TUNGSTEN COATINGS AND FREE STANDING PARTS

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Abstract

Tungsten powders, 20 μm - 100 μm, plasma generated by a water-stabilized spray system WSP®. The molten tungsten was deposited on steel and graphite or boron nitride substrates, whereas the sprayability itself was tested as well as compatibility with other substrates. One of the goals of this experimentation was to gain skills for covering of variously shaped walls of nuclear fusion devices (tokamaks). Also, spraying of free-standing tungsten bodies was realized, by means of substrates easily removable after deposition, such as graphite and BN. Other variant consists of covering of a tungsten mesh or plates armored with tungsten wires. Protection of tungsten against oxidation in the plasma jet was a problem to be solved – the best results were gained with Ar+7%H₂ shroud gas, with substrates placed in graphite cells. The whole spray process was maintained to avoid temperatures over 700 °C when the oxidation is inherent. Spraying onto rotating substrates, when a delamination was prevented, was proved as advantageous. The sprayed products were examined for their structure, density, porosity, content of oxides and also chemical interactions with selected substrates.

Keywords: tungsten coatings; tungsten filters; plasma spraying; shrouding

1. INTRODUCTION

Thermal spraying, and particularly plasma spraying is the most advanced approach to obtain the highest accessible temperatures in the solid materials processing. Refractory materials with the highest melting points \( T_m \) could be processed, such as tungsten metal \( (T_m \approx 3420°C) \) or Zr- and Hf-carbides \( (T_m \approx 3850°C) \). In the present work, we are focused onto production of tungsten coatings on various substrates including metal, ceramics and carbon. Other topic of our paper is spraying of self-supporting forms, such as tubes. And finally, we are also mentioning variously shaped bodies made from spheroidized tungsten filters suitable for a hot media filtration.

2 SOLUTION OF THE PROBLEM

Tungsten is an element very sensitive to oxidation at high temperatures, which is demonstrated by a DTA and TG curves, Fig. 1. Over 700 °C, seriously detrimental oxidation takes place. Also the use of tungsten over such temperature needs protection of inert atmosphere. In plasma spraying, the key point is to prevent oxidation in the plasma and also minimize oxidation of the deposited coating upon cooling. Among the ways how to ascertain this step, air-tight chambers or various types of protective shrouding – by nitrogen, argon, argon-hydrogen mixture are important, as well as so called auto-shrouding that utilizes addition of small amount of tungsten carbide [1,2]. The solution of this problem described here consists of utilization of the central part of the plasma plume only (with a neutral red-ox profile), dimensions of which could be derived from a plasma spray footprint, see Fig. 2. According to the velocity and temperature profiles of tungsten particles fed into a water-stabilized plasma (WSP®), Fig. 3, as recorded by the DPV-2000 apparatus, Fig. 4,
the spray parameters could be specified as: torch power 160 kW, feeding distance 25 mm to 80 mm, spraying distance 190 mm to 300 mm, feed rate 25 kg.h\(^{-1}\) to 40 kg.h\(^{-1}\) [3,4].

Fig.1 DTA and TG curves of tungsten
Fig.2 Spray plume footprint profile (i.e. coating thickness distribution – left and its shape - right)
Fig.3 Spraying with the WSP® generator

Fig.4 a) Typical temperatures and velocities of individual W particles, b) Dependence of W particle temperatures and velocities on spraying distance

3. EXPERIMENTAL PART

3.1 Deposition of tungsten coatings
Tungsten powder (OSRAM Sylvania Towanda) with size distribution 20 µm -100 µm was obtained and oxygen content was analyzed by the fusion in an inert gas (GFA) [5,6] using the analyzer LECO ONH836. In the finest particles, under 20 µm, the oxygen content was 2.78 wt%, whereas in the fraction 50 µm-63 µm it was only 0.028 wt%. This feedstock was in the first variant of the experiment used directly for plasma spraying and in the second variant it was sprayed into a collector filled with liquid nitrogen, to obtain spherical particles [7]. The powders were spheroidized by the following process: A narrow size distribution powder was injected in a plasma jet generated by the plasma torch WSP® operated under 160 kW power (320 V, 500 A). The feeding distance was between 50 mm and 77 mm, the feeding rate of different tungsten powder by two external injectors was between 25 kg.h\(^{-1}\) and 30 kg.h\(^{-1}\). Spraying distance between the nozzle orifice and the substrate as well as the level of liquid nitrogen in the collecting vessel were both between 300 mm and 400 mm. As a carrier gas, nitrogen was employed at a pressure 0.4 MPa. During the flight through the plasma having temperatures up to 30 000 K, tungsten particles melted and spheroidized in course of
solidification due to their surface tension. Spherical particles enabled easier sorting of the size fraction necessary for injection in the narrow central, chemically neutral, part of the plasma plume. The content of bonded oxygen in this size class (mean size 90 µm) was 0.12 wt%. Coatings on steel (standard label CSN 11 373), graphite, boron nitride and aluminum substrates were protected against oxidation and simultaneously cooled by a placement in a graphite chamber with an input window, Fig. 5. The dimensions of the window were made with respect to the spray footprint to allow only the particles traveling in the central part of the plasma to form the coating. The chamber was flushed by Ar with 7 % of hydrogen. Temperature field in individual equipment parts was monitored by the thermal camera Micro-Epsilon TIM 160. After reaching of 450°C-600°C, the spray process was interrupted by the operator and continued just after temperature decrease below 300 °C. Examples of coated parts are in Fig.6, their polished microstructures in Figs. 7 and 8, and properties of the deposits in Table 1.

3.2 Preparation of tungsten free standing parts
Coatings were applied onto aluminum, graphite and hexagonal boron nitride substrates by the process described in the chapter 3.1, but with higher thickness, typically about 2 mm. The spraying was followed by Al-substrate leaching in 30 % solution of warm NaOH. The substrates made from graphite or BN were removed mechanically by careful lathing and brushing. On a contact surface between W and graphite, thin (1µm -3 µm) layer of WC was formed. Its actual thickness was influenced by the duration of the spray process and given by the empirical (x2=Dr) value of the diffusion coefficient of carbon into tungsten, D = 2.11×3.17×10⁻¹² m²s⁻¹. With the BN-substrate, no chemical reaction of tungsten was observed. Another variant of spraying was the armoring of a body based on a skeleton from W-wires fixed on a surface of removable graphite substrate, Fig. 6.
Table 1 Properties of the sprayed tungsten deposits

<table>
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<tr>
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<th>Tungsten coating ad 3.1 process</th>
<th>Tungsten FSP ad 3.2 process</th>
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<tbody>
<tr>
<td>Hardness HV 10N</td>
<td>In cross-section direction 519 ± 5</td>
<td>In spray direction 553 ± 12</td>
</tr>
<tr>
<td>Bulk Density at 0.1 MPa (g.cm⁻³)</td>
<td>15.93</td>
<td>16.92</td>
</tr>
<tr>
<td>Apparent (skeletal) Density (g.cm⁻³)</td>
<td>18.36*</td>
<td>18.97*</td>
</tr>
<tr>
<td>Oxygen content (wt%)</td>
<td>1.76 (R²=0.608)</td>
<td>1.88 (R²=0.802)</td>
</tr>
<tr>
<td>Porosity vol.%</td>
<td>13.1</td>
<td>11.4</td>
</tr>
<tr>
<td>Total Pore Area (m²/g)</td>
<td>0.04</td>
<td>0.021</td>
</tr>
<tr>
<td>Average Pore Radius (2V/A; μm)</td>
<td>0.427</td>
<td>0.638</td>
</tr>
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* note: Relative calibration at the same conditions – compact tungsten Metallwerk Plansee density 18.91 g.cm⁻³

3.3 Preparation of the tungsten filters

Spheroidized tungsten powder (Fig. 9) was used for the experiments. A nitrogen atmosphere above the liquid nitrogen level in a product collector suppressed the tungsten oxidation. Impact on the collector walls may deform some particles with higher kinetic energy. Therefore, a vibration shape classifier was developed and used to select powder products of a defined geometric shape [8]. The preparation of the filters consisted of sintering of shape-classified (spherical) powders of narrow size classes (20 μm - 40 μm) by common metal filter production technologies. Prior to sintering, the powders were compacted into cylindrical plates under 100 MPa pressure with a temporary binder – 6 wt% AC 112 acrylate suspension in alcohol. First set was prepared by hot isostatic sintering in ASEA HIP D 320 apparatus at 1750°C and in Ar protective atmosphere. Mechanically strong filters resulted from the second set, prepared by high pressure compacting in a HP BELT type apparatus at 1950°C (Figs. 10-12). Due to technical limitations of this apparatus, only circular filter plates up to 25 mm diameter were prepared. In the present time, we are verifying sintering of W filters by Spark Plasma Sintering (SPS) technique (up to 2200 °C, 40 MPa).
4. RESULTS AND DISCUSSION

The microstructure of the W coatings on all substrates is the same as on removable substrates, and its lamellar fashion confirms an acceptable melting of the feedstock powder. The main problem is the presence of WO$_3$ inter-layers, which originates during spray interruption applied for cooling of the as-sprayed deposit. In the case of substrates placed in the graphite protective chamber (Fig. 5) and application of an inert gas (Ar + 7% H$_2$), for the single-spray periods duration 15 seconds, the individual layers have thickness 500 µm (Fig. 13). Smaller substrates were more sensitive to the rise of temperature and spray process had to be interrupted each 5 seconds. The spray process consisted of 5 s deposition plus 15 s cooling for small substrates and 15 s deposition plus 25 s cooling for larger samples. As an illustration we will list results of W coating on carbon cylindrical substrate with diameter 20 mm and length 100 mm. From the polished materialographic section, an XRD pattern was recorded and the content of bonded oxygen was measured. A semi-quantitative WO$_3$ content based on XRD corresponds to the GFA data, i.e. 1.52 to 3.05 wt% of oxygen. Tungsten free-standing parts removed from a BN substrate (diameter 10 mm) contained 1.7 wt% to 2.6 wt% of oxygen after the same number of the spray cycles. As a proof that all WO$_3$ is localized in the inter-layers (dark in Fig. 13), Raman microspectrometry (DRX Nicolet) was done. Figure 14 shows the Raman spectra. The Raman mapping was done in the whole sample section with a 5 µm step.

As is known, the position on Raman-active bands depends on the W/O ratio and chemical bond type. Also the variability of all present oxides between WO$_2$ and WO$_3$ can be detected. The sharp peak at 806 cm$^{-1}$ corresponds to W-O stretching and the peak at 274 cm$^{-1}$ to W-O bending vibration, consequently the sharp peaks at 256 cm$^{-1}$ and 316 cm$^{-1}$ are assigned to the bending vibration O-W-O. The Raman peak at 256 cm$^{-1}$ is typical mode indicating the crystalline character of WO$_3$ accessible already at 300 °C [9].

The short extent of this contribution permits us to describe only some properties of the tungsten filter products, to illustrate the applied technology. Pore size distribution of the 20 µm - 40 µm powder sintered by
the HIP and BELT methods is shown in Figs. 11 and 12. Median pore radius of the HIP-ed product is 6960 nm, average pore radius is 6544 nm. Apparent skeletal density is 15.51 g.cm\(^{-3}\), (theoretical density of pure tungsten is 19.3 g.cm\(^{-3}\)), bulk density 8.77 g.cm\(^{-3}\), open porosity 43 %. Air permeability (159.4 mol.m\(^{2}\).s\(^{-1}\) or 21400 cm.min\(^{-1}\) at 0.4 MPa) and water permeability (2480 mol.m\(^{2}\).s\(^{-1}\) or 70 cm.min\(^{-1}\) at 0.110 MPa) of a HIP-ed W-filter was determined. Further, informative mechanical parameters were determined, such as flexural strength modulus (> 208 GPa).

5. CONCLUSIONS

The compacting of tungsten powders or spheroidal particles by plasma spraying could form coatings or robust free-standing parts that all can have a variety of rather complex shapes. As a result, special layered structures can be formed, with alternate layers of nearly pure metal and others with substantial content of oxides. Their thickness and the oxide content is governed by the spray parameters, namely temperature, external cooling intensity and application of a protective atmosphere. Although W forms a variety of oxides on the scale between WO\(_2\) and WO\(_3\), in our samples only hexagonal WO\(_3\) was detected – by Raman spectroscopy as well as by XRD. By plasma spraying without any interruption, a coating formation up to 0.5 mm thickness can be carried out without oxides.

Using tungsten powders, spheroidized in a water-stabilized plasma jet, materials suitable for the preparation of metallic filters can be obtained. Their sintering into filters with satisfactory mechanical strength is possible at temperatures up to 1950 °C by HP methods. In the present time, we reached comparable results also by the sintering of spheroidized particles in an SPS apparatus. The ratio of sintering temperature and pressure has a significant influence on the pore distribution in the final products. This can be optimized by increasing the tungsten particles hardness through the formation of WC or even harder W\(_2\)C core.

ACKNOWLEDGMENTS

Part of this work was supported by a grant no. P108/12/1872 from the Czech Science Foundation.

REFERENCES


