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Formation of carbon composite coatings by plasma spraying

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ABSTRACT

Carbon–silicon–sulfur composite coatings were deposited on stainless steel by atmospheric plasma spraying. The effect of spraying power on the coating microstructure and microhardness was investigated. The surface morphology and elemental composition of as-sprayed coatings were examined by scanning electron microscopy and energy dispersive X-ray spectroscopy. The increase of torch power leads to a lower oxidation degree and reduces the silicon concentration in the coatings. The SEM cross-section measurements indicated that the thicknesses of the coatings were in the range of 10–15 μm. The X-ray diffraction measurements indicated an increase of crystalline graphite phase with the increase of power. The results indicated that the coating roughness decreased, while the microhardness and specific surface area increased with increased power. The highest microhardness value of 314 HV was obtained.

1. Introduction

Recently much attention has been focused on the deposition and investigation properties of various carbon composites or carbon containing coatings. The unique properties such as chemical inertness, low friction coefficient, high hardness, high specific surface area of carbon composites allows use of these coatings in tribological applications, or, in the energy field as energy storage devices [1–4]. Sulfur-doped, carbons are attractive functional materials for application in fuel cells, energy conversion/storage devices and as an anode materials in Li-ion batteries [4–6]. A number of carbon–sulfur nanocomposites for Li–S cathodes have been proposed [4,6]. It was demonstrated that the C/S composites may contain up to 90 wt.% of sulfur depending on the method of preparation [4]. Meanwhile, the addition of silicon carbide can increase the fracture toughness and wear resistance of metal oxides or metal coatings or change the thermal conductivity of these coatings [7–11].

Plasma spraying is a very attractive technique for the formation of the carbon-containing composites using various material powders including even high melting temperature materials such as graphite, tungsten, silicon carbide, titanium oxide and so on [9–15]. The surface morphologies and properties of the plasma sprayed coatings depend on the process parameters, including torch power, powder feed rate, gas flow rate, spraying distance and particle size [10–21]. The torch power is a crucial parameter, because it influences the velocity and temperature of the plasma flow and, in consequence, powder particles directly. The deposition efficiency, interface bonding and mechanical properties of sprayed coatings increases with the increase of particle velocity and temperature [18–25]. It was demonstrated that the as-sprayed coatings show elemental composition different from the initial feedstock powders [7,8,13]. Variation of plasma gun power allows changing and controlling the plasma jet temperature and, consequently, to adjust the melting degree of the feedstock powders [14,25]. Therefore, it is generally considered that the fully melted particles will lead to production of dense with low pore volume coatings [14]. The nature and elemental composition of the initial powders are directly related to the melting temperature [7,13,14]. Therefore it is very important to obtain the optimal spraying process parameters for individual feedstock powders. The investigations concerning the formation of carbon–silicon–sulfur composite coatings from flake-like shape powders by plasma spraying is hard to find in the scientific literature. As a result it is very important to determine appropriate process parameters which will lead to the deposition of coatings with dense structure and high hardness values.

In this study, the effect of torch input power on the surface morphologies, roughness, pore size, pore distribution, and

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microhardness of sprayed carbon–silicon–sulfur composite coatings was investigated.

2. Experimental details

The coatings were deposited on steel substrates at atmospheric pressure using a direct current plasma torch. The plasma torch used in this experiment was developed at the Lithuanian Energy Institute [26–28]. Substrates with the dimensions of 10 × 40 × 1 mm were made from stainless steel. The steel substrates were polished and chemically cleaned by acetone before starting the deposition process. The steel substrates were placed on the water-cooled sample holder. The coatings were sprayed at a torch power of 17.1 kW, 19.4 kW, and 21.0 kW, respectively. The spraying distance was kept at 35 mm. Argon was used as both the primary gas (flow rate of 7.5 g/s) and the powder carrier gas (flow rate of 0.59 g/s). The experiments were performed using a cylindrical shape (0.15 m of length) reactor with the powder injection place (located 0.10 m from the exit) which was situated at the exit of the anode. The mean temperature of the plasma jet at the exhaust of the plasma torch was calculated from the heat balance corresponding to plasma enthalpy:

$$H_f = M\frac{(P_T - P_w)}{G} + H_o \quad (1)$$

where H_f is the plasma enthalpy (kJ mol^{-1}), P_T is torch power (kW), P_W is power used for water heating (kW), G is plasma mass flow rate (kg s^{-1}), M– argon gas atomic mass (kg mol^{-1}), and H_0 is the enthalpy under standard conditions (kJ mol^{-1}).

The mean velocity of the plasma jet at the exhaust of the plasma torch was calculated from Eq. (2):

$$v = \frac{4MGT}{\pi d^2 p} \quad (2)$$

where T is mean temperature of the plasma (K), d – diameter of the exhaust nozzle (m) and p – pressure (m). The average temperature and velocity of the plasma flow at the different torch powers is given in Table 1. Detailed description of the methodology of the plasma temperature and velocity calculation is given in Ref. [29]. The graphite powders with the elemental composition of carbon (C) – 95.9 at%, oxygen (O) – 2.9 at%, silicon (Si) – 1.0 at% and sulfur (S) – 0.2 at% were used as sprayed powders. The graphite powders used in the spraying process were of a non-regular flake-like shape with various sizes from 20 μm to 150 μm, and thickness of ~10 μm (Fig. 1a). The specific surface area of these powders was 1.84 m^2/g. The feedstock powders were grinded and sieved using a 150 μm size grid and were dried for 8 h at ~350 K before starting the deposition process. The feedstock powders were injected into the reactor nozzle at a distance of 100 mm from the exit. The deposition duration was 60 s. The plasma torch was moving in the x-axis direction forward and back during the deposition.

The surface morphology of the sprayed coatings and feedstock powders was analyzed by scanning electron microscopy (SEM) using a JEOL JSM–5600. The elemental composition of deposited coatings and powders was obtained by energy dispersive X-ray spectroscopy (EDS). The surface roughness measurements were investigated using a stylus profiler (Ambios XP-200). The measurements were done 5 times; the length of one measurement was 2 mm. The coating structure was analyzed by X-ray diffraction (XRD) (DRON-UM1 with standard Bragg–Brentano focusing geometry) in a 10–100° range using the CuK$_\alpha$ (λ = 0.154059 nm) radiation. The bonding structure of sprayed coatings was investigated by Raman scattering (RS) spectroscopy ("Jobin Yvon" company). RS measurements were done using a Nd:YAG laser (532.3 nm, 50 mW, spot size 0.32 mm, in the 1000–2000 cm^{-1} range) as an excitation source. The RS spectra were fitted by Gaussian-shape lines in the spectral range of (1200–1800) cm^{-1}. The specific surface area of the coatings was measured by the BET-method in a KELVIN 1042 sorptometer. The microhardness measurements were done using a CSM Micro Scratch Tester with Vickers indenter. The microhardness was measured on the polished coating surface at room temperature by applying a load of 10 mN. The speed of the loading and unloading was 200 mN/min and the pause between the loading and unloading rate was 10 s. 10–12 hardness measurements were taken randomly and the arithmetic mean of measurements was taken as the microhardness of the coatings. Beside the hardness values the elastic deformation work of indentation (W_e), plastic deformation work of indentation (W_p), and total mechanical work of indentation (W_t) were given from the force – penetration depth curves for loading and unloading. The elasticity (elastic part of indentation work) was calculated using Eq. (3) [30]:

$$\varepsilon = \frac{W_e}{W_t}\cdot 100\% = \left(1 - \frac{W_p}{W_t}\right)\cdot 100\% \quad (3)$$

Table 1
Plasma spraying parameters for depositing composite coatings.

Power, kW	I, A	U, V	Velocity, m/s	Temperature, K
17.1	180	95	540 ± 15	3180 ± 50
19.4	200	97	600 ± 15	3520 ± 50
22.0	220	100	670 ± 15	3940 ± 50

3. Results and discussion

Fig. 1 shows the surface morphologies of plasma-deposited composite coatings at different torch powers. The surface of a coating formed at the lowest power is composed from partially melted and solidified flake-like particles (Fig. 1b and e). The number of partially molten particles in the coating decreases with increasing torch power. The ball-like shape particles with size of 1–10 μm appear on the surface at higher power (Fig. 1c, d and f). The appearance of pores and non-regular shape particles could be found in all deposited coatings. The existence of sphere-like shape particles on the surface indicates the higher melting degree of the initial feedstock powders. It is well known that pores in sprayed coatings are generally derived from poorly stacked flat particles and that the state of the flat particles is highly dependent on the melted extent of the feedstock powders and the velocity of the plasma jet [21]. The SEM cross-section measurements indicated that the thicknesses of the coatings were in the range of 10–15 μm. The EDS measurements demonstrated that the oxygen content in the as-sprayed coatings decreased from 44.4 at% to 41.8 at% with increasing power from 17.1 kW to 22.0 kW. The carbon content increased from 31.8 at% to 38.5 at%. It should be noted that, despite the low concentration of Si and S in the initial powders, the sprayed coatings contained quite a high fraction of these elements. The silicon concentration decreased from ~16 at% to ~12 at%, while the sulfur content did not change (~8 at%) in coatings with the increased power values.

In order to evaluate the torch power influence on the surface morphologies surface roughness measurements were performed. The surface roughness investigations indicated (see Fig. 2) that coatings sprayed at the lowest power had the highest surface roughness (R_a = 700 nm, R_q = 1000 nm). The surface roughness