Degradation behaviour of a composite material for thermal protection systems

Part III *Char characterization*

L. TORRE, J. M. KENNY
Institute of Chemical Technology, University of Perugia, Loc. Pentima bassa, 05100, Terni, Italy
E-mail: torrel@unipg.it, kenny@unipg.it

G. BOGHETICH
Applied Chemistry and Environmental Protection Institute, Polytechnic University of Bari, via Orabona 4, 70125 Bari, Italy

A. MAFFEZZOLI
Department of Materials Science, University of Lecce, Via per Arnesano, 73100, Lecce, Italy

In the former parts of this work (*J. Mat. Sci.* **33** (1998) pp. 3137 and 3145) the kinetic characterisation and the mathematical modelling of the behaviour of an ablative material subjected to high heat fluxes were analysed. In this work the structure and morphology of the char produced from the degradation of the same ablative material, occurring as a consequence of plasma torch exposure, are evaluated in order to improve the ablative behaviour of an active protection. Usually the char produced from the degradation of polymeric ablators is weak and brittle, and therefore is susceptible of rapid removal by the mechanical stresses due to the high vehicle speed, this phenomena provokes a reduction of the thermal insulation. Reinforcing fibres and other inorganic fillers must be therefore included in the ablative formulation in order to improve the char stability. One of the roles of the char, which is very important, is to limit oxygen diffusion from the boundary layer to the bulk to prevent the exothermic degradation reactions of the polymeric matrix. Therefore, the mechanical characteristics and the physic-chemical properties of the char are of fundamental importance to ensure good quality of an ablative material. In this paper Scanning Electron Microscopy (SEM) elemental microanalysis (EDAX) and wide angle X-ray diffraction (WAXD) are used to provide respectively the morphological characteristics of the char and further insight on the crystalline structure resulting after quenching at room temperature. © *2000 Kluwer Academic Publishers*

1. Introduction

The kinetic characterisation and the mathematical modelling of the behaviour of an ablative material submitted to high heating flows were analysed in the two previous papers [1, 2]. In particular the mathematical model was experimentally confirmed, by the temperature values measured during a simulation of the ablation process in a plasma torch facility [2].

Charring ablators are the most widely used thermal protection shields and are generally produced using phenolic, epoxy, or silicon resins reinforced with glass, silica or organic spheres and short fibers [3–5]. During the ablation process, the degradation reaction produces the char whose porous structure provides a further insulation layer. The char, whose formation is a function of the local pressure and the heating rate, start to develop at a pyrolisis temperature of the organic components ranging from 250 °C to 600 °C. Then, further heating of the exposed char surface (up to 1600–1800 °C) produces new compounds as a result of the interaction of the inorganic components of the raw materials. At these temperatures the char oxidises or sublimes or is mechanically eroded by external shear forces. During lifting or moderate ballistic re-entry, the oxidation is the main thermochemical mechanism of char removal [2].

In a charring ablator, the char has a very important role, as it provides a thermal barrier to heat diffusion and reduces oxygen diffusion from the boundary layer to the bulk to prevent the exothermic degradation reaction of the polymeric matrix. These functions are accomplished through the creation of a porous skeleton in which the gases produced by the degradation of the matrix can flow out, behaving as a thermal insulator. Therefore, during the formulation of a charring ablative material it is very important to obtain a char whose physical properties are compatible to its working conditions.

The thermal degradation of ablators based only on polymer usually produces weak and brittle char, which is susceptible of rapid removal by the mechanical forces produced as an effect of the elevated re-entry speeds. Reinforcing fibres and other inorganic fillers must, therefore, be included in the ablative formulation in order to improve the mechanical properties of the char.

Besides the porous morphology, the main properties required to the forming char are related to the thermal conductivity, the mechanical resistance and the thermal stability at high temperatures. In particular, for ablative materials based on silicone matrix, crystalline inorganic matter provides a better thermal, chemical and mechanical resistance compared with amorphous phases. However these properties are counteracted by a higher thermal conductivity [6].

In this work the structure and morphology of the char produced from the degradation of the ablative material containing inorganic fillers, occurring as a consequence of plasma torch exposure are analyzed. Scanning Electron Microscopy (SEM) is applied to determine its morphological characteristics; elemental microanalysis (EDAX) and wide angle X-ray diffraction (WAXD) are used to provide a further insight on the phases composition and crystalline structure resulting after quenching at room temperature.

2. Experimental

The study of the ablative material ALS051, kindly provided by ALENIA Spazio S.p.A., is reported in this paper. The average composition of the ALS051 is reported in Table I.

For the char production the equipment, previously described [2], able to simulate the aerodynamic heating occurring during space re-entry, was used. This test represents one of the better conditions to simulate the working condition of an ablative thermal shield leading to high heating rates and providing the measurement of the heat flux and of the stagnation pressure. Tests were carried out imposing a heat flux of 732 KW/m^2 producing a stagnation pressure on the sample of 50 Torr with an argon-air plasma. The char is obtained exposing samples of cylindrical shape (3.5 cm of diameter and 2 cm of thickness) to the gas stream for 125 s. Further details about materials and testing facilities were presented elsewhere [1, 2].

X-ray wide-angle diffractometry (WAXD) was performed by means of a diffraction technique using Cu K$_\alpha$ radiation (XRD Philips). A Scanning Electron Microscope (Philips) equipped with a microanalyser (EDAX) was used for image and elemental analysis.

TABLE I Indicative composition of the ALS051

COMPONENTS	Weight %
Poly (methyl phenyl) siloxane filled with Fe_2O_3	40–60
Hollow phenolic microspheres	15–25
Quartz microfibres	5
Hollow inorganic microspheres (55–60% SiO_2, 30–35% Al_2O_3, 4–10% Fe_2O_3, 2–6% other oxides)	15–25

3. Results and discussion

The diffraction patterns of the ablative material (containing glass and phenolic microspheres and other polymeric components) indicate that crystalline phases are not present. The results of the diffractometric analysis, obtained on the char produced by the ablation test in the plasma arc torch facility, are reported in Fig. 1; the amorphous structure is mainly detected with a small amount of α–crystobalite. Such a structure may be probably due to the presence of iron silicates and aluminates, prevalently non crystalline, produced by quenching which occurs in the plasma arc torch at the end of the test, while the presence of α–crystobalite is mainly due to the high temperature reached during the degradation process. Lower degradation temperatures reproduced in an oven at 900 °C generate a smaller α–crystobalite amount as shown in Fig. 2 where no peaks related to a crystobalite are visible. Furthermore, in addition to the amorphous structure, the presence of the iron contributes to the high background level because of the well-known X-ray fluorescence effect, produced by Cu K$_\alpha$ radiation.

The SEM morphology of the ALS051 before degradation is reported in Figs 3 and 4. The material appears as syntactic foam with a significant porosity arising from the phenolic and silica microspheres; very good
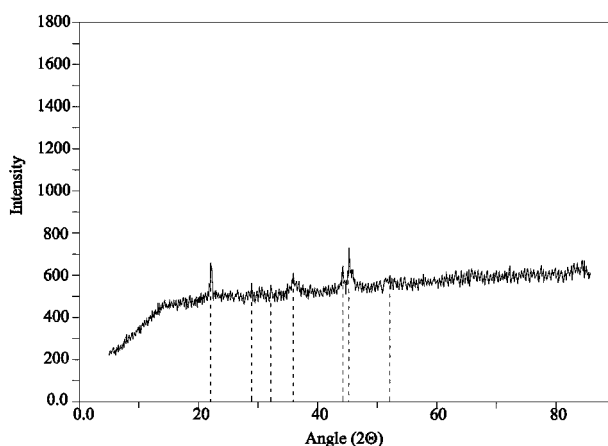
Figure 1 Diffractometric analysis, on the char produced by the ablation test in the plasma arc torch facility (the dotted lines are related to the peaks of α crystobalite).
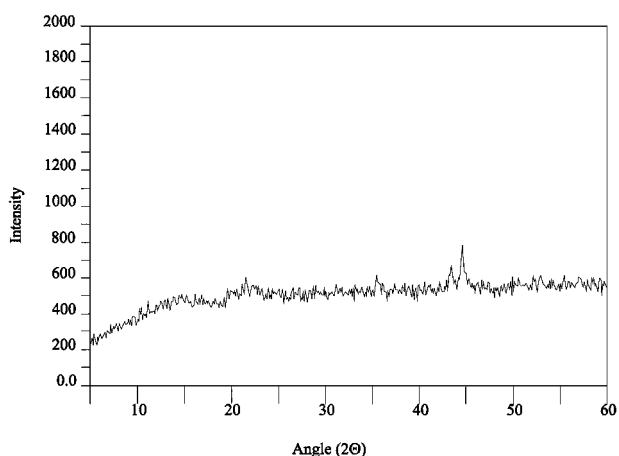
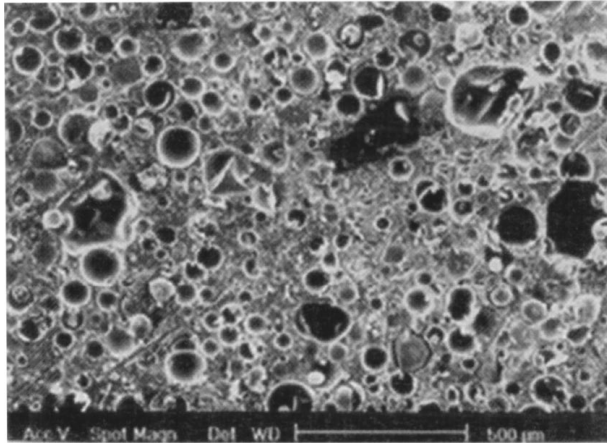*Figure 2* Diffractometric analysis, on the char reproduced in an oven at 900 °C.

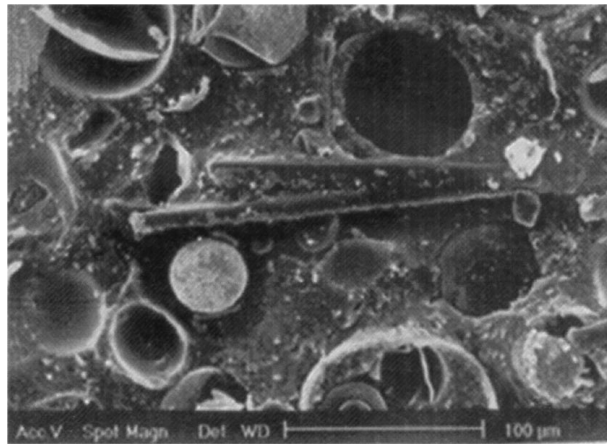*Figure 3* Morphology of the ALS051 before the degradation.

Figure 4 Particular of Fig. 3.

Figure 5 Morphology of the ALS051 after the degradation (the white frame are enlarged in Figs 6 and 7).

Figure 6 Enlargement of a degraded quartz sphere.

Figure 7 Particular of a quartz fiber embedded in a molten char.

adhesion between the silicone matrix and the microspheres is observed. In particular two quartz fibers completely embedded in the matrix are visible in Fig 4. A good adhesion between reinforcements and the rubbery matrix is important because it is responsible of the mechanical properties both of the starting materials and of the material during the different stages of the degradation process. If the matrix is not reinforced by fibres and inorganic fillers the degraded material, such as that in the reaction zone and the char, would be easily eroded [7].

The char morphology, reported in Fig. 5, shows an increased and more irregular porosity respect the original material; large areas of a molten phase are clearly detected. A particular (top-centre) of Fig. 5, reported in Fig. 6, reveals the morphology of quartz fibers embedded in the molten material. Quartz fibres are not affected by degradation and still act as reinforcements in the char. The molten phases of Fig. 6 may be associated with the predominant glassy structure revealed by WAXD. The morphology of a silica microsphere, observed at the centre of Fig. 5, is shown enlarged in Fig. 7. Large cavities and extensive erosion, arising from melting and sublimation of the original inorganic material, are evident.

Elemental microanalysis in the molten zones of Fig. 6 indicates the presence of carbon, oxygen, silicon, aluminium and iron, which are likely to form iron and aluminium silicate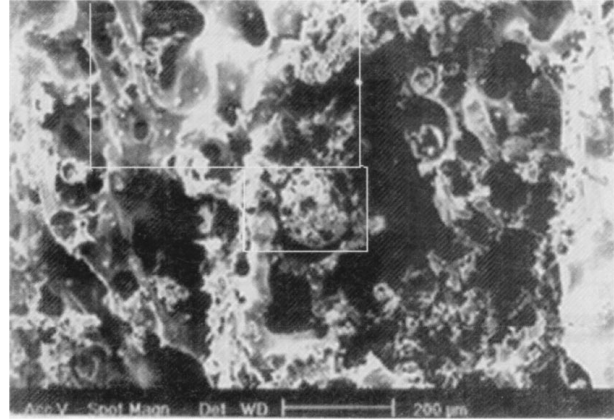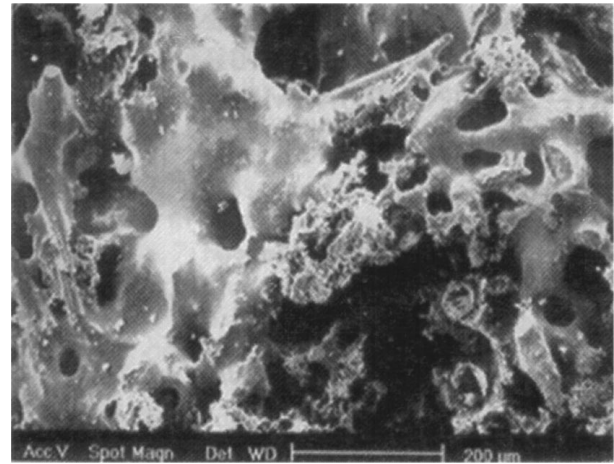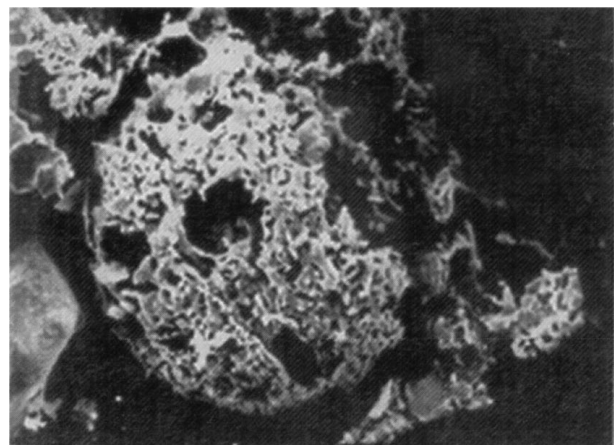s being their molten temperatures lower than 1400 °C [8]. These silicates, acting as low melting phase, may be responsible of the transformation of a small amount of the amorphous silica to α–cristobalite, through a mechanism of dissolution of the metastable amorphous silica and precipitation of the stable crystalline α-cristobalite at temperatures lower than 1720 °C.

4. Conclusions
The SEM images of the starting material showed a good adhesion between the matrix and filler, which ensures

a good mechanical performance of the material. The morphology and structure of the char produced by the ablative degradation of the ALS051 (silicone based ablative composite material) were studied. WAXD analysis of the char revealed a substantially amorphous phase with a small amount of α–cristobalite crystals produced by the presence of melted iron silicates and aluminates at the temperature reached during the plasma torch exposure. This phase was not observed in the low temperature degraded char. The reinforcing action of the fibres, after the simulation of the working conditions is also highlighted in the char by SEM images. Furthermore, this study has shown that, in order to obtain a char with the characteristic properties needed by an ablative material, it may be non-crystalline or poorly crystalline provided that the filler ensures the porosity and the fibres still retain their reinforcing action.

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