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X-ray microanalysis and properties of multicomponent plasma-borided layers on steels

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The structure and chemical composition of composite and multicomponent borided layers obtained by a new method that combines the chemical electroless and plasma boriding techniques are described. Quantitative X-ray microanalysis examinations show that on the surface of nickel–phosphorus coated steel borided at 923 K three boride phases of the type $(Ni_xFe_{1-x})_4B_3$, $(Ni_xFe_{1-x})_2B$ and $(Fe_xNi_{1-x})B$ formed, whereas in the samples borided at 1123 K only two borides $(Fe_{1-x}Ni_x)B$ and $(Fe_{1-x}Ni_x)_2B$ are present. The shape and the distribution of the phases depends on the thickness of the Ni–P layer deposited on the steel substrate before boriding. The thicknesses of boride zones obtained on nickel coated steels are much greater than those obtained on the same steel without nickel coating. Also the diffusion zone between the Ni–P layer and the steel increases during boriding, which improves the adhesion of the layer to the substrate. The composite layers obtained show a high wear resistance, with their resistance to corrosion being markedly greater than that of uncoated and only borided steel. © *1998 Chapman & Hall*

1. Introduction

Diffusion boriding is a thermochemical treatment that permits boride layers of good performance properties to be produced on steels [1–4]. A prospective line for future development of this technique is the production of multicomponent and composite borided layers using, prior to boriding, electroless (autocatalytic) nickel plating of the steel parts to be borided [3, 5]. In this way, one can produce borided layers of type $[(Ni, Fe)_4B_3 + (Fe, Ni)B + (Ni, Fe)_2B]$ or $[(Fe, Ni)B + (Fe, Ni)_2B]$, depending on the parameters of the glow-discharge boriding process (in particular the temperature and time) and on the thickness of the nickel layer deposited on the substrate prior to treatment. The layers thus obtained show a good resistance to frictional wear and to corrosion. The properties of these layers chiefly depend on their phase composition and the distribution of the individual phases within them.

2. Experimental details

Specimens made of AISI 1045 steel, after being coated with 5 and 20 μm Ni–P layers (with a 7–12 wt % P content), were subjected to plasma boriding under glow-discharge conditions at temperatures of 923 and 1123 K. The chemical deposition was conducted in a solution composed of NaH_2PO_4, $NiCl_2$ and sodium citrate at a temperature of 360 K for 1 and 3 h. The boriding process was carried out in the prototype of a universal apparatus for thermochemical treatments under glow-discharge conditions with a resistance-heated anode [5]. The atmosphere was composed of $H_2 + BCl_3$ (up to 5 vol %), the pressure was 5 hPa and the treatment lasted for 4 h.

The chemical composition and the distribution of the phases formed in the surface region of the samples were examined on polished cross-sections of the samples by a Cameca SEMPROBE SU-30 X-ray microanalyser equipped with wavelength dispersive spectrometers, using a 62° take-off angle. The accelerating voltage was 15 kV and the beam current, i, was 20 nA. The analysed microvolumes of the samples varied from about 3.3 μm^2 for boron to 1.1 μm^2 for nickel. Quantitative measurements were performed using Cameca's correction program based on the Pouchou–Pichoir [6] correction method to obtain the exact chemical composition of the phases.

The corrosion resistances of the layers were measured by the potentiodynamic method in 0.5 M NaCl solution at a temperature of 298 K using a Taccusel PRT-20 potentiostat. The reference electrode was a saturated calomel electrode.

The wear resistance was examined using a three rollers-taper method [7], in which friction was applied between three fixed cylindrical specimens (the rollers) and rotating conical counterspecimen (the taper), the hardness of which was about 30 HRC. The surface loads were 200 and 400 MPa, and the rotational speed of the taper was 576 min^{-1}.

3. Results and discussion

3.1. Experimental results

Fig. 1 shows the microstructures of the composite layers produced at a temperature of 923 K on AISI

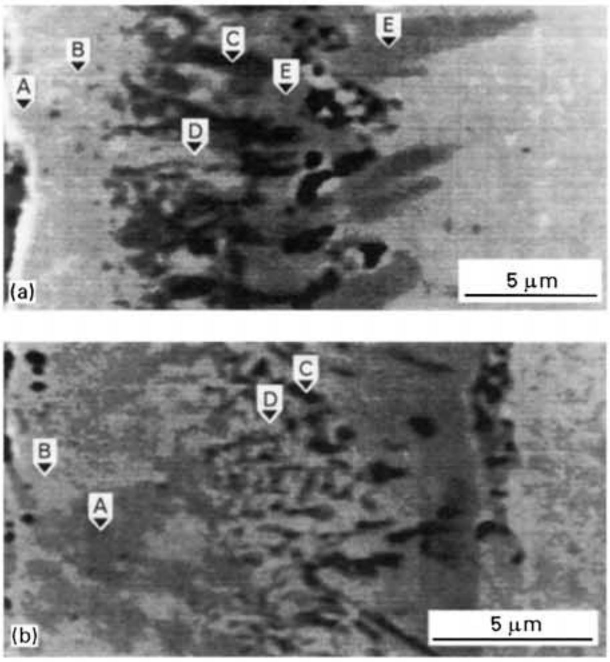

Figure 1 The microstructures of the borided layers produced at a temperature of 923 K on 1045 steel precovered with Ni–P coatings (a) 5 μm and (b) 20 μm thick.

1045 steel precovered with Ni–P coatings 5 and 20 μm thick. The results of quantitative X-ray microanalysis and diffraction [5] examinations have shown that the layers contain borides of the types: $(Ni_{1-x}Fe_x)_4B_3$, $(Fe_{1-x}Ni_x)_2B$ and $(Ni_{1-x}Fe_x)B$. The thicknesses of the zones in which these borides occur, their shape and the phase distribution within them depend on the thickness of the Ni–P layer deposited on steel prior to boriding.

At the surface of the samples covered with a 5 μm thick Ni–P layer, a zone, about 3.5 μm thick, forms; it is composed of a mixture of $(Ni_{1-x}Fe_x)_4B_3$ (Fig. 1a, phase A), $(Ni_{1-x}Fe_x)_2B$ (Fig. 1a, Phase B) borides and very fine phosphorus-rich precipitates. The concentrations of the individual elements in the borides are given in Table I. It was impossible to determine the element concentrations in the phosphorus-rich precipitates, because of their very small sizes. Below the near-surface zone, we observe a 4–5 μm thick zone composed of the $(Fe_{1-x}Ni_x)B$ borides (Fig. 1a, phase C) and microregions of high P concentration (Fig. 1a, phase D). The shape and size of the boride phases within this zone vary with increasing distance from the surface of the sample: from very fine spherical particles to broad needles perpendicular to the surface of the sample. No phosphorus was found in the needles of this boride phase (the vestigial quantities of this element shown by the analysis can be attributed to the insufficient resolution of the technique employed: the needles are so narrow that the excitation zone overlaps partially the phosphorus-rich phases adjacent to them). The $(Fe_{1-x}Ni_x)B$ needles extend into the next zone, which is composed of the $(Fe_{1-x}Ni_x)_2B$ borides (Fig. 1a, phase E) in the form of 5–8 μm long needles that penetrate into the substrate. The Ni concentration within these needles decreases with increasing distance from the surface, and their ends are composed of Fe_2B alone. The spaces between the needles are filled with a zone about 6 μm thick that contains less than 1 at % nickel and phosphorus.

TABLE I Concentration of elements (at %) in selected microregions of the composite layer produced by boriding at a temperature of 923 K on steel precovered with a 5 μm thick Ni–P layer

Phase	Distance from surface (μm)	Concentration of elements (at %)			
		Fe	Ni	B	P
A	2	3.6	57.2	39.2	0.0
B	3	6.2	59.1	34.6	0.1
	5	9.5	57.3	33.1	0.1
C	8	44.9	5.0	48.3	1.8
	9	47.3	3.5	49.1	0.1
D	6	22.1	46.3	6.2	25.4
	8	21.1	45.5	5.3	28.1
	9	35.6	36.4	2.3	25.7
E	12	65.4	1.3	32.8	0.5

The distributions of the boride phases within the samples covered with 20 μm thick Ni–P layer are similar. Near the surface, a zone ~ 6 μm thick forms, which is composed of a mixture of borides: $(Ni_{1-x}Fe_x)_4B_3$ (Fig. 1b, phase A) and $(Ni_{1-x}Fe_x)_2B$ (Fig. 1b, phase B). The concentrations of the individual elements in these borides are given in Table II. Below this near-surface zone, we have a 4–7 μm thick zone composed of $(Ni_{1-x}Fe_x)B$ borides (Fig. 1b, phase C) and phosphorus-rich microregions (Fig. 1b, phase D). The shape and size of the borides in this zone vary with increasing distance from the surface of the sample from very fine spherical particles to long narrow needles that penetrate into the next phosphorus-rich zone. This latter zone is 4–5 μm thick. Below this zone, in the substrate, a zone ~ 6 μm thick containing less than 1 at % nickel and phosphorus is formed.

Fig. 2 shows the microstructures of the composite layers produced by glow-discharge boriding at a temperature of 1123 K on AISI 1045 steel precovered with 5 or 20 μm thick Ni–P layers. Quantitative X-ray microanalysis and diffraction [5] examinations have shown that the layers thus obtained contain borides of $(Fe_{1-x}Ni_x)B$ and $(Fe_{1-x}Ni_x)_2B$ types, in which the Ni

TABLE II Concentrations of elements (at %) in selected microregions of the composite layer produced by boriding at a temperature of 923 K on steel precovered with a 20 μm thick Ni–P layer

Phase	Distance from surface (μm)	Concentration of elements (at %)			
		Fe	Ni	B	P
A	1	1.1	58.9	39.9	0.1
	2	2.4	56.1	41.5	0.0
	6	5.4	52.5	42.0	0.1
B	2	2.2	65.8	32.0	0.0
	6	1.2	64.4	33.9	0.5
C	10	24.4	25.0	44.7	5.9
D	11	43.9	31.4	0.4	24.3
	15	18.9	49.8	1.8	29.5
	18	23.3	43.6	0.0	33.1
	20	27.9	47.3	0.0	24.8

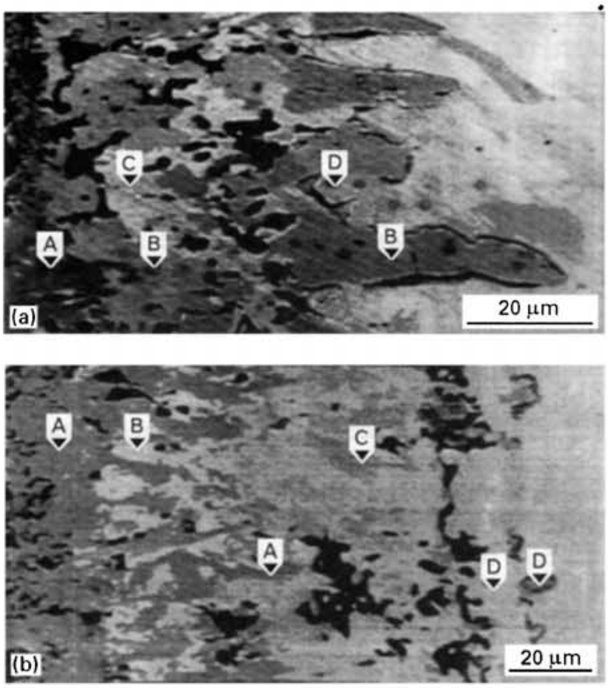

Figure 2 The microstructures of the borided layers produced at a temperature of 1123 K on 1045 steel precovered with Ni–P coatings (a) 5 µm and (b) 20 µm thick.

content decreases and Fe content increases with increasing distance from the surface of the sample. The borides do not contain phosphorus.

In the samples precovered with a 5 µm thick Ni–P layer, the near-surface zone contains borides of the $(Fe_{1-x}Ni_x)B$ type, which first form a 10–15 µm thick layer and then appear as needles that extend to a depth of 26 µm from the surface of the sample (Fig. 2a, phase A). The concentrations of Ni and Fe in these borides at various distances from the surface are given in Table III. In-between the $(Fe_{1-x}Ni_x)B$ boride needles, and behind them, we can see the $(Fe_{1-x}Ni_x)_2B$ boride needles (Fig. 2a, phase B) separated by phosphorus-rich microregions (Fig. 2a, phase C). The needles of this boride phase penetrate into the substrate to a depth of up to 100 µm from the surface of the sample, and their ends do not contain Ni (Table III). In-between the $(Fe_{1-x}Ni_x)_2B$ boride needles penetrating the substrate beneath the phosphorus-rich regions, we find grains (Fig. 2a, phase D) composed of boron, carbon and iron (18.9 at % B, 12.0 at % C and 69.1 at % Fe).

In the samples precovered with a 20 µm Ni–P layer, the $(Fe_{1-x}Ni_x)B$ boride layer is thicker: its thickness ranges from 30 to 35 µm (Fig. 2b, phase A), and the penetration depth of the needles of this phase amounts to 65–80 µm from the surface of the sample. In-between these needles, we can see phosphorus-rich regions (Fig. 2b, phase B), and beneath them a zone, 30–45 µm thick, composed of the $(Fe_{1-x}Ni_x)_2B$ borides (Fig. 2b, phase C) and phosphorus-rich regions. The next zone contains phosphorus-rich regions, Fe–Ni phases and separate $(Fe_{1-x}Ni_x)_2B$ boride needles of low Ni concentration that penetrate into the substrate. The concentrations of the individual elements in the microregions, described above, of a composite layer are given in Table IV.

TABLE III Concentrations of elements (at %) in selected microregions of the composite layer produced by boriding at a temperature of 1123 K on steel precovered with a 5 µm thick Ni–P layer

Phase	Distance from surface (µm)	Concentration of elements (at %)			
		Fe	Ni	B	P
A	1	29.4	23.2	47.4	0.0
	4	37.0	14.8	48.2	0.0
	8	41.7	9.8	48.5	0.0
	19	43.8	7.4	48.8	0.0
B	27	59.7	6.1	33.8	0.4
	31	58.4	7.3	34.0	0.3
	56	64.7	0.4	34.9	0.0
	64	65.1	0.1	34.8	0.0
	100	67.6	0.0	32.4	0.0
C	32	63.0	11.0	6.6	19.4
	35	65.9	8.2	7.9	18.0

TABLE IV Concentrations of elements (at %) in selected microregions of the composite layer produced by boriding at a temperature of 1123 K on steel precovered with a 20 µm thick Ni–P layer

Phase	Distance from surface (µm)	Concentration of elements (at %)			
		Fe	Ni	B	P
A	5	42.5	10.1	47.4	0.0
	15	38.0	14.6	47.4	0.0
	20	39.4	12.2	48.4	0.0
	30	39.1	13.2	47.7	0.0
	47	39.8	11.7	48.5	0.0
	68	43.0	7.6	49.4	0.0
B	52	20.7	53.0	9.0	17.3
	63	21.8	46.5	6.3	25.4
	73	38.2	23.4	26.0	10.4
	85	40.7	22.5	26.1	10.7
	97	28.0	41.5	4.6	25.9
	112	31.9	33.6	12.6	21.9
	128	50.7	24.8	6.3	18.2
C	103	52.2	15.7	32.1	0.0
D	128	61.3	12.4	17.8	8.5
	135	62.7	36.0	0.5	0.8
	137	65.1	0.7	34.2	0.0

3.2. General discussion

When AISI 1045 steel precovered with an electroless Ni–P layer is subjected to glow-discharge boriding, a multicomponent surface layer forms on it; the layer is composed of ferro-nickel borides and phosphorus precipitates, whose chemical composition and distribution can be controlled by modifying appropriately the parameters of the process or the thickness and the chemical composition of the Ni–P layer deposited on the steel prior to boriding. During the boriding process, iron diffuses towards the surface of the sample, while phosphorus is "pushed" into the interior of the material by boron that reacts with nickel and iron to form phosphorus-free borides. As a result, in-between and behind the borides, phophorus-rich regions form, thanks to which the wear resistance of the layer increases and the stress state within it is reduced. It should be noted that nickel and phosphides present in the borided layers reduce the compressive stresses active in them [8].

When, prior to boriding, the steel is covered with an Ni–P layer, the boride zone formed on it is considerably thicker than that obtained at the same temperature on uncovered steel. The thickness of the boride zone formed on precovered steel at a temperature of 923 K is about 15 μm, whereas that obtained on uncovered steel is only 10 μm. In boriding at 923 K, the change of the thickness of the Ni–P layer from 5 to 20 μm has no appreciable effect on the thickness of the boride layer formed but it essentially affects the distribution of the borides. With the thinner Ni–P layer, the $(Fe_{1-x}Ni_x)B$ needles, in which the Ni concentration decreases to 0% towards their ends, penetrate into the substrate and, thus, improve the adhesion of the layer; this effect does not occur with the thicker Ni–P coating. In boriding at 1123 K, on the other hand, the thickness of the boride layer depends on the thickness of the Ni–P coating: with the 5 μm Ni–P coating the boride thickness was 80 μm and with the 20 μm Ni–P coating it was 130 μm, whereas on uncovered steel it was only 30–50 μm. Therefore, depending on the boriding process temperature and the thickness of the Ni–P layer deposited on steel prior to boriding, we can produce borided layers of various thicknesses, phase compositions and properties.

In order to examine how the diffusion processes that take place during the boriding depend on the initial structure of the Ni–P layer deposited on steel, the samples were heated up (at the same rate as during boriding) to the temperatures of the boriding process, i.e. to 923 and 1123 K. The microstructures of the layers thus obtained are shown in Fig. 3.

During the heating, iron diffuses through the layer towards the surface of the sample, whereas nickel and phosphorus diffuse towards the substrate; we also observe the precipitation of Ni–Fe phase particles with low phosphorus contents. Between the layer and the substrate, a diffusion zone forms, in which the concentrations of the individual constituents are varied. In the Ni–P layers heated to a temperature of 923 K, these precipitates have spheroidal shapes and are distributed along the grain boundaries (Fig. 3b). After heating to 1123 K, the 5 μm Ni–P layer contained: a zone, ~ 3 μm thick, composed of about 22 at % phosphorus, 31.5 at % nickel and 46.5 at % iron, and, beneath, a diffusion region in which the Ni and P concentrations decreased with increasing distance from the surface (Fig. 3c). The concentration of phosphorus in this region was below 1 at %. In the 20 μm thick Ni–P layer heated to 1123 K, we observed precipitates with a high iron content, a low phosphorus content (40–42 at % Fe, 57 at % Ni and 0.8–1.6 at % P), and an increased iron concentration (up to 24–30 at % depending on the distance from the surface of the sample) in the layer matrix. The shapes and sizes of the precipitates varied from spheroids of various sizes (from a fraction of 1 μm to several micrometres) to needles or plates (Fig. 3d). In many places the layer had an eutectic structure. Beneath the layer, which had been greatly thickened (to ~ 50 μm), a diffusion zone was observed, in which the concentrations of the individual components were varied.

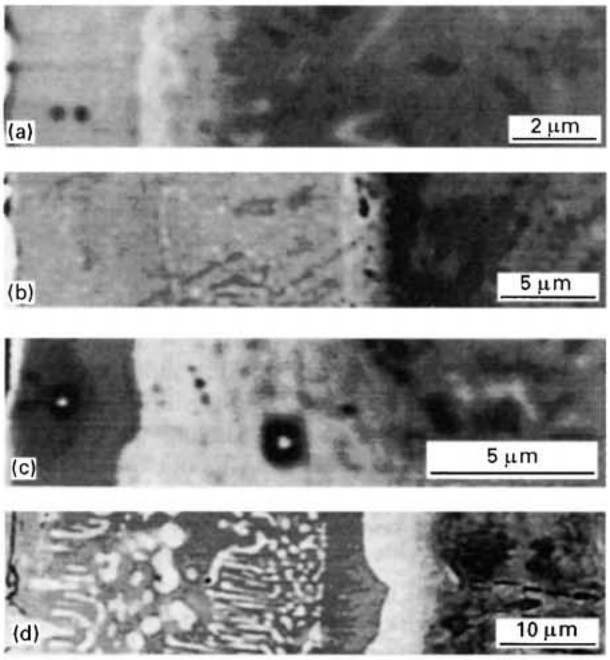

Figure 3 The microstructures of the nickel layers on steel substrate heated to the temperatures of 923 K: (a) 5 μm thick, (b) 20 μm thick and to 1123 K: (c) 5 μm thick, (d) 20 μm thick.

The two-phase structure formed in the Ni–P layer when, prior to boriding, the samples are heated to the boriding temperature has an influence upon the diffusion processes that proceed during the boriding process and upon the formation of phases in the surface layer of the samples (especially when the sample is heated to 1123 K).

3.3. Resistance to wear

The results shown in Fig. 4 indicate that the wear decreases as the boriding temperature increases, which is related to the increasing thickness of the borided layers obtained. Moreover, it can be seen that as the thickness of the nickel layer on steel increases, the wear also decreases. When comparing the resistance to frictional wear of the borided layers produced on steel with and without subjecting it earlier to nickel plating, we can see that the borided layers produced on substrates coated with a nickel layer show a higher resistance to frictional wear. This may be attributed to the fact that probably the stress state that prevails in the composite layer of the $(Ni_xFe_{1-x})_4B_3 + (Fe_xNi_{1-x})_2B$ type is different. This is undoubtedly associated with the complicated diffusion processes that proceed during the temperature of the quaternary B–Ni–P–Fe system.

3.4. Resistance to corrosion

Fig. 5 presents the corrosion current densities measured for borided layers on samples covered with Ni–P layers and without Ni–P plating. The results show that nickel plating before boriding increases the corrosion resistance of borided layers obtained on steel.

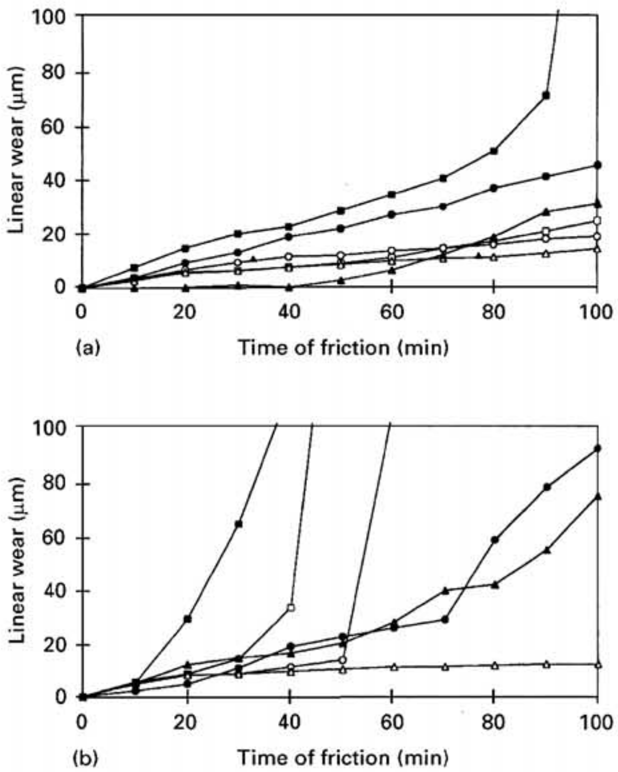

Figure 4 Linear wear of borided layers on steel with and without nickel plating, borided at 923 and 1123 K at (a) 200 and (b) 400 MPa: (■) no Ni, 1123 K; (□) no Ni, 923 K; (●) 5 µm Ni, 1123 K; (○) 5 µm Ni, 923 K; (▲) 20 µm Ni, 1123 K; (△) 20 µm Ni, 923 K.

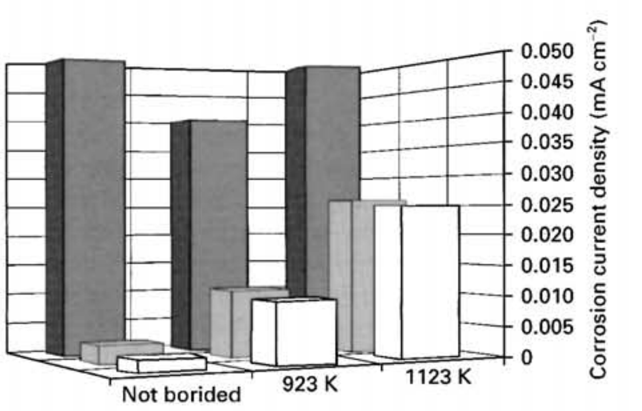

Figure 5 The corrosion current densities measured for borided layers obtained, borided at 923 and 1123 K on steel with and without nickel coating: (■) no Ni coating, (▨) 5 µm Ni, (□) 20 µm Ni.

The thicker the Ni–P layer, the better the corrosion resistance of the borided layers. The best corrosion resistance (for borided layers) was measured for samples covered with a 20 µm Ni layer, borided at the lower temperature of 923 K. This is associated with the presence of Ni boride of the type $(Ni_xFe_{1-x})_4B_3$ on the surface. With increasing boriding temperature (and with time) a slight reduction in resistance to corrosion occurs, due to the higher iron content in the surface zone of the layer and decreasing thickness of the $(Ni_xFe_{1-x})_4B_3$ borides.

4. Conclusions

Glow-discharge boriding applied to parts that have previously been chemically Ni–P plated permits the production of multicomponent boride layers whose chemical and phase compositions and properties can be controlled by modifying the parameters of the process or the thickness and chemical composition of the Ni–P layer deposited prior to the boriding process. Increasing the thickness of the Ni–P layer and using high temperature (1123 K) of the boriding process one can produce thicker borided layers of type $[(Fe, Ni)_2B + (Fe, Ni)B]$ with better wear resistance. Lowering the temperature of the treatment to 923 K makes it possible to obtain borided layers of type $[(Ni, Fe)_4B_3 + (Fe, Ni)B + (Ni, Fe)_2B]$ with better resistance to corrosion. The results of our experiments have shown that plasma boriding under glow-discharge conditions applied to Ni–P plated steel increases its resistance to frictional wear, while retaining at least some of the high resistance to corrosion of the nickel coating, particularly if a lower boriding temperature is chosen. The good mutual solubility of iron and nickel promotes the formation of multicomponent borided layers that show good adhesion to the substrate. These advantages of the layers produced by plasma boriding of nickel-plated steel open new possibilities for their application.

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