

**INVESTIGATION OF CARBURISATION OF TUNGSTEN-CARBIDE FORMATION
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Tungsten filaments were carburised by pyrolytical decomposition of methane and hydrogen over hot filament surface. The carburised filaments were characterized by Raman spectroscopy, X-ray diffraction measurements and scanning electron microscopy. Featureless micro-Raman spectra confirm a formation of tungsten carbide layer after 10-minute carburisation. Strong WC-related peaks in X-ray diffraction spectra are observed for carburisation temperatures of 1600 °C and higher. SEM analysis of filaments fracture indicates a creation of WC layer over W filaments, generation of deep micro cracks in WC region and a preferential creation of WC grains in thin surface layer over bulk of carburised filaments in dependence on carburisation time is observed. Presented results indicate that successful carburisation is practically self-stop process after 5 hours.

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1 Introduction

The “refractory carbides” represent carbides of transition metals in IV-VI groups. Their intrinsic properties, such a high melting point, high thermal stability, high wear-resistance and low chemical reactivity make them an attractive material also for the vacuum technology [1]. Tungsten, molybdenum, tantalum and rhenium are widely used as the “activation filaments” in various chemical vapour deposition processes. These filaments are heated up to high temperature (2000 - 2400 °C) in order to enhance *i*) thermal electron emission and *ii*) rates of chemical reactions acted over the hot surface. Furthermore, the stability of filaments used in achieving of the “hot filament chemical vapour deposition” (HF CVD) plays an essential role in reproducible and well-defined growth of diamond and diamond-like thin films. Therefore, it is necessary to stabilize the

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surface of filaments, which are employed in aggressive gas environments (like carbon consisting gases – methane, ethane, *etc.*). This stabilization process (often called carburisation) is mostly performed via chemical modification of filaments in reactive gas atmosphere.

In the present study, we investigate the dependence of carburisation process of tungsten filaments on process time. The tungsten filaments were carburised by pyrolytical decomposition of the gas mixture of methane and hydrogen in the HF CVD reactor.

2 Experimental

Tungsten “technical” wires (0.6 mm in diameter and 120 mm in length) used for CVD were cleaned in acetone and loaded into the HF CVD chamber. One end of the filament was fixed to the supporting electrode (molybdenum rod, 3 mm in diameter), and other one was connected to the flexible molybdenum electrode (3 mm in diameter) that slides free in the longitudinal direction. It was experimentally confirmed that the fast carburisation process (typically at extreme process parameters, like filament temperature of 2000 °C and higher, methane concentration higher than 3% , and/or dc plasma assisted environment) caused the filament to fail very quickly during the chemical vapour deposition. Therefore, the maximum starting temperature for carburisation was limited to approximately 1600 °C at the dc current of 30 amps per filament. To keep predefined carburisation conditions, the whole process was controlled via PC unit.

The initial filament temperature was measured by the two-colour optical pyrometry in its centre and it was corrected for tungsten emissivity $\varepsilon(W) = 0.4$ at $\lambda = 650$ nm. On the other side, only a negligible correction was used for tungsten carbide emissivity ($\varepsilon(WC) = 0.85$) [2]. It must be noted for the completeness that the filament temperature near electrode rods was lower than that at the centre.

Characterization of filaments was performed by conventional micro-Raman spectrometry using an ISA Labram equipment (Jobin Yvon/Spex/Dilor, Horiba Group) equipped with a 632.817 nm line from a He-Ne laser in the backscattering geometry. A 100x microscope objective was used to focus the laser onto a spot of approximately 1 μm in diameter and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. Furthermore, a confocal hole diameter of 200 μm , a spectrograph entrance slit of 150 μm , and a 1800 grooves/mm diffraction grating were employed. The X-ray diffraction data were collected by a horizontal goniometer HZG3 equipped with a graphite monochromator in the primary beam tuned for Cu-K α radiation ($\lambda = 0.1542$ nm). The cross-section measurements of filaments were observed by DSP powered TESLA BS 300 scanning electron microscope with a spatial resolution of up to ~ 25 nm.

2.1 Carburisation process

Before carburisation process, filaments were heated up to ~ 1600 °C in vacuum for 3-4 min to outgas any filament contaminations and to re-crystallize it from fibre-like to polycrystalline structure (Fig. 1 - point A). Then, a gas mixture of methane and hydrogen was led into a vacuum chamber at the gas flow ratio of 3 : 300 sccm (a standard cubic centimetre per minute). The total gas pressure was adjusted by a needle valve and kept at constant value of 3000 Pa.

After achieving stable pressure conditions, filaments were slowly heated up to temperature of 1600 °C at which the pyrolytical dissociation of methane and hydrogen started over the surface of filaments. The starting point for filament carburisation can be clearly distinguished as an

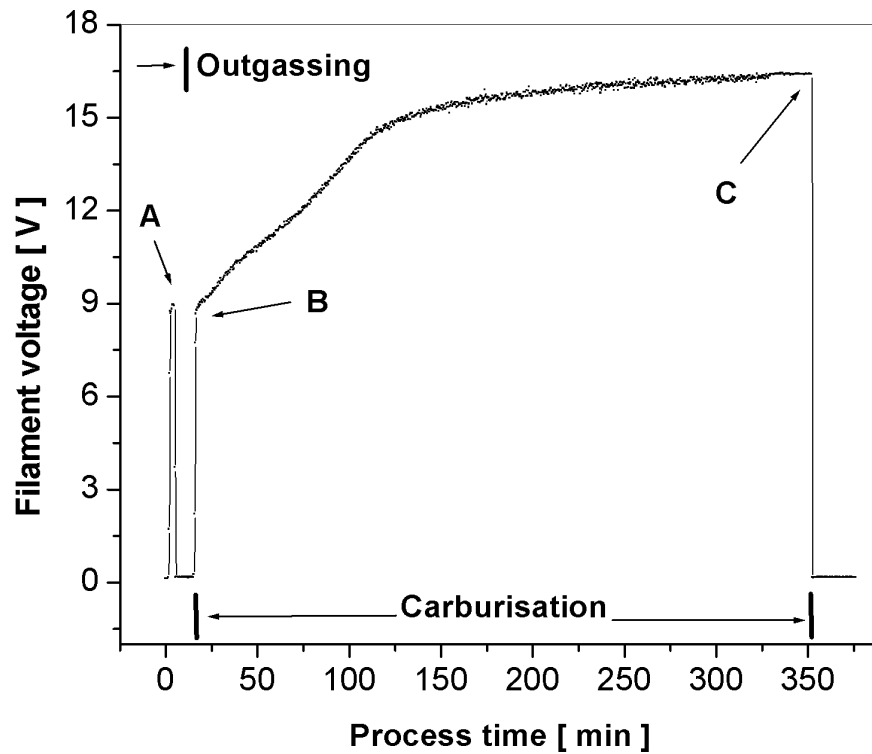


Fig. 1. Time dependence of filament voltage during the carburisation process.

automatic increases in filament voltage for a given DC current (approx. 30 amps per filament in our experiments). Increase in voltage arises from the fact that the resistivity of formed WC layer is importantly higher (up to ten times) than the resistivity of the original tungsten filament. The thickness of WC rises to the centre of filament, total filament resistance increases up and, as a consequence, voltage over the filament saturates (Fig. 1 - point C). At this point, no additional tungsten carbide formation is possible and the carburisation process seems to be the selfstopping process.

After finishing of carburisation, the W/WC filaments appeared light grey in colour. The most inconvenient characteristic of them is brittleness, which can result in short lifetime since a small mechanical disturbance could result in its breakage. During the carburisation process, the treated filament sometimes showed a considerable distortion. When this occurred, the filaments were discarded from the experiments and the carburisation procedure was repeated until the suitable filaments were obtained. The filament cracking was observed for carburisation time of 2 hours and higher, and it occurs due to the volume extension of formed WC phase over the W filament.

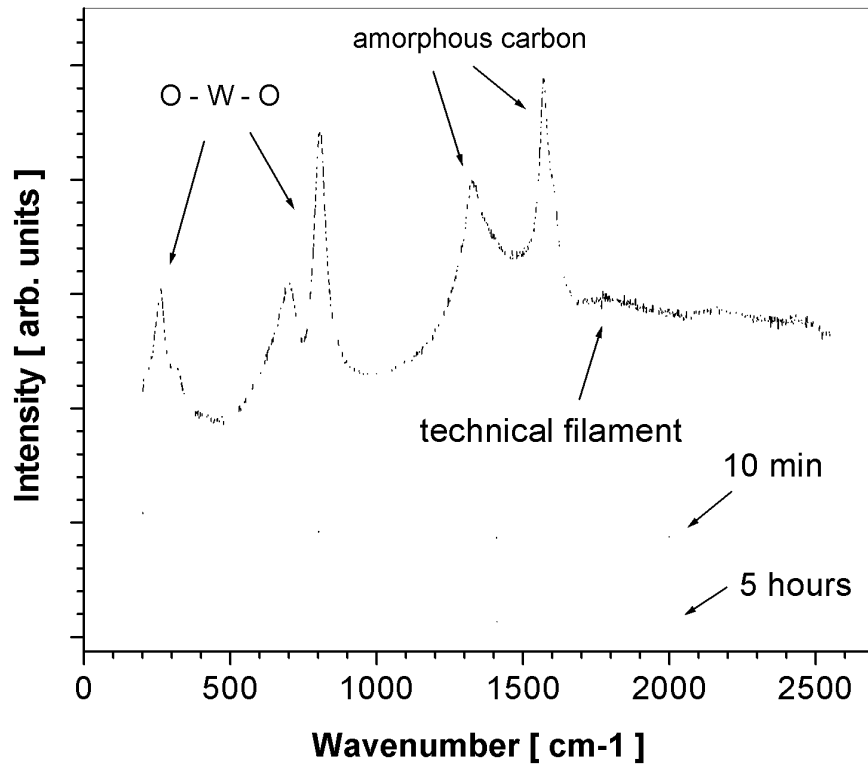


Fig. 2. Raman spectra of non-treated tungsten filament and carburised filaments for 10 min and 5 hours.

The total diameter of filament raised from 0.6 up to ~ 0.7 mm as the carburisation time increased up to 5 hours.

3 Result and discussions

3.1 Raman measurements

Fig. 2 compares Raman spectra of technical tungsten filament and filaments carburised for 10 minutes and 5 hours, respectively.

The Raman spectrum of non-treated filament, *i.e.* of filament measured before loading into the working chamber, shows a few broad bands. The bands centred at 699 and 805 cm^{-1} are attributed to tungsten oxide stretching modes [3]. The additional broad peaks centred at 266 and 325 cm^{-1} are attributed to bending vibration of O-W-O. Furthermore, this Raman spectrum reveals two broad bands centred at 1326 and 1580 cm^{-1} . These broad bands centred are

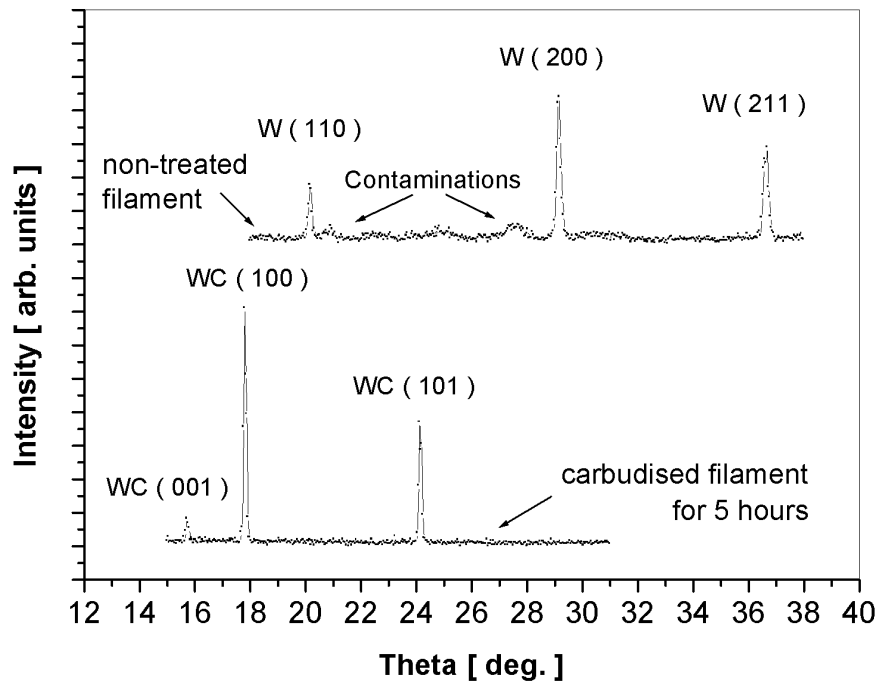


Fig. 3. X-ray diffraction patterns of non-treated filament and carburised filament for 5 hours.

known as D and G band of amorphous carbon [4]. The weakly observable band centred at 1450 cm^{-1} , as found only after fitting by software Labspec 2.08, is assigned to diamond-like-carbon. The observed bands are characteristic only for non-treated filament and represent *i*) an oxide contamination and *ii*) amorphous carbon due to a graphite suspension used as the lubricant in the production of thin tungsten wires.

On the other side, Raman spectra of filaments treated for 10 minutes and 5 hours are similar and show rather featureless spectrum, *i.e.* no surface contamination is detectable. The lost of Raman bands is in good agreement with the fact that metals do not exhibit a Raman signal.

3.2 X-ray diffraction patterns

XRD patterns of the filament before and after the carburisation are shown in Fig. 3. The non-treated tungsten filament shows three sharp W-corresponding lines identified as W(110), W(200) and W(211). Some broad background “bands“ can be related to impurities presented in the W filament and/or on its surface, as was confirmed by Raman measurements. However, the XRD pattern of the same filament, as measured after the finished 5-hour carburisation process, shows

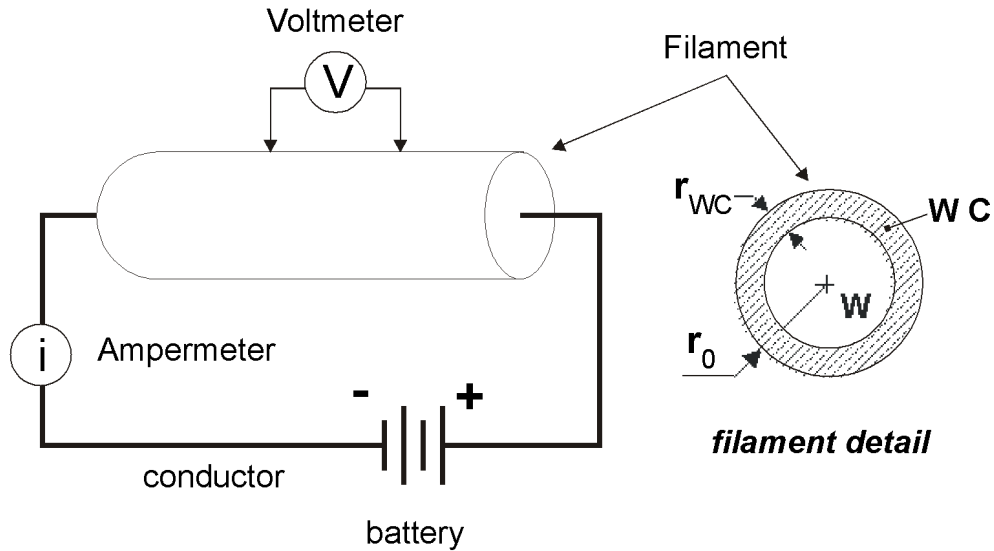


Fig 4. A schematic view of measurement set-up of electrical resistance.

only sharp WC-related lines and no other phases are detectable.

3.3 Electrical resistance

The electrical resistance of filaments was measured by a two-probe method at room temperature, as schematically sketched in Fig. 4. An external loading force of 0.5 N was applied onto the voltage probe to obtain good contact and to avoid a wire breaking. The measured electrical resistance vs. carburisation time is shown in Fig. 5.

The electrical resistance rises with increasing carburisation time. First, it rises slowly from 24 to 36 m Ω with carburisation time increase from 0 to 60 minutes. Next, the curve rises steeper and the resistance achieves value of 178 m Ω for carburisation time of 3 hours. The resistance saturates at value of 200 m Ω for 5 hours.

Further insights come from examining of calculated thickness of tungsten carbide in dependence on the carburisation time. The model is based on previous experiments [5-6], which resulted in observations that the WC phase has been only developed as the dominant tungsten carbide phase in a hydrogen environment at temperatures above 1500 °C. Additionally, it is important to note, that effects of *i*) formation of other carbon tungsten phases (like W₂C), and *ii*) increase in the filament resistance due to defects in filaments are not included in this simplified model.

Generally, the filament resistance of W/WC mixture can be calculated using the Eq. (1)

$$R_{total} = \frac{R_W R_{WC}}{R_W + R_{WC}} \quad (1)$$

where: R_{total} is the total resistance of W/WC mixture (as measured by the two probe method), R_W is the resistance of tungsten filament with the radius of $(r_0 - r_{WC})$, R_{WC} is

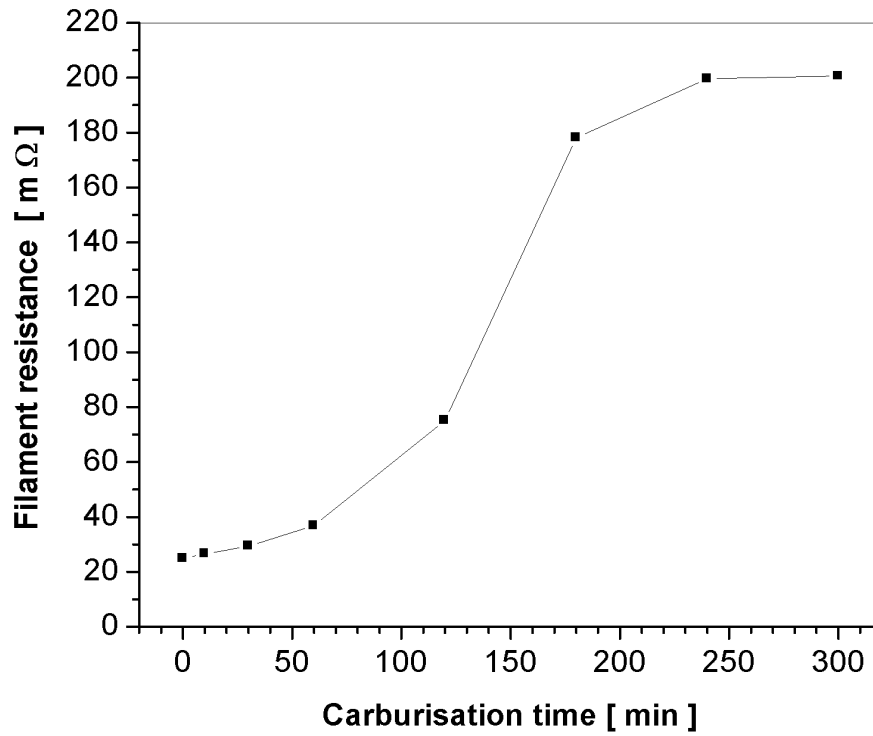


Fig 5. Electrical resistance of filaments vs. carburisation time.

the resistance of the formed WC layer with the layer thickness r_{WC} , and r_0 is the radius of the original tungsten filament ($r_0=0.3\text{ mm}$) (see Fig. 4, filament detail).

Let denote that the R_W and R_{WC} resistance is written as follow:

$$R_W = \frac{l \cdot \varsigma_W}{\pi(r_0 - r_{WC})^2} \quad R_{WC} = \frac{l \cdot \varsigma_{WC}}{2\pi r_0 r_{WC} - \pi r_{WC}^2} \quad (2)$$

where: R_W , R_{WC} is the resistance of tungsten and tungsten carbide, l is the filament length (120 mm), ρ_W and ρ_{WC} is the resistivity of W and WC.

After plug in of all the data into (1) and (2) we get:

$$r_{WC} = r_0 - \sqrt{r_0^2 - \frac{\varsigma_{WC} r_0^2}{\varsigma_{WC} - \varsigma_W} + \frac{l \cdot \varsigma_{WC} \varsigma_W}{\pi(\varsigma_{WC} - \varsigma_W) R_{total}}} \quad (3)$$

Fig. 6 represents the calculated thickness of formed WC layer in dependence on i) carburisation time and ii) WC resistivity. The resistivity of WC depends on layer quality and can vary

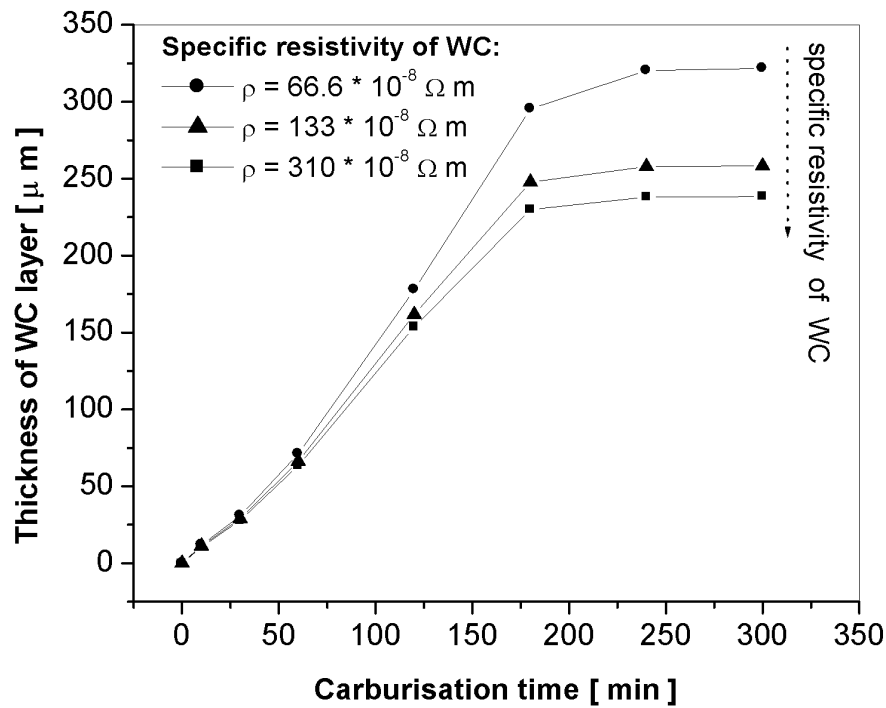


Fig 6. Calculated thickness of formed WC layer in dependence on carburisation time and varied resistivity.

from 20×10^{-8} up to $310 \times 10^{-8} \Omega\text{m}$, and possibly higher [7]. In our case, the calculations have been performed for three different resistivities of WC layer, i.e. 67×10^{-8} , 133×10^{-8} and $310 \times 10^{-8} \Omega\text{m}$, respectively. As could be observed, the calculated thickness of WC layer increases “nearly” independently on resistivity up to approximately 2 hours. Then, these curves saturate at different values of WC thickness in dependence on used resistivity.

Fig. 7 shows a cross-section of the filament carburised for 2 hours, as visualized by SEM in the back-scattered electrons (Fig. 7a) and secondary electrons modes (Fig. 7b). Two different regions are observable after the detail inspection: *i*) approximately $120 \div 150 \mu\text{m}$ thick WC layer at the perimeter of the tungsten core, and *ii*) region of micro-cracks with density rapidly increasing from the depth of approximately $70 \mu\text{m}$ to the surface. These micro-cracks explain a rapid increase in WC layer thickness as carbon can penetrate into the filament bulk across the filament cracks. Additionally, formation of such micro-cracks is responsible for *i*) filament cracking observed for long carburisation times (usually observable after 2 hours) and *ii*) increase in filament diameter from $600 \mu\text{m}$ up to $\approx 700 \mu\text{m}$.

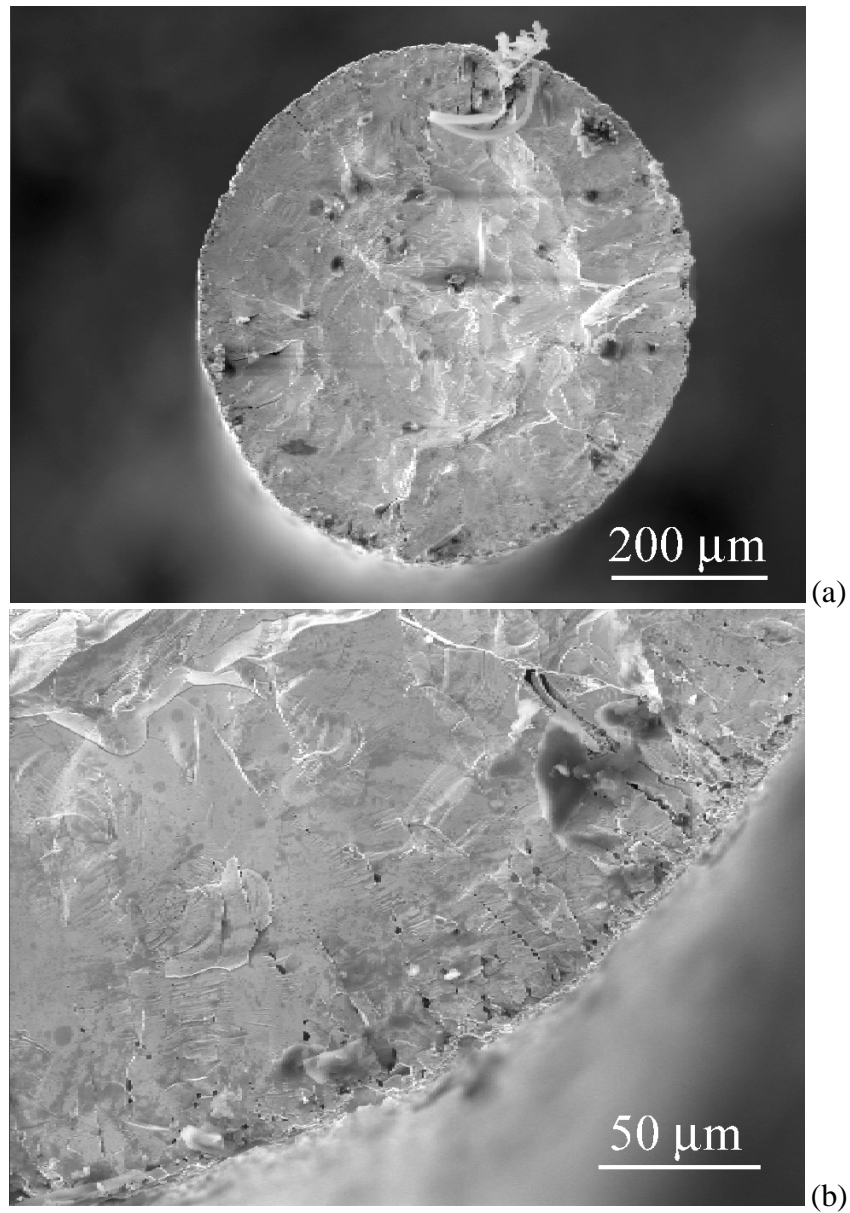


Fig. 7: Cross-section of the filament carburised for 2 hours (a) and detail of the crosssection at the surface (b).

4 Conclusions

Filament carburisation is an important process parameter leading to the reproducible and controllable CVD deposition process. The WC layer successfully formed over the tungsten filament

surface *i*) extends their life time (more than 100 hours lifetime was experimentally achieved), *ii*) reduces tungsten evaporation, and *iii*) stabilizes the carbon flux to the substrate during the CVD diamond growth. The calculated thickness of tungsten carbide in dependence on the carburisation time implies that the growth of WC layer in its early stage does not depend on WC resistivity.

The calculated final film thickness is influenced by the used value of WC resistivity where higher values of ρ_{WC} indicate a trend in decreasing of saturation time of WC. However, this was not our case and the microcracks formed in the filaments were found to enhance the growth rate of WC layer. The complete carburisation of tungsten filament was observed after 5 hours. In addition, such carburised filaments were found acceptable for the reproducible and well-defined diamond growth by the hybrid HF CVD technique [8].

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