BLACK CHROMIA COATINGS ON METAL TUBES FOR THE SOLAR COLLECTORS

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Abstract

This paper describes the results of the first phase of the study preparation, structure and properties of coatings modification of black chromium oxide on copper, aluminium, iron and zirconium tubes for solar collectors. The coatings are prepared by plasma spraying of liquid chromate method which is known as Liquid precursor plasma spraying. Coatings have the function of an energy trap for thermal radiation wavelengths of 1 μm - 3 μm i.e. in the IR region. At the same time, the coating increases the corrosion resistance of metal substrates. The nanometric structure and thickness of the coating depend of the feeding distance and the concentration of chromate precursors. For the deposition of nanometric splats of melt chromium^{III} oxide, a new type of feeder that injects precursors into the water stabilized thermal plasma produced by the WSP® generator has been developed.

Keywords: Solar collector, black chromia, plasma spraying

1. INTRODUCTION

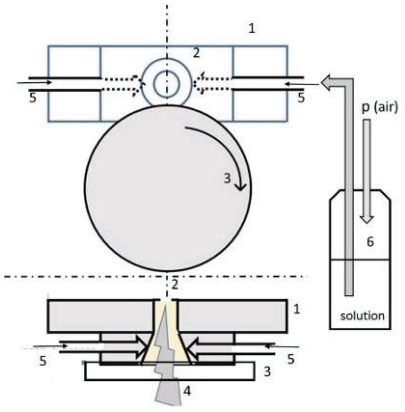
Solar collectors for water heating represent far more efficient use of solar energy than photovoltaics, of course with regard to the geographical and climate conditions at the place of installation. In the Central Europe region, the solar radiation has an average intensity of 620 W / m^2. The efficiency of solar hot water panels is influenced by a wide range of physical and chemical factors. Because solar hot water panels represent a vast group of competing material and construction types there is an ongoing research and development of more efficient materials [1-4]. In general, solar hot water panels can be divided into two groups: flat and tubular. The common denominator for both types is the layer for selective absorption of UV-VIS and IR radiation that covers the surface of metals of which the special heat exchangers are made. An ideal absorption layer should absorb radiation of almost every wavelength but at the same time it should not let heat radiation escape the heated media (water or antifreeze solution). This effect, called energy trap, is described as follows: if water in the collector is heated up to 100 °C, the appropriate emitted IR radiation wavelength is 2.5 μm. So far, the easiest way to meet this requirement is to apply thin black absorption layers, which are close to the definition of the black body. Apart from the opto-spectral characteristics, atmospheric corrosion resistance is required as well. Not so many chemical compounds or special alloys meet the above mentioned requirements. In a large part of solar collectors produced today, ceramic absorption layers from the black modification of chromium^{III} oxide are applied [5, 6]. These coatings are produced by quite complicated and expensive CVD or PVD processes or by chromate coating that use toxic chemical substances. The production is covered by a large number of patents that describe both chemical composition of the coatings and the construction of the solar collector [e.g. 7, 8]. An important novelty is TINOX's Highly selective blue absorbers [9, 10] prepared by PVD, which compared black surfaces show a significantly lower emissivity. Being given the actual recovery of investment in solar water heating [11, 12] of about 7-10 years, the service life both from the point of view of the material and of the construction used must be at least 25 years. An effective technology for the thin ceramic coatings production on metallic materials is the thermal spraying and its newest technique - plasma spraying. This

method uses powder or suspensions/solutions as precursors for the coating preparation [13-20]. Thus, the experimental part of this work summarises the new facts about coating of the functional solar collector parts by black chromium^{III} oxide. This coating meets the majority of requirements for the effective operation and for the cost-effective production.

2. EXPERIMENTAL

The coatings of black chromium^{III} oxide were prepared by plasma spraying of ammonium dichromate on thin metal tubes, which were used for the construction of the laboratory model of solar hot water panel. Aluminium, iron, copper and zirconium tubes of 10 mm in diameter were blasted by corundum of F240 granulometry to obtain surface roughness R_a = 7 µm - 9 µm. Plasma generator WSP® H-500 developed by the Institute of Plasma Physics of the CAS, Prague was used to prepare the plasma deposited chromium^{III} oxide coatings. The device (see **Figure 1** and **2**) was modified to allow the introduction of the liquid precursor immediately into the plasma jet right before it meets the rotary anode; the temperature of the plasma jet in this place is approx. 25 000 K. The plasma jet escapes the generator at approx. 900 m·s^{-1}, the velocity of the seized drops of precursor solution is approx. 80-100 m·s^{-1} (molten product). This setting allows the solution to evaporate, to form molten evaporate (future product) and to be deposited on the substrate in less than 10 ms. The substrate temperature can be regulated either by the deposition rate or by the spraying distance (SD). As the main aim of the experiment was to prepare oxide, no inert or protective atmosphere was used and the plasma deposition took place in normal air. During the short-time deposition, the substrate itself does not undergo undesirable oxidation.

With respect to the electric arc system of plasma generation with arc current of 300 A - 550 A, all parts of the feeder were made from high-temperature ceramic insulator - hexagonal boron nitride. The solution feeding by two opposite nozzles of inner diameter 0.2 mm was regulated via pressure gas inlet into the solution reservoir.



1 - dephlegmator body
2 - conical aperture of plasma torch
3 - rotary anode of WSP generator
4 - plasma
5 - liquid precursor feed
6 - feeder

Figure 1 Scheme (front and side view) on the feeder and the condenser dispenser solutions into the plasma jet

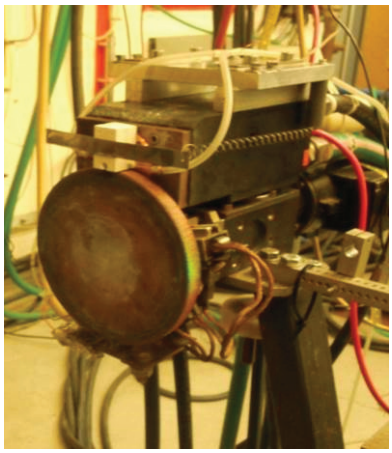


Figure 2 Plasma generator WSP® with dephlegmator body

Surface-blasted tubes were positioned at spraying distance (SD) of 30 cm or 40 cm, the distance of the liquid chromium precursor nozzles (feeding distance, FD) was 10 mm. Boron nitride dephlegmator with conical aperture was capable of creating the deposition track of approximately elliptical shape and solid angle 0.08 sr - 0.1 sr. Water solutions of ammonium dichromate with 5 wt. % and 10 wt. % were used for the deposition. Ammonium dichromate is thermally decomposed by the plasma jet according to the chemical equation

$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + 4\ H_2O + N_2$, to form solid chromium sesquioxide, water vapour and nitrogen. The deposition time was 30 s at SD of 40 cm and 20 s at SD of 30 cm. Morphology of Cr_2O_3 coatings on metallic substrates was studied by means of metallography. Scanning electron microscope EVO MA 15 (Carl Zeiss SMT, Germany, SEM-BSE) was employed for microstructural observations. Phase composition was confirmed by XRD analysis using X´Pert PRO Panalytical. Because of the curved surface of the tubes, the surface roughness was measured by confocal microscope Olympus Lext OLS 3100. Surface density of prepared coatings was evaluated from the results of XRF analysis by PAN Analytical - Axios FAST performed on 0.7 cm^2. Absorbance and colour of Cr_2O_3 coatings on tubes was measured using Color Quest XE Huter Lab USA at D65 (daylight) and viewing angle of 10°.

3. RESULTS AND DISCUSSION

Figure 3, **Figure 4** and **Figure 5** show the surface structure of coatings on metallic tubes sprayed with SD of 30 cm and 40 cm. Morphology of coatings was evaluated by comparison of the surface roughness. Surface roughness was higher in case of samples with SD = 40 cm, with measured maximum of R_a = 21.3 µm (RMS = 33.4 µm) for 1 mm^2 area. Coatings prepared with SD = 30 cm were visibly less porous, more lustrous, with surface roughness R_a = 5.7 µm (RMS = 8.7 µm) on 100 x 100 µm area.

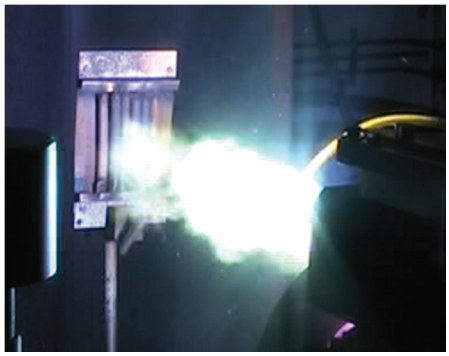


Figure 3 LPPS coating of a set of tubes

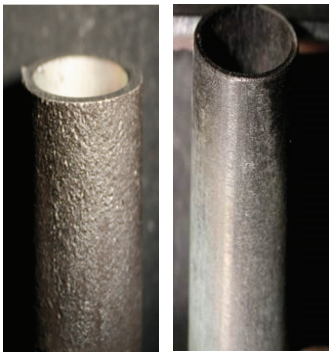


Figure 4 Detail view of Cr_2O_3-coated tubes

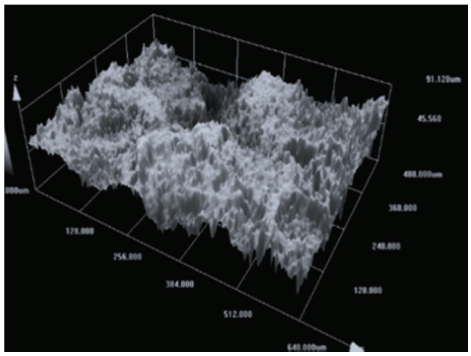


Figure 5 Surface morphology of tubes after LPPS process

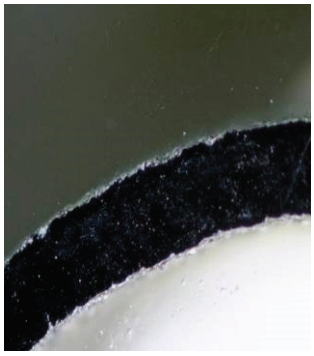


Figure 6 Cross-section of the tube wall

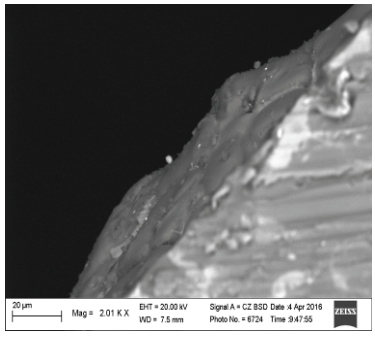


Figure 7 Detail of chromia coating on Al tube

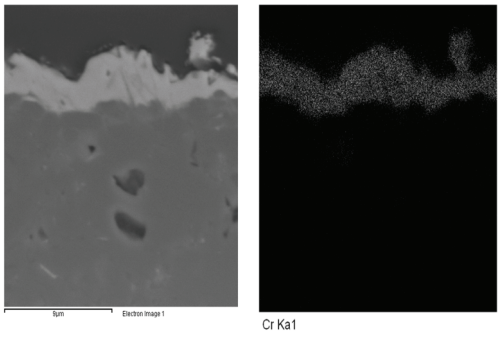


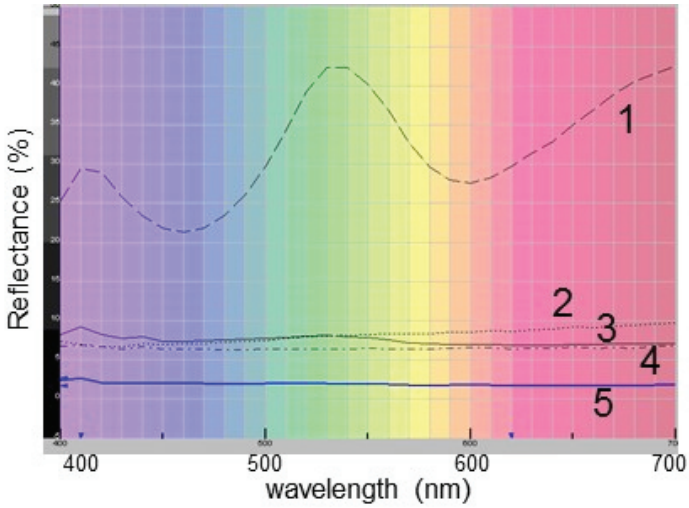
Figure 8 Section of the Cr_2O_3 coating on planar substrate

The coating thickness (**Figure 6, 7, 8**) was evaluated not only from the metallography cross-section samples but also by surface weight measurement using XRF analysis. **Table 1** shows obtained values.

Table 1 Cr^{III} content in surface layer on Al, Cu, Fe, Zr substrates after Cr_2O_3 deposition

substrate	Al /SD 40 cm	Al /SD 30 cm	Cu /SD 30cm	Fe /SD 30 cm	Zr /SD 30 cm	Zr /SD 40 cm
	Al 93.4 %	Al 66.1 %	Cu 91.6 %	Fe 97.6 %	Zr 81.8 %	Zr 96.5 %
	Cr 3.6 %	Cr 31.3 %	Cr 3.2 %	Cr 2.01 %	Cr 13.1 %	Cr 1.8 %
Precursor - 10 % ammonium dichromate solution, spraying time 20 s						

The second property, which is more important for the collector functioning, was coating color. The spectrum can be seen in **Figure 6**.



1 green Cr_2O_3
L* = 64.79 a* =-11.13 b* = 15.15

2 Cr_2O_3 on Al substrate
L* = 34.31 a* = 0.71 b* = 4.25

3 Cr_2O_3 on Cu substrate
L* = 32.94 a* = -2.23 b* = -0.66

4 Cr_2O_3 on Zr substrate
L* = 30.45 a* = 0.46 b* = -0.15

5 standard graphite target EK Topolcany
L* = 14.92 a* = -0.91 b* = -1.26

Figure 6 Spectrum of Cr_2O_3 layers on Al, Cu and Zr metal substrates

Substrates placed in the deposition track extremities were of green colour corresponding to the $chromium^{III}$ oxide (spectrum 1), with the structure of rhombohedral eskolaite R-3c. In the central, i.e. hottest, part of the plasma jet, products of black Cr_2O_3 (spectra 2, 3, 4) were found. Their structure, according to XRD analysis, is the same as in case of green coatings. The crystallinity calculated using Scherrer equation was 80-120 nm in all measured samples. Samples with L*a*b* parameters within the range of spectra 2-4 were selected for further measurement of heat absorption characteristics of coated tubes.

Sets imitating solar collector were constructed from the metallic Cr_2O_3-coated tubes. The bottom of the tubes was sealed and tubes were filled with water or with antifreeze liquid Sheron Stabil containing ethylene glycol and fitted with inner liquid temperature sensor. Sets of tubes were placed in an optical tunnel with unidirectional light and heat flow from different radiation sources. For the purposes of this paper, only the results of the experiment using Philips 4A Type 103 150 W IR lamp are described. **Table 2** shows the time dependence of the temperature of liquid in tubes of the same volume and surface subjected to thermal and light radiation. From the graphical representation of the temperature change in time for the samples exposed up to 45 minutes it can be deduced that the relation between the irradiation time and temperature can be expressed by logarithmic function. In case of other exposition distances and light sources, the same trend was observed as well.

Table 2 Time dependence of the temperature of liquid in tubes irradiated by Philips IR lamp

tube	Cu		Al		Fe		Zr	
λ (W / m·K)	350		237		73		22.6	
Liquid in the tube	water	glycol	water	glycol	water	glycol	water	glycol
Start (1 min)	20°C	20°C	20°C	20°C	20°C	20°C	20°C	20°C
5 min	28	29.3	24.2	26.3	26.0	26.5	22.4	24.2
10 min	32	33.5	26.4	29.2	28.4	28.6	23.9	26.2
15 min	34.5	36.1	27.5	31.0	30.1	30.6	24.8	27.3
30 min	35.8	40.2	29.3	33.9	32.5	33.1	26.2	29.3
45 min	37.5	42.5	30.5	35.6	33.9	35.0	27.1	30.5

4. CONCLUSION

The effectivity of a solar collector in steady conditions is defined as a ratio of the heat output conducted by the heat collector liquid away from the collector to the input of the incident radiation flow. In this paper, only the effectivity of different chromia coating vs. tube construction material couples in stationary state collector was observed. Colour (or more precisely absorption properties) of the Cr_2O_3 coating depends on the plasma deposition temperature. Cr_2O_3 coating produced at lower temperature is green, characterised by L*a*b* parameters 64.79; -11.13; 15.15. Black colour, which is an important requirement for the effective functioning of the solar collector, is produced at deposition temperatures above 700 °C. For these reasons, it is not possible to coat metallic substrates (Al or Cu tubes in this case) with standard high-temperature chromium^{III} oxide thermal spray coating as its melting point reaches 2435 °C [13]. However, our experiments prove that it is possible to produce high-temperature chromium^{III} oxide coating by using LPPS method. General knowledge concerning solar collector function states that the black absorption layer thickness should not exceed 2.5 μm. Layer of such small thickness can be produced or modified by changing the chromate precursor concentration. The coating adhesion to the metallic substrates is to a great extent influenced by the initial surface roughness. The coating method that uses thermal decomposition of liquid precursors can produce ceramic splats of just few nanometres that perfectly imitate the surface of metallic substrate and are able to cover even the smallest asperities. To a large extent, this ultraprecise coating can enhance the corrosion resistance of the coated metal.

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