of the ceramic coatings produced as described above was measured by optical microscopy and scanning electron microscopy (SEM) on the specimen cross-sections, as well as by profilometry (alpha step).[13]

2.4 Adhesion

Adhesion of the ceramic layer on the C/C–SiC substrate was determined by the direct pull method.[14] According to this method, a stamp, which first was sand-blasted and then cleaned in toluene, was pasted on the degreased ceramic layer by means of a mixed adhesive or a cyanoacrylate cement. After hardening of the adhesive, the stamp was pulled off by a force F perpendicular to the substrate surface. The withdrawal installation was fixed on a cardanic mount to prevent shearing strain, which would falsify the result. The velocity of withdrawal was 5 mm min^{-1}. The force F necessary to remove the ceramic layer from the substrate was measured, so that the adhesion σ of the coating on the substrate could be cal-culated using the equation $\sigma = F/A$ with A = 34 mm^2.

Due to the small quantity of cement used, the high viscosity and the rapid hardening of the cement, penetration through the ceramic layer to the substrate could be excluded, as was additionally shown by light micro-scopic inspection of the cross-section of the samples.

2.5 Oxidation behaviour

Oxidation behaviour of the coated C/C–SiC material was investigated thermogravimetrically by measuring the weight-change during heat treatment in air using a Netzsch STA 409 TGA.

3 Results and Discussion

The ability to produce ceramic layers on composite materials by polymer pyrolysis has already been

$$[RSiHNH]_m\,[RSiN]_n \xrightarrow[Ar;N2]{1100^{\circ}C} Si_xC_yN_z + CH_4 + NH_3 + H_2$$

(polysilazane) (amorphous ceramic) (gas)

$R = CH_3, C_2H_5, C_2H_3$

Fig. 2. Schematic description of the decomposition of a polysilazane (e.g. NCP 200).

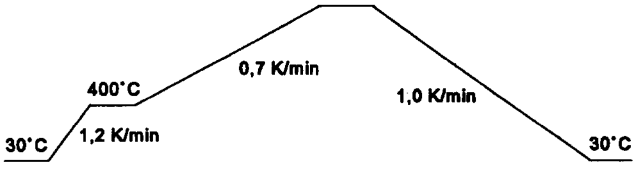

Fig. 3. Heating programme for pyrolysis of the pre-ceramic coating.

reported,[15] yet it was impossible to produce thick (several μm), crack-free and large-area ceramic coatings in one coating–pyrolysis cycle by this method. Also, in our investigations, the use of highly concentrated polymer solutions always led to the formation of cracks. Figure 4 shows a typical result. This layer was prepared by dipping the C/C–SiC substrate into a 67 wt% solution of NCP 200 in toluene, followed by pyrolysis. The velocity v was 2·7 cm min^{-1}.

One reason for the formation of cracks is the volume shrinkage that occurs during pyrolysis. The polymer, with a density of about 1·1 g cm^{-3}, is transformed into an amorphous ceramic with a much higher density of approximately 2·4 g cm^{-3}. In the case of manufacturing ceramic bodies the total volume shrinkage was up to 60%. At the same time, due to the release of volatile reaction products, an open porosity of up to 12% occurred.[16] In the case of ceramic bodies a certain amount of filler can be added to the starting polymer to reduce shrinkage as well as porosity.[17]

Another reason for the formation of cracks is the exceeding of a certain critical layer thickness, h_c. In layers thicker than h_c, the stress energy due to the different thermal expansion coefficients of the substrate and the layer is released by the formation of cracks during the cooling phase.[18]

In our investigations, however, we produced (several μm) thick, almost crack-free, well-adherent ceramic layers on the C/C–SiC composites by adding a certain amount of silicon powder to the polymer solution.[19,20] Silicon is assumed to be a passive filler in the pyrolysis schedule. In an oxygen-containing atmosphere silicon reacts at high temperatures forming silicon dioxide, which may close pores and increase the protective ability of the ceramic coating. The filler content has to be chosen in such a way that the shrinkage of the coating is minimized but the viscosity of the dispersion is usable.

The use of a 60 wt% solution of NCP 200 in toluene with a filler content of 45 vol% (related to the polymer weight) and a withdrawal speed of 2·7 cm min^{-1} leads to an approximately 5 μm thick, almost crack-free ceramic layer after one coating–pyrolysis cycle. This is shown in Figs 5 and 6.

In Fig. 7 the dependence of the layer thickness h on the withdrawal velocity v is illustrated. For this investigation a 37·5 wt% polysilazane solution in toluene with a filler content of 42 vol% (viscosity: 12 mPa s measured at 23°C with a rotary viscosimeter, Haake RV 12, D = 2000 s^{-1}) was used. At lower velocities (<14 cm min^{-1}) the layer thickness does not increase much on raising the withdrawal speed, whereas at higher velocities (>14 cm min^{-1}) a considerable increase occurs. However, the higher the velocity, the higher the number of cracks in the obtained ceramic layer.

The adherence of the ceramic layer on the C/C–SiC material depends on the pre-treatment of the substrate as well as on the pyrolysis conditions. In general, the adhesion of the ceramic coating was determined to be in the range of 6 MPa with highest values up to 14 MPa. The adhesion of the ceramic layers could be increased by 30% by

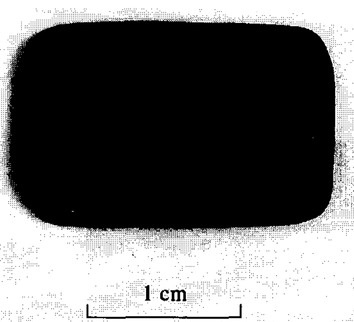

Fig. 5. Non-cracked ceramic layer on C/C–SiC substrate; prepared by dip-coating with a 60 wt% solution of NCP 200 in toluene, 45 vol% silicon powder, pyrolysis up to 1100°C; withdrawal speed = 2·7 cm min^{-1}.

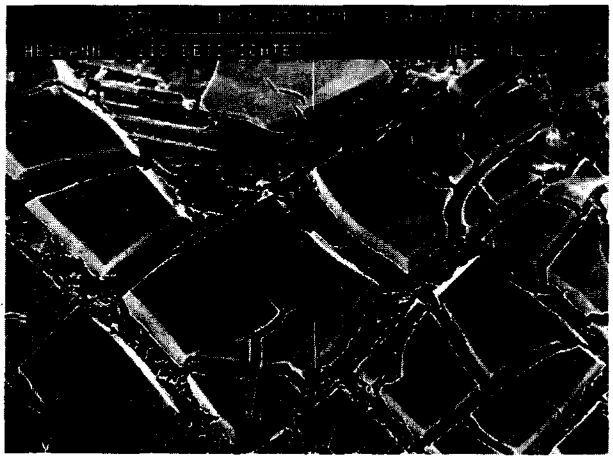

Fig. 4. Ceramic layer on C/C–SiC substrate; prepared by dip-coating with a 67 wt% solution of NCP 200 in toluene and followed by pyrolysis up to 1100°C; withdrawal speed = 2·7 cm min^{-1}.

Fig. 6. Cross-section of the coated C/C–SiC specimen, prepared by dip-coating with a 60 wt% solution of NCP 200 in toluene, 45 vol% silicon powder; pyrolysis up to 1100°C; withdrawal speed = 2·7 cm min^{-1}.

additional annealing of the samples in nitrogen atmosphere at 1350°C. This may due to nitridation of the silicon filler and must be investigated in future work. It should be mentioned that, in most cases, the layer was not pulled off but the substrate was broken (Fig. 8). Thus the real value of σ must be higher than the measured one.

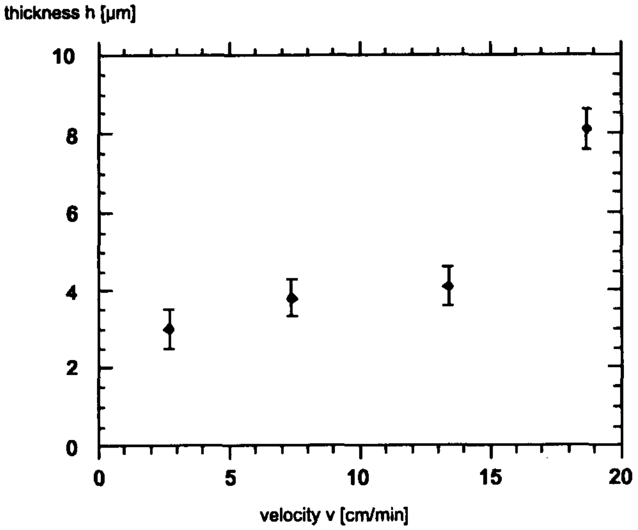

Fig. 7. Thickness h of the ceramic layer vs. withdrawal velocity v. The ceramic layers were manufactured by dip-coating with a 37·5 wt% polysilazane solution in toluene, 42 vol% silicon powder and subsequent pyrolysis up to 1100°C.

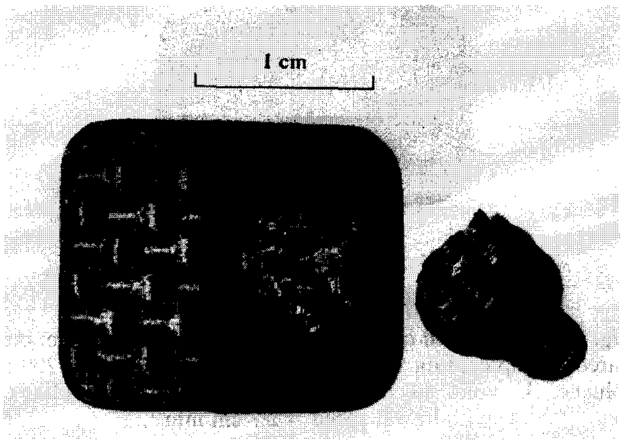

Fig. 8. Coated C/C–SiC sample after direct-pull test. The ceramic layer was obtained by dip-coating with a 60 wt% solution of NCP 200 in toluene, 45 vol% silicon powder; pyrolysis up to 1100°C; withdrawal speed = 2·7 cm min^{-1}. Parts of the substrate were pulled off.

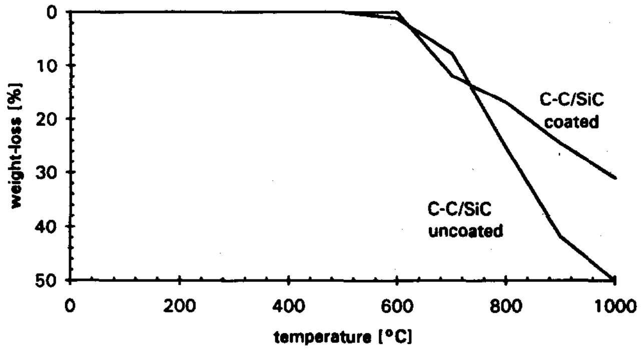

Fig. 9. Thermogravimetric investigation in air at 1000°C.

The oxidation behaviour of the coating and the ability to protect the C/C–SiC substrate against oxidation was investigated using thermogravimetric analysis. Figure 9 shows the weight loss of an uncoated (reference) and a coated C/C–SiC sample during a heat treatment in air at atmospheric pressure up to 1000°C. Both samples were heated up at 1 K min^{-1} and then cooled down at 8 K min^{-1}. After the test the reference sample showed a weight loss of more than 50%, whereas the sample coated with an only 10 μm thick ceramic layer (using a 60 wt% solution of NCP 200 in toluene containing 45 vol% of Si filler; v = 2·7 cm min^{-1}), lost about 30% of its original weight.

The reference sample starts to oxidize at about 500°C. The beginning of oxidation of the coated sample is shifted to approximately 600°C. Up to 750°C the oxidation rate of the coated sample is at least as high as that of the reference, while at higher temperatures the oxidation rate of the coated sample decreases. One reason for this might be a reduction of the porosity of the ceramic coating by the formation of silicon dioxide, leading to a lower diffusion rate of oxygen through the pores.

Cross-sections of both samples are shown in Figs 10 and 11. In the case of the uncoated specimen (Fig. 10) all the C fibres were burned out, while in the case of the coated sample (Fig. 11) carbon fibres are still present.

Thermogravimetrical investigations in flowing air (30 cc min^{-1}) were carried out at 1160 and 1260°C. In Fig. 12 (1160°C) and Fig. 13 (1260°C) the weight loss vs. time is shown; only the part until no further weight loss was observed, i.e. until weight stabilization occurred, is illustrated. The values of weight loss measured (55–61 wt%) are in the same range as the C fibre content in the composite (57–60 wt%). In all cases no fibres could be observed after the test by SEM investigation. In other words, all the carbon

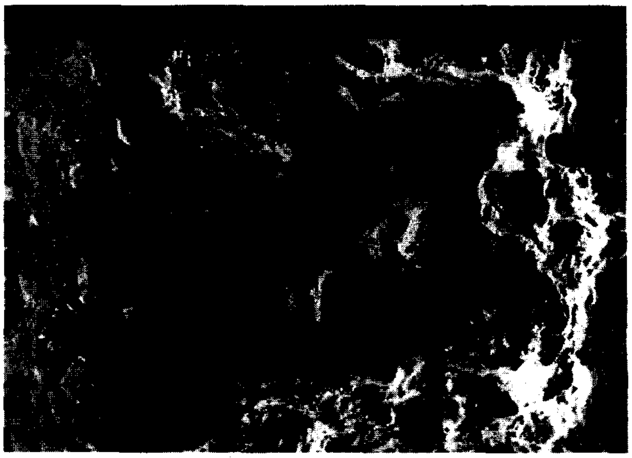

Fig. 10. Uncoated C/C–SiC sample after oxidation test in air.

Fig. 11. Coated C/C–SiC sample after oxidation test in air.

fibres were burned off. The time until weight stabilization is observed was extended by 120% at 1160°C and by 36% at 1260°C by a coating with a thickness of approximately 20 μm obtained after four coating– pyrolysis cycles.

The reasons for the weight loss in the case of coated samples are the porosity of the layer as well as some microcracks that may occur during the cooling phase of the pyrolysis step, due to the difference between the thermal expansion coefficients α of the substrate ($0{\cdot}6$–$0{\cdot}8 \times 10^{-6}$ K^{-1} between 20 and 1000°C in fibres plain) and the coating ($3{\cdot}4 \times 10^{-6}$ K^{-1} between 20 and 1100°C).

Further investigations with other filler materials such as SiC and Si_3N_4 (passive filler) or Ti (active filler), which react with the gaseous species evolved during pyrolysis, will be carried out to examine their influence on the porosity of the ceramic coating as well as on the crack formation. Moreover, new tailor-made polymers leading to a higher ceramic yield and a ceramic residue with a value of α close to that of the substrate ($0{\cdot}6$–$0{\cdot}8 \times 10^{-6}$ K^{-1}) will be used, to minimize crack formation. The synthesis of such a suitable polymer, which leads to a ceramic material in the system Si/B/C/N with $\alpha \approx 1 \times 10^{-6}$ K^{-1} (100–1000°C), has already been reported.[21]

4 Summary

An almost crack-free, oxidation-protective ceramic coating on C/C–SiC substrates was produced by dip-coating, using a 60 wt% solution of NCP 200 in toluene with a filler content of 45 vol% Si powder, followed by pyrolysis of the adherent polymer/filler layer in a nitrogen atmosphere at 1100°C. The thickness of the ceramic layer was up to 5 μm after one coating– pyrolysis cycle. For the adhesion of the coating on the substrate, values up to 14 MPa were measured using the direct-pull method. Oxidation tests showed that the durability of coated samples in air at 1160°C and 1260°C was much higher than that of uncoated samples.

Acknowledgments

This work was supported by the DFG and is the summary of a report[19] written within the scope of SFB 259 'Hochtemperaturprobleme rückkehrfähiger Raumtransportsysteme'. The authors would like to thank Professor Dr F. Aldinger, Universität Stuttgart, Institut für Nichtmetallische Anorganische Materialien, for helpful conversation and support; Professor Kochendörfer and co-workers at

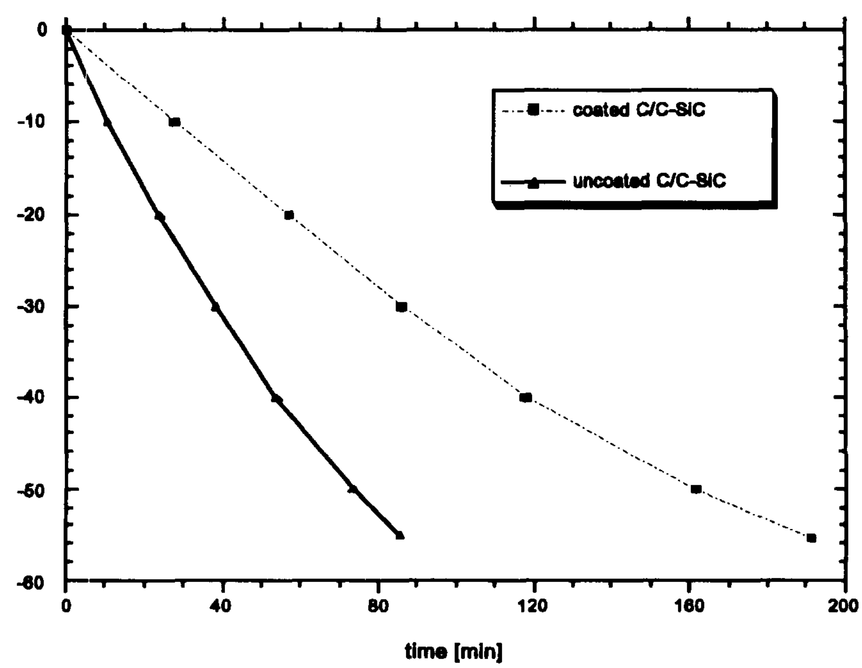

Fig. 12. Thermogravimetric investigation in flowing air at 1160°C.

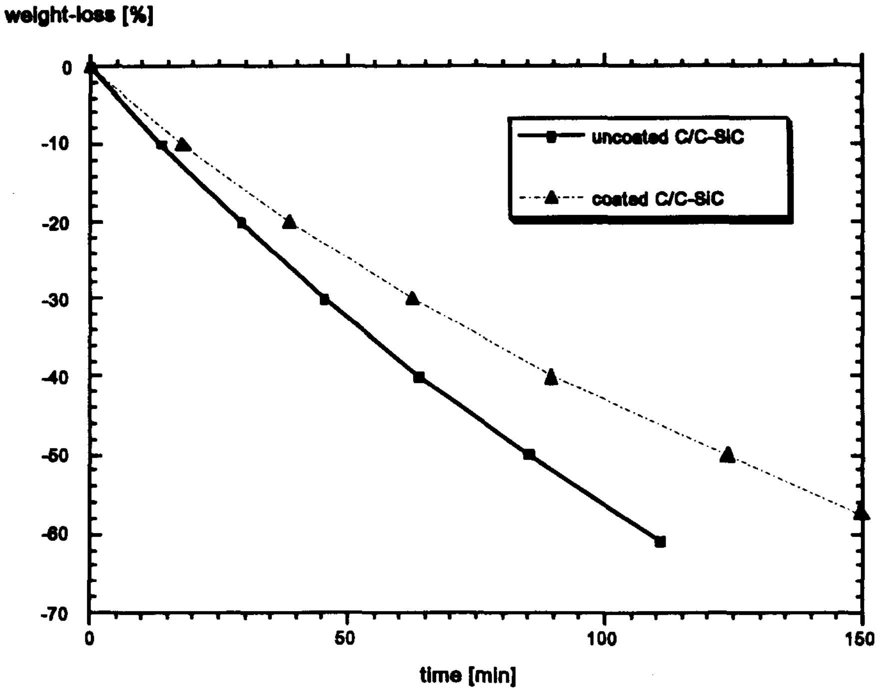

Fig. 13. Thermogravimetric investigation in flowing air at 1260°C.

DLR, Institut für Bauweisen- und Konstruktionsforschung, Stuttgart, for supply of the C/C–SiC composite materials; and Professor Dulog, Dr Rösler, Mr Klinke and co-workers of the Institut für Pigmente und Lacke e.V., Stuttgart, for performing the direct-pull measurements.

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