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The effect of dissolved oxygen on the deposition process in electroless cobalt plating

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This paper describes the effect of dissolved oxygen on the deposition process in electroless cobalt solutions. In ammonia alkaline solutions, the deposition rate decreases as the dissolved oxygen content increases. The dissolved oxygen mainly affects the nucleation rate, and affects the growth rate only slightly.

1. Introduction

Recently, electrolessly-plated cobalt alloy films have become of interest as promising materials for magnetic storage devices [1, 2]. Various alloy solutions have been developed to obtain films which have the required magnetic properties [3–5]. In the cobalt alloy solutions, deposition generally proceeds only in the alkaline region [6], because the driving force of the reducing agent is not sufficient in the acid region [7]. As a pH control agent, sodium hydroxide or ammonium hydroxide is usually used. For practical applications, alkaline ammonia solutions are considered to be superior, due to their high resistance to spontaneous decomposition and their high solvent power for additional metal ions [8]. In alkaline ammonia solutions, however, there is a problem in that deposition rates vary considerably with time. This may cause a variation in the magnetic properties of the films deposited from these solutions.

In order to promote the application of the electroless method, it is important to investigate the cause of this problem. It has already been reported that the initial film growth in electroless deposition can be monitored by measuring the variation in transmissivity of He–Ne laser light [9]. In this study, this technique is applied to improve the understanding of the deposition effects.

2. Experimental details

Four types of electroless cobalt plating solutions were used with different combinations of the pH control agents and complexing agents, namely an alkaline ammonia – tartrate solution [10], an alkaline ammonia – pyrophosphate solution [11], a caustic alkaline – tartrate solution [12] and a caustic alkaline – citrate solution [12], here abbreviated as A–T, A–P, C–T and C–C, respectively. The composition and operating conditions of the solutions are shown in Table 1. The solutions were prepared using pure grade reagents and distilled water. Prior to all experiments, dissolved oxygen was purged from the solutions via an initial nitrogen bubbling. An ageing treatment of the solutions was carried out at a temperature of 293 K. Oxygen gas, of purity 99.9%, was passed through the solutions using a bubbler. The rate of inflow was kept constant at a value of $5\,\mathrm{cm^3\,s^{-1}}$ with a regulator. All experiments were carried out in Pyrex cells of volume $500\,\mathrm{cm^3}$. As substrate material, polyethylene terephthalate film (thickness: $t = 25\,\mu\mathrm{m}$) was used. Sput-

Table 1. Composition and operating conditions of electroless cobalt plating solutions

Plating solutions/mol m^{-3}		*A -T*	*A -P*	*C -T*	*C -C*
Cobalt sulphate	($CoSO_4$)	50	100	50	100
Sodium hypophosphite	(NaH_2PO_2)	20	20	20	20
Sodium citrate	($Na_3C_6H_5O_7$)	–	–	–	20
Sodium tartrate	($Na_2C_4H_4O_5$)	50	–	50	–
Sodium pyrophosphate	($Na_4P_2O_7$)	–	30	–	–
Ammonium sulphate	($(NH_4)_2SO_4$)	50	50	–	–
Boric acid	(H_3BO_3)	–	–	50	50
pH		10.2	10.2	9.2	7.5
pH control agent		NH_4OH	NH_4OH	NaOH	NaOH
Operating temperature	(K)	323	323	333	343

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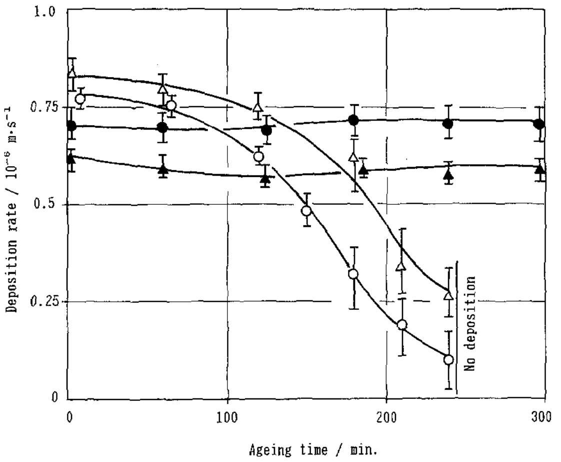


Fig. 1. Effect of ageing time on deposition rate. Solutions: (○) A–T; (△) A–P; (●) C–T; (▲) C–C.

tered palladium nuclei were formed on one side of the film only as a catalyst. The deposition rate was determined from the weight gain of the films per unit area and unit time ($10\,\mathrm{cm}^2\,\mathrm{min}^{-1}$). An induction time and a time to attain a continuous film were measured by the method described by Matsuda *et al.* [7]. The spectrochemical study was carried out using a Nihon bunkoh spectrophotometer (U-BEST 30).

3. Results and discussion

3.1. *Effect of ageing time*

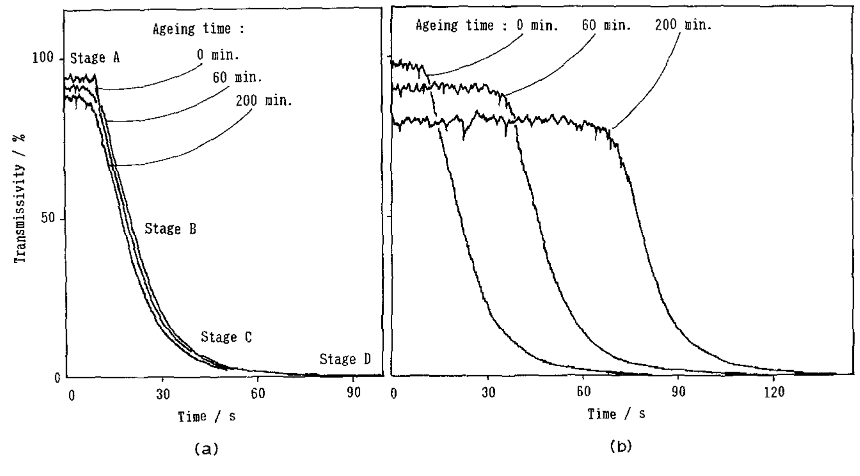
Figure 1 shows the relation between the deposition rate and ageing time after the formation of the solutions. The deposition rate of the caustic alkaline (C–T, C–C) solutions is practically independent of the ageing time. For the alkaline ammomnia (A–T, A–P) solutions, the deposition rate decreases as the ageing time increases, and eventually the deposition stops at an ageing time above 240 min.

In general, the deposition rate is determined from the nucleation rate and growth rate. To obtain more detailed information, variations in the transmissivity of light from a He–Ne laser with time elapsed after the immersion of the substrate were measured. Typical results are represented in Fig. 2a and b. Under all conditions, the transmissivity varies as follows. Initially the transmissivity remains approximately constant (stage A). After this initial period it decreases linearly (stage B), then the transmissivity curve slopes gently (stage C). Eventually the transmissivity levels off to zero (stage D). As shown in Fig. 2, the obvious effect of ageing time was observed only in the transmissivity curve of the A–T solution.

From the TEM observations and magnetic measurements, it has been confirmed that the curves obtained show the change in film structure and that the period of stage A corresponds to the induction time for nucleation (τ_i) and that the period of stages B plus C correspond to the formative time for continuity (τ_f) [9]. The measured values of τ_i and τ_f in the four solutions are plotted as a function of the ageing time in Fig. 3. As shown in Fig. 3a, τ_i is independent of the ageing time in the caustic alkaline (C–T, C–C) solutions. In the case of alkaline ammonia solutions, τ_i increases significantly as the ageing time increases. With regard to τ_f, (Fig. 3b), a slight increase is observed only in the alkaline ammonia solutions. It is noticeable that the ageing time mainly affects τ_i only in the ammonia alkaline solutions. The induction time generally increases as the nucleation rate falls. This means that longer ageing times inhibit the nucleation rate, and hence the nucleation step is considered to be the rate-determining step of the deposition rate in the aged alkaline ammonia solutions.

3.2. *Oxygen charge to solutions*

The inflow of atmospheric oxygen in the period of the ageing time is a possible cause of the increase in τ_i. In order to investigate the effect of oxygenation, τ_i, τ_f and the deposition rate were measured after oxygen had been passed through the solutions for a given time. The results are shown in Fig. 4. In the C–T solutions, Fig. 4(a), the change of τ_i, τ_f and deposition rate is not significant. In the A–T solution, Fig. 4(b), an obvious



(a) (b)

Fig. 2. Effect of ageing time: transmissivity against time curve. Solutions: (a) C–T; (b) A–T.

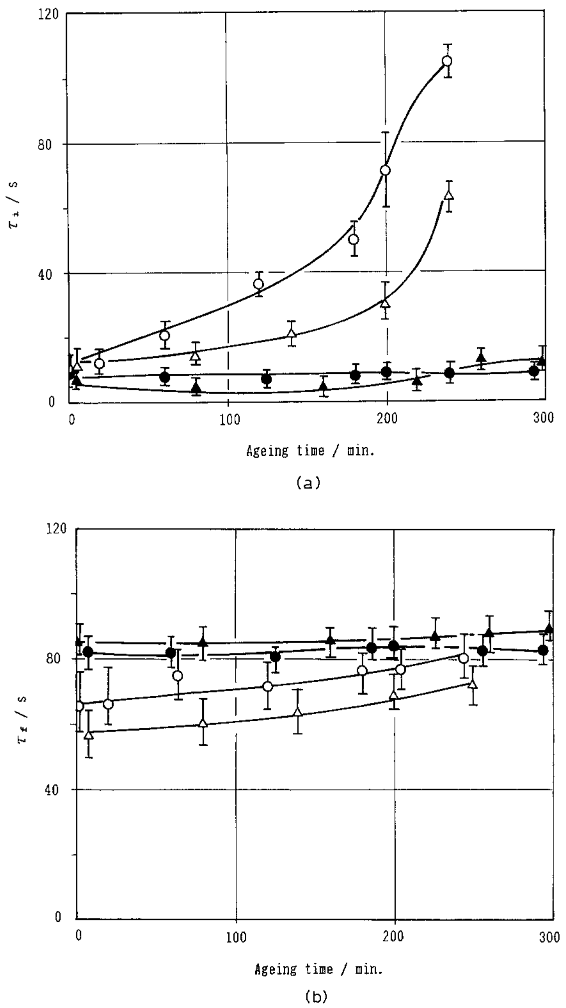


Fig. 3. Relation between ageing time and (a) τ_i, (b) τ_f. Solutions: (○) A–T; (△) A–P; (●) C–T; (▲) C–C.

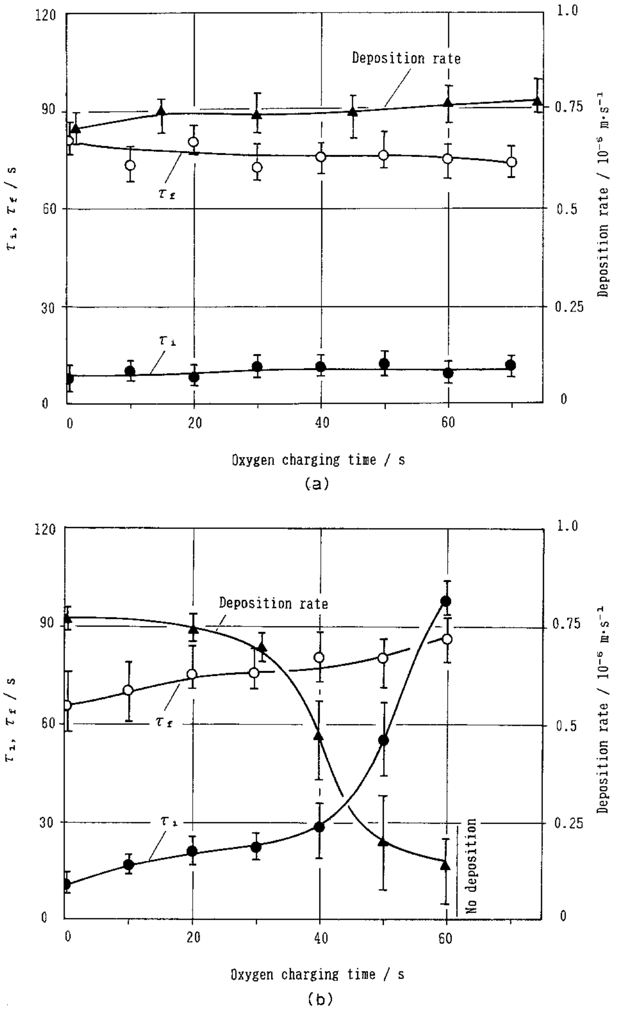


Fig. 4. Relation between oxygen charging time and τ_i, τ_f. Solutions: (a) C–T; (b) A–T.

increase of τ_i and a slight increase of τ_f are observed as the charging time increases. The deposition rate reduces, in contrast to the increase of τ_i, and levels off to zero at charging times over 60 s. These facts suggest that the increase in induction time (τ_i) in the alkaline ammonia solutions originates from the increase in dissolved oxygen.

It may be concluded that the concentration of dissolved oxygen gas is an important factor in determining the deposition rate of the alkaline solutions and that it mainly affects the nucleation rate, but not significantly the growth rate.

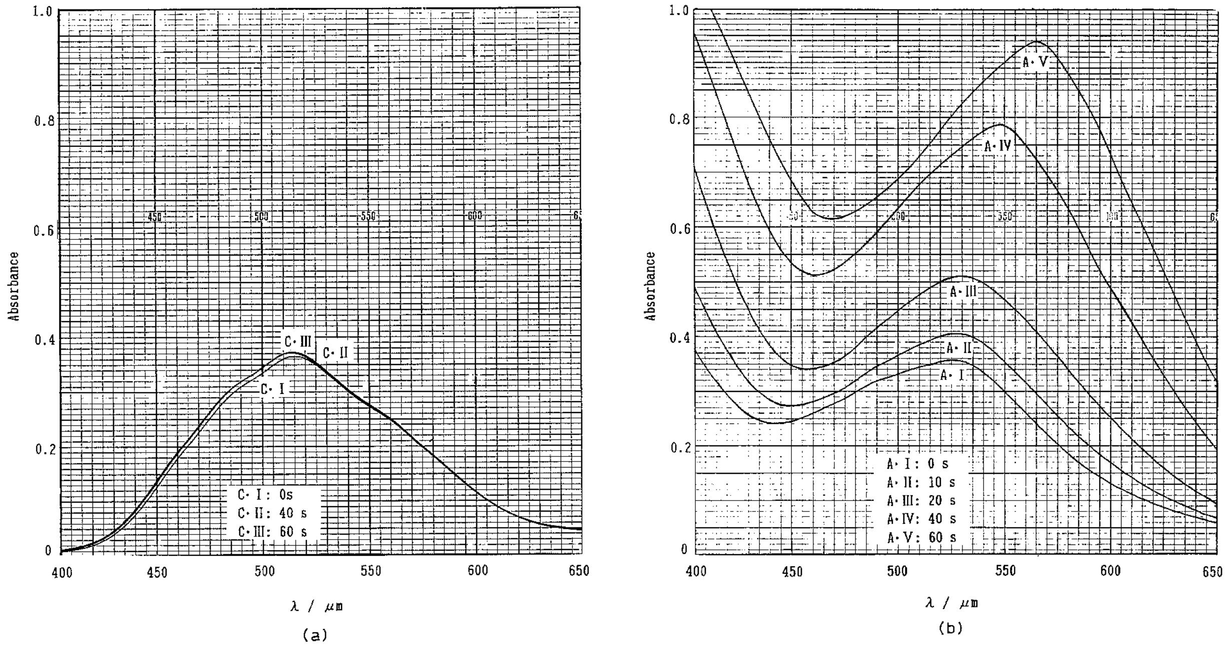
3.3. *Spectrochemical study*

Figure 5 presents the wavelength–absorbance spectra of the caustic alkaline (C–T) solution and alkaline ammonia (A–T) solution. In both solutions, the metallic complex salts, which exist before the oxygen charge, have been identified as a cobalt – tartaric acid complex and a cobalt–ammine–tartaric acid complex, respectively [13, 14]. As is obvious from Fig. 5a, insignificant changes in the spectrum are observed with the charging time in the caustic alkaline solution. For the alkaline ammonia solution, (Fig. 5b), the absorbance peak becomes higher, and gradualy shifts to a longer wavelength in the spectrum as the charging time increases. It has been reported that the cobalt (II))–citrate–ammine complex easily changes, in the presence of dissolved oxygen, to a cobalt (III)-citrate–ammine complex [15]. Similar structural changes should occur in the cobalt–ammine–tartaric acid complex. An attempt was made to identify such a structural change; however, no unknown complex could be identified.

It was also discovered that the deteriorated deposition rate due to the oxidation of the solution can not be restored to the original level by a succeeding nitrogen gas charge, that is, the oxidation reaction is irreversible. However the deterioration of the solutions due to oxygen inflow can be arrested with a continuous nitrogen gas charge during both the ageing and deposition processes, and consequently the deposition rate can be maintained at the original level. This fact is considered to have a significant implication for the practical application of the alkaline ammonia solutions.

4. Conclusion

The dissolved oxygen content is an important factor in determining the deposition rate of alkaline ammonia



(a)

(b)

Fig. 5. Wavelength against absorbance spectra of electroless cobalt plating solutions: (a) C–T and (b) A–T.

electroless plating solutions. The dissolved oxygen mainly affects the nucleation rate. The deterioration of the solutions due to oxygen inflow can be arrested with a continuous nitrogen gas charge during the deposition.

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