PREPARATION OF PYROCARBON COATED CARBON FIBRES FOR USE IN LIGAMENT REPLACEMENT

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Introduction

Successful experiments with carbon fibres as tendon and ligament replacement were first reported by H.R. Jenkins (1976). The biological inertness, the high specific tensile strength and the pliability of carbon filaments constitute this material to take charge of damaged or absent tendons. The implanted fibre tows act furthermore also as a scaffold for regenerating tissue, which is growing around, along and through the fibre bundle. But also a partial disintegration of the fibre is observed and the removed carbon particles are transported primarily into lymph ducts. Nevertheless it is not yet cleared up, where these particles are finally deposited. It can not be excluded, that the mechanical degradation of fibres occurs before the tissue is regenerated. The mechanical properties of implanted carbon fibres are not completely utilized. It is obvious to try to improve the fibre surface properties, e.g. its resistance against splitting and breaking. The aim of the present work was, to obtain such modifications of the carbon fibres by pyrocarbon depositions. The fibres then were tested "in vivo" in animals.

Principles of pyrocarbon deposition on the monofilaments of carbon fibre yarn

Carbon fibre yarn, consisting of several thousand monofilaments, are geometrically complicated systems with a large inner surface area. Figure 1 shows schematically the cross section of a part of fibre bundle after pyrocarbon deposition. The average slit width between the monofilaments can be assumed to be about 1 µm. The overall deposition rate must be controlled by the chemical reaction and not by the diffusion of the gas molecules to and from the fibre surface in order to obtain uniform coatings (AGGOUR et al. 1974; FITZER et al., 1973). Otherwise the carbon deposition will take place on the outer shell of the bundle, causing the formation of carbon bridges between the monofilaments, which will not only reduce the flexibility of the yarn, but may also prevent the ingrowth of fibrous tissue in implanted yarns. It was found experimentally, that these carbon bridges can be avoided only if the coating thickness does not exceed about o,3 µm (FITZER et al., 1973; SAHEBKAR, 1973). From this result one can conclude, that a slit width of o.6 µm seemed to be present between the filaments during deposition process. This value is confirmed by the average bundle diameter of about 1,o mm in the case of 1o.ooo and o,5 mm for 3ooo monofilaments. As a consequence the deposition gas must penetrate the bundle up to a depth of o,5 mm and o,25 mm respectively.

A deposition apparatus was developed basing on the experience in SiC deposition from methylchlorosilanes /hydrogen mixtures (AGGOUR et al., 1974). It was shown, that this penetration depth can be realized even in the case of pore diameters of 1 µm. Theoretical calculations, using the THIELE modulus $\sqrt{k \cdot (L^2/D)}$, have confirmed this result (FITZER et al., 1973). The transfer of these experiments on pyrocarbon deposition from methane has shown, that hot wall arrangements must be used in that case. In cold wall arrangements with directly heated fibre bundles inhomogeneous deposition was found by SAHEBKAR (1973).

The deposition apparatus

The continous CVD of pyrocarbon from methane was performed in a tubular reactor with hot wall arrangement and inductive heating. The apparatus (fig. 2a) consists of an outer quartz glass shell, a graphite tube as susceptor of inductive heating and a device for fibre transport. The residence times of the fibres can be varied between 10 sec. and some minutes. The gaseous feed enters through whirl-nozzles, as shown in part b of fig.2, in order to separate somewhat the monofilaments and to avoid adhering during deposition.

Experiments

Commercially available PAN based carbon fibres type II, SIGRAFIL HF with 10000 filaments (fibre diameter: 8-9 µm, tensile strength: 2200 MN/m^2) and TORAY T300 with 3000 filaments (fibre diameter: 7-8 µm, tensile strength: 2560 MN/m^2) were used as substrates. Both fibre types have nearly circular cross sections of monofilaments. A deposition temperature of 1300°C, a methane feed of 10 l/h, and a residence time of the substrate of 180 sec. were applied.

Results

Carbon black formation was avoided by argon addition to the reaction gas. The optimal deposition conditions are indicated in fig. 3. It was found, that a minimum coating thickness of o,15 µm was necessary in order to achieve homogeneous coatings on each monofilament. A coating thickness of more than o,3 µm decreases the flexibility of the fibre bundle. The average coating thickness was measured by weighing: 0,15 µm for SIGRAFIL HF with 10 000 monofilaments and 0,35 µm for TORAY T 300 with 3000 monofilaments.

Table 1 shows the mechanical properties of the fibres before and after coating. In the case of TORAY T 300 the coating resulted in a small increase of the tensile strength of 8%, in the case of SIGRAFIL HF of 4%. YOUNG's modulus and strain to failure are not influenced by deposition. These results are similar to former observations of FITZER at al.,(1973), who reported, that an improvement of the fibre strength by PC deposition can only be achieved in the case of low strength fibres, and here up to 30%.

Medical Investigations

Medical experiments were performed on 20 rabbits, aged 12 weeks. The medial collateral ligament of the knee joint of the animals was resected. Bone screws were placed into the point of origin and insertion of the medial collateral ligament in the tibia and femur. These screws were tied together with the carbon fibres in a figure 8 fashion.

Furthermore on 10 rabbits only the medial collateral ligament was resected and 10 rabbits were used as control group for the "only resected" and "carbon fibre replaced" animals. Histological investigations after 3 months have shown the incorporation of the fibres in the tissue.

Indications were found for some fibres being removed, which is a symptom, that breaking of the fibres could not be avoided completely. The full knee joint function was maintained (WOLTER et al., 1977). The animals are still under observation. It is expected that the final results of the present test will allow to draw some conclusions on the effect of the coatings.

References

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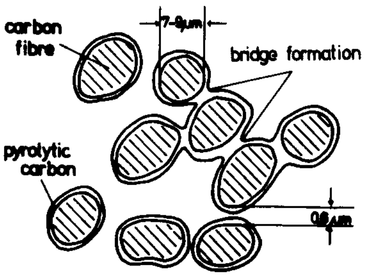

Fig.1: Schematic of a PC-coated carbon fibre bundle

a)

b)

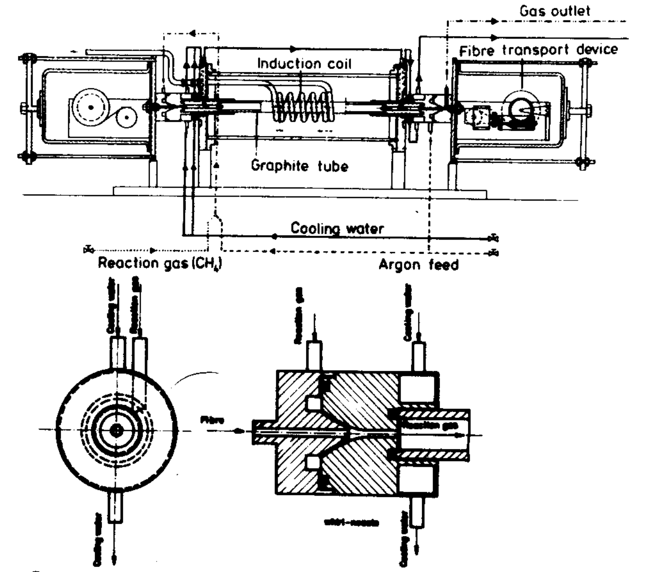

Fig.2: Deposition apparatus (a) Whirl-nozzle (b)

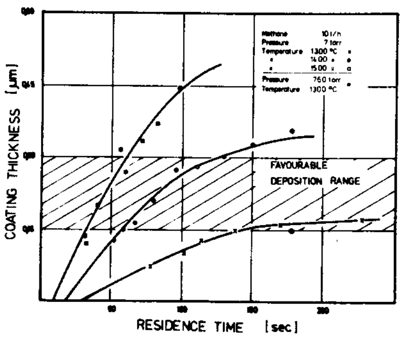

Fig.3: Coating thickness as function of temperature and residence time

Fibretype		TORAY T300/90A	SIGRAFIL HF
Tensile strength [MN/m²]	without coating	2560	2220
	with PyC coating	2760	2310
Youngs modulus [MN/m²10³]	without coating	218,8	185,4
	with PyC coating	224,6	186,6
Strain to failure [%]	without coating	1,17	1,27
	with PyC coating	1,23	1,18

Table 1: Mechanical properties of carbon fibres before and after deposition