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Effects of Heating by Arc Discharge on Structure and Chemical Composition of Coatings Formed Using High Velocity Oxygen Fuel and Flame Spraying Processes

Eitvydas GRUZDYS[1,2], **Šarūnas MEŠKINIS**[1*], **Sigitas TAMULEVIČIUS**[1], **Tomas GRINYS**[1]

[1] *Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, LT-50131, Kaunas, Lihuania*
[2] *JSC „Technologija“, Breslaujos 3B, 44403 Kaunas, Lithuania*

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In this study thermal effects in tungsten carbide/cobalt (WC-Co), chromium carbide/nickel chromium (Cr_2C_3-NiCr) and tungsten carbide/cobalt with nickel chromium boron silicon WC-Co/NiCrBSi coatings were investigated. Coatings were heated using electric arc discharge in hydrogen-argon atmosphere. XRD analysis was accomplished before and after heating. Changes of the structure and elemental composition were observed. In the case of Cr_2C_3-NiCr coating, heating increased crystallization thus increasing coating's resistive properties. In the case of the WC-Co coatings, small changes of the structure were observed only after the heating at 1090 °C temperature. Amorphisation of the Cr_3C_2-NiCr occurred during the coating deposition process, while following heating by arc discharge at 1000 °C temperature resulted in recrystallization of the Cr_2C_3 and, especially, Ni phases. Amount of the crystalline Ni phase in WC-Co/NiCrBSi coatings increased only after the arc heating at 1030 °C temperature. Flame remelting of the flame sprayed WC-Co/NiCrBSi coatings resulted in formation of the more crystalline coatings in comparison with coatings heated by arc discharge and increased crystallinity not only Ni phase, but Ni_3B, CrB, WC phases as well.

Keywords: protective coatings, spray deposition, annealing by arc discharge, XRD, XRF, SEM.

1. INTRODUCTION

Coatings, formed using thermal spraying process, are widely used in many industrial areas where resistance to wear, glide, erosion and other destructible processes are at work [1, 2]. Tungsten carbide (WC) and chromium carbide (Cr_3C_2) are between the materials most often used for such a purpose [1 – 6]. Parts of industrial devices and tools coated with tungsten carbide become more wear-resistant [3]. However, WC as well as Cr_3C_2 are relatively brittle despite their hardness [4]. Additional elements are used to make these coatings more ductile, such as cobalt, nickel, and iron as well as different alloys based on materials mentioned above. One of the main problems related with protective WC-Co and Cr_3C_2-NiCr coatings are their tendency to fracture when high loads, high mechanical tensions or high temperature are applied. To solve that problems different post-spraying treatment processes are used. The most common ones are remelting with flame or plasma. Significantly improved wear resistance [5, 6] and reduced residual stress as a result of the heat treatment in inert atmosphere or vacuum has been reported for WC-Co and Cr_3C_2-NiCr coatings [5]. Another possible way to solve the problem is application for coating deposition of different binder element instead of Co, Ni or NiCr. Recently nickel alloy NiCrBSi achieved considerable interest of the researchers. Chromium in this alloy increases resistance to high temperature corrosion and oxidation. Boron decreases melting temperature and is one of the components of the hard compounds formed during the protective coating synthesis process. Silicon is added to maximize quality of melting process. NiCrBSi resistance to corrosion is greater at high temperature than at room temperature. It is possible to increase mechanical properties of this coating using flame heating or heating in the inert gas environment.

The goal of the present study was to examine and compare WC-Co, WC-Co/NiCrBSi, Cr_3C_2-NiCr properties of the coatings and their dependencies on the spraying process parameters. Changes of the morphology, structure and chemical composition before and after the heating of the coatings at different temperatures by electric arc discharge were evaluated.

2. EXPERIMENTAL

WC-Co (chemical composition in mass percents: 88 % WC, 12 % Co) and Cr_2C_3-NiCr (chemical composition in mass percents: 75 % Cr_2C_3, 25 % NiCr) coatings were formed using high velocity oxygen-fuel (HVOF) method. Gas flame spraying equipment has been used for deposition of the WC-Co/NiCrBSi. Powder used to form WC-Co/NiCrBSi coating consisted of 30 % WC and 70 % NiCrBSi.

Deposition parameters for the WC-Co and Cr_2C_3-NiCr coatings are shown in Table 1.

Table 1. Gas flows during deposition of WC-Co and Cr_2C_3-NiCr coatings

Gas flows during deposition			Spraying speed (g/min)
C_3H_8 (l/min)	O_2 (l/min)	N_2 (l/min)	35
33.3	142.6	10	

To eliminate high temperature oxidation process effects the coatings were heated using electric arc discharge in hydrogen and argon atmosphere. The heating parameters are shown in Table 2. Temperature was adjusted by

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[*] Corresponding author. Tel.: +370-37-327605, fax.: +370-37-314423.
E-mail address: *sarunas.meskinis@fei.lt* (Š. Meškinis)

changing distance between the sample and plasma source (200 mm – 260 mm). Temperature measurements were performed using a pyrometer ЛОП-72. Accuracy of the pyrometer measurement was ±50 °C.

Table 2. Technological parameters of heating using arc discharge

Discharge current	690 A
Discharge voltage	26 V
Gas pressure	1178,2 Pa
H_2 gas flow	6 l/min
Ar gas flow	25 l/min

Phase composition of the formed coatings was evaluated using X-ray diffractometer DRON-3 (XRD). X-ray lamp 2.0BSV-24Cu with a copper anode (characteristic wave length $\lambda = 0.154178$ nm) was used as X-ray radiation source. Phase composition of the coatings was evaluated using Fullprof program comparing interplanar distances d and corresponding reflexes with data from JCPDS database.

Chemical structure of deposited coatings was evaluated using X-ray fluorescent spectrometer VRA-20. Rh Kα anode was used for the fluorescence excitation; current was 26 mA, voltage 35 kV. Duration of the measurement was 100 s, and each measurement was repeated 3 times.

Surface morphology and structure were investigated using a scanning electron microscope (SEM) JEOL JSM-IC25S and optical microscope with a digital camera attached.

3. EXPERIMENTAL RESULTS

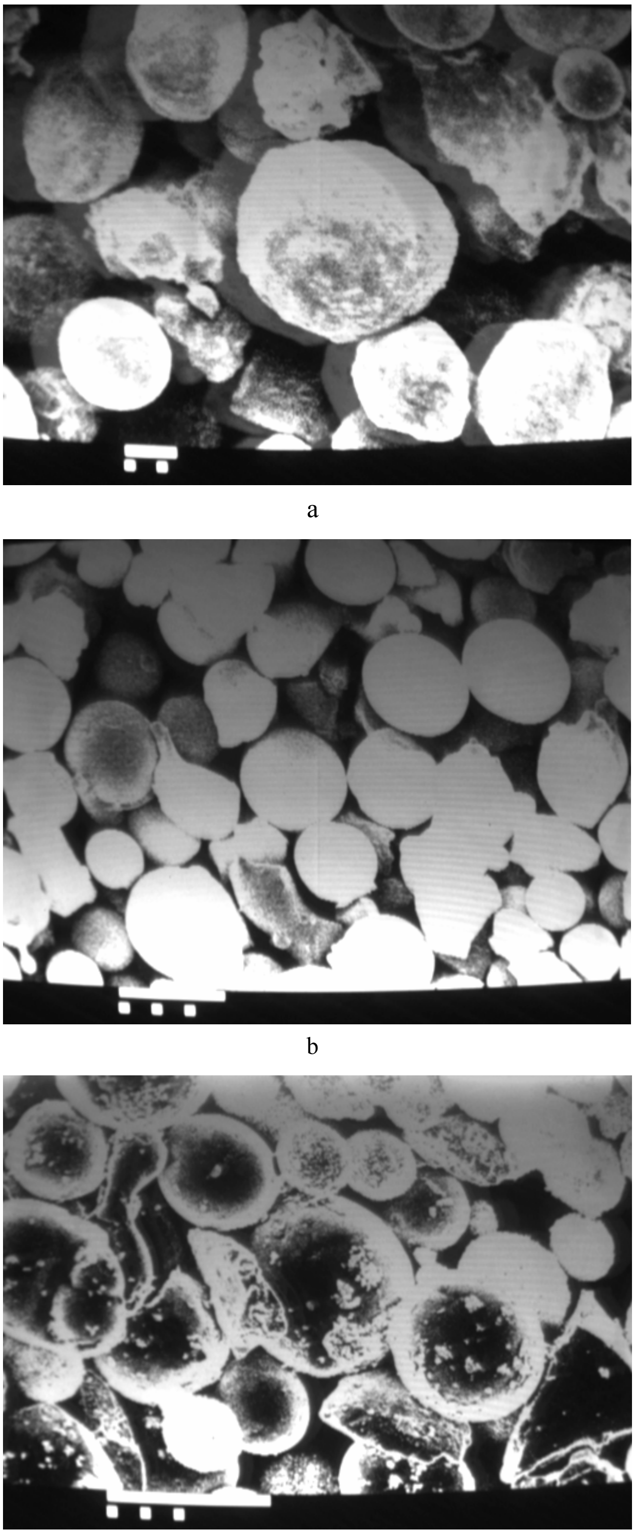
3.1. Analysis of Powders Used in Thermal Spray Processes

Powders used for the deposition of the protective coatings were investigated by means of the XRF, XRD and SEM analysis. SEM pictures of the powders are presented in Fig. 1. As we can see in all cases particle size varied from several tens of micrometers in the case of the Cr_3C_2-NiCr up to 100 μm and more for NiCrBSi and WC-Co-NiCrBSi.

Table 3. Elemental composition of the powders used for deposition of coatings

Powder	Elemental composition (%)					
	Ni	Cr	W	Co	Fe	Other
Cr_3C_2-NiCr	24.4	62.6	-	-		13
NiCrBSi	81	13.1		0.1	3.6	2.2
WC-Co-NiCrBSi	21.9	2.6	64.7	2.5	0.7	7.6

It revealed, that Cr_2C_3-NiCr powder consists of 62.6 % Cr, 24.4 % Ni and 13 % of chemical elements, which cannot be identified using XRF (C in particularly) (Table 3). Ni dominated in NiCrBSi powder, while W dominated in the mixture of WC-Co and NiCrBSi powders. It can be associated with gradual separation between the components of the compound – NiCrBSi particles settles at the bottom, while WC stays on the surface. It should be mentioned, that investigation of the WC-Co/NiCrBSi powder has been performed several days after the mixing of the powders. While WC-Co/NiCrBSi coating deposited using just formed powder mixture, consisted of 70.2 % Ni and 19.7 % W. XRD spectra of Cr_2C_3-NiCr, NiCrBSi and


a

b

c

Fig. 1. SEM pictures of powders used for thermal spray process: a – WC-Co (mark length 10μm); b – Cr_2C_3-NiCr (mark length 100 μm); c – WC-Co/NiCrBSi (mark length 100 μm)

WC-Co/NiCrBSi powders are shown in Fig. 2. In the case of Cr_2C_3-NiCr powder Ni and Cr_2C_3 related peaks can be observed. In the NiCrBSi spectra narrow and strong Ni peak can be seen. There are also less stronger peaks of Ni_3B and CrB. XRF analysis has shown that powder contains 13 % Cr. That allows to suggest that Cr is in amorphous phase. After blending of WC-Co and NiCrBSi powders new peaks of WC and W_2C occur at the time, Ni peak stays strong at about 44°.

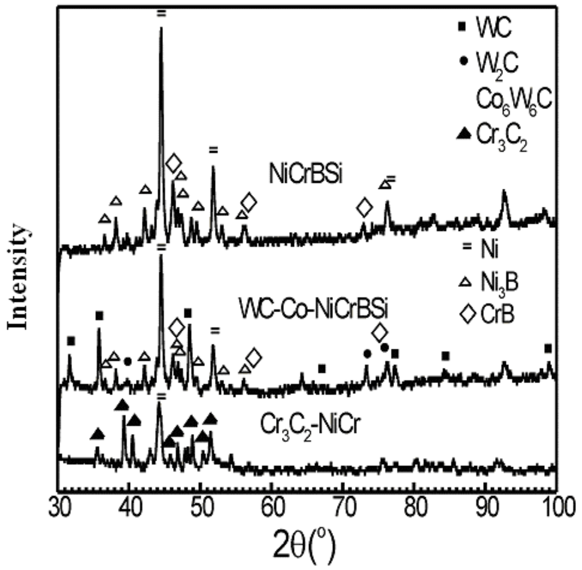


Fig. 2. XRD spectra of Cr_2C_3-NiCr, NiCrBSi and WC-Co/NiCrBSi powders

3.2. Structure of coatings before and after the heating

As we can see in Fig. 3, heating of the WC-Co coatings to 600 °C using electric arc discharge for 30 s, had no influence on the structure of the coatings. After 60 s of heating at 1090 °C temperature, Co_6W_6C peaks appear (Fig. 3).

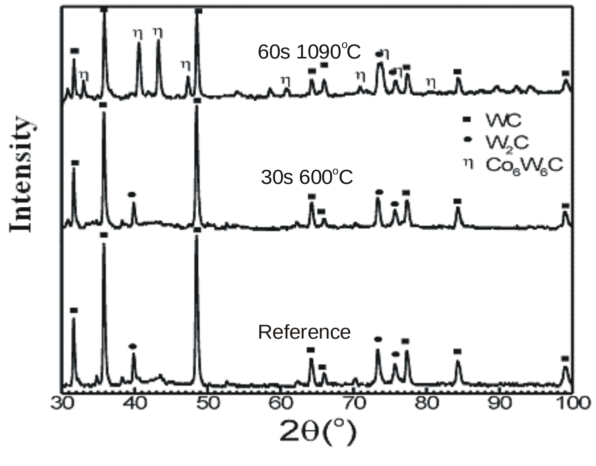


Fig. 3. Influence of electric arc discharge annealing on the structure of WC-Co coating

Similar results were reported in [5], where XRD spectra of WC-Co coating did not change after heating for 48 min at 600 °C and after heating at 800 °C for 48 min Co_6W_6C appeared. On the other hand, in other research [7] after 1 hour of heating in 950 °C temperature in vacuum no peaks were observed, and only at 1000 °C cobalt tungsten carbide peaks appeared. As we can see, the use of electric arc discharge in hydrogen and argon mixture enables to achieve the same results as with heating in vacuum or argon but for much shorter time.

After comparison of the Cr_2C_3-NiCr coating XRD spectra with powder XRD spectra, we can see that in the case of powder spectra, XRD peaks are stronger and sharper (Figs. 2, 4). Especially Ni peak around 44° is strong. Amorphisation already occurred in the process of the forming of the coating. Other authors reported similar behavior in [8]. Heating in the air and heating in the hydrogen and argon with electric arc discharge have changed the XRD spectra significantly. As we can see in Cr_2C_3-NiCr XRD spectra, after 1min of heating by electric arc discharge in hydrogen and argon at 1000 °C temperature, intensity of peak of Ni and some peaks of Cr_2C_3 increases. It seems like in the process of heating, some part of Cr_2C_3 and significant part of Ni have crystallized. XRD spectra become more similar to the XRD spectra of powder (Fig. 2). Yet, unlike in the XRD spectra of the powder, in the case of coating spectra, Ni peak is much more intensive than Cr_2C_3 peak. XRD spectra of the sample that has been heated for 1 hour at the 900 °C temperature in air is very similar to the XRD spectra of the coating, which has been heated using electric arc discharge in hydrogen and argon. The only difference is that in the case of heating in the air - some weak $NiCrO_3$ related peaks appeared.

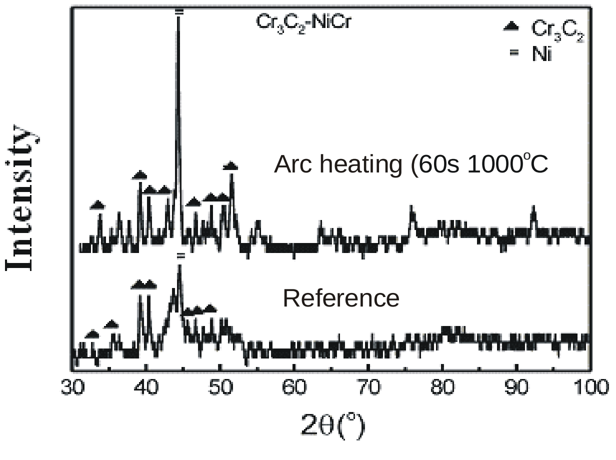


Fig. 4. Influence of electric arc discharge on the structure of Cr_2C_3-NiCr coating

It is much more difficult to analyse the XRD spectra of WC-Co/NiCrBSi and NiCrBSi powders with spectra of the WC-Co/NiCrBSi coating (Fig. 5) due to the already mentioned separation between the particles in powder. An XRD spectrum of the WC-Co/NiCrBSi coating is more similar to the spectra of the NiCrBSi powder. Heating using electric arc at 800 °C temperature has not changed the XRD spectra of the coating. But, judging by the XRF data (appearance of iron), some blending between the substrate and coating occurred. After increase of heating temperature to 1090 °C, intensity of Ni peaks increased. XRD peaks of Ni_3B, CrB, WC stayed relatively the same. In other words, W and Cr compounds in this coating are expected to be in amorphous phase. In the spectra of the

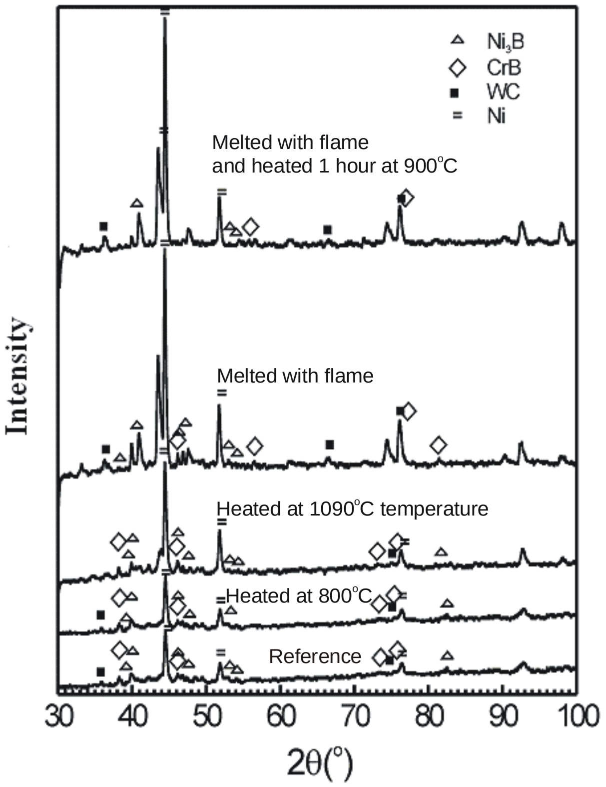


Fig. 5. Influence of electric arc discharge on the structure of WC-Co/NiCrBSi coating

coating melted using flame the dominance of Ni peaks can be observed. These peaks are significantly stronger than the Ni peaks in XRD spectra of the coating heated for 1 min 1090 °C using electric arc discharge. It is likely that duration of melting was too short, or the temperature was lower than NiCrBSi melting temperature. Peaks characteristic to Ni_3B, CrB, WC were also of increased intensity in the case of flame melting. 1 hour heating in the air had almost no effect on the flame melted coating – no change in intensity of existing peaks or appearance of new peaks was observed.

CONCLUSIONS

In conclusion, effects of the heating by arc discharge on the structure of WC-Co, Cr_3C_2-NiCr, WC-Co/NiCrBSi were investigated. In the case of the WC-Co coatings some changes of the structure (formation of the Co_6W_6C phase) were observed only after the heating at 1090 °C temperature. Some amorphisation of the Cr_3C_2-NiCr occurred during the HVOF deposition process of coating. Arc discharge heating of Cr_3C_2-NiCr coating at 1000 °C temperature resulted in recrystallization of the Cr_2C_3 and, especially, Ni phases. Flame remelting of the flame sprayed WC-Co/NiCrBSi coatings resulted in formation of more crystalline coatings in comparison with the coatings heated by arc discharge. Cr_3C_2-NiCr and flame remelted WC-Co/NiCrBSi coatings were resistant to the heating at 900 °C temperature in the air (high temperature oxidation). It means that coatings formed using HVOF and flame-spraying processes are suitable as high temperature protective coatings. Results show that technological conditions of the process of deposition can be further improved to increase durability of the coating.

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