OXIDATION RESISTANCE OF NOVEL
CARBON-SILICON ALLOY FIBRES

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Introduction

The high temperature application of carbon fibres is restricted because they are prone to oxidation at temperatures above 450°C. There have been many attempts to protect carbon products by coatings that form oxidation barriers [1-3]. However, these coatings often crack in use exposing the underlying carbon to oxidising gas [4]. High performance SiC fibres are produced from polycarbosilane precursors [5]. It is possible to incorporate this precursor into pitch to produce isotropic C/Si alloy fibres with useful mechanical properties [6]. This paper shows how these novel carbon fibres alloyed with silicon have in-situ oxidation resistance enabling them to generate and regenerate protective outer layers.

Experimental

The silicon-containing polymeric precursor, prepared by reacting a petroleum pitch (Ashland A240) fraction with polydimethylsilane (PDMS) [6], was melt spun into fibres. The spun fibres were oxidatively stabilised in O_2 and then pyrolysed at 1200°C under argon atmosphere. The pyrolysed fibres are referred to as carbon-silicon alloy (CSA) fibres. The CSA fibres were heated to 1200°C under an argon atmosphere and then exposed to oxygen for a short period of time (< 10 min), as a result the fibres exhibited a remarkably improved oxidation resistance, presumably because an impermeable silica layer developed on the fibre surfaces. This process could also be carried out during pyrolysis at 1200°C by adding oxygen into the argon stream. These fibres are called control oxidised carbon-silicon alloy (CO-CSA) fibres. TGA, SEM/EDX, FTIR and tensile testing were used to characterise the CSA fibres, and CO-CSA fibres respectively.

Results and Discussion

Figure 1 shows typical stress/strain curves of the fibres. Stabilised fibres (300°C in O_2) show plastic deformation, indicating their polymeric nature at this stage. The elongation, at 4%, is remarkably high and far superior to that of stabilised isotropic and mesophase pitch fibres. CSA fibres show a massive increase in the tensile strength and the onset of brittle fracture behaviour, due to the substantial structural change that takes place during the pyrolysis process, in which the basically organopolymeric structure is converted into carbon-ceramic structures. CO-CSA fibres show reduced tensile strength and lower fracture strain, indicating increased flaw sizes and more brittleness due to the outer silica layer.

Figure 2 shows a comparison of the oxidation behaviour of CO-CSA fibres, CSA fibres and a laboratory prepared isotropic pitch-based carbon fibre (Aerocarb 75). The CO-CSA fibres do not show any oxidative weight loss until 700°C, and the overall weight loss at 1000°C is less than 5 wt%. The pitch-based carbon fibres begin to oxidise in air rapidly at temperatures of 400 - 500°C. The CSA fibres also begin to oxidise in this temperature region due to the accessibility of the carbon phase. The pitch-based carbon fibres are completely oxidised at around 700°C. On the other hand, the CSA fibres lose weight more gradually to a maximum weight loss of about 40 wt%, attained at 900°C and are thus more oxidation resistant than the carbon fibres. This is partly because the silicon is oxidised to form silica, the resulting weight increase balancing the weight loss caused by carbon oxidation. The net weight loss that would result if the carbon is completely oxidised and the silicon is fully converted into silica is shown in the figure. It can be seen that the CSA fibre weight loss curve reaches this point indicating that they are converted into silica fibres.

This experiment also demonstrates that the SiO_2 produced at temperatures below 1000°C is not sufficiently mobile to form a coherent glassy film that can protect the residual carbon against oxidation so in the control oxidation process a higher temperature than this value is necessary for the desired mobility of the SiO_2.

The SEM observations showed that the CO-CSA fibres have smooth outer surfaces similar to those of the CSA fibres. Examination of transverse sections by the SEM showed no clear evidence of an outer layer of SiO_2.

However, EDX analysis of the fibre surface and the internal area of the fibre showed that the surface has a significant oxygen peak, whereas there is no appreciable oxygen detectable in the internal area (Figure 3). Thus, a very thin adhesive SiO_2 layer is present. When measuring the electrical resistance of the CO-CSA fibres, it was noted that the outer surface acts like an insulation layer but the inside has a resistivity value typical of the original CSA fibres. This is also a good evidence of the presence of the silica outer layer. The absence of a clearly discernible silica coating suggests that there is not a clear-cut visible interface between the protective layer and the inside structure of the CO-CSA fibres. This could be beneficial to the fibres since the layer will not behave like an artificial coating that tends to crack in use. The tensile properties of the CO-CSA fibres depend mainly on the characteristics of the spinning precursor, spinning conditions, stabilisation extent and control oxidation conditions. The control oxidation process reduced the tensile strength of CSA fibres by 20-30%, but increased the Young's modulus by a factor of 20% due to the introduction of the impermeable silica layer. This implies that the control oxidation reaction introduced additional flaws or increased the size of the existing defects. The CO-CSA fibres still maintain approximately 70% of the initial strength after being exposed in air at $1000°C$ for 20 hours.

Conclusions

When the CSA fibres were heated to $1200°C$ under argon atmosphere and then exposed to oxygen for a short period of time, an oxidation resistant silica layer could form on the fibres. The presence of the silica layer was indirectly proved by EDX analysis and the electrically insulative surface also indicates the existence of the silica layer. The CO-CSA fibres have a tensile strength of 800 - 1100 MPa with greatly enhanced oxidation resistance.

References

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3. Hoffman, W. P., Phan, H. T. and Groszek, A., Carbon, 1995, 33, p 509.
4. Fergus, J.W. and Worrell, W.L., Carbon, 1995, 33,p 537.
5. Yajima, S., Hayashi, J. and Omori, M., Chem. Lett., 1975, No. 9, p 931.
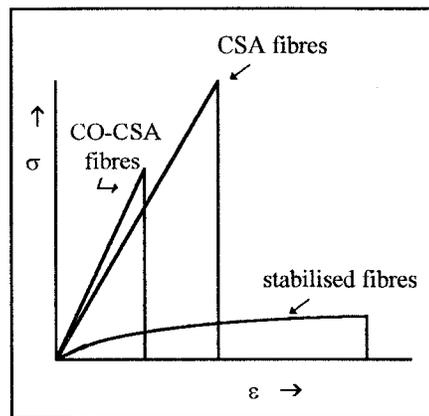6. Lu, S., Rand, B. and Bartle, K.D. in Carbon'96 (Ext. Abstr.) Newcastle Upon Tyne, 1996, p 620.

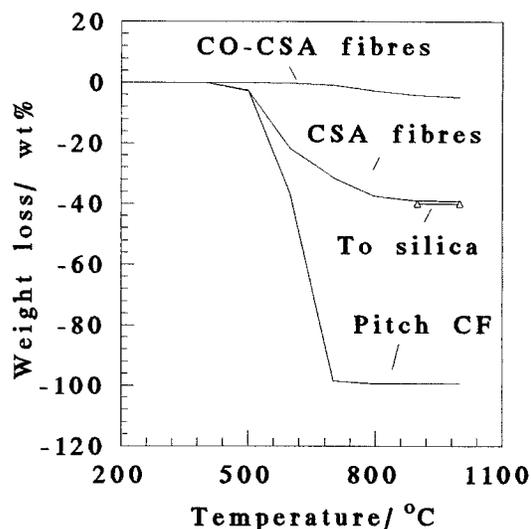Figure 1. Typical stress/strain curves of fibres

Figure 2. Comparative thermogravimetric analysis of fibres in air at a heating rate of $5°C/min$ to $1000°C$
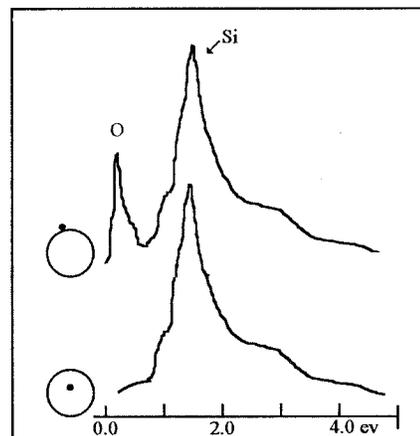

Figure 3. EDX analysis of the surface and internal area of CO-CSA fibre (• measuring point)