SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF COMPOSITE GALVANIC Ni WITH CARBON NANOMATERIALS AND PVD Mo COATINGS

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Double layer coatings Ni – Mo were obtained by electrolytic deposition of galvanic Ni and following arc PVD deposition of molibdenium. The ion plating coatings Mo on Ni foil and composition electrolytic Ni coatings with carbon nanomaterials (CNM) deposited on mild steel has been also investigated. Composite galvanic Ni coatings with CNM and ion plating coatings Mo contain separately obtained cubic α-Mo phase as well as fragmentary solid solution Mo in Ni. Such coatings exclude hydrogenation of Ni foundation in alkaline solution and possess enlarged electrocatalytic properties while emitting hydrogen and oxidgen. Availability of carbon based nanomaterials in combined coatings is cause of an active absorbtion hydrogen after cathodic polarization. A formation on the surface layer of nanostructure solid solution (Ni, Mo) after compression plasma flows treatment with fixed parameters of patterns Mo/Ni/ mild steel take place.

Introduction

There is a possibility for thermal Ni–Mo alloy to applicate it as electrocatalitic coating in the most aggressive FH- and other media because of wide properties spectrum of Ni–Mo alloy. The technology of deposition of Ni-Mo alloy by preliminary obtaining of Ni–Mo sublayer in many layers Ni–Al–Mo, Ni–Mo–Ti–Al, Ni–Mo–Zn, Ni–Mo–Si–Al–O alloys is used for catalisators [1]. It is carbon nanomaterials (CNM) that take part in it. From this points of view complex formation based on nanotubes, nanofibres and others which may be used as electrode materials for hydrogen reaction [2], hasn't been enough investigated.

Experimental

An attempt to obtain nanocoatings of alloy Ni–Mo with its incorporation on the surface layer of electrolytic Ni coatings by cathode arc physical vapour deposition (PVD) technigue [3] and following compression plasma flows (CPF) treatment of coating has made. CPF technigue needed to reach alloy synthesis temperature.

Double layer coatings Ni-Mo were obtained by electrolytic deposition of galvanic Ni and following arc PVD deposition of molibdenium with thickness smaller than 1 μm. The ion plating coatings Mo on Ni foil and composition electrolytic Ni coatings with CNM deposited on mild steel has been also investigated. The patterns were also executed by CPF. CPF were formed in the magnetic plasma compressor with following parameters [4]: vacuum chamber was filled with nitrogen under pressure 500 Pa. The velocity of plasma in flow was $7 \cdot 10^4$ m / s. Plasma flow temperature varied from 10^4 to 10^5 K. Pulse duration was 100 μs, number - from 1 to 5. Assorted energy density was ~40 and 13 J / sm^2 during impulse accordingly.

Nanocarbon materials with the spatial density to 0,8 g / sm^3, which consist of amorphous carbon (more than 59 %), carbon nanofibers with diameter 20 – 40 nm and length 1 – 15 μm, multiwall nanotubes with diameter 20 – 80 nm and length 1 – 10 μm, are used for passive phase of composition electrolytic coatings with CNM. This nanocarbon materials were obtained in unbalanced plasma of arc discharge, a methan – air mixture vapor is created by an arc discharge between two carbon electrodes with a catalyst. Nanotubes self-assemble from the resulting carbon vapor under atmosphere pressure.

Mo coatings were formed by condensation from a plasma vapor phase in a vacuum with the ion bombardment of the Ni samples surface in a residual nitrogen atmosphere under pressure 10^{-1} Pa. Arc current was 180 A, bias voltage – -120 V. Prior to the deposition, the surface of the Ni samples is bombarded by Mo ions at high voltage bias -1 kV and under pressure 10^{-3} Pa. Temperature at the deposition of coatings corresponded to 400 – 450 °C.

Morphology of formed coatings and its element composition are determined by means of SEM and EDXA methods using scanning electron microscopy instrument LEO-1455VP. The phase composition was studied by XRD.

The corrosion and electrocatalytic behaviour was determinated by cyclic voltamperometry in 1 M KOH solution at temperature 20 °C. The line velocity of potential changing was 0,05 V / s.

Results and discussion

It is established that PVD molibdenium deposition on Ni foil is formed as a single-phase cubic α – Mo without any interactions with the basis. After CPF treatment of the samples a surface layers heating is occurred with the velocity ~10^7 K / s [5]. Then the heat of surface coatings takes place and both components are mixed in a liquid phase finally.

XRD analysis revealed the formation of solid solution Mo in Ni with considerable Ni predominance onto Ni foil surface after CPF treatment at fixed parameters. The formation of solid solution (Mo, Ni) at increase power CPF is observed.

XRD analysis shows that increasing power CPF lead to decrease of Mo concentration on the surface layer of Ni coating. A formation on the surface layer of nanostructure solid solution (Ni, Mo) with considerable Ni predominance after CPF treatment with

fixed parameters of patterns Mo/ Ni/ mild steel has been occurred.

The investigations of cyclic potentiodynamic iE-curves of galvanic Ni/ PVD Mo after CPF treatment showed, that at potentials of -0,05 V in 1M KOH a small dissolution of molibdenium occurred only at first cycle of the line velocity of potential changing.

XRD analysis shown as the formation of solid solution (Mo, Ni) in Ni matrix of composite electrolytic coating, which is a component of double PVD Mo coating / Ni coating with CNM on steel base.

Mo PVD coatings onto Ni coating with CNM show more stable electrocatalytic properties while emitting hydrogen and oxidgen after 7 – 8 cycles of polarization in the field of potentials -0,8 – +0,9 V (fig. 1a). It is determined that unstructured molibdenium content dissolves during first 7 – 8 cycles at potential -0,2 V.

Availability of carbon based nanomaterials in combined coatings is the cause of an active absorbtion hydrogen after cathode polarization. It shoud be noted that among the potentials the thermodinamic potential hydrogen electrode is the more positive. These results are in accordance with the data obtained earlier for hydrogen sorbtion and electrocatalytic activity of a composite Ni coating with carbon based nanomaterials [2]. Cyclic potentiodynamic iE-curves of duble layer PVD Mo/Ni coating with carbon based nanomaterials after CPF treatment are demonstrated in a sensitive scale, that in the field of potentials -0,7 – -0,1 V (fig. 1b) the strongly marked picks of current absorbtion hydrogen are already observed after first cycle of polarization.

Conclusion

The investigations of composition and properties PVD Mo coatings onto various Ni patterns which also consist of carbon nanomaterials with CPF treatment showed that these coatings are formed by a single-phase cubic α-Mo. The fragmentary solid solution Mo in Ni with considerable Ni predominance is formed on electrocalytical Ni coating after CPF treatment with the following fixed parameters: number of pulse that is from 1 to 5 at energy density of plasma flows ~ 40 and 13 J / sm^2 during impulse accordingly.

For PVD Mo coatings in alkaline solution after cathode polarization the hydrogenation is practically excluded in comparison with a bare Ni base. These results are very important, because the decrease of hydrogenation steel and others materials is a topical problem in industry and hydrogenation leads to accelerated corrosion materials.
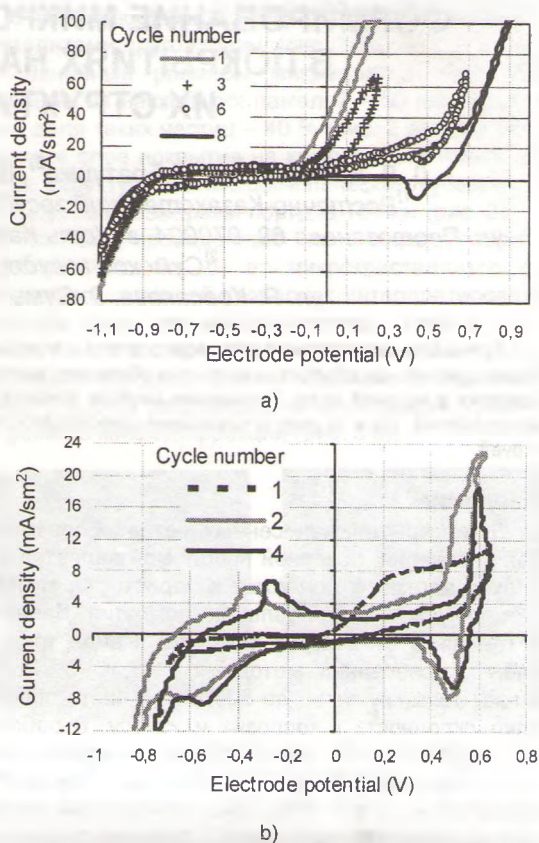

a)

b)

Fig. 1. Cyclic potentiodynamic iE-curves of PVD Mo coatings / Ni coatings with CNM / steel before (a) and after (b) CPF treatment

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