
APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Wear Resistance of Electrolytic Nickel–Boron Alloy Deposited from a Chloride Electrolyte

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Abstract—Dependence of the wear resistance of an electrolytic nickel–boron alloy deposited from a chloride electrolyte on the alloy composition, thermal treatment temperature, and specific load on friction surfaces was studied.

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The conventional chromium plating can produce solid chromium coatings with good physicochemical properties, such as corrosion resistance, wear resistance, hardness, and low friction coefficient. However, chromium plating electrolytes based on hexavalent chromium salts have serious disadvantages. These are the low throwing power (TP), high toxicity, exceedingly low current efficiency in electrodeposition of chromium coatings, and poor hardness at elevated temperatures. Standard chromium plating electrolytes based on chromic acid are among the most dangerous electrolytes in modern industry.

Replacement of these electrolytes with those based on trivalent chromium salts is not a solution because the latter are also toxic, and, moreover, coatings formed from electrolytes developed so far cannot replace coatings deposited from standard chromium plating electrolytes primarily in those cases when the functional properties of chromium coatings are required, e.g., their high wear resistance.

Chromium-containing compounds are among substances that are the most hazardous to a human organism. Their detoxication is only possible by conversion to poorly soluble compounds. No typical equipment and methods have been suggested for this purpose, and, therefore, any particular plant has to solve this problem fully on its own. As a rule, this cannot improve the ecological situation in a region. Technical and economic calculations show that it is considerably more profitable to preclude penetration of

chromium compounds into wastewater, compared with its complicated, energy consuming, and expensive purification.

Recently, techniques have been intensively developed for electrolytic deposition of nickel alloys with boron, indium, and phosphorus, which can replace chromium coatings. Coatings of this kind should have a low friction coefficient, high wear resistance, and sufficient protecting capacity under various working conditions.

EXPERIMENTAL

The wear resistance of the coatings was studied on an end-type friction test machine. St.45 steel was used as a counterbody.

Electrolytic coatings based on a nickel–boron alloy were deposited from a chloride electrolyte of the following composition (g l^{-1}): nickel chloride hexahydrate 200–300, nickel sulfate 2.5–5.0, boric acid 25–45, Chloramine B 0.5–1.5, potassium dicarboxylate (BSD) 0.5–4.0, at pH 1.0–5.0, temperature of 18–40°C, and cathode current density of 0.5–9 A dm^{-2} [1–3].

The wear resistance of coatings with the same content of boron in the alloy increases by nearly a factor of 3 upon a thermal treatment at a temperature of 400°C (Fig. 1) and tests for 24 h, which corresponds to the dependence of the microhardness on thermal treatment (Fig. 2). The microhardness is at a maximum

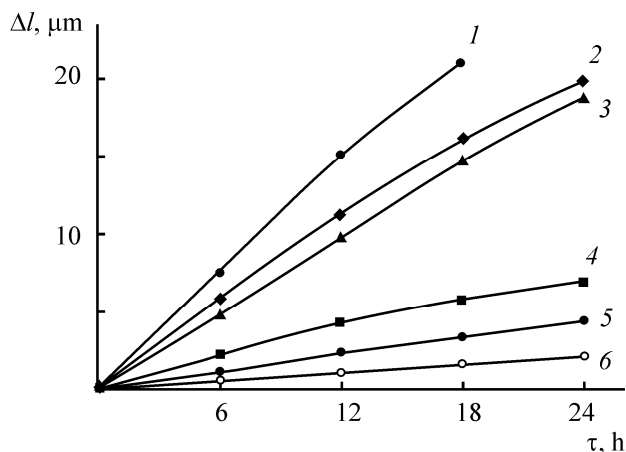


Fig. 1. Amount of wear, Δl , of (3–6) Ni–B coatings and (1, 2) reference samples vs. the testing time τ under boundary friction conditions at a load of 40 MPa. (1) St.45 steel, (2) St.40Kh steel, (3) Ni–B coating (2.8% B) in the initial state, (4, 5) the same coating kept for 1 h at (4) 400 and (5) 500°C, and (6) Ni–B coating (5% B) kept at 500°C for 1 h; the same for Fig. 3.

for coatings thermally treated at about 400°C (14–15 GPa). Further wear resistance tests of the coatings were performed with the optimal thermal treatment conditions for alloys of various compositions taken into account.

The data in Fig. 1 demonstrate that the wear resistance of the coatings is determined not only by their hardness, but also by other factors.

It was shown in [4, 5] that the wear resistance of steel depends on the quality of both martensite (plastic component) and carbides (solid component). The quality of martensite primarily depends on its chemical composition, and that of carbides, on the chemical composition and dispersity.

The wear begins with wearing-away of martensite (as the softer component), with the result that carbide crystals form the surface profile and take-on the entire load. If martensite is sufficiently plastic, carbide crystals are pressed into it; if not, carbide crystals are disintegrated to become an abrasive that promotes an enhanced wear. The coarser carbide crystals, the more pronounced the wear.

An X-ray phase analysis of nickel–boron alloys demonstrated that, before being thermally treated, the optimal, as regards its wear resistance, alloy contains a boron-containing Ni_3B phase in addition to the $\alpha\text{-Ni}$ phase (solid solution of boron in the cubic nickel lattice).

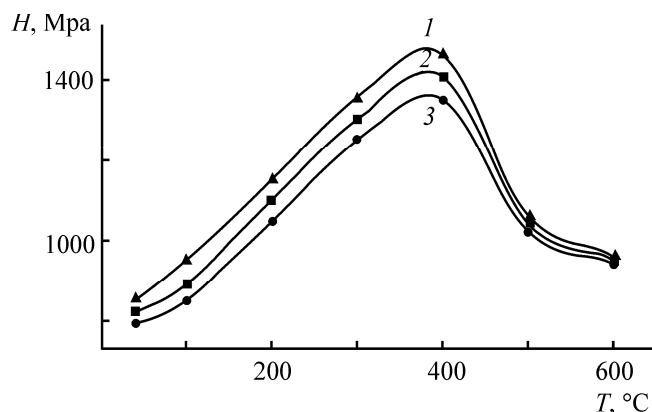


Fig. 2. Microhardness H of thermally treated Ni–B coatings deposited from a chloride electrolyte at various BSD concentrations vs. the thermal treatment temperature T . BSD concentration (g l^{-1}): (1) 0.5, (2) 2.0, and (3) 4.0.

In the course of a thermal treatment of the alloy at 300–400°C, Ni_3B is presumably converted to the tetragonal Ni_2B phase. It should be noted that there is a preferable orientation of crystallites of the Ni_2B phase, which can be determined in X-ray diffraction patterns from anomalously intense diffraction lines with hkl indices 002 and 004. These lines in the X-ray diffraction pattern correspond to reflections from crystallographic planes of the Ni_2B phase with a high reticular density. In [6], possible ways in which Ni_3B and Ni_2B phases are formed were reported.

Thermally treated nickel–boron alloys can be regarded as composite eutectic structures that are similar to alloyed steels and have a solid boride phase uniformly distributed in the plastic nickel phase. As demonstrated by results of tests, the wear resistance of the coatings grows with the boron content of an alloy, which is due to an increase in the content of the solid boron component. This results from formation of Ni_3B boride for alloys with a low content of boron (1 wt %) and Ni_2B for alloys with a high content of boron (4–5 wt %). Thus, the wear resistance of thermally treated nickel–boron alloy coatings substantially exceeds that of reference samples of various steels. For a thermally untreated coating, the amount of wear is approximately on the same order of magnitude as that of St.40Kh steel containing chromium as alloying additive and somewhat exceeds that of St.45 in which manganese is the alloying additive.

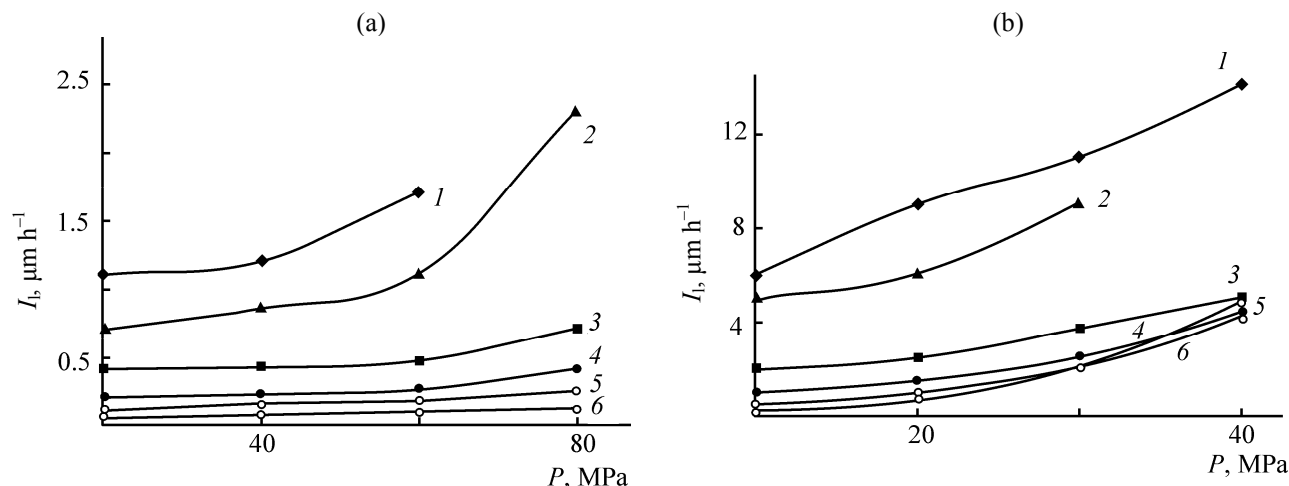


Fig. 3. Linear wear rate I_l of (3–6) Ni–B coatings and (1, 2) reference samples vs. the load P under (a) boundary and (b) abrasive friction conditions.

It should be noted that the dependence of the amount of wear of thermally untreated coatings on the working time shows a deviation from linear behavior. A possible reason is that, in the course of a test, the temperature in the friction zone increases and reaches values sufficient for a boride to be formed, with the result that the wear resistance becomes higher. In particular, measurements of the temperature in the friction zone demonstrated that it grows with the load to become 120–200°C, which is sufficient for the Ni_3B and Ni_2B phases to be formed and leads to an increase in the microhardness and wear resistance.

Raising the specific load from 20 to 80 MPa makes more pronounced the wear of nickel–boron alloy coatings, with the wear of coatings with a low boron content increasing faster than that of coatings with a large amount of boron (Fig. 3a).

The study demonstrated (Fig. 3b) that, in the case of abrasive wear, coatings containing a smaller amount of boron in the alloy, i.e., those composed of a mixture of crystals of nickel and a boride Ni_3B , are worn to a greater extent. It can be assumed that an insignificant amount of the boride phase in a coating of this composition results in that the more plastic component, nickel phase, primarily suffers a stronger wear under the action of abrasive particles. This facilitates the course of the next stage, crumbling of the brittle boride, with the intensity of wear strongly increasing as the specific load is raised. Deposits with a higher content of the boride phases (3–5 wt %), obtained upon introduction of potassium dicarboundecaborate (4.5–7.0 g l⁻¹) into the electrolyte, suffer a smaller abrasive wear at both low and high specific loads. However, it

is interesting to note that coatings with 5 wt % boron are less subject to wear at low specific loads. As the load is raised, the intensity of their wear grows considerably more rapidly, compared with coating containing 2.8 wt % boron. This suggests that, in abrasive wear at low loads, the wear intensity is determined by the amount of the solid phase, with the plastic deformation of the matrix being less important. As the specific load is raised, coatings with a high content of boron (5 wt %) and, consequently, with a higher content of the boride phase, are subject to a stronger wear because of the brittle crumbling of borides, which, finding themselves in the friction zone, enhance the wear.

Comparative wear resistance tests of chromium and nickel–boron alloy coatings in pair with steel, with SOZh RV-2 lubricant used in an amount of 3%, demonstrated that the total amounts of wear of both pairs are almost the same. The friction coefficient is 0.80 for coatings with chromium and 0.78 for nickel–boron alloy coatings. The dry friction coefficient for a pair constituted by an electrodeposited alloy and St.45 steel is 0.22–0.36 under loads of 10–100 MPa.

CONCLUSIONS

(1) Upon a thermal treatment of a nickel–boron alloy coating at temperatures of 350–450°C, the microhardness of the coating increases from 780–830 to 1300–1450 MPa.

(2) The wear resistance of a nickel–boron alloy containing 2.8% boron increases upon a thermal

treatment at 400°C by approximately factor of 3 in a test during 24 h.

(3) The dry friction coefficient for a pair constituted by an electrodeposited alloy and St.45 steel is 0.22–0.36 under loads of 10–100 MPa.

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