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STUDIES OF HARDNESS FOR THE ELECTRODEPOSITED NICKEL FROM WATTS BATHS WITH ADDITION OF POLYVINYL PYRROLIDONE (PVP)

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This work presents a study about the influence of polyvinyl pyrrolidone (PVP) addition on the hardness of electrodeposited nickel from Watts baths. PVP is a wetting agent which improves the quality of deposited layers. Its action seems to be closed with inhibition of adsorption of $(NiOH)^+$ species on the cathode surface. Even there are some studies about the influence of PVP in electrochemical processes, this trend is new and our results could promote this additive for future commercial applications.

INTRODUCTION

The additives are intensively used in nickel electroplating processes, because they permit to achieve a better quality and better properties. Polyvinyl pyrrolidone (PVP) is a relative new agent used and it acts primarily like a wetting agent.

Many processes of nickel electroplating are carried out from classical baths with compositions proposed by Watts. To obtain decorative coatings on a like-mirror surface, special additive recipes have been developed, consisting in organic substances such as surfactants, brightness agents and leveling agents. The current efficiency is almost 100% for a large current densities interval.[1,2] However, in practice it is difficult to obtain a uniform layer thickness distribution because of the non-uniformity of the current density during electrolysis. For the majority of applications it is necessary a hardness as good as it is possible, which could be achieved using additives carefully selected. This work presents a study about the influence of polyvinyl pyrrolidone (PVP) addition on the hardness of electrodeposited nickel from Watts baths. We mention that this additive was previously used[3-7] and the change of the electrolysis current function on concentration, temperature and composition of the deposited films was studied.[5,6]

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EXPERIMENTAL

Nickel electrodeposition was performed using a Watts bath with the following composition: nickel sulphate ($NiSO_4 \cdot 6H_2O$) 240 $g \cdot L^{-1}$; nickel chloride ($NiCl_2 \cdot 6H_2O$) 45 $g \cdot L^{-1}$ and boric acid (H_3BO_3) 30 $g \cdot L^{-1}$. All substances were Merck reagents.[3,4,7] In order to improve the properties of electrodeposited layer 5 $g \cdot L^{-1}$ polyvinyl pyrrolidone was added in the Watts bath, as wetting agent. We worked at diferent temperatures in the range from 45°C to 65°C. The experimental device used a potentiostat-galvanostat PARSTAT 2273 Advanced Electrochemical System with special software for data processing, an electrolytic cell, a thermostat Lauda 003, and a magnetic stirrer. The reference electrode was a saturated calomel electrode and the contraelectrode was a high purity nickel plate. For processing data recorded during the electrodeposition a software ORIGIN 7.5. was used.

The working electrodes are copper plates (2 cm^2) of which the thickness was measured with a micrometer. Their surface was mechanically processed with emery paper and felt. The copper plates were washed with a solution containing sulphuric acid 500 $g \cdot L^{-1}$, nitric acid 500 $g \cdot L^{-1}$ and sodium chloride 5 $g \cdot L^{-1}$, at 25°C temperature, for

2 minutes, then washed with distilled water, dried and weighted.[8]

There were made measurements of Vickers micro-hardness using a Shimadzu device with indenter Vickers (pyramid form of the diamond with an angle between opposite faces of 136º). This type of measurement has to be performed on a small and without defects zone of the sample. The applied forces range are between 98.7 mN and 19.61N. An electric engine moves up and down the diamond indenter on the way to fix and removes the weight. To measure the indentation hardness on the sample an optical microscope is used (magnification 400X for high precision), determining the distances between two lines of the indentation.

Scanning electron microscope (SEM-Zeiss EVO 20) was also used for obtaining micrographs at very high magnification.

RESULTS AND DISCUSSION

Before nickel electrodeposition the potentiostatic polarization curves were recorded to establish the optimum potential range for nickel ions discharge.

Figs. 1 and 2 show polarization curves for two types of solutions, Watts bath without additives and with addition of polyvinyl pyrrolidone (PVP). A slow moving to the region of highest negative potentials was observed in the case of addition of PVP.[9]

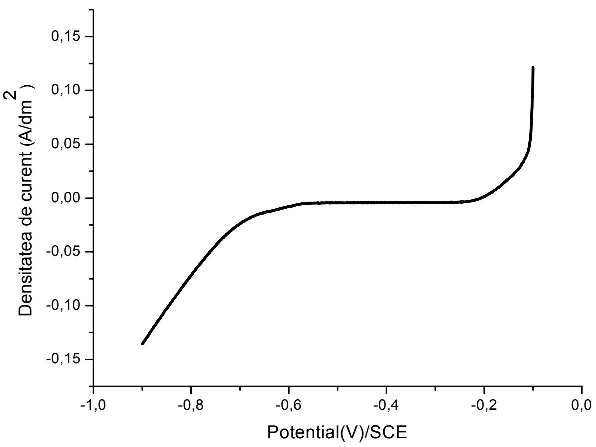

Fig. 1 – Polarization curve for nickel in a Watts bath for the potential range from -100 mV to -1200 mV, 65°C temperature.

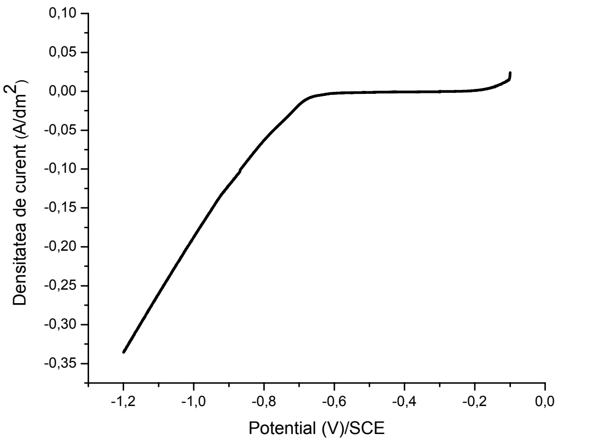

Fig. 2 – Polarization curve for nickel in a Watts bath with 5 g·L^{-1} PVP adding for the potential range from -100 mV to -1200 mV, 65°C temperature.

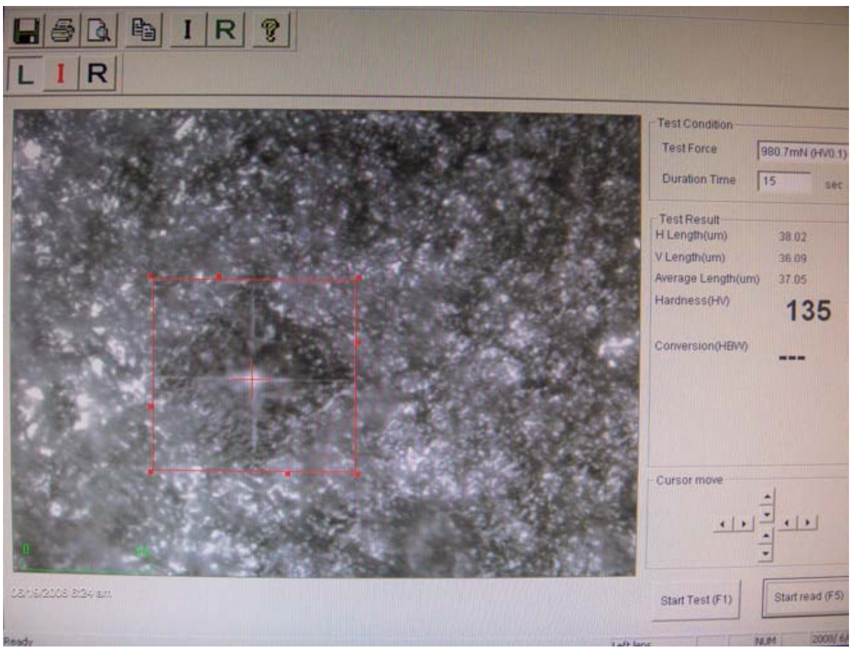

Fig. 3 – Measurement of an imprint of a sample of nickel electrodeposited from a Watts bath with addition of PVP at -1000 mV, 65°C temperature, and 15 minutes time. Applied force 0.1N (Shimadzu HMV).

In experiments of Ni electrodeposition during 15 minutes electrolysis we searched the influence of deposition potentials and of additive (PVP) upon properties of the deposited layer. The results were presented in Table 1.[9]

In the first set of determinations it was measured the hardness of samples of nickel electrodeposited from a Watts bath with addition of polyvinyl pyrrolidone (PVP), at 65°C temperature and different potentials, -800 mV, -900 mV and -1000 mV vs. SCE. In the second set was measured the hardness of nickel samples electrodeposited from Watts bath without PVP addition, using -700 mV, -800 mV, -900 mV and -1000 mV potentials, and 65ºC temperature. Exemples of optical microscopy image are presented in Figs. 3-5.

Table1

Results of the Vickers micro-harness measurements for nickel layers on copper, 15 min. electrolysis

No. of the sample	Applied force (N)	Deposition potential (mV)	Deposition temperature (°C)	Micro-hardness (HV)
4 (PVP)	0.1	-1000	65	132.396
5 (PVP)	0.1	-900	65	115.685
6 (PVP)	0.1	-800	65	117.873
13	0.1	-900	65	107.497
18	0.1	-1000	65	109.962
20	0.1	-800	65	96.7772
21	0.1	-700	65	94.3739

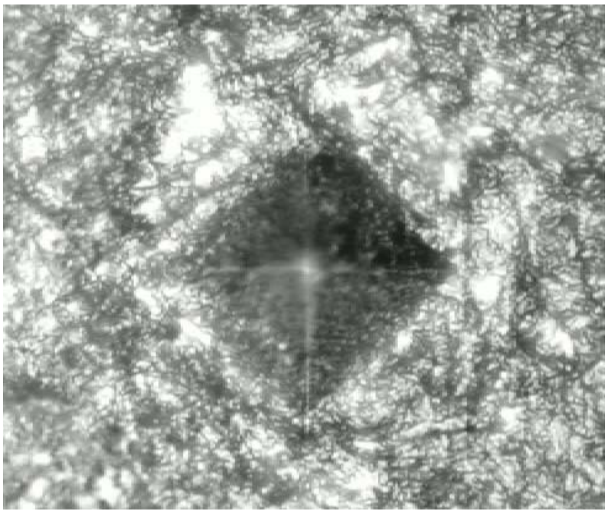

Fig. 4 – Photo of a hardness measurement for a sample of nickel deposited on a copper substrate from a Watts bath with addition of PVP, at -1000 mV potential and 65°C temperature (Shimadzu HMV, 400X optic magnitude).

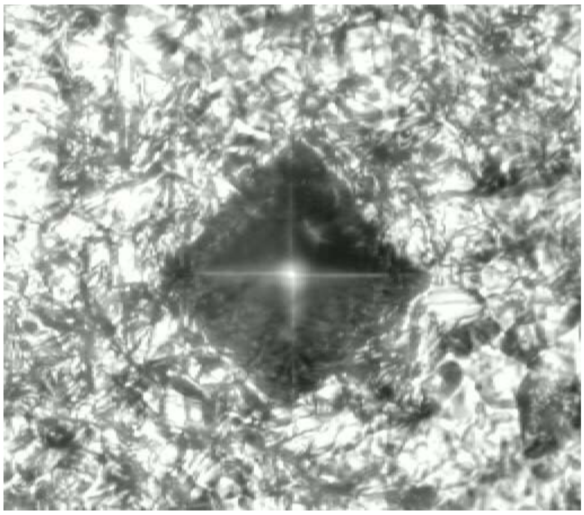

Fig. 5 – Photo of a hardness measurement for a sample of nickel deposited on a copper substrate from a Watts bath without additive, at -1000 mV potential and 65°C temperature (Shimadzu HMV, 400X optic magnitude).

As it can be observed, from Table 1 the values of Vickers hardness increase with shift of deposition potential, towards more negative values; so, the greater value was found for the samples deposited at -1000 mV (Table 1), in both sets of experiments. For accuracy of measurements we applied always the same force, 0.1N to the indenter diamond. The photo of the hardness indentation shows a good quality of the deposited layer, too, and there was not observed "the anvil effect". By comparing two kinds of measurements a good quality of the nickel deposited layer for samples performed from a Watts bath with addition of PVP was noticed.

Similar with the case of addition of PVP, the hardness value in Watts baths without PVP increases by shifting the deposition potential, in negative direction, but the absolute values are diminished. The smallest value is recorded for -700 mV potential (Table 1).

Regarding the dimensions of grains, the images obtained using SEM microscope (Fig. 6, Fig. 7) show that addition of PVP induces a decreasing in dimensions comparing with the case of electrodeposition without this additive. So, the hardness increases substantially, because smaller grains mean higher hardness, a result well known in materials science.

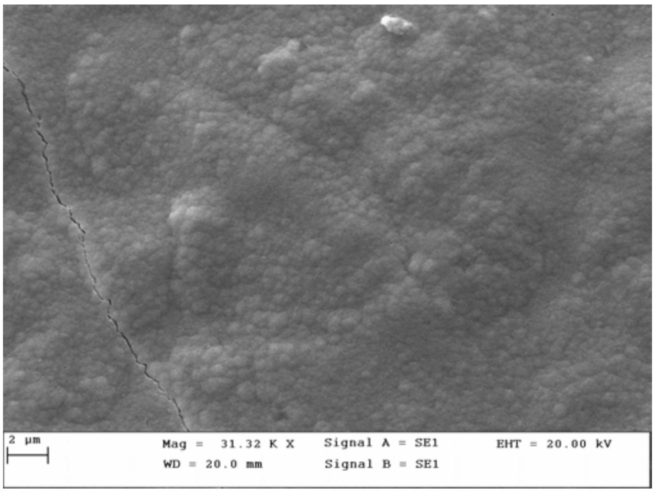

Fig. 6 – SEM image of a nickel layer electrodeposited from a Watts bath with addition of PVP (sample 4) at -1000 mV potential, 65°C temperature, 10 minutes, with magnetic shaking of the electrolyte (SEM-Zeiss EVO 20, 31320X magnification).

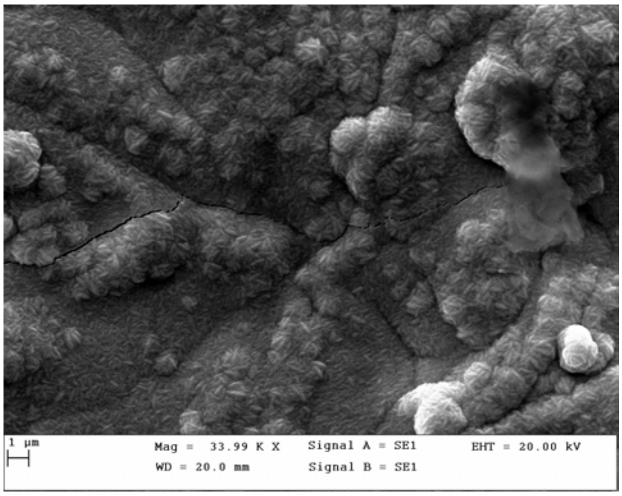

Fig. 7 – SEM image of a nickel layer electrodeposited from a Watts bath without additives (sample 12) at -1000 mV potential, 65°C temperature, 10 minutes, with magnetic shaking of the electrolyte (SEM-Zeiss EVO 20, 3399X magnification).

Both groups of images (Figs. 4, 5 and Figs. 6, 7) prove that grains are smaller in case of using PVP (left side images, Figs. 4 and 6) comparing with the case of electrodeposition without PVP additive (right side images, Figs. 5 and 7).

CONCLUSIONS

We can suggest that the polyvinyl pyrrolidone as addition agent in Watts bath for nickel electroplating proves good properties of electrodeposited layers because it inhibits the adsorption of $(NiOH)^+$ ions existing in bath. The results demonstrate that it can be used for commercial applications, where a high microhardness is desired.

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