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The Study of Electroless Ni–P/Ni–B Duplex Coating on HVOF-Sprayed Martensitic Stainless Steel Coating

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High velocity oxygen fuel sprayed stainless steel coatings have been widely used in various industries to repair damaged components. However, its broad application is limited due to its comparatively low hardness and inferior tribological properties. In this work, electroless Ni–P/Ni–B duplex coating with a thickness of $\approx 40 \mu\text{m}$ was deposited on surfaces of HVOF-sprayed 420 martensitic stainless steel substrate, and its structural, corrosion and tribological properties were characterized. Experimental results showed that upper Ni–B coating deposited on the surface of first Ni–P layer by duplex treatment exhibited superior hardness, wear and corrosion resistances as compared to the HVOF-sprayed 420 martensitic stainless steel coating with a thickness of about $150 \mu\text{m}$.

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1. Introduction

The high demand for high velocity oxygen fuel (HVOF) sprayed coatings comes from the necessity of repairing damaged components of power plants, hot working dies, and tools because it is possible to deposit a depth in the micrometer range and minimize thermal effects on the substrate compared to the coatings obtained by other thermal spray processes (plasma or wire arc spray) [1]. Unfortunately, its broad application is limited due to the undesirable properties, such as the formation of micropores upon solidification and the “weak links” caused by the oxide veins [2].

Electroless deposition process is one of the most technologically feasible and economically superior techniques for the production of dense metallic nanocrystals. Among the various types of electroless plating, electroless Ni–P coating has received attention as a functional coating in industrial applications due to its high hardness, uniform thickness, as well as excellent corrosion and wear resistance [3]. However, electroless duplex coatings designed to achieve advantages of both Ni–P and Ni–B coatings have better capabilities than usual electroless coatings for use under high shear and load conditions [4–6].

Duplex coating consisting of thick hard Ni–B deposited over a thin ductile Ni–P may protect industrial parts subjected severe wear and corrosion conditions. According to the available literature, the Ni–P/Ni–B duplex coatings deposited on difficult substrates have many challenges in the plating processing and there is no such report on the thermal sprayed coating. In the present study, the HVOF-sprayed 420 martensitic stainless steel coating has

been subjected to duplex-treatment with Ni–P and Ni–B coating and then its structural characterization, dry sliding wear and corrosion properties have been evaluated.

2. Material and method

Surface of plain carbon steel plates in the size of $20 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$ was roughened by sand blasting and then coated with an intermediary Ni–Cr layer that increases the adhesion of coating. Martensitic stainless steel coating was applied by HVOF thermal spray process on the steel plates. The average coating thickness was $\approx 150 \mu\text{m}$. The HVOF-sprayed 420 martensitic stainless steel coating was used as the substrate material for the preparation of electroless Ni–P/Ni–B duplex coating. To generate a Ni–P/Ni–B duplex coating, the surface of the HVOF-sprayed 420 martensitic stainless steel coating was prepared for plating by mechanical grinding, acetone degreasing and etching in a 30 vol.%HCl solution for 1 min. A continuous Ni–P deposit was applied to form the first layer before immersion in the electroless Ni–B bath for the second layer. By the preparation of Ni–P coating, a commercial Ni–P electroless solution (Durni-Coat DNC 520-9) was used. The stirring rate of plating bath was about 250 r/min, using a magnetic stirrer and a polytetrafluoroethylene (PTFE) coated magnet with 2 cm length and 5 mm in diameter. The deposition was carried out in a 100 ml thermostated double wall beaker at 90°C and pH 4.6 for 2 h to achieve a thickness of $\approx 3.5 \mu\text{m}$. The Ni–B plating took place at 95°C and pH 13.5 for 2 h to achieve a thickness of $\approx 36 \mu\text{m}$ in a thermostated cell with a volume of 100 ml. The electroless Ni–B bath used for this study uses sodium borohydride as a reducer, nickel chloride hexahydrate as a nickel source, ethylene diamine as a complexing agent and lead nitrate as a stabilizer. More details on the bath composition have been given by Bulbul [7]. The cross-section of the coating was included in epoxy resin and polished by metallographic procedures.

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Characteristics of the HVOF-sprayed martensitic stainless steel coating and duplex treated coating were investigated by microscopic examinations, X-ray diffraction (XRD) analyses, microhardness measurements, dry sliding wear and corrosion tests. The cross-sectional microstructure of the coatings was inspected with an optical microscopy (OM) and a scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS). The cross-sectional microhardness measurements were carried out using a Vickers microhardness tester (Shimadzu) with a load 50 g and a dwell time of 10 s.

Dry sliding wear performances of the coatings were performed on a reciprocating wear tester operating in ball-on-disc configuration at room temperature. In this configuration, an Al_2O_3 ball with a diameter of 10 mm was sliding forward and backward against the coatings with a sliding speed of 1.7 cm s^{-1} . Normal load of the test, sliding amplitude (wear track length) of the reciprocating motion, and overall sliding distance were 5 N, 10 mm, and 50 m, respectively. During the wear tests, the temperature and the relative humidity were maintained as $20 \pm 5^\circ\text{C}$ and $30 \pm 5\%$, respectively. The friction coefficient force was continuously recorded during the tests. After the wear test, the wear tracks formed on the coatings were detected by a surface profilometer (SurfTest SJ 400). The wear of the Al_2O_3 balls were evaluated by an OM examination of their contact surfaces. To evaluate wear mechanisms, wear tracks of the coatings were further studied using a SEM.

The electrochemical corrosion tests of the coatings were performed utilizing a typical three electrode potentiodynamic polarization test unit in the corroding media of aerated solution of 3.5 wt% NaCl at room temperature. Before potentiodynamic polarization measurements, an initial delay of 45 min was employed in order to measure the open circuit potential between working and reference electrodes. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV s^{-1} , starting from -0.25 up to $+0.25 \text{ V}$. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method. Finally, the surface images of the corroded coatings were examined using an OM in order to determine the morphology of the developed corrosion.

3. Results and discussion

The chemical composition of the Ni-P and Ni-B deposits can be seen in Table I. The Ni-P deposit contains 13.43 wt% phosphorus and 86.57 wt% nickel, whereas the Ni-B deposit contains 5.95 wt% boron, 1.89 wt% phosphorus, and 92.16 wt% nickel. It is also noted that electroless Ni-B coating containing 4 wt% or more boron is generally amorphous by Vitry et al. [5].

The XRD patterns of the examined coatings are shown in Fig. 1. After electroless duplex plating on the HVOF-sprayed 420 martensitic stainless steel coating, Ni-B fully

TABLE I

Chemical composition [wt%] of the Ni-P and Ni-B coatings.

Coating	Nickel	Phosphorus	Boron
Ni-P	86.57	13.43	—
Ni-B	92.16	1.89	5.95

coated the surface as shown in XRD pattern of the Ni-P/Ni-B deposit. XRD pattern of the Ni-P/Ni-B deposit exhibits a single broad peak indicative of the amorphous nature of the coating (Fig. 1).

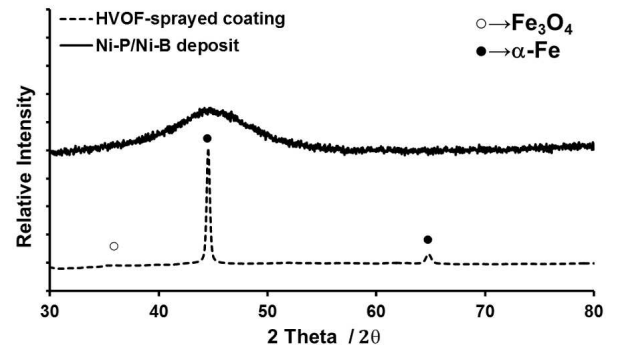


Fig. 1. XRD patterns of the examined coatings.

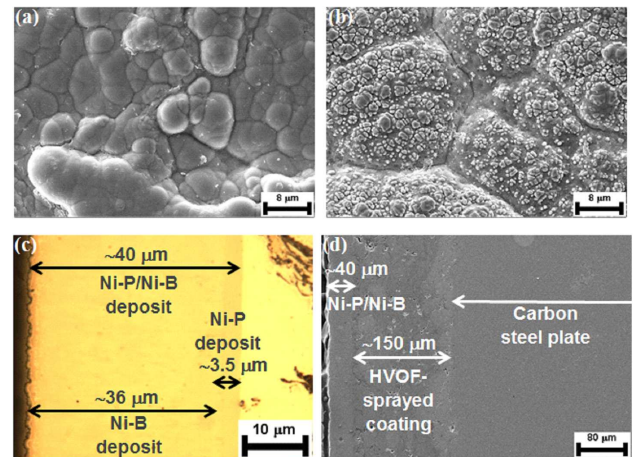


Fig. 2. Surface morphologies of (a) Ni-P, (b) Ni-P/Ni-B deposits, and (c), (d) cross-section views of Ni-P/Ni-B deposit and HVOF-sprayed 420 martensitic stainless steel coating analyzed by OM and SEM.

The surface morphology of the electroless Ni-P deposit with an average globular size of about $5\text{--}8 \mu\text{m}$ was shown in Fig. 2a, which fully covered the HVOF-sprayed 420 martensitic stainless steel coating. Ni-B presented a cauliflower-like morphology consisting of globular grains (Fig. 2b) and its thickness was about $36 \mu\text{m}$ (Fig. 2c). It can be seen from Fig. 2c,d that the Ni-P/Ni-B duplex coating is uniform and compact, and good adhesion exists

between the Ni-P and Ni-B layers. The coating thickness and porosity achieved by HVOF process are greater than for the Ni-P/Ni-B duplex coating. The HVOF-sprayed coating can be as thick as $\approx 150 \mu\text{m}$, while the Ni-P/Ni-B duplex coating is typically up to $\approx 40 \mu\text{m}$ thick and free of porosity.

Figure 3 shows the cross-sectional hardness values of the Ni-P/Ni-B duplex coating. On the cross-section, hardness varied in between $495 \text{HV}_{0.05}$ and $616 \text{HV}_{0.05}$ within the distance of about $30 \mu\text{m}$ starting from the outermost surface. At depths in between 30 to $40 \mu\text{m}$, hardness value was measured as about $400 \text{HV}_{0.05}$. An increase in the hardness can be attributed to the formation of interstitial solid solution developed by boron in the nickel matrix [8].

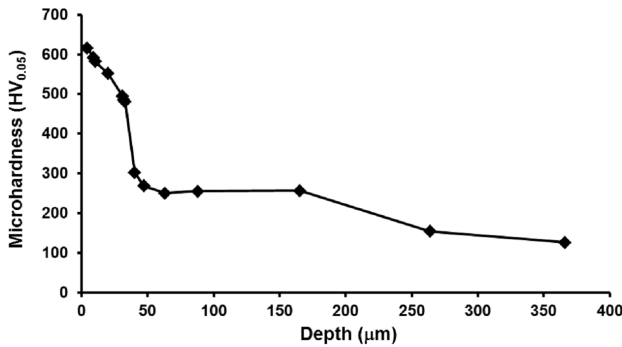


Fig. 3. Cross-sectional hardness variation of the Ni-P/Ni-B duplex coating.

Appearances of the wear tracks developed on the coatings and their corresponding testing balls along with the friction curves are shown in Fig. 4. Wear track for the HVOF-sprayed 420 martensitic stainless steel coating is characterised by the longitudinal grooves along the sliding direction and the wear of Al_2O_3 ball is relatively serious (Fig. 4a). In contrast, SEM image of the shallow wear track for the Ni-P/Ni-B duplex coating shows that the surface is polished on the path and the wear of Al_2O_3 ball is very low (Fig. 4b). This situation benefits from the solid-lubricating properties of Ni-B layer [9, 10]. The friction curve of the HVOF-sprayed 420 martensitic stainless steel coating fluctuated in a broad range and continuously increased, while that of the Ni-P/Ni-B duplex coating was very smooth and decreased after making a maximum at the beginning of the test (Fig. 4c).

When examining the wear rate (calculated by considering width and depth of wear track) of their wear tracks (Fig. 5), the Ni-P/Ni-B duplex coating exhibited lesser wear rate than the HVOF-sprayed 420 martensitic stainless steel coating. Since the bonding between each droplet deposited on the steel substrate was not strong enough, a large amount of material has fallen out from the surface of the wear track (Fig. 4a). Superior wear resistance of the Ni-P/Ni-B duplex coating compared to the HVOF-sprayed 420 martensitic stainless steel coating may be attributed to the nearly homogeneous and lubricant cauliflower-like structure of Ni-B layer [5, 9].

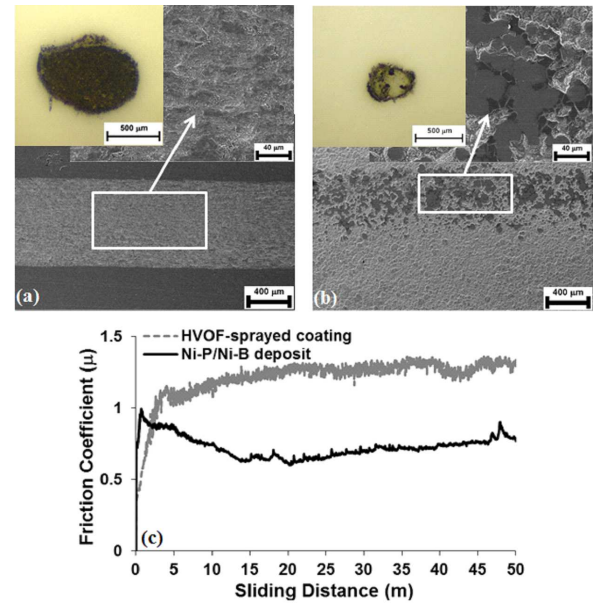


Fig. 4. Low and high magnification SEM micrographs of wear tracks generated on the (a) HVOF-sprayed 420 martensitic stainless steel coating, (b) Ni-P/Ni-B deposit, and OM images of their corresponding testing balls, (c) friction coefficient curves recorded during wear tests.

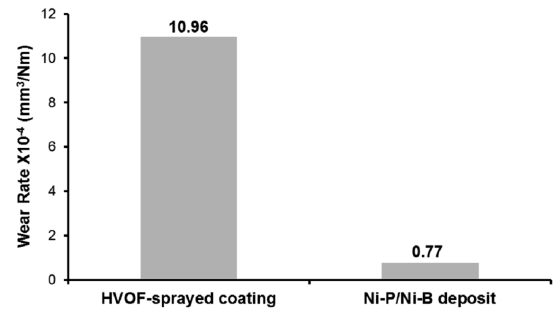


Fig. 5. Wear rates of the examined coatings.

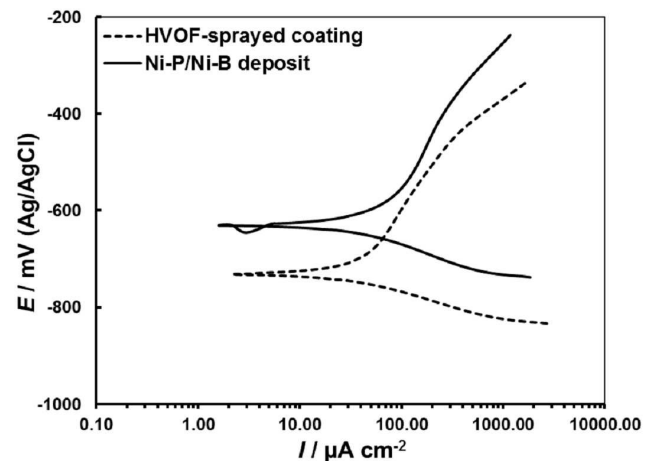


Fig. 6. Potentiodynamic polarisation curves for the examined coatings in a 3.5 wt% NaCl solution.

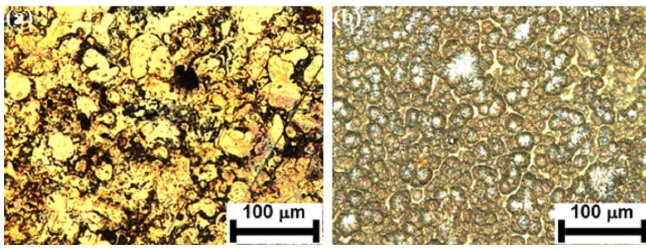


Fig. 7. OM images of the (a) HVOF-sprayed 420 martensitic stainless steel coating and (b) Ni-P/Ni-B deposit after polarization test.

TABLE II

Corrosion potential and corrosion current density values obtained from the polarization curves

Coating	E_{corr} [mV]	I_{corr} [$\mu\text{A cm}^{-2}$]
HVOF-sprayed coating	-732	46.5
Ni-P/Ni-B deposit	-633	3.75

Figure 6 showed the electrochemical polarization curves for the coatings in a 3.5 wt%NaCl solution. The corrosion potential and corrosion current density of the examined coatings obtained from the electrochemical polarization curves were summarized in Table II. The Ni-P/Ni-B deposit showed great positive shift in corrosion potential and evident decrease in corrosion current density in comparison with the HVOF-sprayed 420 martensitic stainless steel coating. The lower corrosion tendency of the Ni-P/Ni-B deposit could be a consequence of the presence of the protective Ni-P underlayer [5] and its amorphous structure [11]. However, the low corrosion resistance of HVOF-sprayed 420 martensitic stainless steel coating may be owing to the high porosity of the coating induced by the HVOF process (Fig. 2d) [12]. The surface of the HVOF-sprayed 420 martensitic stainless steel coating shows some small areas of corrosion (Fig. 7a), while the Ni-P/Ni-B deposit is mostly free of such spots (Fig. 7b).

4. Conclusion

Ni-P/Ni-B deposit with the thickness of about 40 μm on the HVOF-sprayed 420 martensitic stainless steel coating was prepared by electroless deposition using

dual baths. OM and SEM of the cross-section views of the Ni-P/Ni-B deposit revealed that the coating was uniform, compact, and the compatibility between the layers was good. Extremely hard (about 616 $\text{HV}_{0.05}$) Ni-P/Ni-B layer was developed on the surface of HVOF-sprayed 420 martensitic stainless steel coating with a thickness of about 150 μm . Under dry sliding conditions, the Ni-P/Ni-B layer exhibited superior tribological performance against the Al_2O_3 ball by greatly lowering both the wear rate and the friction coefficient. The Ni-P/Ni-B duplex coating showed a more noble electrochemical compartment than the HVOF-sprayed 420 martensitic stainless steel coating.

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