CATALYTIC ACTIVITIES OF SUBSTRATE METALS IN A Ni–B–SiC ELECTROLESS COMPOSITE BATH①

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ABSTRACT

The catalytic activities of different substrate metals in Ni–B–SiC electroless composite bath was investigated by means of measuring stationary potentials, potential-time curves and EPMA. The mechanism of electroless plating taking place in the substrate metals at initial stage was investigated. Experimental results showed: (1) In addition to the stationary potential of the substrate metal and the temperature of the bath, the change of the surface state of metal, e.g., its passivity, is one of the factors for deciding catalytic activity of a substrate metal. (2) the transition time is helpful in determines the degree of catalytic activity. (3) If the substrate metals possess catalytic activity, the coating rates of electroless plating are mostly equal.

Key words: Electroless plating substrate metals stationary potential catalytic activity passivity.

1 INTRODUCTION

Electroless plating is a method by which metal ions are reduced on the surface of a catalytic metal by a chemical reductor without electric energy. The electroless bath is a thermodynamically unstable system which exibits a tendency of taking place as an oxidation-reduction reaction. However it is a quasistatic system. If only the surface of the substrate metal has catalytic activity, the reaction can take place. So, electroless plating exibits the characteristics of choice deposition and instable bath. In order to avoid the disintegration of bath, it is necessary that the bath be filtered often during the process of electroless plating to remove some solid pieces. But, in the technology of electroless composite plating, large amounts of solid powder must be introduced. That is very harmful to the stationary bath[1].

In the research of electroless nickling, the stationary potential of the substrate metal and the temperature of the bath are considered to determine the catalytic activity of the metal[2, 3]. The catalytic activities of the substrate metals in electroless composite baths have not been studied.

The stationary potential and the change in the passivity of the metal are researched in a Ni–B–SiC electroless composite plating bath. The experimental results are different from those for electroless nickling.

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2 EXPERIMENTAL PROCEDURES

2.1 *Composition of the Bath and Conditions of Deposition*

$NiCl_2 \cdot 6H_2O$	30 g / L
NaOH	40 g / L
$NH_2CH_2CH_2NH_2$	36 g / L
O / V	0.5–4.0 dm^2 / L
KBH_4	1.0 g / L
$PbCl_2$	20 ppm
Temp.	75 ± 1 ℃
SiC Size	1.5(dia.1.0–1.5)μm

Added amount of SiC:4.0 g / L

2.2 *Measurement of the Stationary Potential*

Substrate metals treated normally before deposition were used as research electrodes. The stationary potential and potential–time curves were measured with a digital PZ–36 potential meter and LZ3–20XY recording instrument at 75 ℃. The stainless steel was 1Cr18Ni9Ti.

2.3 *Inducing Method*

The inducing metal that was pretreated for activity was inserted into the bath and touched with substrate metal.

2.4 *Electron probe X–ray Micro Analysis*

The initial coating of Ni–B–SiC electroless composite plating on the stainless steel after induction was analysed with a 810Q EPMA.

3 RESULTS AND DISCUSSION

3.1 *The Determination of the Stationary Potential*

It was found that the potentials of the metals change with time. This change corresponds to the change from substrate metal to composite plating. The initial stationary potentials were considered to be the stationary potentials of the substrate metals in the article. The stationary potentials of copper and six other metals or alloys were measured, their values are given in Table 1.

According to the experimental result, the order of the catalytic activities of the metals is Ni–B–SiC(Ni–B) > copper > brass > iron > stainless steel > Ni–P. Copper, brass, iron, Ni–P and Ni–B can be plated directly. But in the case of stainless steel, the induction by a catalytic metal is needed.

Although the stationary potential of stainless steel is more negative than that of Ni–P alloy at suitable temperatures, it is not catalytically active. The results show that the stationary potential is not a simple parameter by which to estimate the catalytic activity of substrate metals in electroless baths. This result is different from the case of Ni–P electroless nickling.

The stationary potential of the Ni–B–SiC coating is equal to that of the Ni–B alloy.This result shows that the embedment of SiC powder does not affect the stationary potential of Ni–B alloy.

3.2 *Change of Stationary Potential*

The potential-time curves of the substrate metals are presented in Fig.1. The results show that the potential of the catalytic metal undergoes three stages (Fig.2). In stage I, the potential of the metal reaches fast its stationary potential in two seconds. This value represents the activity of the clean surface of the substrate metal. Of course, the surface has a adsorbed film that consists of coordinated ions and solvent molecules[5]. The adsorbed film can probably affect the formation of the passive film and electroless composite coating.

In stageⅢ, the potentials of every metal reach −1.21 V and do not change.At this time, based on the experimental observation composite coatings have been plated on the substrate metals. The scanning analysis of EPMA of Ni on stainless steel(Fig.3) shows that Ni has nucleated well-distributedly after induction for 1 min. After

Table 1 Stationary potentials of some substrate metals in a Ni–B–SiC electroless composite plating bath. 4

substrate metal	Cu	Brass	Fe	Ni–P alloy	Stainless Steel	Ni–B alloy	Ni–B–SiC
Stationary Potential / V	−1.12	−1.08	−1.01	−0.96	−0.97	−1.21	−1.21

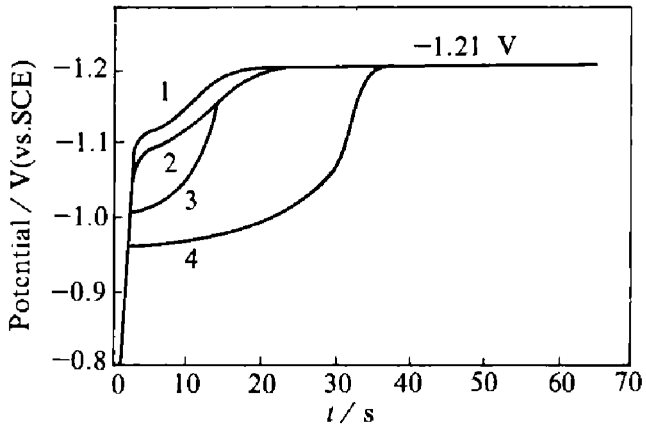

Fig. 1 Potential-time curves of some substrate metals

1—Cu; 2—Brass; 3—Fe; 4—Ni–P alloy

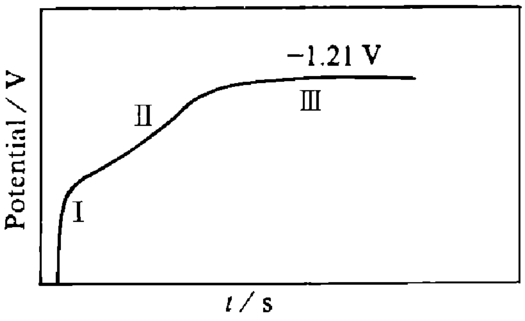

Fig. 2 Sketch map of potential-time curve

this time, all substrate metals have essentially been covered by a Ni–B–SiC electroless coating.

Stage II is a transition period as the surface state changes from the substrate metal to electroless composite coating. This process involves some changes in the desorption, passivity and nucleation of the electroless coating. The synthetical contribution of every factor determines the time and slope of the change of the potential to −1.21V. This time is called the transition time. The transition times of copper and other metals are shown in table 2. The results show that the shorter the transition time, the stronger the catalytic activity of the metal.

It can also be seen from the slopes of the curves (Fig. 1) that the rate of electroless coating formation is slower during the initial period of the tansition process. The reason is that electroless deposition requires the removal of the adsorption film, and the activation energy is higher. After some atoms of Ni and B have plated, the rate of coating increases because of the lower activation energies. The adsorption of SiC to the surface of Ni–B alloy and the deposition of Ni–B result in the embedding of powerd SiC[6].

Fig. 3 Scanning micrograph of EPMA of Ni on stainless steel after induction for 1 min

Table 2 Transition times of some substrate metals

Substrate metals	Cu	Brass	Fe	Ni–P alloy
Transition time / s	18	22	27	38

3.3 *The effect of Catalytic Activity on the Deposition Rate*

Table 3 shows that the deposition rate of electroless composite plating is the same if the substrate metal is catalytically active. This is a result of very small differences in transition times. The greatest difference in time in the test was about 20 seconds. This short time can be virtually neglected in comparism to the whole plating time (3 600 s). So, the rate of deposition is termined by the time required for forming one layer of electroless coating.

Table 3 also shows the rate of deposition of Ni–B–SiC decreased with the increase of SiC powder. The reason is that the SiC powder that has no catalytic activity is adsorbed to the surface of the Ni–B alloy and decreases the effective area of reaction.

Table 3 Deposition rate of Ni–B–SiC on Cu and Fe

Substrate Metal	added amount of SiC / g • L^{-1}				
	1.0	2.0	4.0	6.0	8.0
Cu	6.08	5.21	4.54	3.82	3.34
Fe	6.19	5.23	4.44	3.87	3.35

3.4 *Relative Catalytic Activity of the Substrate Metals*

The conditions of the bath have a direct bearing on the catalytic activity of the substrate metal. One substrate metal may have catalytic activity in one bath, but may not be cetalytically active in another bath. Table 4 shows again that the stationary potential of the metal and the temperature of the bath can not completely determine the catalytic activity.

Table 4 Stationary potentials and catalytic activities of some metals

metal	Kind of bath	Stationary Potential / V	catalytic activity
Cu	HEDP bath	−0.22	Ineffective
	Ni–B–SiC bath	−1.12	Effective
Brass	HEDP bath	−0.22	Ineffective
	Ni–B–SiC bath	−1.08	Effective
Fe	HEDP bath	−0.75	Effective
	Ni–B–SiC bath	−1.01	Effective
Ni–P alloy	HEDP bath	−0.72	Effective
	Ni–B–SiC bath	−0.96	Effective
Stainless steel	HEDP bath	−0.83	Ineffective
	Ni–B–SiC bath	−0.97	Ineffective

Ni–P bath temp.80 ℃

3.5 *The Factors Affecting the Catalytic Activities of Substrate Metal*

The experimental results show that the stainless steel does not have the catalytic activity although the stationary potential is less than that of the Ni–P alloy and the temperature of the bath is high enough. The potential-time curve of stainless steel in the Ni–B–SiC electroless composite bath was investigated in order to understand the reason. The result shows that the potential of stainless steel goes through five periods (Fig.4).

In period Ⅰ, the potential of stainless steel reaches −0.97 V in a bring time after the stainless steel is inserted into the bath. This potential value represents the value of the clean surface of stainless steel. In period Ⅱ, the potential moves up to −0.83 V. This course probably represents the passivation of the stainless steel. The potential (−0.83 V) is the value of a passive film in the bath. In period Ⅲ, the stainless steel is induced by copper. The potential moves quickly to −1.12 V after a small positive increase. The value (−1.12 V) is the stationaary potential of copper. The mechanism of the process is shown below[7]: copper makes up a short circuit cell with $Ni(en)_3^{2+}$ in the bath and the following reaction takes place.

$$Cu+Ni(en)_3^{2+} \longrightarrow Ni+Cu(en)_2^{2+} \qquad (1)$$

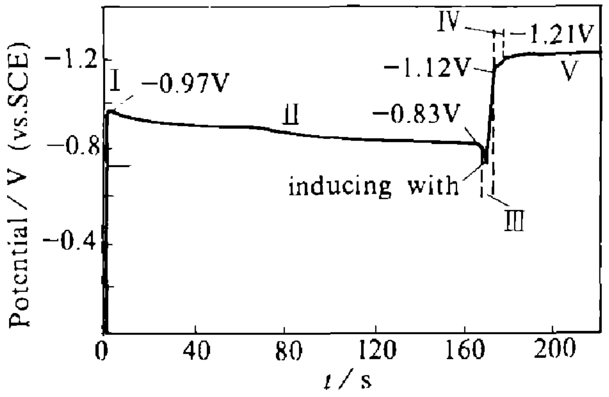

Fig. 4 Potential change curve of stainless steel

The electrons from copper can also transplant to the surface of stainless steel. Meanwhile, $Ni(en)_3^{2+}$ can obtain electrons from the surface of stainless steel.

$$Ni(en)_3^{2+}+2e \longrightarrow Ni+3en$$

Ni has catalytic activity and induces the following reactions

$$BH_4^-+4Ni(en)_3^{2+}+8OH^- = 4Ni+BO_2^-+12en+6H_2O$$

$$2BH_4^-+4Ni(en)_3^{2+}+6OH^- =$$

$2NiB+12en+6H_2OH_2$

The transportation of electrons suddenly decrease the potential to −1.12 V.

At the moment of inducing the potential of the stainless steel moves suddenly from −0.83 V to −0.72 V and then moves to −1.12 V. Perhaps it is related to the surface reactions. The detailed mechanism should be researched further. Period Ⅳ is the transition stage that has been discussed before. Period Ⅴ is the period when the Ni−B−SiC electroless composite plating occurs continuously.

The experimental results indicate that the passivity of the surface is one of the factors determing the catalytic activity of the substrate metal besides the stationary potential and temperature of the bath.

4 CONCLUSIONS

The obtained results are summarized as follows:

(1) Besides the stationary potential of the substrate metal and temperature of the bath the passivity of the surface of substrate metal determines its catalytic activity;

(2) The transition time and slope of the potential−time curve are useful for judging the catalytic activity of a substrate metal;

(3) The deposition rate of Ni−B−SiC electroless composite plating is almost the same on the catalytic metal.

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