COMPARATIVE STUDIES OF COMPOSITE COATINGS WITH CeO_2 AND Nd_2O_3 IN COPPER MATRIX BY ELECTROLESS PLATING

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Abstract: *The study presents the influence of CeO_2 and Nd_2O_3 particles as dispersed phase in copper coatings. These coatings were obtained by electroless deposition from copper sulphate electrolyte bath. Advantages of electroless plating include excellent uniformity, bulk processing capability and ability to produce unique catalytic coatings. The main disadvantage of electroless plating method is the fact that thin layers are obtained and the working time is long enough. The concentration of CeO_2 particles was between 5-50g/L. Similar samples were made using the same concentration of Nd_2O_3 particles in bath solution. Many factors, like the nature of electrolyte and concentration of the dispersed phase in the electrolyte, methods of codeposition contributed to the obtaining of qualitative coatings. The embedded particle of dispersed phase in the copper matrix determines changes of surface coatings and also of their properties. Morphology is an important property of electrodeposited composite coatings and was studied by scanning electron microscopy (SEM) and EDAX analysis. The mechanical properties of the composite coatings were investigated. The Vickers microhardness was measured in cross section. The results are compared with copper coatings without oxide particles to understand the effects of dispersed phase on the properties of composite coatings. The obtained composite coatings properties are increased in comparison with the metal copper coatings.*

Keywords: *electroless, composite coatings, electrolyte bath.*

Introduction

Composite coatings consist of a metal matrix with small particles (or fibres) like a dispersed second phase in the matrix. These composites are developed for a large scale of applications. Composite coatings have been developed primarily for their physical and chemical properties because they combine the properties of the metal matrix and dispersed phases: high temperature strength, good resistance to thermal fatigue, good shock resistance, high thermal conductivity and low coefficients of thermal expansion. Metal matrix composite coatings have been attracted considerable attention because of their relatively low cost and the simple manufacture facility in the case of codeposition in an electroplating bath.

Composite coatings can be obtained by the following methods: vapor phase chemical deposition (CVD), vapor phase physical deposition (PVD), electrodeposition, electroless. In this paper are discussed the easiest methods, like: chemical codeposition and electrochemical codeposition.

The composite coatings deposition from solutions without an external current source, that means a chemical reduction of the substances being in ionic state, was studies since 1969 [1].

The electroless deposition is a simple method usually used for metallic layer depositions on metallic support, with a low price, for extended surfaces. It is specially used for the obtaining of thin layers, with usability in electronic and electrotechnical industry (for circuit and multicip modules obtaining) [2]. Pure copper and copper composite coatings can be deposited by wet chemical plating techniques such as electroplating and electroless plating.

These techniques have the advantage of low cost of tools and materials, low processing temperature, high quality material and high throughput of the process. It has a very high selectivity, it uses a very thin seed layer, and it has excellent step coverage and good trench filling capability that does not need any electrical contacting of wafers during deposition.

It was used the electroless plating method both for obtaining pure metal coatings and efficient composites that need simple installations and accessible reactives. In the same time, the structural properties of these obtained coatings are improved because of a bigger uniformity found at the deposited layers than obtained through electrochemical procedures [3].

Materials and methods

The installation utilized for chemical depositions is simple and the metal covering is deposited by a simple metallic support immersion in electrolyte. The electrolyte for deposition is composed of soluble metal salt, reducing agent and additives such as complexing agents, buffers, bath stabilizers and rate promoters. The copper electroless plating has been prepared using an electrolyte with the chemical composition: $CuSO_4 \cdot 5H_2O$-30g/L; Na_2CO_3 anh.-12g/L; Na and K-tartrat 150g/L, NaOH-50g/L, EDTA - 6g/L [7]. The formic aldehyde (37%) was used as reducing agent and its amount was 20 g/L HCHO. The pH of the electrolyte was 13, 50 at the temperature of 20-25^{0}C [7]. Carbon steel was used as metallic support for copper deposition. In the electrolyte there were added particles of Nd_2O_3 with a concentration between 5-50g/L or CeO_2 particles with a concentration between 5-50g/L.

Therefore, the plating bath is capable of plating receptive surface, including plating tank and equipment surfaces. To maintain a constant plating rate, high control of pH and temperature are necessary. Metal and reducing agent concentration must also be kept at optimal specified levels [4].

Deposition of copper was obtained on carbon steel as metallic support with an effective area of 25 cm^2. The samples were cleaned mechanically by polishing with abrasive papers, organically (with acetone) and chemical degreased (at 70-80^{0}C for 5 minutes in alkaline solution), washed with hot distilled water and finally, for the activation of surface, treated with HCl 15% (2 minutes) [5].

In this study we used formic aldehyde as reducer. The copper chemical deposition can be performed from alkaline solutions only, and reacts according to the chemical equation below:

$$Cu^{2+} + 2HCHO + 40H^- \rightarrow Cu + 2HCOO^- + H_2 + 2H_2O$$
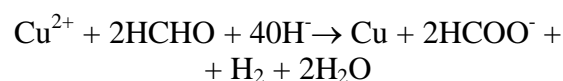
Molecular hydrogen occurs from the reaction, the Cu / H_2 ratio being 1 [6].

Copper chemical deposits from electrolyte with and without particles in suspension were tested by optical microscopy in cross section.

Surface morphology and composition were studied by scanning electron microscopy (SEM) with an X-ray analyzer (EDXS) from Leo Instruments.

The results are compared with pure copper coatings to understand the effects of particles dispersed on the microstructure and properties of composite coatings during the electroless crystallization.

Results and Discussion

Advantages of electroless plating include excellent uniformity, bulk processing capability and ability to produce unique catalytic coatings. The main disadvantage of electroless plating method is the fact that it was obtained thin layers and the working time is long [7], [8]. By this

consideration, the obtaining of composite layers by electroless plating methods was less studied. Another consideration consist the instability of solutions of depositions and low deposition speed that interaction create a bigger activity of copper reducing reaction represent another reason. They are thus suitable methods for low-cost processing. Electroless plating occurs simply by immersion of the samples in a plating bath. No rectifiers, batteries or anodes are involved. The essential elements of the solution are soluble metal salt, and reducing agent, additives such as complexing agents, buffers, bath stabilisers and rate promoters.

Electroless plating is an autocatalytic process; that means that metal deposition serves to catalyse the reaction [9], [10].

a. Structural aspects

The structure of copper coatings was investigated by light microscopy and scanning electron microscopy (SEM) in cross section. Thin layers of copper deposits between 3-18 μm were obtained.
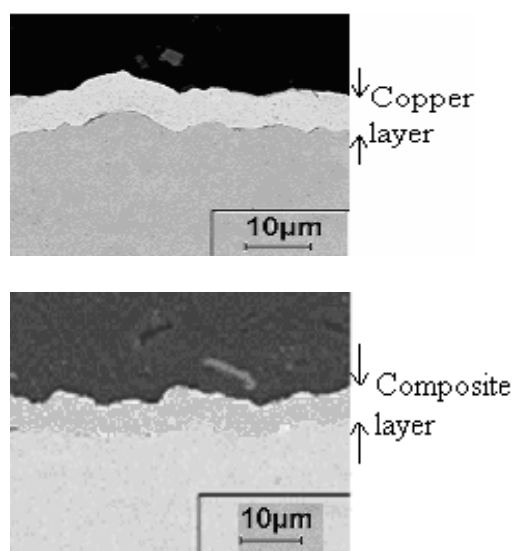

Fig.1. Optical microscopy for copper and copper composite deposition

The layer thickness depends on the immersion time of samples in solution. The aspect of layers is not completely uniform but this can be explained by destruction of

metallic support during the preparation of samples for optical analyses (Fig. 1).

Composites coatings structure is modified by the presence of Nd_2O_3 and CeO_2 particles in copper matrix. SEM micrographs of composite layers were obtained by chemical deposition. An Nd_2O_3 particles agglomeration with their concentration increase was observed. The copper matrix structure is modified, the particles presence conduce to the surface polishing that was also demonstrated by the roughness measurements.

The presence of Nd_2O_3 and CeO_2 particle affects the mechanism of the copper reduction by electroless plating.

When the Nd_2O_3 particles are added in solution, the particles of oxide were embedded in the copper deposits in a satisfactory amount. The results of the investigations confirm that Nd_2O_3 was embedded into copper matrix by electroless plating. The EDX analysis in point of Nd_2O_3 also indicated the presence of particles in copper matrix (Fig.2, Fig.3). From experimental date it was observed a growth amount of Nd_2O_3 in deposit with the amount of oxide in the electroless solution.
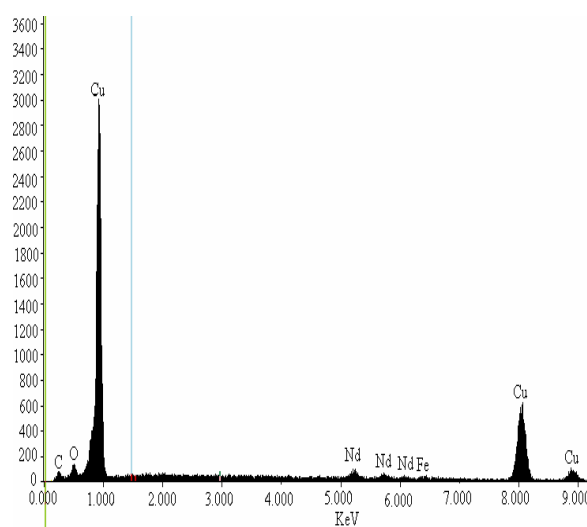

Fig.2. EDAX analysis (in point) on Nd_2O_3 particles included in copper matrix

Table 1.
Composite coatings Cu/ CeO₂ obtained from the electrolyte containing 5g/L CeO₂

Element	Atom (%)	Weight(%)	Error (±)	Norm (%)
Cu	41.92	9.73	1.09	43.19
Ce	20.74	10.61	0.64	47.12
O	37.34	2.18	0.16	9.69
Total:	100.0	22.52		100.0

When CeO_2 was added into solution, the particles of oxide were included in the copper deposits in a very small amount.

The results of the investigations have shown that cerium oxide was included into copper matrix by electroless plating. The EDAX analysis in point of CeO_2 also indicated the presence of copper. (Fig.4)
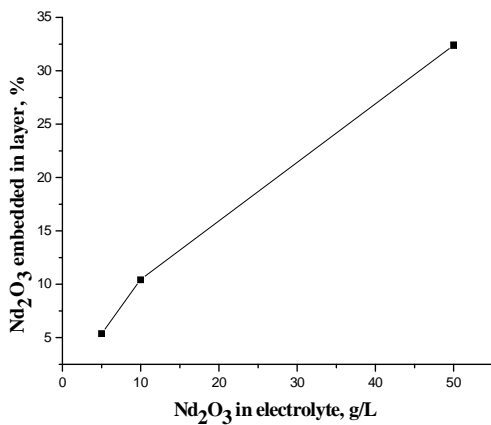
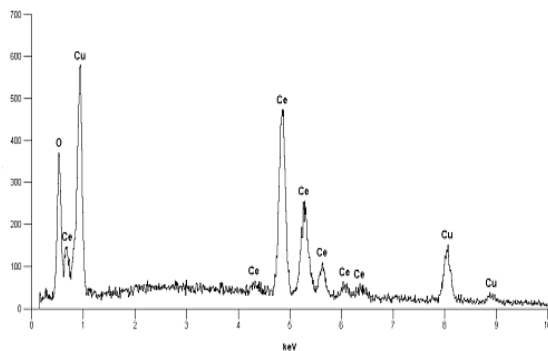**Fig. 3 Nd₂O₃ amount content (percentage by weight) in the copper coatings**

Fig.4 EDAX analysis on CeO₂ particles included in copper matrix

The standard analysis realized in point by X ray tests referring to CeO_2 inclusion percentage in the composite coatings went to the following results:

Table 2.
Composite coatings Cu/ CeO₂ obtained from the electrolyte containing 10g/L CeO₂

Element	Atom (%)	Weight(%)	Error (±)	Norm (%)
Cu	9.41	2.67	0.69	10.26
Ce	30.48	19.05	0.76	73.25
O	60.10	4.29	0.23	16.49
Total:	100.00	26.00		100.00

Composites coatings structure is modified by the presence of particles oxides in copper matrix. SEM micrographs of composite layers obtained by chemical deposition are showed in fig.5, fig.6 and fig.7.
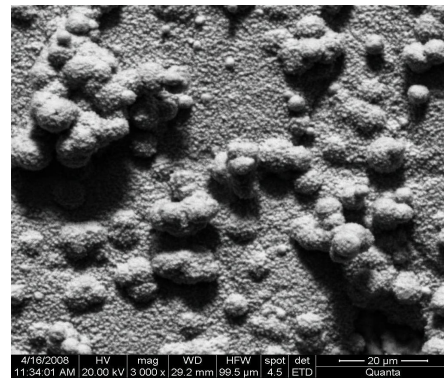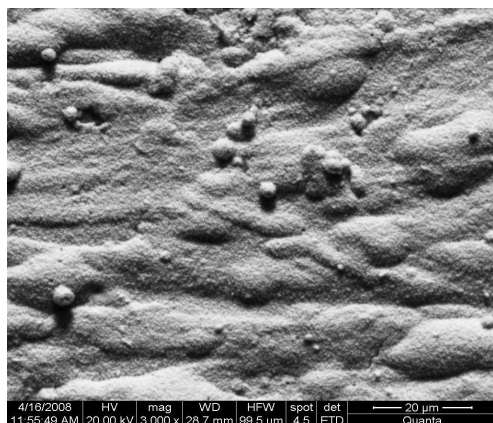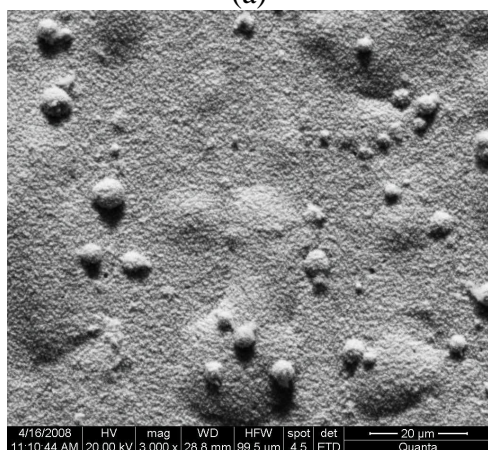

(a)
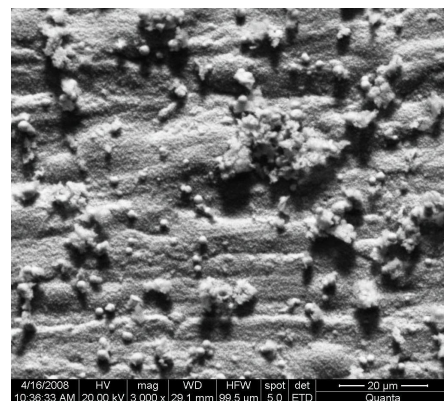
(b)

Fig.5. SEM micrographics: a) Cu; b) Cu-Nd₂O₃ (1 g/L in electrolyte)

The copper matrix structure is modified, the particles presence conduce to the surface polishing that was also demonstrated by the roughness measurements.


(a)

(b)

Fig.6 SEM micrographics: a) Cu-Nd$_2$O$_3$ (5 g/L in electrolyte); b) Cu-Nd$_2$O$_3$ (10 g/L in electrolyte)

The presence of Nd$_2$O$_3$ and CeO$_2$ particles affects the mechanism of the copper reduction by electroless plating. When Nd$_2$O$_3$ is added in solution, the particles of oxide were embedded in the copper deposits in a satisfactory amount. The results of the investigations confirm that Nd$_2$O$_3$ and CeO$_2$ particles were embedded into copper matrix by electroless plating.

More studies are necessary to understand the phenomena occurring during the electroless plating in order to find the optimal parameters for deposits with better
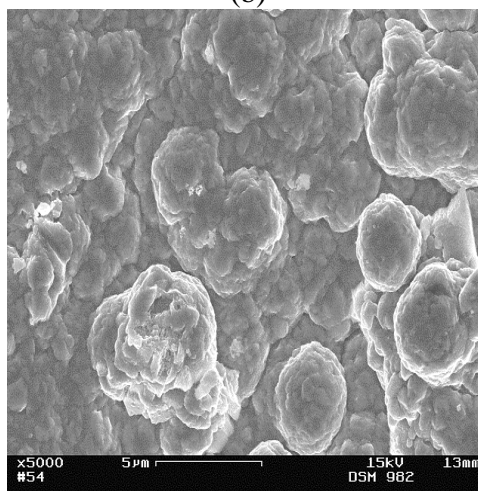
properties such as corrosion resistance and good wear resistance.
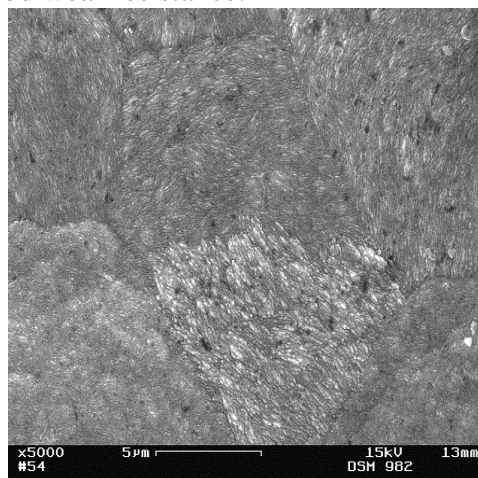
(a)
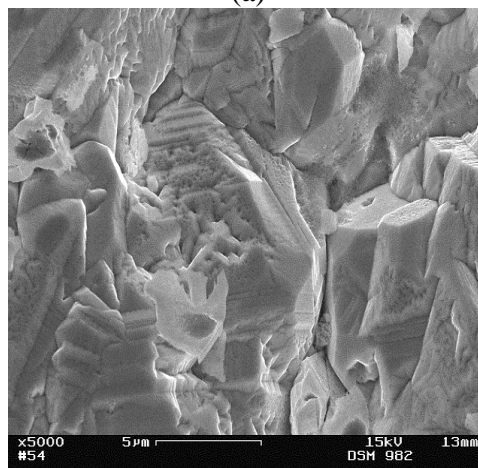
(b)

(c)

Fig.7 SEM analysis on the surface for the deposits Cu-CeO$_2$: a) metallic Cu; b) 10g/L CeO$_2$; c) 50g/L CeO$_2$

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b. *Microhardness*

The Vickers microhardness ($HV_{0.025}$) of coatings in copper matrix was studied. The presence of dispersed particles in the electrolyte and in coatings modifies the microhardness of layers and can be correlated to the amount of dispersed phase in the deposit. The content of particles in the electrolyte influences the microhardness of the coatings.

The Vickers microhardness ($HV_{0.025}$) of coatings in copper matrix was studied. The presence of dispersed phases in the electrolyte and in coatings modifies the microhardness of layers and can be correlated with the amount of dispersed phase in the deposit. Figure 8 shows the results obtained for copper coatings with CeO_2 particles in electrolyte. The amount of CeO_2 in the electrolyte influences the microhardness of the coatings.

The microhardness of the coatings obtained with 5g/L and 10 g/L CeO_2 in electrolyte has increased smaller in comparison with that of the copper deposits without particles in the electrolyte. A decreasing in the microhardness of the layers obtained with 50 g/L CeO_2 in the electrolyte was observed.
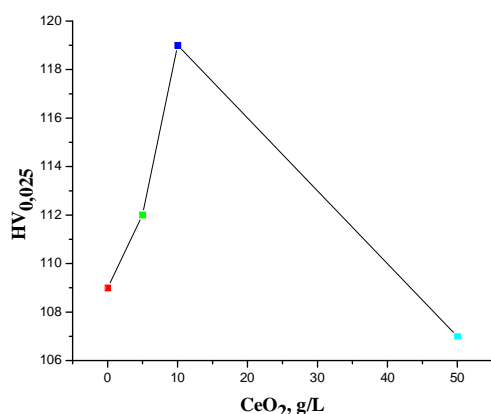

Fig.8. Microhardness variation of copper coatings with CeO_2 particle in electrolyte

The dispersed phase content in a larger amount of electrolyte modifies the metal electroless deposition process. Considering that neodinium oxide is a hard one, it would be expected that the composite layers hardness to increase a lot but this is not happening. It was observed a slow microhardness increase at the samples obtained by electrodeposition, due to the small inclusion degree. For a large microhardness increase, the inclusion degree should be for at least 15%. Even a slowly microhardness decrease can be observed at the samples obtained by electroless. This behaviour can be explained both by the structural changes due to the oxide particles presence in copper matrix and the structural differences determined by the inclusion method.

Table 3.

Microhardness of layers in matrix of copper with and without Nd_2O_3 particles in the electrolyte

Disp. phase	Conc. of DP, (g/L)	HV min.	HV max.	HV$_{mediu}$	Standard deviation
-	-	98	115	108	6.3
Nd_2O_3	5	102	118	110	5.4
Nd_2O_3	10	104	121	113	4.6
Nd_2O_3	50	115	134	125	5.3

Conclusion

1. The experiments were performed to study the obtaining of copper coatings matrix with and without CeO_2 and Nd_2O_3 particles from a copper sulphate electrolyte with formaldehyde as reducing agent.
2. The dispersed phase of CeO_2 and Nd_2O_3 was included in copper layers but in a very small amount.
3. The layers and the properties of coatings presented differences and this fact depended on the amount of particles oxide in electrolyte.
4. The composite layers properties are improved but not in a spectacular way, probably due to the small amount of included particles.

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