Original Article

Effect of heat treatment on the hardness and wear resistance of electrodeposited Co-B alloy coatings

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Abstract

Cobalt-boride (Co-B) alloy coatings with different boron contents (7.31–15.33 at.% B) were electrodeposited onto an AISI 1018 steel electrode using dimethylamine borane (DMAB) as the boron source and then heat treated at various temperatures ranging from 200 to 500 °C for 60 min under air atmosphere. The composition and morphology of the coatings were analyzed using glow discharge spectroscopy (GDS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The tribological characteristics, such as the hardness, friction coefficient, and wear resistance, were also studied. The results showed that the boron content in the coatings increased as the concentration of DMAB in the electrolytic solution increased. Amorphous Co-B coatings with hardness values ranging from 700 to 820 HV, depending on the boron concentration in the coating, were obtained. When the coatings were heat treated over the temperature range of 200–400 °C, the hardness increased considerably and the wear volume decreased. The XRD patterns of the coatings revealed that the thermal treatment caused a structural change in the Co-B alloys, from an amorphous structure to a crystalline Co metal and a Co-B alloy. The maximum hardness (1280 HV) and the minimum coefficient of friction (0.08) were obtained when the Co-B coatings (15.16 at.% B) were thermally treated at 400 °C.

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1. Introduction

One of the major problems of the metal components for machinery exposed to high stress in highly hostile environments is surface degradation. The surface degradation of these components causes a decrease in their mechanical properties, such as hardness and wear resistance, which results in device malfunctions. In order to avoid surface degradation and to increase the useful life of metal parts, these parts are commonly protected with functional coatings, such as nickel, cadmium or chromium. Because chromium coatings have a high intrinsic hardness (600–1000 HV) and a low coefficient of friction (<0.2), they have been used for decades as functional coatings, primarily to provide wear resistance...
and to repair worn or undersized parts [1]. Currently, electroplated hard chromium coatings are used extensively in critical aerospace applications, e.g., aircraft landing gear, hydraulic actuators, gas turbine engines, actuators, helicopter dynamic components, valves and propeller hubs. Despite the excellent characteristics of hard chromium coatings, their use has been restricted due to environmental regulations because the electrolytic process to obtain hard chromium coatings uses chromic acid (H2CrO4) as the chromium source. Chromic acid is considered a carcinogen and a highly toxic compound; thus, the U.S. Environmental Protection Agency (EPA) has classified the hard chrome electroplating process as being environmentally unfriendly [2,3]. In addition, new legislation by the U.S. Department of Labor’s Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit for all CrVI-containing compounds from 52 to 5 μg.m−3 as an 8-h time-weighted average. These environmental restrictions have stimulated research for the development of new environmentally friendly processes that produce coatings that are superior or equal to the tribological characteristics of hard chromium coatings.

In recent years, alternatives such as the electrodeposition of Cr from electrolytic baths of trivalent chromium [4,5], Co-W alloy coatings, ternary alloys (Zn-Ni-Cd) [6], nitride-based coatings (Cr-N) as well as multilayer coatings [7] have been investigated.

In addition, electrodeposited and electroless Ni-P [8,9] and Ni-B [10–12] alloys, with amorphous and nanocrystalline structures, have been considered as potential replacements for hard chromium coatings. Several studies have shown that Ni-P and Ni-B coatings are amorphous in their as-plated condition and upon heat treatment at temperatures below 300 °C. However, when the coatings are treated at temperatures above 300 °C, the hard phase nickel phosphide (Ni2P) [3,13] and nickel boride (Ni3B) [14,15] are produced in the respective coatings. Depending on the temperature of the heat treatment and the elemental concentration of the new phase (Ni2P or Ni3B), the hardness of the coatings increased from 850 to 1300 HV [16,17].

Although nickel compounds endow the coatings with good performance and durability, the EPA lists nickel as a priority pollutant, and it is considered one of the 14 most toxic heavy metals. Thus, coatings containing nickel are a short-term solution.

Recently, Prado et al. [1] proposed nanocrystalline cobalt-phosphorous (nCo-P) coatings as an alternative to hard chromium coatings due to their properties of high hardness, low wear rates, and high deposition rates. With the advantage that the cobalt is not considered to be a heavy metal that negatively affects human health [18].

Moreover, Boron (B) exhibit unique and very interesting properties that find applications in various technology fields. Thanks to their extreme hardness (30–60 GPa) [19] metal-B alloys can be exploited as protective coatings.

It has also been reported that in the presence of a boron source, it is possible to form the cobalt-boride (Co-B) alloy, which tends to form the intermetallic compounds CoB6, Co2B, and CoB after thermal treatment at temperatures ranging from 200 °C to 500 °C [20,21].

Co-B alloys can be prepared using several methods. Hui et al. [22] prepared Co-B nanochains by chemical reduction of cobalt ions in an aqueous medium by using borohydride as the reducing agent. Similarly, amorphous Co-B alloy was produced by simple chemical reduction from its respective salts [23]. Lu et al. [24] synthesized Co-B alloy nanowires by applying a magnetic field via the reduction of CoCl2 with NaBH4 in solution. Additionally, Lui et al. [25] using an arc melting method prepared various Co-x-B (x = 1, 2, 3) compounds.

On the other hand, several authors [26–29] have shown that Co-B alloys present high discharge capacity in alkaline medium, attracting attention as high energy density anodes and catalysts for hydrogen production via the hydrolysis of Boron hydrides [29].

Despite the aforementioned technological applications of Co-B alloys, only a few studies on their electrodeposition and without description of their tribological properties have been reported. The preparation of Co-B coatings by electrodeposition from aqueous solutions present several advantages over above mentioned techniques: the equipment is not expensive, uniform coatings can be obtained on substrates of complex shape, the deposition rate is relatively high and the thickness and morphology of coatings can be controlled by electrochemical parameters. In this regard, Subramanian et al. [30] studied the effect of the applied current density on the concentration of boron in the amorphous Co-B alloy, obtained from an alkaline medium in the presence of citrate. Also, Bekish et al. [31] using the decahydro-closo-decaborane anion as the boron source, produced a Co-B alloy by electrodeposition, in addition, from XPS studies the authors proposed a chemical interaction between boron and cobalt atoms. In a previous work [32], we reported the formation by electrodeposition of the Co-B alloy with an intrinsic hardness of 818 HV, which is comparable to that of hard chromium (860 HV).

The aim of this work was to study the effects of the heat treatment temperature on the physical properties of electrodeposited Co-B coatings, such as their composition, crystalline structure, wear resistance, friction coefficient and hardness.

2. Experimental

Co-B alloy coatings were obtained by galvanostatic deposition from a base solution, \( S_0 = 0.14 \text{M CoCl}_2\cdot 6\text{H}_2\text{O} + 0.32 \text{M H}_3\text{BO}_3 + 2.8 \text{M KCl} \) at \( \text{pH} = 5.0 \pm 0.2 \) + x gL−1 dimethyamine borane (DMAB) as a boron source (x = 0, 1, 3, 5, 7 or 10 g·CL−1). All solutions were prepared immediately prior to each experiment using deionized water (18 MΩ·cm) and high purity analytical grade reagents (J.T. Baker). For the electrodeposition of the Co-B coatings, a methacrylate parallel-plate cell with an interelectrode distance of 5 cm was used and the temperature of the electrolytic bath was at 25 °C. As the anode a graphite plate was used and AISI 1018 steel plates with an exposed area of 2.5 × 5.5 cm² were used as cathodes. The cathode was cleaned with a degreasing solution before each experiment. The electrodeposition current density of 0.011 A·cm⁻² over 40 min was selected based on additional tests (the results are not presented here) using a Hull cell. The coating thickness was approximately 3.0 μm. The Co-B coatings were then
annealed in air for 60 min at one of six temperatures (i.e., 200, 300, 350, 400, 450 or 500 °C).

Thermal analysis of Co-B alloys was performed by using Netzsch STA 449 Jupiter apparatus, in which Co-B alloys of each composition were placed in alumina crucibles and were heated from room temperature up to 600 °C in a flow of air using a heating rate of 10 °C min⁻¹. An empty pure alumina crucible served as an inert reference.

Glow discharge spectrometry (GDS) (Horiba, model GD Profiler 2) was used to determine the elemental composition of the coatings as a function of thickness. The morphology of each coating was evaluated using scanning electron microscopy (SEM) (JEOL, model JSM-6510LV) in conjunction with energy dispersive X-ray spectroscopy (EDS) (Bruker, model Quantax 200). The topography of the coatings was analyzed by a profilometer (Contour GT-K3D, Bruker). X-ray diffraction was performed using a Bruker D8 Advance diffractometer.

The hardness measurements were performed using a Matsuzawa MXT-ALFA Vickers microhardness tester with a 10-g load applied for 15 s. The final value reported for the coating hardness was the average of ten measurements.

Wear tests were performed using a reciprocating ball-on-disk tribometer (CSM tribometer) in air at a temperature of approximately 25 °C and a relative humidity of approximately 39% under dry, without lubrication. As the counter body in the wear tests, balls (3-mm diameter) composed of tungsten carbide (WC) with a hardness of 3500 HV were used. All wear tests were performed under a 2-N load at a sliding speed of 4.2 cm s⁻¹. The friction coefficient and sliding time were automatically recorded during the tests. The wear volume was measured according to the ASTM G99 standard method [33]. Three wear tests were conducted for each sample.

3. Results and discussion

3.1. Electrodeposition and characterization of the chemical composition by glow discharge spectroscopy (GDS) of the Co-B coatings

The Co-B coatings were electrodeposited under galvanostatic conditions (0.011 A cm⁻² for 40 min) from \( S_0 + x \) g L⁻¹ DMAB solutions, where \( x = 0, 1, 3, 5, 7 \) or 10, at \( \text{pH} = 5.0 \pm 0.1 \).

To determine the influence of the DMAB \( ((\text{CH}_3)_2\text{NH})\text{BH}_3 \) concentration in the electrolytic solution on the relative concentration and distribution of the elements cobalt (Co), boron (B), carbon (C), and nitrogen (N) in the Co-B obtained coatings, the depth profiles of these elements were measured using the GDS technique.

Fig. 1 shows typical GDS elemental-distribution profiles of the atomic percentage (at.%) variation of the elements as a function of the Co-B coating thickness obtained from a solution of \( S_0 + 7.0 \) g L⁻¹ DMAB. In Fig. 1, the lines corresponding to H, C, and N were multiplied by a factor of 10, and the line corresponding to B was multiplied by a factor of 2. Coating analysis was stopped once the substrate signal (Fe) was constant. At the beginning of the analysis, the presence of Co and oxygen was observed on the coating surface, indicating the formation of an oxide film that was approximately 250-nm thick, which was attributed to surface oxidation due to the adsorption of oxygen molecules from the air on the Co surface. After removing the oxide film, the presence of Co (≈80 at.%) and B (≈15 at.%) was detected. The concentrations of these elements display a constant trend with the coating thickness (≈3.0 μm), and they decrease abruptly at the beginning of the growth of the Fe substrate signal, indicating the onset of the developing interface zone between the coating (Co-B) and the substrate (AISI 1018 steel). Additionally, across the entire evaluated deep range, the signals of N and C behave similarly to that of B but at lower concentrations (0.5 and 0.9 at.%, respectively). The trend observed in the elemental composition profiles shows that under the working conditions used, the codeposition of both metals, Co and B, occurred. A similar trend was observed at all studied DMAB concentrations. In a previous study [32] and based on the results obtained by GDS and XPS, it was proposed that the formation of bonds between Co and B produced the Co-B alloy.

In this regard, Brenner [34] proposed that for an aqueous electrolyte solution, the electrodeposition of boron on the cathode surface is possible only when the boron is alloyed with another stable metal, such as cobalt; this type of deposition is known as induced codeposition. The mechanism of boron incorporation into Co-B coatings prepared by the electrodeposition technique has been reported. In a study by Onora et al. [35] on the formation of Ni-B alloy proposed that boron was incorporated in the Ni-B coating due to the adsorption of DMAB produced after the Nickel surface is formed and the subsequent decomposition to elementary boron is occurred.

Fig. 2 shows the variation of B, N, and C (at.%) in the Co-B coatings obtained as a function of the DMAB concentration in the electrolytic solution. The amount of B, N, and C in the coating was increased proportionally to the DMAB concentration in the electrolytic bath. The maximum content of B in the coating was 15.33 at.%. This value is similar to that reported by other authors [36] during the electrodeposition of the Ni-B alloy using DMAB as a boron source. In addition, at concentrations greater than 7 g L⁻¹ DMAB, no significant change of the B content in the coating is observed. Note that N and C have a similar behavior and that the ratio of the
C/N concentrations increases from 1.6 to 2.7 by increasing the DMAB concentration in the solution from 1 to 10 g L⁻¹, respectively. In a previous study, using the XPS technique, we showed that the presence of N and C inside the coating is associated with the DMAB occlusion in the metal matrix during the formation and growth of the Co-B coating [32].

3.2. Effect of the heat treatment temperature on the composition, crystalline structure, hardness, wear resistance and friction coefficients of the Co-B coatings

In order to evaluate the effect of the heat treatment temperature on the morphological and tribological characteristics of the produced Co-B (x at.% B, x = 0, 7.31, 10.90, 12.24, 15.16 or 15.33) coatings, the coatings were heat treated over the temperature range of 200–500 °C for 1 h under air atmosphere.

3.2.1. XRD analysis

Fig. 3 shows the XRD diffractograms of the Co-B (15.33 at.% B) coatings before and after heat treatment at different temperatures. For comparison, the XRD diffractogram of a Co coating without B was added. For this coating, the XRD diffractogram shows the characteristic peaks of the different crystalline phases of Co: α-Co (ICDD 01-089-4307), β-Co (ICDD 01-089-4308) and Co (ICDD 00-015-0806). The behavior is radically altered when the Co-B alloy is formed by the incorporation of B into the metal matrix of Co, in which only a broad peak that is characteristic of an amorphous structure is observed. The maximum value of this peak occurs at 2θ = 44.72°, which is slightly shifted to the right with respect to the α-Co (2θ = 44.25°) peak observed for the Co coating. When the Co-B coatings were treated at temperatures between 200 and 450 °C for 1 h, the structure became crystalline, and new peaks corresponding to crystalline Co₂B (ICDD 03-065-2414) appeared. These behaviors can be attributed to the crystallization of pure cobalt followed by the precipitation of cobalt-boride (Co₃B) from the supersaturated Co-B solid solution; therefore, the onset of the allotropic transformation of the Co-B alloy occurred between 200 and 450 °C. It is important to note that as the heat treatment temperature increases from 200 to 500 °C, the characteristic peak of the amorphous Co-B alloy observed at 2θ = 44.72° becomes sharper and shifts to the left to reach a value of 2θ = 44.25° (500 °C HT), similar to that observed in the Co coating. Likewise, when the heat treatment temperature is 500 °C, the peak associated with the Co₂B alloy disappears, and the peaks corresponding to the different phases of cobalt reappear, demonstrating the decomposition of the intermetallic compounds Co-B and Co₂B in this temperature range.

3.2.2. GDS analysis of the composition of O and B

To analyze the effect of the heat treatment on the elemental composition in the produced Co-B (x at.% B, x = 0, 7.31, 10.90, 12.24, 15.16 or 15.33) coatings, a GDS analysis was performed on the thermally treated coatings. Fig. 4 shows the variation of the B content in the coatings after thermal treatment at various temperatures for 1 h. For all coatings with different B contents, the B content in the coating clearly decreases with increasing heat treatment temperature. This trend is attributed to two factors: the decomposition and the evaporation of the DMAB (boiling point 66 °C) occluded in the coating matrix, as well as to the decomposition of Co-B and Co₂B. About, Oomori and Hashimoto [37] reported the thermal decomposition at 845 °C of a solid sample of Co₂B with 25 at.% B, obtained from the molten salts of Co and B. In this way, Boron produced by thermal decomposition reacts with the oxygen of the air to form the amorphous compound B₂O₃, which is partially volatile at temperatures near 500 °C [38,39], remaining a fraction of this oxide onto the surface.

Also, Fig. 5 shows the GDS results for the oxygen content variation in the Co-B (x at.% B, x = 0, 7.31, 10.90, 12.24, 15.16 or 15.33) coatings after the heat treatment. When the Co-B coatings were heat treated between 200
and 400 °C, the O concentration decreased to values ranging from 0.1 to 1.5 at.%. At higher heat treatment temperatures, a considerable increase of oxygen content in the coatings is observed, indicating the formation of oxides. It is important to note that at temperatures exceeding 400 °C, the amount of oxygen present in the coatings after the heat treatment decreases with increasing B content in the coatings, suggesting that the presence of B produced by the decomposition of Co3B reacts with the oxygen to form the compound B2O3, thus inhibiting the formation of oxides on the surface of Co, which corroborate the behavior observed in Fig. 4. A different trend was observed in pure Co coatings, for which, after being heat treated at temperatures above 300 °C, the amount of oxygen present in the coating increased considerably, indicating the oxidation of the coating.

To support the above results, after heat treating the coatings at 500 °C, an XRD analysis of the Co coatings without and with different B contents was performed. Fig. 6 shows the XRD patterns obtained in the absence of B, revealing the characteristic behavior displayed in the presence of cobalt oxides. For the Co coatings with different B contents, after the heat treatment, the intensity of the peaks associated with cobalt oxides decreases when the amount of B in the coatings increases, confirming the inhibition of the formation of oxides by the presence of B, as well as the generation of the Co coating.

3.2.3. Thermal analysis
Fig. 7 show the TGA curves for Co-B coatings (0, 10.9, 15.33 at.% B) heated from room temperature to up 600 °C with a heating rate of 10 °C min⁻¹. In the temperature range from 0 to 200 °C, the Co coating present a mass loss associated with water desorption. Subsequently, in the range of 200–300 °C, the formation of a peak mass gain is observed which is associated to the formation of Co3O4 species, the same behavior is obtained for Co-B coatings. From the study by XRD, it is possible to propose that the above behavior corresponds to the formation of both species: Co3O4 and CoB. At temperatures up 350 °C, a constant increase in mass gain is observed for all coatings, indicative of surface oxidation. It is important to
note that this mass gain is lower as the concentration of B in the coatings increases. These results are in agreement with those obtained by GDS and show that the presence of B in the coatings partially inhibits the formation of oxides on the surface.

3.2.4. SEM analysis
Fig. 8 shows the surface morphology of Co-B coatings (15.33 at.% B) after the heat treatment at different temperatures under air atmosphere for 1 h. Two important changes in morphology are observed as a function of temperature. Without heat treatment, the Co-B coatings are uniform and have a granular morphology with semicircular clusters of different sizes (Fig. 8a). Also, the roughness parameter Rp (distance from the highest peak to the deepest valley) was evaluated with an obtained value of 1169 nm. When these coatings were treated at temperatures ranging from 200 to 350 °C, a significant change was observed in their morphology: the coatings were plate-like, more homogeneous, and smooth (Rp = 876 nm) (Fig. 8b). When the coatings were treated at temperatures greater than or equal to 400 °C, the formation of a granular structure with surface cracks was again observed (Rp = 1224 nm) (Fig. 8c). This feature was most pronounced when the temperature increased to 500 °C (Rp = 1342 nm) (Fig. 8c). This behavior is associated with the decomposition of the compounds Co-B, Co3B and DMAB occluded in the coating. The same behavior was observed for all Co-B coatings studied.

3.2.5. Tribological properties
3.2.5.1. Microhardness of Co-B electrodeposits. The dependence of the Co-B coating microhardness on the heat treatment temperature over the range of 200–500 °C is shown in Fig. 9. Two regions are clearly observed. In the first region, over the temperature range of 25–400 °C, the microhardness values show a considerable increase until a maximum value is reached. This trend is associated with the crystallization of Co and the precipitation of Co3B, occurring between 200 and 400 °C, as shown in the XRD study. At heat treatment temperatures exceeding 400 °C, the microhardness values decrease due to the formation of cracks in the surface of the coatings and the decomposition of the Co-B and Co3B hard compounds, as confirmed by the GDS composition analyses and the XRD diffractograms.

In addition, the hardness of the coatings increases with an increasing B content. The maximum microhardness value of 1281 HV was obtained by the Co-B coating with 15.16 at.% B.
after thermal treatment at 400 °C. Note that unlike the other produced coatings, the coating with the maximum content of B (Co-B, 15.33 at.%) showed a maximum hardness value of 1220 HV at a temperature of 350 °C. The results show that the Co-B coatings have a hardness value comparable to that of hard chromium coatings (850–1200 HV [40,41]), either without or with heat treatment.

3.2.5.2. Wear volume. Fig. 10 shows the trend of the wear volume of each produced Co-B coating. The wear volume depends on two factors: the heat treatment temperature and the B content in the coating. Contrary to the microhardness behavior observed, the wear volume decreases when the coatings were treated over the temperature range of 200 and 400 °C. At thermal treatment temperatures above 400 °C, the wear volume increased.

Thus, in general, it can be proposed that over the temperature range of 25–300 °C, the wear volume decreases with an increasing B concentration in the Co-B coating. However, at higher temperatures, no regular trend is observed as a function of the B concentration due to the decomposition of Co-B and Co3B.

These results demonstrate the relationship between hardness and wear volume since a lower wear volume is observed for the Co-B coating with 15.16 at.% B and heat treated at 400 °C, which correspond to the same conditions under which the maximum hardness value was obtained.

3.2.5.3. Coefficient of friction. The values of the coefficients of friction (μ) obtained during the wear tests indicate the wear resistance of the coatings. The average μ values of the Co-B coatings with different B contents and as a function of the heat treatment temperature are shown in Fig. 11. When the heat treatment temperature was between 200 and 300 °C, in general the values of μ decreased with increasing temperature and increased with the B content in the coating. Over the range of 350–400 °C, an anomalous behavior was observed, mainly for coatings with a higher B content. In the latter region, over the range of 450–500 °C, the μ values increased with increasing temperature and B content in the coating. This behavior is associated with the decomposition of the intermetallic compounds Co-B and Co3B, as well as the formation of the αCo phase between 450 and 500 °C.

The lowest coefficient of friction (approximately 0.08) was obtained from the Co-B coating with 15.16 at.% B, heat treated at 400 °C; this value is comparable to the values reported for Cr (0.1–0.2) [38] and Cd (∼0.2) coatings.

4. Conclusions

Co-B coatings were produced by electrodeposition using DMAB as a boron source. The concentration of B in the Co-B coatings increases by increasing the DMAB concentration in the electrolytic solution, thus obtaining Co-B coatings with a B concentration ranging from 7.31 to 15.33 at.% B. When the Co-B coatings were heat treated over the temperature range of 200–400 °C, the hardness increased due to Co crystallization as well as the formation and precipitation of the Co3B intermetallic compound. The hardness values obtained ranged from 780 to 1280 HV. When the heat treatment temperature exceeded 400 °C, the hardness of the coatings decreased due to the decomposition of Co3B. The maximum hardness value of 1280 HV was obtained by the Co-B coating (15.16 at.% B) with a heat treatment at 400 °C in air. The same coating had a μ value of 0.08. These hardness and coefficient of friction values are comparable to those of hard chromium coatings (1200 HV and 0.15 μm, respectively). Thus, Co-B coatings are a clear and viable alternative to hard Cr or Cd coatings. However, during the heat treatment, a partial loss of B in the coating and inhibition of oxide formation due to the presence of the remaining B in the coatings were observed.

Conflicts of interest

The author declares no conflicts of interest.
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