FRACTURE TOUGHNESS OF PYROLYTIC CARBON-GRAPHITE COMPOSITES FOR BIOLOGICAL APPLICATIONS

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Fracture toughness indentation experiments performed on Si - alloyed LTI PyC - graphite layered composites for biomedical applications have allowed to fully assess the sequence of damages induced in the top pyrolytic carbon layer while increasing the applied load. FEM analysis has indicated a compressive residual stress pattern in PyC. K_c data obtained at different applied loads pertain to composites with a different residual stress level, what is the cause of the large scatter usually found in K_c values while performing such a type of experiments.

A procedure to single out a unique K_{Ic} value for heart-valve screening and design purposes is illustrated.

INTRODUCTION

In the fifties and sixties pyrolitic carbon (PyC) deposited from hydrocarbons in a fluidized bed had considerable technological importance in the nuclear field for use as coatings on various oxide and carbide fuel particles. Today PyC composites have great interest for biomedical applications. Artificial heart valves fabricated with PyC-graphite composite have been seen at times affected by sudden ruptures; renovated attention has therefore been devoted to the problem under the impulse of regulatory bodies.

Heart valves should be designed for a life span of at least 25 years, i.e. for 10^9 cycles, which calls for an adequate fatigue life. Previous analysis had considered fatigue non existent in ceramics and had hypothesised a coincidence between tensile strength and fatigue endurance limit (Schoen (1)). Yet more recent studies developed in the USA (Odell et al (2), Klepetko et al (3)) demonstrated the contrary, calling for greater attention in handling heart valves to avoid inducing cracks that could propagate in a relatively short time. Studies on fracture toughness and fatigue resistance both of PyC and PyC composites have followed ever since (Ritchie et al (4), Dauskardt et al (5) (6), Giplin et al (7)).

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The complex of results indicate a large scatterband occupied by published K_{Ic} values as well as the extreme steepness of the line averaging Paris approach fatigue results (m values ranging to over 100), which might set doubts on the occurrence of a real Paris regime. Also evidence of corrosion fatigue has been presented (4). Restricting ourselves to PyC-graphite composites, such a high brittleness may be strongly influenced by the residual stress pattern as induced by the fabrication procedure and by the layers stiffness ratio which varies in various heart valves leaflets available on the market, as depending on different layer thicknesses foreseen in design.

In the framework of a large research program aimed at assessing the influence of residual stress patterns on fracture toughness of PyC composites for biological applications, results pertaining to a first series of experiments are hereby presented.

BASIC MATERIAL PROPERTIES

Deposition from hydrocarbon gases at atmospheric pressure is adopted for PyC fabrication, with density of carbon layers being strongly affected by the substrate; highest densities are obtained while coating ceramics. For biomedical application the temperature-range in fluidized bed furnaces is 1300-1900 °C; hydrocarbon gas is added with methyl-chlorine silane to get Si-alloyed low temperature isotropic (LTI) Pyrolitic Carbon. The silicon is present in the structure of LTI PyC as sub-micron particles of β-SiC that may lie in preferred directions. Silicon enhances the elastic modulus, without affecting strain to rupture; thus, higher fracture resistances, and conversely hardnesses, are achieved. Temperature strongly influences the residual stress pattern and hence fracture propagation resistance; in fact, if the thermal expansion coefficient (α) of the substrate is larger than the one pertaining to the coating, compressive residual stresses develop, whereas the contrary occurs if PyC has α values larger than graphite. Deposition temperatures have an effect on PyC α values (Bokros (8)), whereas α values of graphite should not be affected by the permanence in the fluidized bed furnace. Deposition temperatures in the vicinity of 1400 °C should yield PyC α values lower than the graphite ones, thus generating a beneficial compressive stress pattern at top layers.

EXPERIMENTAL

Deposition temperatures of 1400-1450 °C have been adopted in the production of disk shape specimens; graphite thicknesses have been kept at about 0.4 mm (in a few cases at 0.2 mm) with the coatings being about 0.8 mm thick. To provide a smooth surface for hardness indentation readings, one side has been polished to yield a 0.4 mm ca. thick coating, as ascertained by lateral sectioning. The other side has been ground to obtain a 0.6 mm ca. thick coating. The residual stress pattern has been evaluated by an axial-symmetric FEM model inserting average values of substrate and coating thermal expansion coefficients related to the 1450 °C ÷ RT range. Fracture toughness values have been determined by the indentation method adopting the procedure described in (5) using the Anstis formulae (Anstis et al (9)). Vickers hardness indentations have been effected either by common hardness testing machines at various fixed loads or by an ad-hoc adapted servo-hydraulic machine to generate continuous low rate load increments (cross head rate = 0.2 mm/min) and to be able to interrupt the test at various not predetermined loads.

Subsequent abrasions of the indented specimens surfaces have allowed to follow, by optical and electronic metallography of the exposed layers, crack morphology evolution and crack propagation at increasing depths up to the coating substrate interface.

RESULTS AND DISCUSSION

FEM analysis performed in the case of 0.2 and 0.4 mm substrate thickness and coating to substrate thickness ratios between 0.5 and 2.0 has signalled that a compressive radial stress pattern develops at the outer surfaces and proceeds with little variations up to the coating - substrate interface; opposite to this, an obvious tensile stress pattern develops in the graphite. The analysis also indicates a potential dangerous zone at the disk circular rim, where the above described stress pattern inverts and tensile stresses develop in the Si-alloyed LTI PyC coating. An analogous pattern is followed for circumferential stresses, which, furthermore, do not change sign at the disk rim.

Surface observations after hardness tests at 10, 15, 20, 30 and 31.25 kg applied loads indicate that first nucleated cracks appear in directions parallel to the sides of the indentations with 15 kg applied loads; at 20 kg occasional radial cracks emanate from the indentation tips, whereas at 30 or 31.25 kg very long radial cracks are always present. Having singled out that the critical force range for radial crack development lied just after 200 N, it was decided to apply a pyramid indenter to a servo hydraulic machine equipped to generate a continuous load-indenter displacement diagram. It was noticed that in the 200 ÷220 N range a distinctly audible ‘clack’ consistently occurred with a distinctive load drop developing in the recorded diagram soon after the clack was heard. From that point on serrations in the diagram continued to develop, accompanied by later clacks and smaller load drops at not consistent load levels. It was then decided to perform tests being ready to interrupt at various “clack-load levels” with the hope to observe just nucleated cracks that had not let propagate under too a large load. Surface observations performed on specimens corresponding to tests interrupted at various stages indicate that 4 radial cracks emanating from the indentations corners occur only at quite large load levels (in the vicinity of 250 N); the first clack does not correspond to any radial crack nucleation, which instead occurs later, showing nucleation first from a pair of corners and then from the other pair.

To investigate on the cause of the first clack, which also signals a distinctive variation in the load-displacement curve, successive abrasions were performed on specimens undergone test interruption after the first load drop. Upon abrading top surface layers (about 25 μm) four radial cracks were discovered with their direction coinciding with the diagonals of the pyramid indenter. Their length, being small at the first plane of their appearance, increased soon after at increasing abrasion depths and then remained constant up to the coating - substrate interface where the cracks stopped without propagating into the graphite. Analogous observations effected on specimens corresponding to tests interrupted at larger loads have allowed to ascertain that upon increasing the load a further system of cracks emanating at the surface from the indentation corners develops and coalesces with the previous one. Concurrently with the second system of radial cracks, a few partial conical cracks develop below the surface, which finally yield a third system of cracks this time of complete conical shape. Such a system has an average opening angle of 68°, in full agreement with what can be seen while performing indentations on open structure ceramics

(Cook and Pharr (10)). Further radial and conical cracks form at even larger loads. These observations confirm what has been illustrated in the works by Ely et al. (11); a doubt arises on the reason why the first system of crack does not extend upward to the specimen surface and instead stops at same distance from it. It is suggested that the reason resides in the triaxial compressive stress field at the root of the indenter, which reduces after the development of the first cracks, but does not annihilate completely if the carbon coating is adequately thick. Then further loading is required to form radial cracks at the surface. Conversely if the coating is relatively thin the first system of cracks emerges to the surface, as probably in the case of experiments performed by Ritchie et al. who were using composites with 0.25 mm ca. Si-LTI PyC coatings.

Cracks visible on the surface are therefore forming when the displacements induced at the corner of the indenter while increasing the load are able to generate stress intensity factors (SIF's) large enough in adjacent material; it has to be born in mind that local SIF's result from the algebraic sum of the applied SIF and the residual SIF due to the pre-existing residual stress pattern, as resulting from the fabrication procedure and the previous cracking systems occurrence. Cracks will stop when the local total SIF reduces to the local fracture toughness of the coating.

Proposed formulae (Ponton and Rawlings (12)) for indentation fracture mechanics are based on the applied load, crack length and the Young's modulus to hardness ratio; no provision is made to single out any residual stress patter influence. Thus, calculated fracture toughness values do not pertain to the material in general, but to the pre-stressed material as generated by the composite fabrication procedure as well as the complex cracking evolution. Therefore published values of fracture toughness cannot be considered intrinsic proprieties of the various polycarbon materials as produced by different makers but have to be assumed as the apparent fracture toughness of the top layers of very specific carbon graphite composites.

Fracture toughness results obtained by us using the Anstis formulae and its lower limit limitation for crack lengths (9) have been collected in a diagram as a function of measured crack lengths (figure 1). Considering that conical cracks induce a strong damage to the layer similar to that hypothesised by Anstis when considering the indentation influence, it has been decided to exclude from the acceptable cracks those whose crack semi-lengths (c) were less than the average diameter (2d) of the cone outlined by conical cracks measured at the indentation root level (290 μm ca in our case). It can be seen from the diagram that the range of acceptable K_c's is 0.3-2.2 MPa$\sqrt{m}$. Such a range may be considered too large to be of practical use. Yet, the fact that the entire set of experimental points lies in effect on a single interpolating line reflects a continuous phenomenon that causes a continuous reduction of recorded K_c's. The only continuous phenomenon being the continuous increase of the damage to the coating as the applied load increases, it may well be that the increase of the damage is the controlling mechanism for fracture toughness reduction. On the other hand, as the residual compressive stress field at top layers reduces its intensity as damage accumulates beneath, it may be possible that its beneficial effects tend to vanish. Then, we may interpret the falling K_c's as pertaining to different Si-LTI PyC-graphite composites characterised by different compressive residual stress patterns. Since for practical design purposes an heart valve has to be judged in its integrity, without taking into account extensive damage caused by impossible high loads, a conventional assessment procedure for their fracture toughness screening is hereby proposed.

Having performed a number of tests on specimens fabricated like the heart valves with the same coating to substrate ratio as real leaves, the fracture toughness is taken as the intersection value of the interpolating line drawn as in figure 1 and the vertical exclusion line based on the average diameter of the cone outlined by conical cracks measured at the indentation root level. Applying such a procedure to the set of our tests a unique K_{Ic} value of 2.3 MPa$\sqrt{m}$ can be obtained (see the dotted horizontal line in figure 1).

CONCLUSIONS

Vickers hardness indentations performed on Si-alloyed LTI PyC-graphite composite specimens and subsequent optical as well as scanning electron microscope observations at various distances from the surfaces have allowed to ascertain that 3 different systems of cracks develop while increasing the load applied to the indenter:

i) a system of radial cracks originating from the coating-substrate interface, with directions parallel to the diagonals of the indentation; such a system stops at some distance from the surface if the coating is thick enough (at least 0.35-0.4 mm); otherwise it emerges directly to the surface;
ii) a system of surface radial cracks emanating from the corners of the indentation which coalesces with the first one;
iii) a concurrent system of conical cracks originating just below the root of the indenter.

Further cracks develop as the applied load increases, thus increasing the damage to the coating.

Absolute fracture toughnesses of the polycarbon layer cannot be measured since they are hindered by the residual stress pattern originating in the coating by the fabrication procedure and controlled by the difference of thermal expansion coefficients of the coating and the substrate while cooling the specimen to RT. Instead, K_c values measured by surface indentation reflect the particular type of composite that has been obtained by its specific fabrication procedure and by the extent of damage in the coating prior to surface crack nucleation and extension. Basing upon the above considerations, a procedure for assessing fracture toughness of heart valves by surface indentation is proposed.

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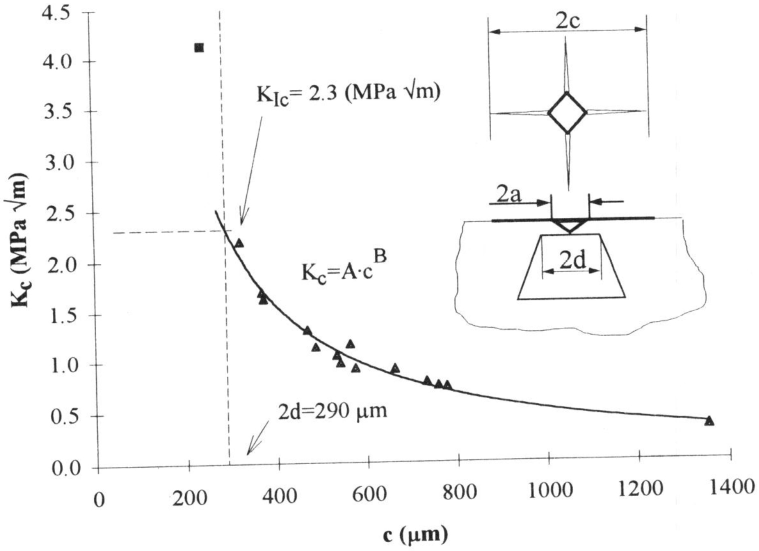

Figure 1 PyC-graphite composite fracture toughness as a function of the crack length