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Technical Note

Copper-Tungsten Composites Sprayed by HVOF

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Copper and copper-tungsten composite coatings were produced by high-velocity oxy-fuel spraying (HVOF). After initial optimization of the spraying parameters, coatings of various compositions were made and their structure, composition, mechanical, thermal, and electrical properties were characterized. The HVOF technique was able to produce rather dense coatings with minimal oxide content and relatively good mechanical and thermal properties compared to, for example, plasma-sprayed coatings; however, the achieved tungsten content was quite low.

Keywords composite materials, high velocity/electric arc sprayed coatings, HVOF spray parameters

1. Introduction

Copper-tungsten composite coatings can be utilized in various thermal management applications (Ref 1-3), for example, plasma-facing components for fusion reactors. Tungsten as a refractory metal provides the plasma-facing surface resistant to high heat and particle fluxes, whereas copper with its high thermal conductivity ensures efficient heat removal. Coatings with variable composition would help reduce the stress concentration at the interface (Ref 2, 4, 5). Various techniques for production of these composites already exist—for example, plasma spraying (Ref 2, 6), laser deposition (Ref 7), cold spraying (Ref 1), powder metallurgy (Ref 5, 8, 9), etc. HVOF was chosen in this study as a promising alternative, thanks to its ability to produce dense and highly conductive coatings.

This article reports on the processing and characterization of HVOF-sprayed copper-tungsten coatings. Their properties are compared to those produced by other techniques.

2. Experimental

The coatings were sprayed using a Tafa JP-5000 HVOF spraying equipment at Skoda Research. Pure copper was sprayed first as a baseline for comparison. Pure tungsten coatings could not be deposited due to the low temperature of the flame (~2800 °C, compared to 3400 °C, melting point of tungsten). Copper-tungsten composites were sprayed from a feedstock with 50 and 75 vol.% tungsten at several spraying conditions. For pure copper, the settings recommended by the torch manufacturer were used. For different feedstock compositions and feed rates, powder injection had to be optimized to ensure proper particle trajectory along the centerline of the flame. The procedure described in (Ref 10) was used: a stationary deposition pattern was obtained at each torch setting and its height profile was measured in the direction parallel to the powder injectors. The sharpest profile, that is, with the most material deposited in its center, was selected for the coating production. As a quantitative criterion, a normalized moment of inertia of the profile was used:

$$M = \frac{\sum y_i(|x_i - x_c|)}{\sum y_i}, \text{ with } x_c = \frac{\sum x_i y_i}{\sum y_i}$$

where x_i are the ordinates at which the heights y_i were measured and x_c is the center of gravity of the profile.

The spraying parameters used for each type of coating are listed in Table 1. Parameters common for all types of coatings were: 10 cm (4 in.) barrel, combustion chamber pressure 630 kPa (91 psi), kerosene flow rate 16 L/h, oxygen flow rate 987 L/h. Copper 38-75 μm (Stamont, Zilina, Slovakia) and tungsten 20-63 μm (Osram, Bruntal, Czech Republic) powders were used as feedstock. Plain carbon steel coupons with the dimensions 2.5 × 25 × 100 mm were used as substrates. Spraying distance was 380 mm, torch traverse speed was 400 mm/s, spraying pattern was a rectangular meander of 6 lines with 6 mm offset. Air cooling from nozzles adjacent to the torch was applied during the spraying, and additional manual air cooling was applied between the torch passes, to reach about 50 °C.

Coating structure was observed in a Camscan 4DV SEM; porosity and tungsten content were assessed by image analysis. In-plane Young's modulus of the coatings was determined by 4-point bending in an Instron 1382 universal testing machine; the substrate and coating contributions to the total stiffness were separated according to

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Table 1 Spraying parameters that were varied between coating types

Coating type	Powder feed rate, g/min	Carrier gas flow, slpm
Cu	76	9.9
W + Cu 50/50 CGF8	Cu: 76	10
	W: 70	8
W + Cu 50/50 CGF12	Cu: 76	10
	W: 70	12
W + Cu 50/50 MIX	Cu + W: 73	9
	Cu + W: 73	9
W + Cu 75/25	Cu: 30	7.5
	W: 82	9

Powders were fed from two powder feeders through two radial internal injectors. The label CGF reflects the carrier gas flow for tungsten powder; MIX means that 50/50 mixture (by volume) of both materials was used in both feeders.

Table 2 Results of the measurements of stationary deposition profiles (copper)

Powder feed rate, g/min	Carrier gas flow, slpm	Deposition profile moment
38	6	13.8
38	8	*5.2*
38	10	9.1
76	10	*8.2*
76	12	8.3

Lower moment means sharper curve, indicating better powder injection (in italics).

Harok and Neufuss (Ref 11). Electron probe microanalysis (EPMA) was used to deteremine the composition on a micro-scale and to help identify the phases present; cuprite (Cu_2O) was used as a reference. Qualitative phase analysis was performed by X-ray diffraction (XRD) on a Siemens D-500 diffractometer with Cu radiation. Thermal diffusivity and conductivity were determined by the laser flash method (Ref 12) on a Holometrix Microflash instrument. Thermal expansion was measured in a Setaram Setsys 16/18 dilatometer under Ar atmosphere. Electrical resistivity was determined by the 4-electrode method in two laboratories (Siemens and Czech Technical University).

3. Results and Discussion

Results of the stationary deposition profile measurements are shown in Table 2. From these, the best carrier gas flow for a given powder feed rate was chosen.

Typical structures of coatings made from pure copper, 50% Cu + 50% W and 25% Cu + 75% W (feedstock composition) are shown in Fig. 1. Properties of the coatings are summarized in Table 3. For comparison, selected values of these properties for coatings produced by other methods are shown in Table 4.

The porosity of all these coatings is very low, which is typical for HVOF deposits. The pores were concentrated

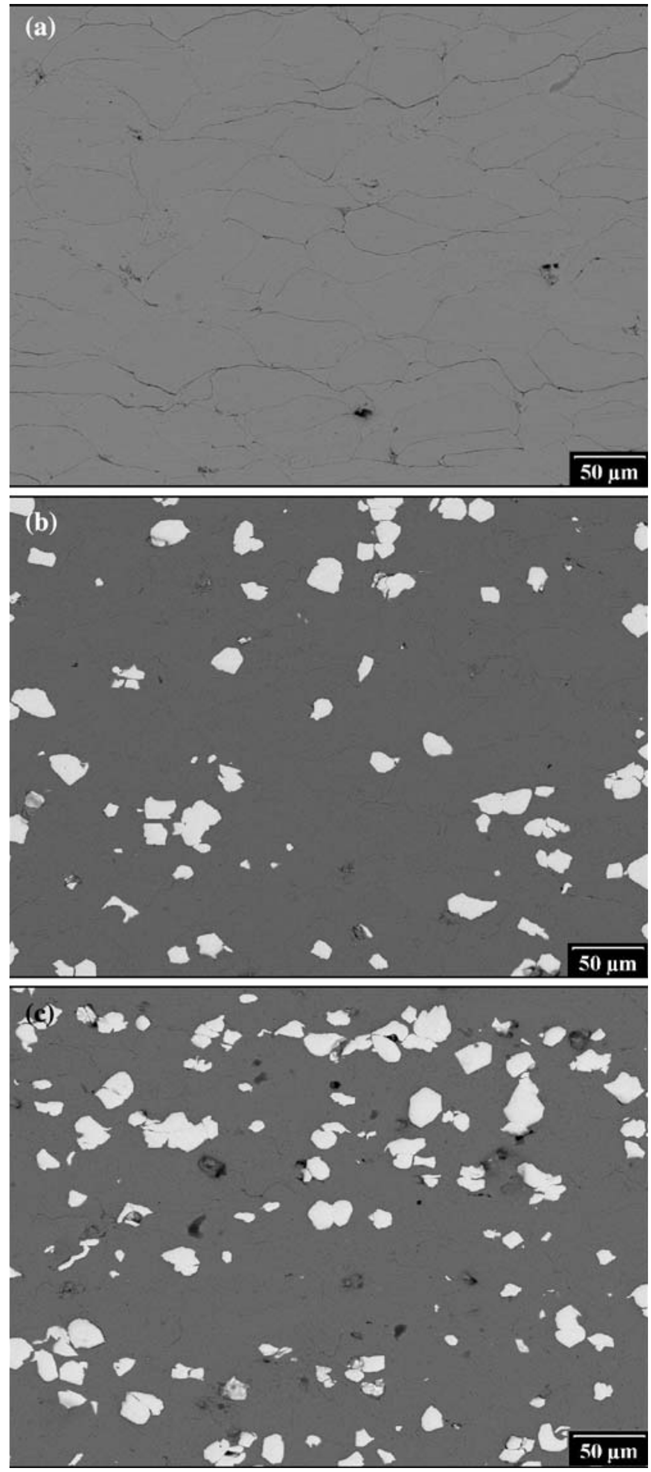

Fig. 1 Typical structures of the coatings: (a) pure Cu, (b) W + Cu 50/50 mix, and (c) W + Cu 75/25

mainly around the tungsten particles. The slightly higher porosity in pure Cu coating—and somewhat lower thermal conductivity, contrary to expectations—may be a consequence of barrel wear (the barrel was replaced just before producing the composites). The tungsten content was

Table 3 Properties of the HVOF coatings sprayed in this study

Coating type	Porosity, %	W content, vol.%	Young's modulus, GPa	Thermal conductivity, W/m K	CTE (150-600C), E-6	Oxygen content EPMA, wt.%	Electrical resistivity SIE, 10^{-8} Ω m	Electrical resistivity CTU, 10^{-8} Ω m
Pure Cu	4.3	0.0	65	78	20.1	0.36	5.4	8.8
W + Cu 50/50 MIX	2.1	7.7	84	101				
W + Cu 50/50 CGF12	3.0	6.4	85	107	18.4	0.31		4.4
W + Cu 50/50 CGF8	3.6	7.6	82	95				
W + Cu 75/25	2.8	13.0	102	69				
Typical std. dev.	0.5	1	1	1		0.08	0.1	

SIE, measured at Siemens; CTU, measured at Czech Technical University.

Table 4 Properties of similar coatings prepared by other technologies

Composition range	Material type	Porosity, %	W content, vol.%	Young's modulus, GPa	Thermal conductivity, W/m K	CTE (150-600C), E-6	Oxygen content EPMA, wt.%	Electrical resistivity ref., 10^{-8} Ω m	Electrical resistivity SIE, 10^{-8} Ω m	Electrical resistivity CTU, 10^{-8} Ω m	Reference
Pure Cu	Bulk Cu			128	398	19.3		1.7 (a)		2.1 (b)	13, 14
	WSP Cu	2-4		30-40	90-120		3-4		4.2 (c)	11.6 (c)	
	PS Cu alloy	9									15
	VPS Cu					18					2
	CS Cu	0.2-0.8						5.5–20			16
	CS Cu							2.8			17
W ~25%	WSP W + Cu	0.5	8	59	58	15.4					6
	VPS W + Cu 40/60	8	16								18
	VPS W + Cu		22	170	145-165	15.5					2
	PM W + Cu	1	27		330						9
	PS W + Cu 72/28	5-10	24-35			10-11					19
W ~50%	CS W + Cu 75/25	1	38								1
	VPS W + Cu		48	125	140-155	10.5					2
	PM W + Cu	3	41		300						9

Only data from the copper-rich side are provided here for comparison; data from the tungsten-rich side may be found in the references. WSP, water stabilized plasma spraying; PS, plasma spraying; VPS, vacuum plasma spraying; CS, cold spraying; PM, powder metallurgy.
(a) Tabular value for high purity copper.
(b) Experimental value for a commercial purity material.
(c) These resistivity values were determined on two different types of WSP coatings.

found to be significantly lower than in the feedstock. The likely cause is that a majority of the (unmelted) tungsten particles bounced off the substrate, while only some were 'captured' by the well-molten copper. Increase in the feedstock tungsten content to 75% resulted in about two-fold increase in the coating tungsten content, which nevertheless remained well below the feedstock. This was also accompanied by a reduction in deposition efficiency. As a consequence of the low tungsten content, the mechanical and thermal properties are rather similar to those of sprayed pure copper. The values for the various 50/50 composites were also similar, except for porosity, where the lowest value was achieved for the powder mixture. An increase in Young's modulus with increasing tungsten content can be attributed to higher modulus of bulk tungsten (400 GPa vs. 128 GPa for copper). In the same way, reduced thermal conductivity would be expected (163 W/m K for bulk tungsten, 398 W/m K for copper), but was observed only between the 50/50 and 75/25 composite coatings. Both of these properties, however, are also affected by the quality of bonding between the splats. EPMA indicated very low oxygen content, about 10 times lower than in a representative plasma sprayed coating. Qualitative XRD comparison indicated a similar ratio; Cu_2O was identified as the prevalent oxide phase, with only a trace of CuO.

As shown in Table 4, the properties of these HVOF coatings are—from the application point of view—generally better than typical air plasma sprayed coatings, roughly comparable to cold sprayed or vacuum plasma sprayed ones, and worse than bulk materials. The reduction in thermal and mechanical properties is mainly governed by the interfaces between the molten particles. The degree of interparticle bonding, the amount of porosity and oxides are quite favorable in the case of HVOF.

4. Conclusions

Copper and copper-tungsten composite coatings were produced by high-velocity oxy-fuel spraying. The HVOF technique produced rather dense coatings with minimal oxide content and relatively good mechanical and thermal properties compared to, for example, plasma sprayed coatings. However, the achieved tungsten content was quite low, due to lack of melting and bouncing-off of the tungsten particles. Its increase may be possible by the use of composite powders (copper-clad tungsten core).

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