The corrosion-resistant Ni-based coatings and their tribological properties

Korózne odolné povlaky na báze Ni a ich tribologické vlastnosti

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Ni-based coatings can be successfully applied under abrasive and adhesive conditions as a substitute for environmentally harmful chrome coatings. The research has been carried out for thermally flame sprayed Ni-based coatings with remelting (so-called the two-step process) with the different chemical composition of starting powders. The structure of coatings was evaluated by optical and scanning electron microscopy. Both the three-body abrasive wear test, according to ASTM G65-4 (Dry-Sand Rubber Wheel Test) and dry sliding wear test by the Falex tester, were performed. The results show the influence of the effective chemical composition of the metal powders on improving the properties of the coating. The higher hardness of the coatings leads to a lower tendency for the creation of adhesive bonds, and as a result, leads to a lower tendency to scuffing. A similar trend shows the influence of higher coating hardness on the increasing of abrasive wear resistance.

Povlaky na báze Ni je možné úspešne aplikovať pre abrazívne a adhézne podmienky ako náhradu za environmentálne škodlivé chrómové povlaky. Výskum bol uskutočnený pre žiarovo plameňom striekané povlaky na báze Ni s pretavením (tzv. dvojkrokový proces) s rôznym chemickým zložením východiskových práškov. Štruktúra povlakov bola vyhodnotená optickou a skenovacou elektrónovou mikroskópiou. Realizovaný bol test abrazívneho opotrebenia pri trojbodovom dotyku podľa ASTM G65-4 (Dry-Sand Rubber Wheel Test) a test na opotrebenie kĺzaním pomocou Falex testera. Výsledky ukazujú vplyv chemického zloženia kovových práškov na vylepšenie vlastností povlakov. Vyššia tvrdosť povlakov vedie k nižšej tendencii vytvárania adhézných spojov a v dôsledku toho k nižšej tendencii k odieraniu. Podobný trend ukazuje vplyv vyššej tvrdosti povlaku na zvýšenie odolnosti proti abrazívnemu opotrebeniu.

INTRODUCTION

Thermally sprayed Ni-base coatings are currently considered to be a potential and environmentally friendly substitute for conventional electroplated hard chromium layers. Electro deposited hard chromium plating is generally used to produce hard and wear-resistant coatings but, the plating baths contain hexavalent chromium, which has adverse health and environmental effects [1,2].

Thermal spraying involves many deposition processes, such as flame spraying, plasma spraying, high-velocity oxy-fuel (HVOF) spraying, and cold spraying to produce the coatings with various chemical composition, structure, and thickness [3,4].

The flame sprayed coatings are prone to the formation of interconnected elongated pores due to the lack of the fusion between sprayed particles or due to the expansion of gases generated during the spraying process. Subsequently, lower adherence to the substrate can deteriorate the quality of these coatings. One of the possible methods of reducing porosity, improving adhesion and mechanical and tribological properties of thermally sprayed coatings is the application of the

remelting process (flame treatment, thermal treatment, laser post-treatment, etc.) [4-6].

Ni-based alloys are used in wide range of applications, especially requiring wear resistance combined with resistance to oxidation or corrosion at high temperatures [7]. Chromium promotes resistance to oxidation and high-temperature corrosion and increases the hardness of the coating by forming hard precipitates. Boron brings down the melting temperature and helps the formation of hard phases. Silicon is added to increase self-fluxing properties. Carbon produces carbides with high hardness levels that improve the wear resistance of coatings. It is important to provide an effective and economical amount of alloying elements in the starting powders. However, it was also reported that the abrasive resistance can vary for different types of materials and coatings even for materials with very similar hardness [4,8].

Ni-based coatings are generally applied to provide higher wear protection, and therefore, it is important to study their tribological properties. The tribological properties of materials are influenced by mechanical properties (e.g. elastic modulus, yield strength, hardness

or fracture toughness) that are well defined for metallic materials. However, there are no simple equivalents of these properties for thermally sprayed coatings. This is due to the complexity of the structure of the thermally sprayed materials (e.g. hard phases, cracks, lamellar structure, pores) [9].

In the present work, the aim was to obtain information about the influence of remelting (two-step technology) on resistance to scuffing and abrasion of selected Ni-based self-fluxing alloy coatings made of two innovative starting powders. The tribological performance of tested coatings by two test methods, i.e., the three-body abrasion test and the Falex scuffing test, are compared and discussed.

EXPERIMENTAL

Materials

The innovative metallic Ni-based self-fluxing alloy powders with an average grain size of $-100\ \mu\text{m} + 45\ \mu\text{m}$ and the melting point of $1010\ ^\circ\text{C}$ were used as the coating material (Welding Research Institute, PI, Slovakia). The chemical composition of the studied powder materials (marked as A and B) is given in Table 1. The shape of powder grains is shown in Figure 1. The transverse section of the coatings was polished using the standard

metallographic procedure. The powder particles showed a spheroidal shape. The powder of type B contains the hard chromium carbides in the Ni matrix [10].

Coatings

Coatings were deposited on the plate (dimensions $100 \times 150 \times 8\ \text{mm}$) made of hot rolled low carbon steel S35530 EN10027-1 (1.0553). The surfaces of the blocks were shot blasted to remove grease and oxides and to stimulate adherence of the layers to be sprayed. The surface roughness of approximately $R_a \approx 5.0\ \mu\text{m}$ was chosen to provide adhesion and the proper contact properties. The number of samples for each experimental test was three.

The samples before spraying were preheated to a temperature between $90\ ^\circ\text{C}$ and $100\ ^\circ\text{C}$. A suitable substrate temperature increases the adhesion of the thermally sprayed coating.

The SuperJet Eutalloy oxy-acetylene thermal spray system was used for the flame spray process at a pressure of 100 kPa for the oxygen and 70 kPa for the acetylene. The spray distance between the gun and the substrate was 200 mm. Flame remelting consists of applying an oxy-acetylene flame to the coatings until a melting temperature of $1025\ ^\circ\text{C}$ is reached.

Methods

The structure of thermally sprayed coatings was investigated by cross-sectioned specimens with the Neophot 21 optical microscope and SEM. The etching with a mixture of HF (10 ccs) and HNO_3 (100 ccs) was carried out. The Rockwell hardness measurements were carried out after grinding. Microhardness measurements on cross-sectioned specimen were performed by the Hanemann's hardness tester HV0.3 with a constant load of 300 g.

Tab. 1. Chemical composition of powders / *Chemické zloženie práškov*

A	C: 0.25, Si: 3.9, Mn: 0.08, P: 0.001, Cr: 0.12, Mo: 0.01, B: 0.98, S: 0.006, Fe: 0.51, W: 0.02, Cu: 0.1, Co: 0.02, Ti: 0.02, Nb < 0.0, Ni: 94.49
B	C: 0.21, Si: 3.52, Mn: 0.07, P: 0.057, Cr: 8.85, Mo: 1.30, B: 1.48, S: 0.012, Fe: 2.63, V: 0.01, W: 0.02, Cu: 0.73, Al: 0.004, Co: 0.02, Ti: 0.01, Ni: 81.4

Fig. 1. Transverse section of powder A (left) and B (right)
Obr. 1. Priečny rez práškom A (vľavo) a B (vpravo)

The study of the tribological performance of the coatings was carried out by two test methods. The originally designed three-body abrasion tester, according to the ASTM standard G65-4, known as the Dry-Sand Rubber Wheel (DSRW), was used Figure 2a [11]. The principle of the test is shown in Figure 2b. The parameters of the test were as follows: sliding distance: 1031 m, wheel speed: 2.3 m s^{-1} , load: 35.5 N. As abrasive, angular SiO_2 particles (hardness 1000-1200 HV) with 0.36 mm average size were used. The abrasion test was repeated three times for the materials used, and the average mass loss Δm [g] was calculated.

The Falex tribometer – journal and vee block tester – (IT-09 ITE Radom) was used to evaluate the tribological properties of tested samples under dry sliding according to ASTM standards (Fig. 3a). The dimensions of coated samples with the groove on the face surface (V-blocks) were as follows: diameter $D = 12.7 \pm 0.05 \text{ mm}$, length $L = 10.0 \pm 0.05 \text{ mm}$ [10].

a)

b)

Fig. 2. Three body wear test: a) view on tribometer [11], b) scheme of tribometer

Obr. 2. Skúška opotrebenia strojovým dotykom: a) pohľad na tribometer, b) schéma tribometra

a)

b)

Fig. 3. Falex tribometer a) view on tribometer, b) pin and vee block of tribosystem

Obr. 3. Falex tribometer a) pohľad na tribometer, b) kolík a V-blok tribosystému

Fig. 4. The cross-section of coating A before remelting (left) and after remelting (right)
 Obr. 4. Prierez povlaku A pred pretavením (vľavo) a po pretavení (vpravo)

Fig. 5. The cross-section of coating B before remelting (left) and after remelting (right)
 Obr. 5. Prierez povlaku B pred pretavením (vľavo) a po pretavení (vpravo)

RESULTS AND DISCUSSION

Structure and hardness

The layer thickness of coatings was approximately 1.5-2 mm. Light microscopy images presented in Figures 4 and 5 show cross-sections of coatings: (i.) after flame spraying in and (ii.) after remelting. As is documented, the structures of coatings A and B contain pores, unmelted particles, gaps between the splats, and elongated splats. The coatings are mechanically bonded to the substrate [4, 8, 12-15].

The porosity or splat boundaries of thermal sprayed coatings can be successfully eliminated by different methods of remelting (González et al., 2007). The structures of the coatings A and B after remelting show the elimination of the pores and splat boundaries – Figures 4b and 5b [8,12].

The interface between coatings and the substrate after remelting is without defects, pores, and with the metallurgical bond. Adhesion has been reinforced using

the substrate preheating process and remelting for suitable bonding strength [16-18].

The structure of middle region of remelted coatings is shown in Figure 6. The figure displayed the microstructure of coatings A with increased grain size, which may be influenced by a heat treatment time [4].

As reported by González et al. (2007) it is difficult to control the temperature-time cycle, the final through-thickness microstructure is not homogeneous [19, 20]. Darker areas in Figure 6a indicate fewer precipitates in coating A. The remelting of the coating reduces porosity and creates a strong metallurgical bond [4, 8, 17]. The elimination of the pores by remelting was confirmed (Fig. 6). The precipitates in coating B are dissolved in the Ni matrix.

Table 2 presents the results of tribological tests and the hardness of tested coatings. The micro-hardness of A coating is approximately 290 ± 36 HV0.3, which is slightly lower than the hardness of B coating 409 ± 43 HV0.3. The chemical composition of the starting powders

(Tab. 1) corresponds to the quantity and size of the hard precipitates in the Ni matrix, which are responsible for the differences of the hardness of the coatings.

Wear testing

Tab. 2 presents the results of abrasive wear of coatings A and B under three-body abrasion tests. The better resistance to abrasive wear was recorded for B coating compared to coating A. The coating B exhibits lower mass loss, i.e., higher wear resistance, which is consistent with its higher hardness. The chemical composition of the starting powders influences on the creation of the hard phases in the Ni matrix. However, it is also important to use optimized parameters of thermally sprayed processes. Phase diagrams, e.g., NiCr, NiB, and NiSi provide information on the effects of individual alloying elements. They show that the presence of Cr, Si, and B plays a role in the formation of hard phases [21, 22]. The Ni coatings contain hard phases, the matrix phase is a solid solution of Ni with hard precipitates,

mainly of Cr. The coating B with a higher addition of 2.63 wt.% Fe exhibits better wear resistance properties, which is consistent with [12].

The tendency to form carbides and borides at higher content of these elements (coating B) is connected with higher microhardness and increased wear resistance. Many researchers have identified carbides and borides of chromium (mainly Cr_7C_3 and CrB) in solid solution of Ni. The higher hardness of coating B can be attributed to the strengthening effect provided by the precipitates, such as CrB and Ni_3B phases [6, 8, 22, 23].

Tab. 2. Tribological properties of coatings / Tribologické vlastnosti povlakov

Coating	Mas loss Δm [g] ASTM G65-4	$F_{\max}$ [N]	Microhardness HV0.3
A	0.0672 ± 0.019	890 ± 42	290 ± 36
B	0.0389 ± 0.011	1176 ± 32	409 ± 43

a)

b)

Fig. 6. Structure of middle region – coating A (left) and coating B (right)
Obr. 6. Štruktúra strednej oblasti – povlak A (vľavo) a povlak B (vpravo)

Fig. 7. Scuffing resistance $F_{\max}$ for coating A
Obr. 7. Odolnosť proti zadieraniu $F_{\max}$ pre povlak A

Fig. 8. Scuffing resistance $F_{\max}$ for coating B
Obr. 8. Odolnosť proti zadieraniu $F_{\max}$ pre povlak B

The results of scuffing resistance are presented in Tab. 2 for both coatings tested, where $F_{\max}$ is the maximum force when scuffing occurs. The selected graphical outputs from Falex tests (Figs. 7 and 8) show that $F_{\max}$ for coating A recorded a lower value compare to coating B. There are differences in the graphic outputs for tested coatings.

Figure 7 shows the load force for coating A. It can be seen that the oscillations increase with increased load force during the tests. The course of the loading force of coating A shows that, under dry friction conditions, oscillations lead to high scuffing, the scuffing occurred at $F_{\max} = 890$ N.

The higher hardness of coating B leads to a lower tendency to oscillations, and therefore, to the lower tendency to form adhesive bonds and to the lower tendency to scuffing (Fig. 8). Wear resistance was determined as a maximum force when scuffing occurred, and the test was stopped. The scuffing occurred at $F_{\max} = 1176$ N.

The friction force oscillations are more intense for coating A compared to coating B, resulting in lower scuffing resistance of coating A. Under dry sliding test in steel pin and V-block configuration, coating A showed lower scuffing resistance, while coating B with higher hardness recorded a higher scuffing resistance value.

CONCLUSIONS

Based on the experimental research of the thermally sprayed Ni-based coatings by a two-step process, the following conclusions can be drawn. The coatings prepared of the Ni-based starting powders showed that an efficient amount of alloying elements (chromium about 8-9 %, boron about 1.5 %, and Fe) contributes to the formation of hard phases and to increase in hardness. Experimental tests have shown that the higher hardness of the coatings had a positive effect on increasing the abrasive wear resistance. The higher hardness of the coating resulted in a reduction of adhesive bond formation and thus improvement of scuffing resistance under the Falex test. Two experimental tests performed have confirmed the importance of efficient and economical alloying of starting powders for the tribological behavior of flame deposited coatings with remelting. The obtained results showed that thermally sprayed coatings by two-step technology and optimized chemical composition contribute to improved interface bonding, elimination of splat-structure, reduced porosity, and offer improved tribo-mechanical behavior.

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