

The Forming Conditions and Structure Characteristics of the Nickel–Molybdenum–Boron Chemico-Catalytic Coatings

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Abstract—The effect of the components of chemico-catalytic reduction solutions on the formation rate, composition, and structure characteristics of Ni–Mo–B-alloy coatings is studied. The chemical state of elements and the composition of the surface and bulk layers of the coating containing 11 to 22 wt % of molybdenum and 1.0 wt % of boron are studied using XPS combined with layer-by-layer profile analysis. The alloys have crystalline nanostructure stable at temperatures of up to 500°C. Molybdenum is incorporated into the coatings preferably in its completely reduced form, as a supersaturated solid solution in the nickel matrix. Yet at the same time, the deposits absorb a substantial amount of the absorbed intermediate products of the molybdate reduction to Mo(IV).

INTRODUCTION

The interest attracted to the Ni–Mo–B-alloys and their preparation methods is mainly due to their heat and wear resistance, and good electrocatalytic properties. Their practical applications may still be widened by looking for new methods of their manufacturing and studying in detail their phase structure, chemical state of components, relaxation processes in the alloys, especially at elevated temperatures. Vitreous metals based on the Ni–Mo–B-alloys can be obtained by in a flash quenching vaporized or liquid alloys [1] or by chemico-catalytic reduction of the metal ions with dimethylamine borane (DMB) as reducing agent [2]. In [2], the deposition conditions of preparing Ni–Mo–B-alloy films highly enriched in molybdenum (up to 30 wt %), as well as some data on the process kinetics are given. However, the effect of the preparation conditions on the phase and chemical state of the alloy components (which eventually determine physico-chemical and mechanical properties of the coatings) were not investigated.

In this work, the effects of solution composition, including triethanolamine (TEA) as a surfactant, on the kinetics of partial reactions of nickel, molybdenum, and boron reduction are complexly studied. These studies are combined with those on the phase structure and chemical state of the elements in the Ni–Mo–B-coatings obtained by chemico-catalytic reduction of pyrophosphate solutions with DMB. The sampled coatings were investigated as-prepared and upon vacuum annealing.

EXPERIMENTAL PROCEDURES

The 20 to 30 μm -thick coatings were deposited on nickel or copper substrates from solutions of the following composition (g/l): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ —28, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ —1.8 to 3.6, $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ —50, $\text{C}_6\text{H}_{15}\text{O}_3\text{N}$ (triethanolamine)—0 to 18, DMB—3.5; pH 10 (by adding NH_4OH); temperature—75°C.

The total molybdenum content in the coatings was determined by colorimetric analysis of the extract of molybdenum thiocyanate complex in isoamyl alcohol [3]; that of boron, by acid–alkaline titration in the presence of glycerol [4]. The alloys composition determined by the chemical analysis coincided with that obtained by x-ray spectral microanalysis and x-ray photoelectron spectroscopy (XPS). The deposition rate was estimated gravimetrically.

The Ni–Mo–B-coatings' chemical state and composition in near-surface layers was studied with XPS, using a spectrometer with magnesium cathode. The spectrometer chamber was evacuated to no less than 10^{-7} Pa during the measurements. The coating structure was studied by x-ray diffraction, using a JDX-10PA diffractometer with copper filtered radiation. To analyze the bulk layers, they were layer-by-layer scratched in the spectrometer chamber with a knife made of the WCo hard alloy, thus preventing any oxidative effect of atmosphere on the metal. The layers were analyzed to a depth of no less than the coating half-thickness. Additionally, the near-surface layer composition was profiled by sputtering the coatings by argon ions with an energy of 3 keV. The relative concentrations of the elements detected in the XPS spectra were evaluated from the factors of relative sensitivity. Their chemical state

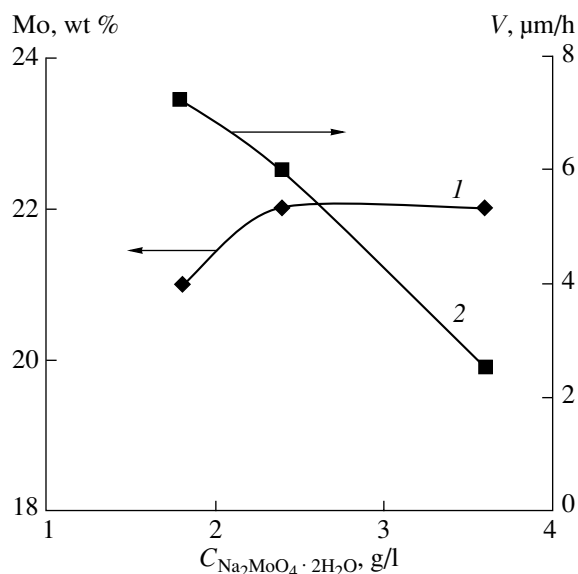


Fig. 1. Effect of the sodium molybdate concentration in TEA-free solution on (1) the molybdenum content in Ni–Mo–B alloy and (2) its deposition rate.

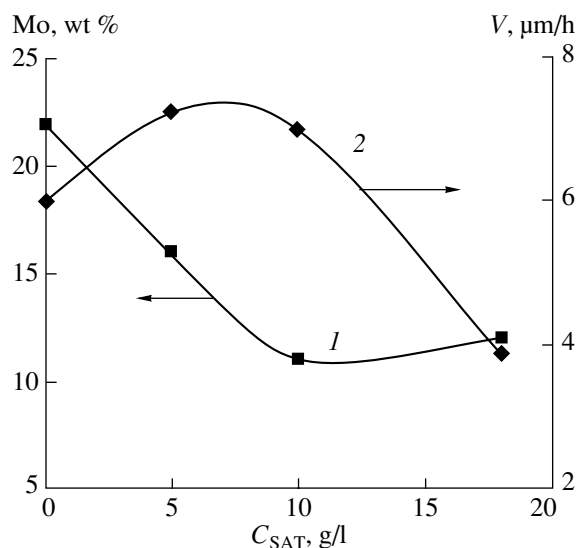


Fig. 2. Effect of the TEA concentration on (1) the Mo content in Ni–Mo–B alloy, and (2) the alloy deposition rate.

was judged from the positions of photoelectron lines in the spectra of the core level electrons Mo3*d*, Ni2*p*, O1*s*, B1*s*, and C1*s*. It is these elements that were detected in the surface and bulk layers of the Ni–Mo–B-coatings.

Prior to investigating the effect of vacuum annealing on the state of the coatings, already in the evacuated spectrometer chamber, we scratched their altered superficial layer off the surface. The annealing was carried out in the same chamber with the use of its resistive heater under programmed conditions, up to a temperature of 400°C or 500°C for 1 h, or 600°C for 6 h. The

coatings were analyzed after their cooling down to room temperature.

EXPERIMENTAL RESULTS

The dependence of the molybdenum content in the alloy on the sodium molybdate concentration in the TEA-free solution is given in Fig. 1.

We see that this quantity depends but weakly on the molybdate concentration in the solution over a range of 1.8 to 3.6 g/l; at higher concentrations, it remains virtually constant (21–22 wt %). Meanwhile the coating deposition rate decreased rather markedly with an increasing in the sodium molybdate concentration.

On adding TEA (0 to 10 g/l) to the solutions, the molybdenum content in the coatings decreased significantly (Fig. 2). Further increasing the TEA concentration has no effect on the molybdenum content in the alloy. The alloy deposition rate increases with an increase in the TEA concentration up to 5 g/l to decrease, with an increase over 10 g/l.

X-ray diffraction patterns of freshly deposited coatings of different composition have only one pronounced broad reflection in the angle range close to the position of the (111) line from the Ni fcc lattice (Fig. 3). The crystallite size estimated by the reflection broadening (disregarding the crystal lattice distortion caused by the difference in the nickel, molybdenum, and boron atomic radii) came to 5–10 nm. It follows from the x-ray diffraction data that the structure of the Ni–Mo–B-coatings remained unchanged after the annealing at temperatures up to 500°C. Only the additional annealing at 600°C results in an agglomerating recrystallization that manifests itself in markedly narrowing and intensifying the (111)-reflection and emergence of a (200)-reflection in the angle range characteristic of the fcc phase in the Ni-based alloy (Fig. 3). However, even after the annealing at 600°C, the agglomerating recrystallization is not completed: besides the sharp (111)-peak in the lower segment of the intensity-distribution integral curve, a reflection broadening is observed, which evidences the presence of a highly dispersed phase in the deposit (Fig. 3). The reflection peaks are arranged identically in the spectra of as-deposited and annealed samples (Fig. 3). The crystal lattice period calculated from the (111)-line is ca. 0.36 nm, which corresponds to a molybdenum solid solution in the nickel lattice. The molybdenum concentration in the solid solution, calculated for this lattice period by the Vegard rule, came to ~14 at % (nearly 20 wt %), which agrees with the results of the alloys' chemical analyses. Thus, the entire molybdenum reduced is incorporated into the nickel-based solid solution lattice. The anomalously low intensity of the (200)-reflection observed for the annealed alloy, as well as its absence in the as-deposited coatings, can be explained by a well pronounced [111] texture.

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