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Hydrofluoric–nitric–sulphuric-acid surface treatment of tungsten for carbon fibre-reinforced composite hybrids in space applications

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ABSTRACT

Hybrid material systems, such as combinations of tungsten foils and carbon fibre-reinforced plastic (CFRP), are replacing metal alloy concepts in spacecraft enclosures. However, a good adhesion between the tungsten oxide scale and the epoxy resin used is required. Here, the effects of a hydrofluoric–nitric–sulphuric-acid (HFNS) treatment on tungsten oxides and subsequent adhesion to CFRP are analysed using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and fracture testing. The work shows that HFNS treatment results in decreased oxygen content, over 50% thinner tungsten trioxide (WO_3) layer and increased nano-roughness on thin tungsten foils. Fracture testing established a 39% increase in the average critical strain for tungsten–CFRP specimens after HFNS treatment was carried out on tungsten. The effect of the oxide scale modification regarding the critical strain energy release rate was $\Delta G_c \approx 8.4\,J/m^2$.

1. Introduction

Spacecraft structures are subjected to tremendous electron and proton radiation as well as bombardment by alpha and beta particles from the space environment. Protection against radiation is the reason why enclosures in spacecrafts are seldom built of pure carbon fibre-reinforced plastics (CFRPs) but of metal alloys instead. Several solutions to hybridize traditional aluminium and pure CFRP designs using fibre modification or metallic components have been developed [1,2]. Tungsten is an ideal element for enhancing the attenuation of electrons in a composite since it has a very high atomic weight and excellent bulk properties [3,4]. The stacking sequence of a CFRP laminate with embedded tungsten layers can be optimized to achieve the required dimensional accuracy, rigidity and radiation protection [5].

Tungsten has been studied extensively in the existing literature and the surface characteristics of tungsten and many tungsten alloys have been reported. Also, the structure and chemistry of the oxides on pure tungsten is rather precisely known. The oxide scale mostly consists of WO_3, although WO_2 following the reduction from WO_3 and also traces of $WO_{2.72}$ and $WO_{2.9}$ due to inadequate oxidation and crystallization defects can exist [6–8]. At room temperature, an approximately 60 Å thick, blue-black coloured and well adhered scale prevails; the activation energy of oxidation and the respective thickening of the scale increases significantly with increasing temperature [9]. Micro-cracking and spalling in the growing oxide scale, especially at temperatures above 625 °C, have been reported [10,11]. In addition, the effects of different chemical treatments and immersions with aqueous mediums have been published [12,13].

The structural integrity of hybrid systems require an enhanced chemo-mechanical compatibility of tungsten with CFRPs. The morphology and chemical state of the oxide scale play an important role in the metal–polymer adhesion during the formation of structural interfaces [14–16]. Adhesion can be increased by applying chemical or electro-chemical surface treatments that modify the oxide scale properties [17,18]. However, the surface treatments of tungsten and also the related interaction with polymers are annoyingly scarce in the existing literature. A sodium-hydroxide treatment, a sol–gel treatment, a hydrofluoric–nitric–sulphuric-acid (HFNS) treatment and special coatings have been introduced for tungsten substrates [19–21]. Recently, it was found that the HFNS acid treatment increases the total surface tension and polarity of pure tungsten surfaces [21]. The increases in the total surface energy

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Table 1
The HFNS surface treatment process, derived from a procedure suggested by Guttmann [19], of tungsten foils in the study.

Treatment	Action	Medium	Duration
Degrease #1	Wiping	Methyl ethyl ketone (MEK)	–
Degrease #2	Immersion	Methanol	2 min
Rinsing	Immersion	MilliQ water	2 min
Etching	Immersion	Hydrofluoric acid (sg 1.18) 5 ppw; nitric acid (sg 1.41) 30 ppw; sulfuric acid (sg 1.84) 50 ppw; MilliQ water 50 ppw; few drops of hydrogen peroxide	67 s
Rinsing	Immersion	MilliQ water	2 min
Dehydration	Oven 70 °C, vertical positioning	Air	15 min

sg = specific gravity, ppw = part per weight.

and polarity of metallic substrates is typically expected to result in stronger adhesion with adhesives and coatings [22,23].

In this study, we analyse the influence of the HFNS surface treatment method on the oxide scale of tungsten using atomic force microscopy and X-ray photoelectron spectroscopy. In addition, the mechanical behaviour of the structural interfaces between CFRP composite parts and tungsten foils in cracked-lap shear specimens is studied. The work addresses the changes in the layer structure of the tungsten oxide scale due to the HFNS treatment and reports that the fracture of the interface is a competition between tungsten–epoxy de-adhesion and carbon fibre–epoxy de-adhesion processes.

2. Materials and methods

2.1. Tungsten surface treatment and specimen preparation

Tungsten of 99.95% purity was obtained in the form of mechanically thinned (rolled) foil with a nominal thickness of 50 μm and planar dimensions of 500 mm × 100 mm (Alfa Aesar GmbH, Germany). The foil was cut into two pieces in order to prepare two different test series. First, a series representing bare tungsten foil (*Bare*) was degreased using methyl ethyl ketone. The second series was surface treated using the hydrofluoric–nitric–sulphuric-acid treatment (*HFNS*). The HFNS method included six treatment steps, as described in Table 1, and it essentially corresponds to the method originally described by Guttmann [19]. Samples were also extracted from the two tungsten foil pieces for subsequent surface characterization.

The tungsten foil pieces were laminated into a carbon fibre-reinforced composite material (CFRP) in order to prepare specimens for fracture testing. The CFRP was acquired in the form of pre-preg tape with a nominal thickness of 0.29 mm, 300 g/m^2 areal weight and 68% (weight/weight) fibre content (Advanced Composites Group, Umeco, UK). The CFRP pre-preg tape consisted of MTM® 57 epoxy resin (ACG, UK) and was unidirectionally reinforced by high-modulus M40J(12K) carbon fibres (Toray, USA). For preparing cracked-lap shear specimens (see Section 2.4), the tape was cut into slices of 20 mm × 180 mm. Likewise, the tungsten foil pieces were cut into slices of 20 mm × 180 mm. The CFRP pre-preg and tungsten slices were laminated by applying a lay-up of (0_5/W/0_5) for each specimen (substrate and lap). Tetrafluoroethylene–ethylene release film (thickness 25 μm) was used for making 20 mm long pre-cracks between the lap and the substrate. An eight-piece aluminium-brass mould was used to control the dimensional accuracy and finally, a vacuum bag was fixed over the entire moulding setup. The specimens were cured inside an autoclave (no overpressure was used) by applying the cure cycle demonstrated in Fig. 1. The lay-up, dimensions and strain gauge instrumentation are illustrated in Fig. 2.

2.2. Atomic force microscopy (AFM)

The effect of the HFNS treatment on tungsten oxide morphology was studied using atomic force microscopy (Dimension 5000 – Nanoscope 5, Veeco Instruments, USA). Tungsten foil samples (10 mm × 10 mm) were fixed on steel substrates and the tungsten surfaces were directly analysed without further preparations. The AFM measurements were performed in tapping mode; single cantilever probes with a silicon crystal tip were used (NSC 15, 10 nm nominal tip radius, 46 N/m stiffness, Micromasch, Estonia). The tip velocity was adjusted during the measurement, to improve tip tracking, over a range of 2–10 μm/s. The tip quality was verified before and after each measurement session using a calibration sample (TGT 01, Micromasch, Estonia).

2.3. X-ray photoelectron spectroscopy (XPS)

A comparative analysis of the surface chemistry of the oxide layer prior-to and after applying the HFNS treatment was performed using the AXIS Ultra electron spectrometer (Kratos Analytical, UK). Data was recorded using monochromatic Al Kα X-rays at 100 W. Surveys were recorded at 160 eV pass energy and 1 eV step and the high resolution regions at 20 eV pass energy and 0.1 eV step. A fresh cellulose sample was used as an in situ reference with each measurement batch [24]. CasaXPS software was used in the XPS data analysis. The aliphatic carbon component of C 1s, at 285.0 eV, was used for the correction of binding energy (BE) scale. In the case of W 4f peaks, the high resolution spectra were fitted with three Gaussian doublets.

The effect of the HFNS treatment on the oxide layer thickness was studied in the context of a homogenous oxide overlayer on a semi-infinite tungsten substrate and thin contamination layer on

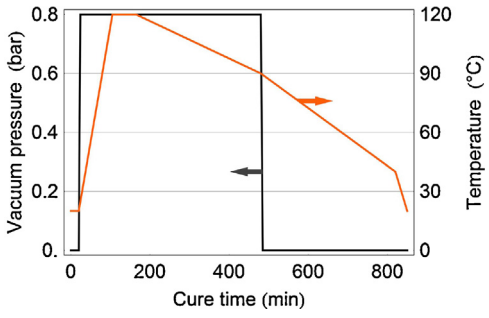

Fig. 1. The autoclave cure cycle used in the preparation of tungsten–CFRP hybrid specimens in the study.