

1 Article

2 Electrodeposition of Co-B/SiC composite coatings: 3 Characterization and evaluation of wear volume and 4 hardness

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16 **Abstract:** In the present paper, Co-B/SiC composite coatings were obtained via electrodeposition
17 from colloidal suspensions with different concentrations of SiC particles and subsequent heat
18 treatments at 350 °C. The composition, morphology and structure of the Co-B/SiC composite
19 coatings were analyzed using glow discharge spectrometry (GDS), scanning electron microscopy
20 (SEM) coupled with energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Hardness
21 and tribological properties were also studied. The results showed that an increase in the SiC
22 concentration in the colloidal suspensions resulted in both an increase in the SiC content and a
23 decrease in the B content in the obtained Co-B/SiC coatings. The Co-B/SiC coatings were adherent,
24 glossy and soft and exhibited a homogeneous composition in all thicknesses. By contrast, an increase
25 in the SiC particle content of the Co-B/SiC composite coating from 0 to 2.56 at.% SiC reduced the
26 hardness of the film from 680 to 360 HV and decreased the wear volume values from 1180 to 23 μm^3
27 $\text{N}^{-1} \text{m}^{-1}$, respectively (that is, the wear resistance increased). Moreover, when the Co-B/SiC coatings
28 with SiC content ranging from 0 to 2.56 at.% SiC were subjected to a heat treatment process, the
29 obtained coating hardness values were in the range of 1200 to 1500 HV and the wear volume values
30 were in the range of 382 to 19 $\mu\text{m}^3 \text{N}^{-1} \text{m}^{-1}$.

31 **Keywords:** Co-B/SiC composite coatings; electrodeposition; hard coatings; wear volume

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33 1. Introduction

34 Surface degradation is one of the main damages experienced by the metallic parts of machinery
35 exposed to high stress in hostile environments. The surface degradation of these components causes
36 a deterioration in their mechanical properties, such as their wear resistance and hardness, which
37 results in machinery malfunctions. For many decades, hard coatings such as cadmium (Cd), nickel
38 (Ni) or chromium (Cr) have been widely used to protect metal components and tools against wear.
39 Although Cd, Ni, and Cr coatings are excellent protective coatings with good performance and
40 durability, the U.S. Environmental Protection Agency (EPA) lists these elements as priority
41 pollutants, and they are considered to be among the 17 most toxic heavy metals [1]. For these reasons,
42 alternative materials have been studied for many years. In this sense, composite coatings have
43 recently been studied as an alternative to hard Cr coatings. Composite coatings are formed by two
44 phases: the metal matrix as the main phase and as the second phase; micro or nanoparticles occluded

45 in the metal matrix [2, 3]. The insoluble micro or nano particles occluded in the metal matrix can be
46 nitrides, oxides and carbides (Si_3N_4 , SiO_2 , Al_2O_3 , TiO_2 , SiC , WC , graphite) and its function is to
47 increase the wear resistance and hardness of the coatings [4, 5, 6, 7, 8, 9]. These phenomena are
48 mainly attributed to the hardening of the metal matrix by finely dispersed ceramic particles. Ogihara
49 *et al.* [10] reported that composite films with Ni-B as the matrix material and SiC particles as the
50 second phase exhibit hardness values of 845 HV without heat treatment and 1490 HV with heat
51 treatment. Balaraju and Seshadri showed that, when the content of Si_3N_4 particles occluded in a Ni-P
52 metal matrix is increased, the wear resistance of the Ni-P/ Si_3N_4 coating increases substantially [11].
53 Min-Chieh *et al.* [9] reported that the addition of SiC particles to a Ni-P metal matrix reduces the
54 residual stress of the deposits and therefore eliminates surface cracking. Also, several studies on
55 Ni/SiC composite coatings have reported significant improvement in the wear resistance when SiC
56 particles are added in the nickel matrix [12, 13]. In another study, the addition of B_4C particles to the
57 matrix of the metallic Ni-P(9 %) alloy was found to increase the wear resistance of Ni-P(9 %)/ B_4C
58 composites [14].

59 Recently, nanocrystalline cobalt (Co) coatings and Co alloys have been identified as good
60 candidates for replacing the hard coatings of Cr, Cd or Ni because of their similar or improved
61 mechanical properties [15, 16]. Additionally, Co is not considered a heavy metal that negatively
62 affects human health [17]. In a previous work [18], we reported the formation of Co-B hard coatings
63 with hardness values between 760 and 800 HV (very similar to those of hard Cr), depending on the
64 content of B in the coating.

65 The novelty of the present work, consists in the preparation of Co-B/SiC composite coatings by
66 electrodeposition method due to the need of coatings with low friction and an improved wear
67 resistance for its application in fabrication of machines, parts and metal structures exposed to high
68 stress and severe erosion conditions. The aim was to elucidate the effect of incorporated SiC particles
69 in the Co-B metal matrix on the wear volume, friction coefficient, and hardness. The effect of
70 thermally treated Co-B/SiC composite coatings was also studied.

71 2. Materials and Methods

72 2.1. Stability measurements of SiC particles in suspension

73 The stability analysis of SiC particles suspended in the electrolytic baths containing the
74 dispersant cetyltrimethylammonium bromide (CTAB) was carried out using colloidal suspension of
75 composition S_0 (= 0.14 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 2.8 M KCl + 0.32 M H_3BO_3 + 0.19 M Dimethylamine borane
76 (DMAB) (DMAB was used as a boron source) + 27.4 mM CTAB) + $x \text{ g L}^{-1}$ SiC ($x = 0.0, 0.15, 0.6, 2.5, 5.0,$
77 10.0, 15.0) at pH 5.0. The solutions were prepared using distilled ultrafiltered water (18 M Ω cm
78 resistivity) and analytical-grade reagents (Sigma-Aldrich). The average size of the SiC particles was
79 100 nm (SkySpring Nanomaterials, Inc.).

80 This study was carried out with a Turbiscan analyser (mod. Lab Expert, Formulation Co.,
81 France) and cylindrical glass vials with a sample height of 43 mm. The analysis of the obtained
82 transmittance profiles vs. vial height was performed as described in Ref. [19]. The scanning of the
83 transmittance (T) along the glass vial was performed at intervals of 5 min for 8 h. From the graph of
84 the transmittance (T) profiles vs. vial height, the thickness of the clarifying layer (ΔH (mm) = $H_{\text{sup}} -$
85 H_{inf}) was calculated (see Fig. 1). H_{inf} (mm) was obtained by arbitrarily fixing the T_f (fixed
86 transmittance) value at 1% T ($T_f = 1\% \text{ T}$) and measuring the value of the distance in the vial where the
87 intersection occurs between the T of the sweep (as a function of time) and the value of T_f . H_{sup} , the
88 length of the sample in the glass vial, was equal to 43 mm. The difference between the two distances
89 measured in the glass vial ($\Delta H = H_{\text{sup}} - H_{\text{inf}}$) is indicative of the precipitation of the SiC particles. High
90 values of ΔH are indicative of an unstable suspension, whereas small values are indicative of a stable
91 suspension.

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94 2.2. Electrodeposition and characterization of the Co-B/SiC composite coatings

95 The Co-B/SiC composite coatings were electrodeposited from colloidal suspensions $S_0 + x \text{ gL}^{-1}$
96 SiC ($x = 0.0, 0.15, 0.6, 2.5, 5.0, 10.0, 15.0$) at pH 5.0 using a parallel-plate cell of 50-mL capacity and
97 with an inter-electrode distance of 5 cm. AISI 1018 steel plates ($2.5 \times 5.5 \text{ cm}^2$ of exposed area) were
98 used as the cathodes and graphite plates were used as the anodes. The coatings were deposited under
99 galvanostatic conditions by applying 8.6 mA cm^{-2} for 56 min at $25 \text{ }^\circ\text{C}$. The current density was selected
100 from additional tests (not presented here) using a Hull cell for each of the electrolytic baths.

101 The deposited phases of the Co-B/SiC composite coatings were analyzed by X-ray diffraction
102 (XRD) using a Bruker diffractometer (model D8 Advance) in the Bragg-Brentano arrangement with
103 Cu K α radiation ($\alpha = 1.54 \text{ \AA}$). The 2θ range from 30° to 150° was recorded at a scan rate of 0.2° s^{-1} .
104 The morphologies of the coatings were evaluated using scanning electron microscopy (SEM) (JEOL
105 JSM-6510 LV) coupled to an energy-dispersive spectroscopy (EDS) analyser (Bruker Quantax 200).
106 The elemental composition profiles of the Co-B/SiC composite coatings as a function of the thickness
107 of the coatings were obtained using the glow discharge spectroscopy (GDS) technique (Horiba, model
108 GD Profiler 2).

109 Hardness tests of the obtained Co-B/SiC composite coatings were carried out using an automatic
110 hardness testing system (Matsuzawa, mod. MXT-ALFA) under an applied load of 25 g for 15 s. The
111 final hardness values reported are the average of six measurements.

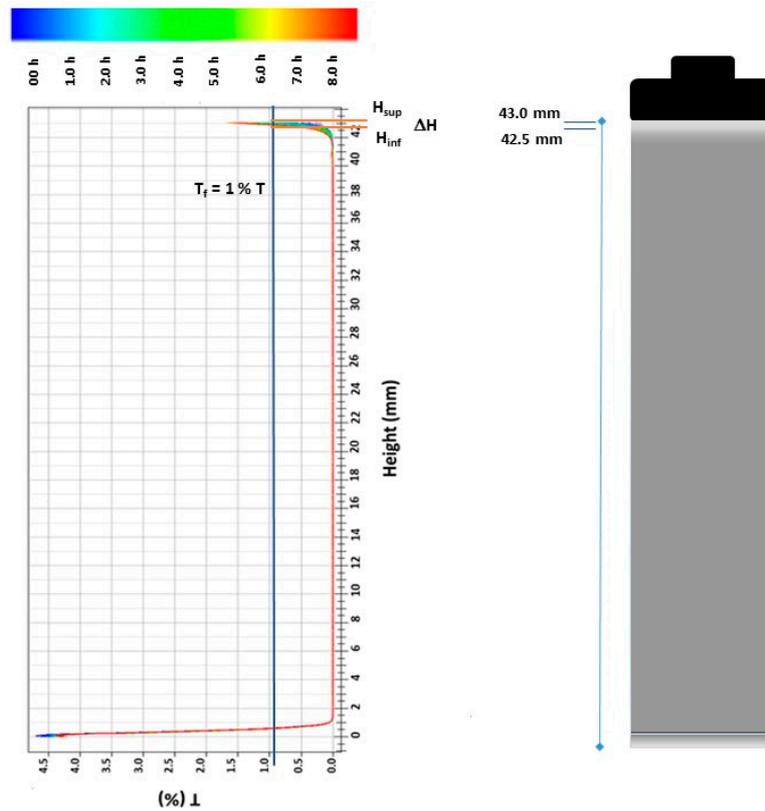
112 The wear volume tests were performed using a ball-on-disk tribometer (CSM instruments) in air
113 at $25 \text{ }^\circ\text{C}$ and a relative humidity of approximately 39 % in dry conditions, without lubrication. Balls
114 made of WC (6-mm diameter) (Anton-Paar) with a hardness of 3500 HV were used as the counter
115 body in the wear tests. All wear volume tests were performed under a 2-N load at a sliding speed of
116 4.2 cm s^{-1} . The wear volume tests were performed in triplicate and in accordance with standard ASTM
117 G99 [20]. During the tests, the sliding time and friction coefficient were automatically recorded.

118 3. Results and Discussion

119 3.1. Stability analyses of the system SiC particles/CTAB in colloidal suspensions

120 To uniformly occlude the SiC particles in the metallic matrix during the electrodeposition
121 process of Co-B/SiC composite coatings, the SiC particles must be kept suspended in the electrolytic
122 solution, which is achieved using a dispersant, preferably of the cationic type, i.e., CTAB. Therefore,
123 before the electrodeposition of the Co-B/SiC composite coatings, the stability of the SiC particles in
124 an electrolytic bath with CTAB as a dispersant was studied.

125 The stability of the SiC particles suspended in colloidal suspensions $S_0 + x \text{ gL}^{-1}$ SiC ($x = 0.0, 0.15,$
126 $0.6, 2.5, 5.0, 10.0, 15.0$) at pH 5.0 was analyzed at $25 \text{ }^\circ\text{C}$ using a dispersion-stability analyser. The
127 analysis was based on the transmittance (T) profiles vs. the vial height obtained at different times.
128 Typical transmittance profiles (obtained at different times) vs. the vial height of the SiC particles in a
129 colloidal suspension are shown in Fig. 1. A small increase in $\sim 5 \%$ T is observed in the region from 0
130 to 1 mm (bottom of the vial); this behavior indicates the formation of a clarifying zone in this region.
131 In the region from 1 to 42 mm, transmittance values close to zero ($\sim 0 \%$ T) are observed during the 8
132 h of the experiment, indicating that the solution is opaque in this range because the SiC particles form
133 a stable suspension. Finally, a small clarifying zone (ΔH) is formed in the range from 42.5 to 43 mm
134 (top of the vial). Therefore, when CTAB was used as a dispersant, stable suspensions of SiC particles
135 were obtained during a period of 8 h.



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Figure 1. a) Transmittance profiles of the colloidal suspension S_0 ($= 0.14 \text{ M CoCl}_2 \cdot 6\text{H}_2\text{O} + 2.8 \text{ M KCl} + 0.32 \text{ M H}_3\text{BO}_3 + 0.19 \text{ M DMAB} + 27.4 \text{ mM CTAB}$) with $10 \text{ g L}^{-1} \text{ SiC}$. Data are reported as a function of time (0 to 8 h) and sample height (0 to 43 mm). b) Schematic representation of the dispersion of SiC particles in the S_0 solution with $10 \text{ g L}^{-1} \text{ SiC}$.

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Fig. 2 shows the thickness variation of the clarifying layer (ΔH) in the colloidal suspensions as a function of time for different concentrations of SiC particles. An increase in the concentration of SiC particles in the colloidal suspensions causes a significant decrease in the values of the thickness variation of the clarifying layer (ΔH) as a function of time. Lower values of ΔH were obtained for the highest concentrations of SiC particles (15 and 10 g L^{-1}). After 8 h of experimentation, the ΔH value of the aqueous suspensions with both 15 and $10 \text{ g L}^{-1} \text{ SiC}$ was only 0.5 mm, whereas for the suspension with $0.15 \text{ g L}^{-1} \text{ SiC}$, ΔH was 37 mm in the same period of time.

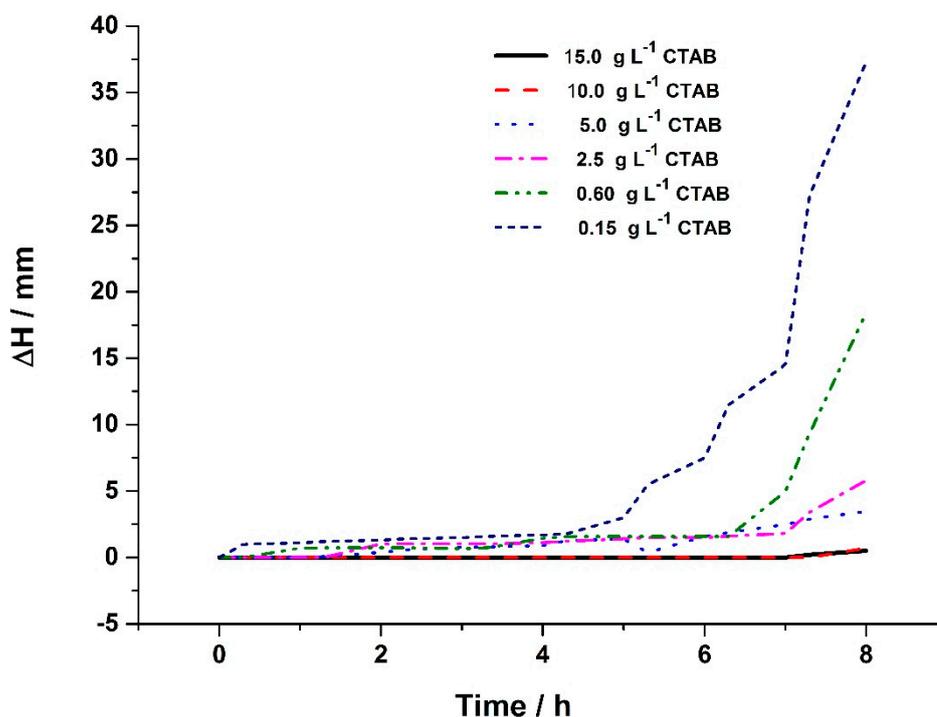
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The greater stability of the SiC particles in the colloidal suspensions is associated with the adsorption of CTAB molecules on their surface. Due to its hydrophilic functional groups and its spatial structure, the adsorbed CTAB increases the steric hindrance and electrostatic repulsion among the SiC particles [21].



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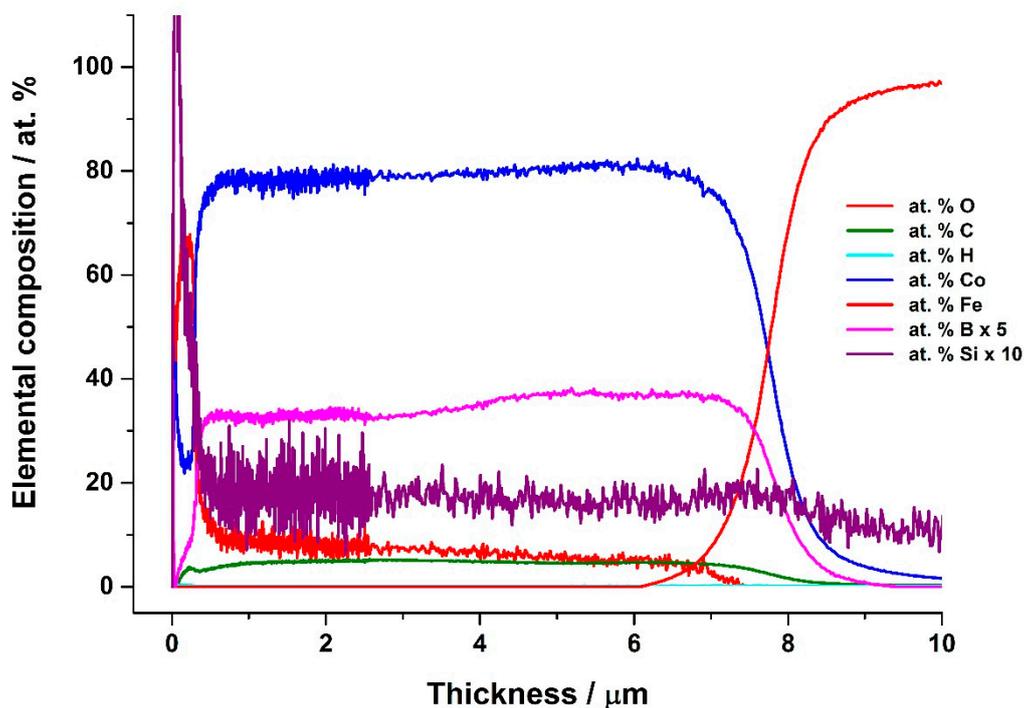
153 **Figure 2.** Effect of the SiC concentration in the colloidal suspensions on the clarifying layer thickness
 154 (ΔH) as a function of time (0 to 8 h).

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156 3.2. Co-B/SiC composite coating composition

157 The Co-B/SiC composite coatings were electrodeposited under galvanostatic conditions (8.6 mA
 158 cm^{-2} for 56 min) from colloidal suspensions $S_0 + x \text{ g L}^{-1} \text{ SiCP}$ ($x = 0.0, 0.15, 0.60, 2.5, 5.0, 10.0, 15.0$) at a
 159 $\text{pH} = 5.0$. The thickness of the coatings was $7.3 \pm 1.3 \mu\text{m}$, which was measured by X-ray fluorescence.

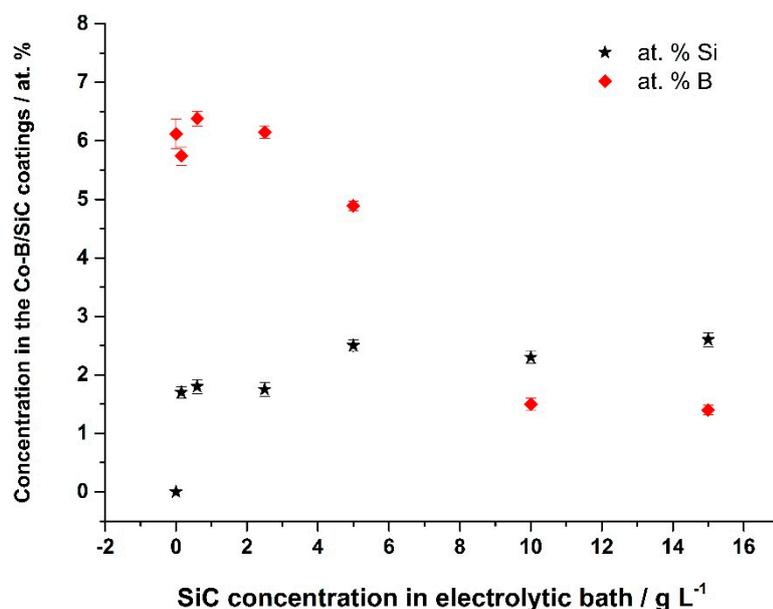
160 GDS was used to analyse the influence of the SiC particle concentration in the colloidal
 161 suspensions on the distribution and relative concentration of the elements Co, B and Si in the obtained
 162 Co-B/SiC composite coatings. For this analysis, we assumed that the detected Si signal corresponds
 163 to SiC. Moreover, coating analysis was stopped once the substrate signal (Fe) was constant and close
 164 to 100 at.%. Fig. 3 shows GDS profiles of the atomic percentage (at.%) variation of Co, B, Si, O and C
 165 as a function of depth of a Co-B/SiC composite coating obtained from a colloidal suspension $S_0 + 2.5$
 166 $\text{g L}^{-1} \text{ SiC}$. In Fig. 3, to better observe the behavior of the elements, the signal corresponding to B was
 167 amplified by a factor of 5 and the signal corresponding to Si was amplified by a factor of 10. On the
 168 surface of the coating, the formation of a surface oxide film of approximately $0.45 \mu\text{m}$ in thickness
 169 was observed. After the surface oxide layer was removed, the signals of C (~ 5.0 at.%), O (~ 7.0 at.%),
 170 Si (~ 1.7 at.%), Co (~ 75.0 at.%) and B (~ 7.0 at.%) were detected. These signals are practically constant
 171 throughout the thickness of the Co-B/SiC coating (approximately $7 \mu\text{m}$). Subsequently, they decrease
 172 rapidly, while the substrate signal (Fe) increases, forming an interface zone between the substrate
 173 (Fe) and the Co-B/SiC coating. At depths greater than $8 \mu\text{m}$, the substrate signal (Fe) remains constant
 174 and close to 100 at.%. In addition, the behaviors of the signals corresponding to Si, C, and B are similar
 175 to that of the Co signal. This behavior demonstrates the simultaneous co-position of Co, B, and Si.
 176 Moreover, Fig. 3 clearly shows the homogeneous distribution of all the elements inside the coating.
 177 A similar behavior was observed for all of the investigated SiC concentrations.



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179 **Figure 3.** GDS elemental-distribution profiles of a Co-B/SiC composite coating electrodeposited from
 180 colloidal suspension S_0 ($= 0.14 \text{ M CoCl}_2 \cdot 6\text{H}_2\text{O} + 2.8 \text{ M KCl} + 0.32 \text{ M H}_3\text{BO}_3 + 0.19 \text{ M DMAB} + 27.4 \text{ mM}$
 181 CTAB) with 10 g L^{-1} SiC.

182 From the GDS analyses of the obtained coatings, Fig. 4 shows the variation in the content of B
 183 (at.%) and Si (at.%) in the Co-B/SiC composite coatings as a function of the SiC particle concentration
 184 in the colloidal suspensions. This figure shows that the Si content in the coating increases and reaches
 185 a saturation point of $2.5 \pm 0.06 \text{ at.}\%$ Si when the concentration of SiC in the electrolytic bath was
 186 greater than or equal to 5 g L^{-1} . In contrast, the content of B in the coating decreases as the
 187 concentration of SiC in the electrolytic bath increases. At concentrations greater than or equal to 10 g
 188 L^{-1} , the B content remains constant at $1.5 \pm 0.08 \text{ at.}\%$. An equivalent behavior for the variation in P
 189 during the electrodeposition of the Ni-P-SiC composite has been observed by other authors [9, 22,
 190 23].



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Figure 4. Changes in the B (at.%) and Si (at.%) contents in the Co-B/SiC composite coatings according to the concentration of SiC in the colloidal suspensions.

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3.3. Co-B/SiC composite coating morphology

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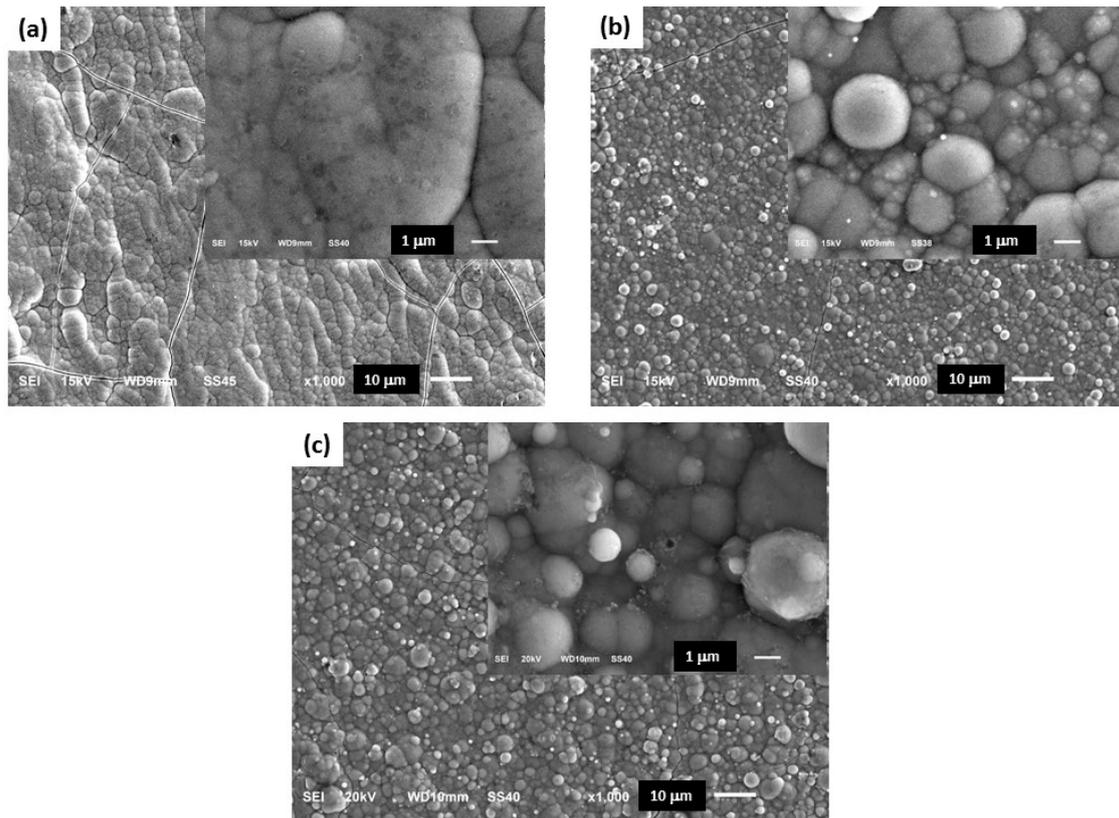
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Fig. 5 shows SEM images of the Co-B/SiC composite coatings obtained from colloidal suspensions containing different concentrations of SiC (i.e., coatings with different at.% SiC). In the absence of SiC in the electrolytic bath (Fig. 5a) (0 at.% SiC in the coating), a compact, smooth, adherent, and shiny Co-B coating is formed. Additionally, the surface of the coating shows superficial microfissures, likely due to the inner coating stress. The inset of Fig. 5a shows the amorphous structure of the Co-B coating. Furthermore, occlusion of SiC particles in the metal matrix causes a change in morphology towards an amorphous-crystalline structure of the Co-B/SiC composite coatings obtained (see Fig. 5b (1.76 at.% SiC), Fig. 5c (2.56 at.% SiC)). Semi-spherical structures of nanometric size were formed on top of the clusters. In addition, by increasing the content of SiC particles in the coatings, the size of the surface micro-fissures decreased, which is indicative of a lower level of internal stress inside the coatings. This behavior is associated with the inhibition of the hydrogen evolution reaction, due to the adsorption of the CTAB dispersant on the surface of the substrate.



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Figure 5. a) SEM images of the Co-B coatings obtained from colloidal suspension S_0 ($= 0.14 \text{ M CoCl}_2 \cdot 6\text{H}_2\text{O} + 2.8 \text{ M KCl} + 0.32 \text{ M H}_3\text{BO}_3 + 0.19 \text{ M DMAB} + 27.4 \text{ mM CTAB}$); b) SEM images of the Co-B/SiC composite coatings obtained from the colloidal suspension $S_0 + 2.5 \text{ g L}^{-1} \text{ SiC}$; and c) SEM images of the Co-B/SiC composite coatings obtained from the colloidal suspension $S_0 + 15 \text{ g L}^{-1} \text{ SiC}$.

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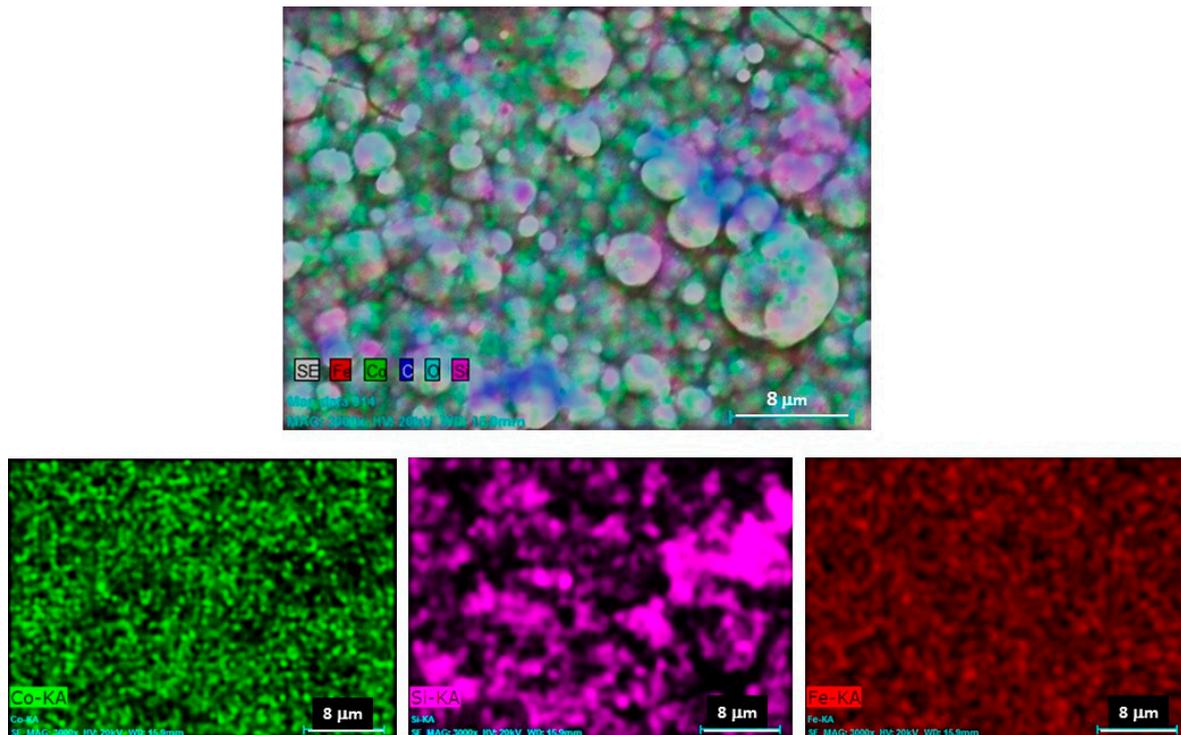
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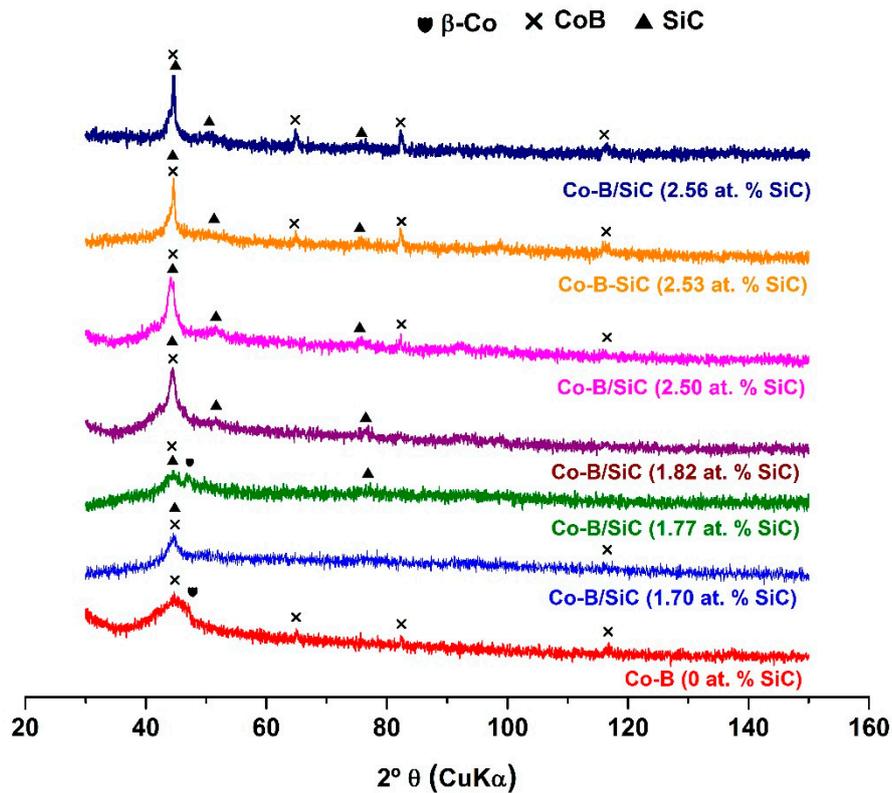
The elemental mapping analysis obtained from the surface of the Co-B/SiC (2.56 at.% SiC) coating (Fig. 6) showed that the SiC particles were homogeneously distributed on the surface of the coating. These results, together with the GDS results shown in the previous section, confirm the homogeneous occlusion of the SiC particles in the Co-B coating matrix; the same behavior was observed for all concentrations of SiC particles studied. This behavior is the result of improving the migration of the SiC particles towards the negatively charged electrode surface (cathode), due to the increase in the positive electric charge of the SiC particles that occurs because of the adsorption of the cationic dispersant CTAB on the surface of the SiC particles [24].



221
 222 **Figure 6.** Elemental mapping profile of a Co-B/SiC composite coating obtained from a colloidal suspension S_0
 223 with 10 g L^{-1} SiC.

224 3.4. XRD Analysis

225 The structural changes of the Co-B/SiC composite coatings were characterized by XRD. Fig. 7
 226 shows the corresponding XRD diffractograms. For the Co-B (0 at.% SiC) coating, the XRD
 227 diffractogram shows a broad peak at $2\theta = 44.44^\circ$, which is characteristic of an amorphous Co-B
 228 structure. This behavior is altered when the Co-B/SiC composite is formed by the occlusion of SiC
 229 particles into the Co-B alloy. When the amount of SiC particles in the Co-B matrix was increased, the
 230 crystallinity of the Co-B/SiC composite increased. These results corroborate the behavior observed in
 231 the SEM micrographs in Figs. 5a-c. Bozzini *et al.* observed a similar phenomenon during the occlusion
 232 of B_4C particles in the matrix of Ni-P alloy; this behavior was tentatively explained by the particles
 233 promoting crystallization at low temperatures by providing nucleation sites for the precipitation of
 234 nuclei in the amorphous matrix [14, 25, 26].

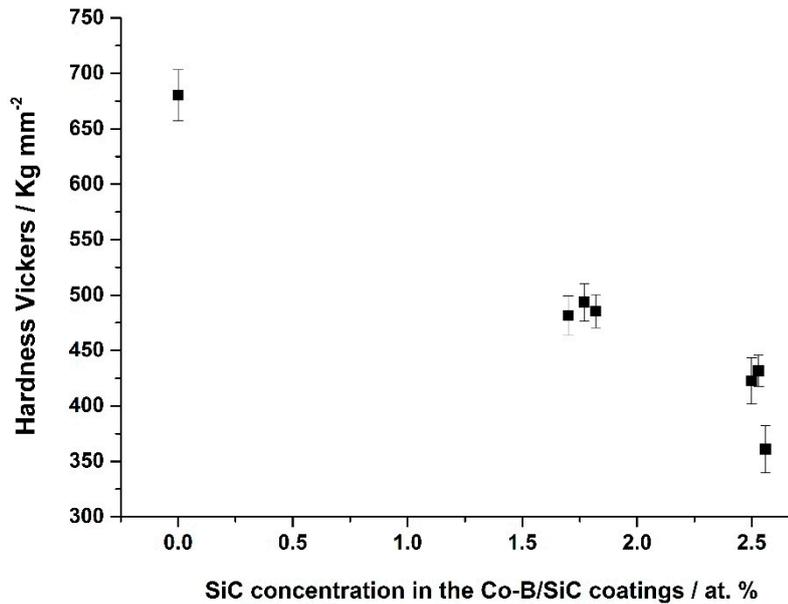


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236 **Figure 7.** Normalized XRD patterns of Co-B/SiC composite coatings with different SiC contents (at.%)
 237 obtained under galvanostatic conditions (8.6 mA cm⁻² for 56 min). β Co (JCPDS 01-089-4308), CoB
 238 (JCPDS 01-089-4308), SiC (JCPDS 00-042-1360).

239 3.5. Microhardness of the Co-B/SiC composite coatings

240 Fig. 8 shows the behavior of the microhardness of the Co-B/SiC composite coatings produced as
 241 a function of the content of SiC particles in the coating. The microhardness of the Co-B/SiC coatings
 242 decreases with increasing SiC content in the Co-B/SiC composite. This behavior can be associated
 243 with a decrease in the content of B by increasing the content of SiC particles in the coating (see Fig.
 244 4). In previous studies, the hardness of Co-B coatings was found to increase with increasing B content
 245 in the coating due to the formation of the hard intermetallic compound Co-B [18, 27]. In the present
 246 study, the results in Fig. 4 show that increasing the content of SiC particles in the colloidal
 247 suspensions increases the content of SiC particles and reduces the B content in the coating. Thus, the
 248 observed decrease in microhardness can be caused by the decrease in the B content in the coating.



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250 **Figure 8.** Variation in Co-B/SiC composite coating hardness as a function of the SiC content in the
 251 coatings.

252 3.6. Tribological behavior

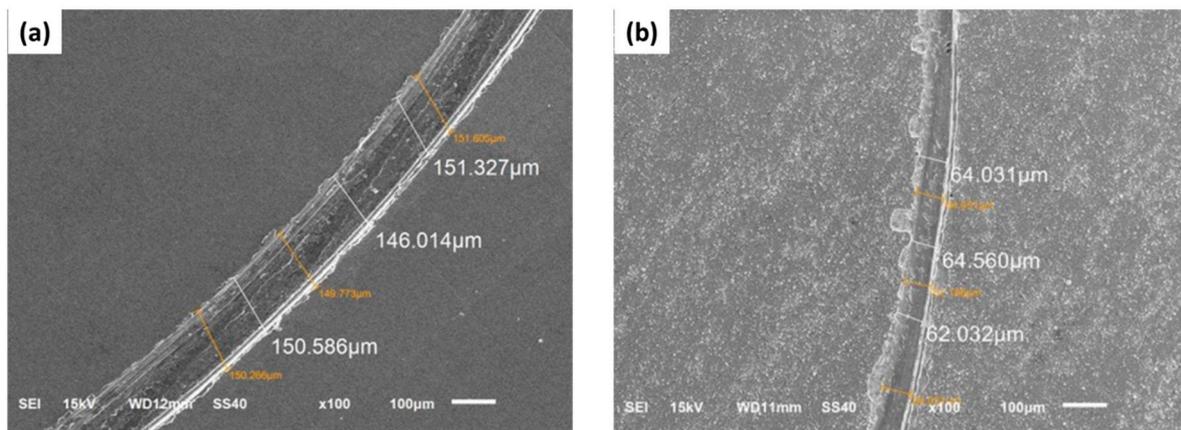
253 Table 1 shows the average values of the wear volume measured at the end of the test (300 m
 254 sliding distance) as a function of the amount of SiC particles in the obtained Co-B/SiC coatings. The
 255 wear volume decreased (i.e., the wear resistance increased) by increasing the content of SiC in the
 256 coatings. The lowest wear volume value (23.0 $\mu\text{m}^3/\text{Nm}$) was obtained for Co-B/SiC (2.5 at.% SiC)
 257 coating; this value is lower than that reported for different systems, such as Ni-P-FGD composite [28],
 258 Ni-B [29], NiP/SiC [30], Ni-P(9 %)/B₄C [14], Co-P [15] or Co-B [18] and is similar to that of a hard Cr
 259 coating [28].

260 **Table 1.** The relationship between the SiC content in the Co-B/SiC composite coatings and the wear
 261 volume and friction coefficients of the Co-B/SiC coatings deposited under galvanostatic conditions
 262 (8.6 mA cm⁻² for 56 min).

SiC concentration in the colloidal suspensions (g/L ⁻¹)	SiC in the coatings (at.%)	Wear volumen loss ($\times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$)	Friction Coefficient (μ)
0	0	11.80 ± 0.13	0.444 ± 0.03
0.15	1.70	3.49 ± 0.19	0.417 ± 0.008
0.60	1.77	2.83 ± 0.21	0.353 ± 0.012
2.50	1.82	0.46 ± 0.12	0.304 ± 0.008
5.00	2.50	0.23 ± 0.08	0.312 ± 0.010
10.00	2.54	0.23 ± 0.10	0.313 ± 0.010
15.00	2.56	0.27 ± 0.11	0.312 ± 0.082

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264 To understand the wear mechanism of the coatings, we analyzed the worn surface of the Co-
 265 B/SiC composite coatings with different SiC content by SEM. In the Co-B coatings (Fig. 9a), the
 266 presence of torn patches and some detachment within the worn tracks is typical evidence of that a
 267 plastic deformation was carried out in this process, which is indicating that the principal mechanism
 268 is adhesive wear. The results show that increasing SiC particles content up to 2.5 at.% SiC (Fig. 9b) it
 269 is possible to observe the formation of the thinner grooves on the worn surface. This behavior is an
 270 evidence of beneficial effect of the incorporation of SiC, which improved wear resistance and low
 271 friction. A similar behavior was observed in the wear tests of the Co-B/SiC composite coatings.
 272 Compared with the other Co-B/SiC coatings, the Co-B/SiC coating with 2.5 at.% SiC (Fig. 9b) exhibited
 273 the narrowest width and shallowest plough lines. These findings indicated that this coating exhibited
 274 the best wear resistance.



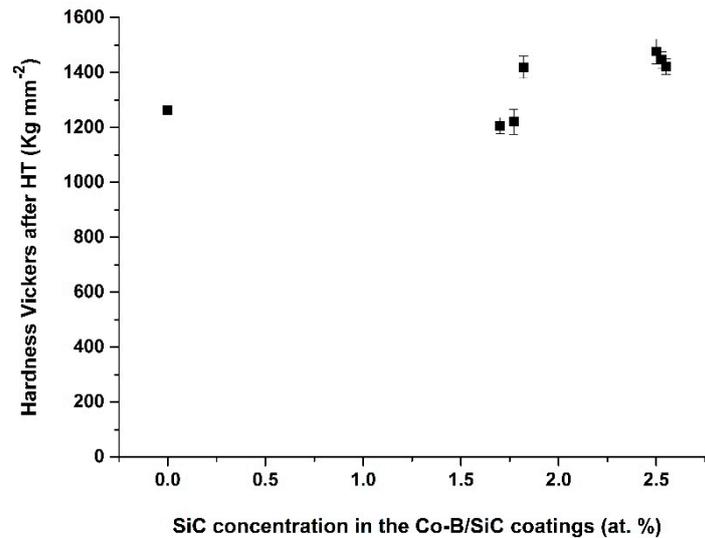
275
 276 **Figure 9.** Typical SEM micrographs of the wear track pattern of coatings in their as-deposited
 277 condition: a) Co-B coating and b) Co-B/SiC (2.5 at.% SiC) composite coating.

278 Likewise, the average values of the coefficients of friction (μ) of Co-B/SiC coatings, which were
 279 obtained simultaneously during the wear test, decreased with increasing SiC content in the coating
 280 and reached a constant value of approximately 0.31 at the highest concentrations of SiC. The obtained
 281 coefficient-of-friction values are lower than those reported for systems such as Ni-P/SiC [30,23,12],
 282 Ni-B [31], Ni-B-diamond [32], Ni-P/B₄C [14], and Ni-SiC [33] but are higher than those reported for
 283 Ni-P-GDF and hard Cr coatings [19]. The above results imply that the SiC particles occluded in the
 284 coating matrix, act as a lubricant, since by increasing the content of SiC particles in the Co-B/SiC
 285 coatings, these increase the lubricating properties of the coatings.

286 3.7. Effect of heat treatment on the hardness, wear volume and coefficients of friction (μ)

287 The effect of a 1-h heat treatment at 350 °C in an air atmosphere on the hardness, wear volume
 288 and coefficient friction of the Co-B/SiC composite coatings was studied.

289 The microhardness results are shown in Fig. 10. As expected, the hardness of the coatings
 290 increased considerably after they were thermally treated; hardness values from 1200 to 1500 HV were
 291 obtained over the entire range of SiC concentrations (0 to 2.56 at.% SiC, respectively). Thus, the
 292 presence of SiC particles in the coatings has little influence on their hardness.



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Figure 10. Variation in the Co-B/SiC composite coating hardness as a function of the SiC content in the coatings after heat treatment at 350 °C for 1 h.

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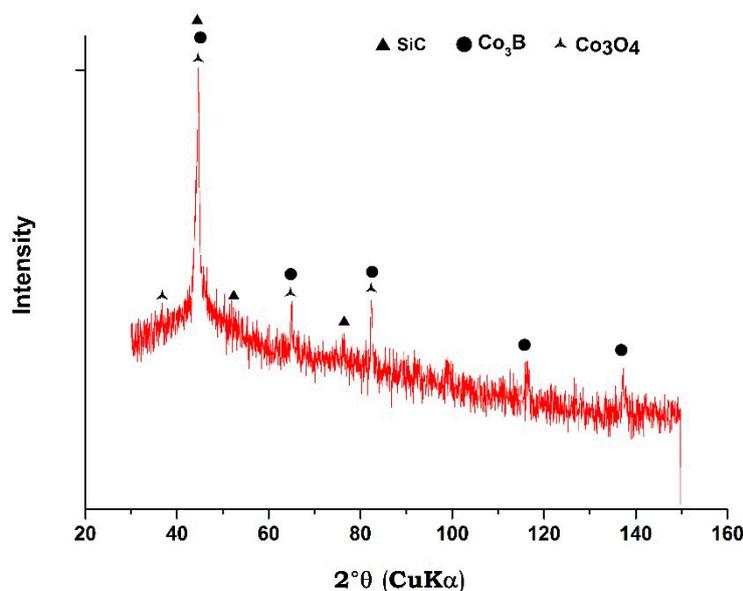
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Therefore, the increase in hardness is mainly associated with the crystallization of the hard intermetallic species Co_3B , which occurs between 200 and 400 °C, which is further confirmed by XRD patterns (Fig. 11). In Fig. 11, the XRD patterns show that when the Co-B/SiC (2.56 at.% SiC) coating was thermally treated at 350 °C, the structure became crystalline and peaks corresponding to crystalline Co_3B and Co_3O_4 appeared. A similar behavior was obtained in all Co-B/SiC coatings analyzed.

The GDS analysis performed on the Co-B/SiC (2.56 at.% SiC) composite coating after being heat treated at 350 °C, presented the following composition: 2.13 ± 0.3 at.% SiC, 1.66 ± 0.13 at.% B, 0.7 ± 0.2 at.% O.



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Figure 11. Normalized XRD pattern of the Co-B/SiC (2.56 at.% SiC) composite coating after heat treatment at 350 °C. SiC (JCPDS 00-042-1360), Co_3B (JCPDS 03-065-2414), Co_3O_4 (JCPDS 00-043-1003).

308 Table 2 shows the values of wear volume and friction coefficient obtained for Co-B/SiC coatings
 309 with different SiC contents and heat treatment at 350 °C. Both values decrease with increasing SiC
 310 content in the coating. Additionally, the values obtained are similar to those obtained for Co-B/SiC
 311 coatings without heat treatment (see Table 1). Therefore, the heat treatment strongly influences the
 312 hardness of the coatings due to the formation of the Co₃B intermetallic species but has little influence
 313 on the volume of wear and the coefficient of friction, which are mainly decreased by the incorporation
 314 of the SiC particles into the metal matrix.

315 **Table 2.** The relationship between the SiC content in the Co-B/SiC composite coatings and the wear
 316 volume and friction coefficients of the Co-B/SiC coatings deposited under galvanostatic conditions
 317 (8.6 mA cm⁻² for 56 min). Values obtained after thermal treatment the coatings at 350 °C for 1 h.
 318

SiC concentration in the colloidal suspensions (g L ⁻¹)	SiC in the coatings at.%	Wear volume loss after HT (x 10 ⁻⁷ mm ³ N ⁻¹ m ⁻¹)	Friction Coefficient After HT (μ)
0	0	3.82 ± 0.09	0.260 ± 0.03
0.15	1.70	2.72 ± 0.11	0.255 ± 0.01
0.60	1.77	1.32 ± 0.08	0.245 ± 0.03
2.50	1.82	0.93 ± 0.10	0.238 ± 0.03
5.00	2.50	0.44 ± 0.08	0.213 ± 0.08
10.00	2.54	0.35 ± 0.10	0.215 ± 0.02
15.00	2.56	0.19 ± 0.07	0.208 ± 0.01

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321 4. Conclusions

322 The objective of this work was to obtain Co-B/SiC composite coatings with different contents of
 323 occluded SiC particles via electrodeposition. The composition, hardness, wear volume (wear
 324 resistance) and coefficient of friction of the coatings before and after heat treatment at 350 °C for 1 h
 325 were analyzed. The results showed that Co-B/SiC composite coatings of homogeneous composition
 326 were obtained by electrodeposition using CTAB as a dispersant in a colloidal suspension. When
 327 studying the influence of the concentration of SiC particles in the colloidal suspensions on the
 328 composition of the obtained Co-B/SiC coatings, we found that the amount of occluded SiC particles
 329 in the coatings increased and the content of B decreased with increasing concentration of SiC particles
 330 in the colloidal suspensions. The variation in the composition of the coatings substantially affected
 331 their physical characteristics. Co-B/SiC coatings with a higher B content and a lower SiC particle
 332 content presented a higher hardness and lower wear resistance, whereas coatings with a lower B
 333 content and a higher SiC particle content exhibited a lower hardness and greater wear resistance.
 334 Therefore, the occlusion of SiC particles in the metal matrix increases the wear resistance of the
 335 coatings.

336 The heat treatment at 350 °C for 1 h had little influence on the wear volume or coefficient of
 337 friction of the Co-B/SiC coatings because the values obtained after the heat treatment were similar to
 338 those obtained without the heat treatment. However, the hardness of the coatings increased
 339 considerably from 1400 to 1500 HV for Co-B/SiC coatings with a SiC particle content in the range of
 340 0 to 2.56 at.%, respectively. This behavior was attributed to the formation of the hard intermetallic
 341 compound Co₃B.

342 From the obtained results, it is possible to propose the Co-B/SiC composites coatings can be
343 applied for the protection of steel parts against wear. Also, it is possible to propose that the coatings
344 obtained in this work are an excellent alternative to replace to the coatings of Cr.
345

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