Bulletin of Electrochemistry 17 (9) September 2001, pp 405-408

0256-1654/2001/$ 3-50

VALIDITY OF ADSORPTION MECHANISM FOR ELECTRODEPOSITED ZINC COMPOSITES

G N K RAMESH BAPU AND T THIRUCHELVAM

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 23 March 2001 Accepted: 08 June 2001]

The two successive adsorption steps, proposed by Guglielmi for the mechanism of codeposition of Molybdenum disulphide (MoS_2) and Kaolin particles from sulphate zinc bath was experimentally demonstrated and the relationship between the electrolytic conditions and the extent of codeposition was verified. From the relationship, the importance of reduction of zinc ions adsorbed onto the particles is shown.

Keywords: Electrodeposition, adsorption mechanism, molybdenum disulphide, kaolin, zinc plating, sulphate bath

INTRODUCTION

The advantages of incorporating inert particles from electrolytic baths have received much attention of researchers, technocrats and material scientists. Improved properties were shown for the composite deposits containing inert particles onto a metallic matrix. The electrodeposition of inert particles from nickel, copper and other baths [1-3] have already been well established. However, studies on codeposition from zinc plating baths [4,5] are very limited.

Eventhough considerable attempts have been made to codeposit inert particles by conventional electrodeposition route, the mechanism of codeposition is still obscure and yet to attract the researchers. This may be due to the lack of physical explanation of the deposition of inert particles together with metal ions. Number of mathematical explanations and mechanisms were proposed by several group of researchers [6-13]. All the above proposed models were based on certain assumptions and no one holds good for practical considerations. However, a model proposed by Guglielmi [14] is found to be simple and valids good for several systems of codeposition [15-17].

According to Guglielmi, the codeposition of inert particles is based on two successive adsorption steps. In the first step, the inert particles, surrounded by adsorbed metal ions and solvent molecules are loosely adsorbed on the cathode and are in equilibrium with the particles in the suspension. In the second step, the particles are strongly adsorbed on the cathode and the metal ions are reduced electrochemically. The inert particles are now bound permanently to the cathode and embedded in the deposit. He derived the following mathematical model based on two adsorption steps:

$$\frac{C}{\alpha} = \frac{Wi_0}{n F d \nu_0} \times e^{(A-B)\eta} \times \left(\frac{1}{k} + C\right) \qquad (1)$$

where W is the atomic weight of the electrodeposited metal, d & n are the density and valency of the metal, F is the Faraday constant, η is the overpotential of the metal, C is concentration of particles in suspension and α is volume fraction of particles in the deposit.

The parameters ν_0 and B are related to the particle deposition and plays a symmetrical role with parameters i_0 and A which are related to the metal deposition. On plotting C/α against C, a sheaf of straight lines having the common intersection on the point 1/k of the 'C' axis can be obtained.

In the present investigation, an attempt has been made to codeposit kaolin/molybdenum disulphide particles with zinc matrix using sulphate bath. The relationship between the particle concentration in suspension and the volume percent incorporation of particles are related using the above adsorption model. Based on the results obtained, the Guglielmi's adsorption model is verified experimentally.

EXPERIMENTAL

For codeposition, acid sulphate bath consisting of 350 g/l zinc sulphate and 30 g/l ammonium sulphate was used. The pretreated Kaolin (5.3 μm size)/molybdenum disulphide (MoS_2) (5 μm size) particles were added individually to the plating solution. By means of a mechanically controlled glass stirrer, the particles were thoroughly stirred for 8 hours and kept in uniform suspension.

The codeposition was carried out in a 1 litre glass beaker. The extent of particle incorporation in zinc was studied with respect to particle concentration and current density ranging from 4 to 8 $A.dm^{-2}$ at *p*H 4 and bath temperature of 303 K. Two 5 mm thick zinc plates were used as anodes. Stainless steel specimens, 7.5 x 5 x 0.1 cm served as cathodes, from which the Zn-Kaolin/Zn-MoS_2 composite deposits could be easily stripped off for analysis. The zinc contents of the composites were determined by analysing the solutions using atomic absorption spectrometry with a high degree of accuracy. The volume percent (vol %) incorporation of the particles were obtained from the volume of zinc and volume of particles in the composite deposits as described elsewhere [18].

From the results, the following plots were drawn

- The volume percent (Vol %) incorporation of particles (α) versus the Vol% particle in suspension (C)
- The ratio C/ α versus the particle concentration (C) in the suspension.

From these plots, the results are discussed.

RESULTS AND DISCUSSION

Zinc Kaolin codeposition

From Fig. 1, it can be seen that the codeposition is maximum (21.3%) at current density 6 $A.dm^{-2}$ with 0.23 Vol% of Kaolin particles in the suspension. The curves follow the Langmuir adsorption isotherm.

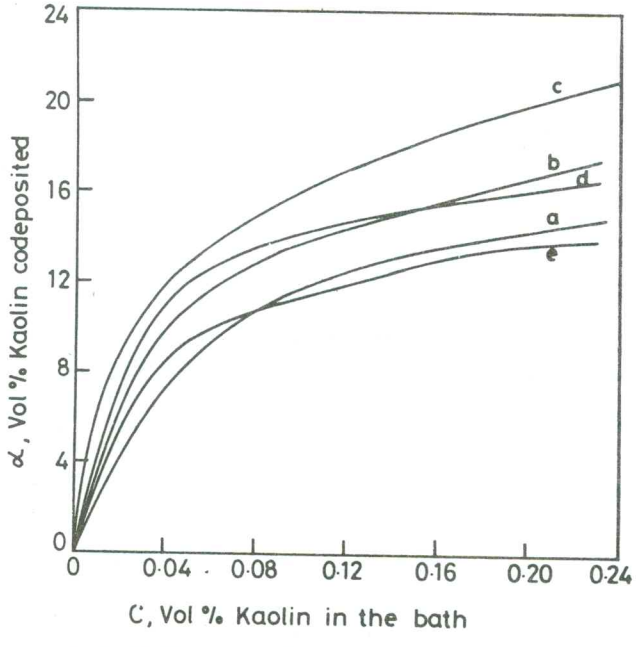

Fig. 1: Variation of Vol% Kaolin codeposited (α) as a function of Vol% Kaolin in the bath (C)
(a) 4 A/ dm^2 (b) 5 A/ dm^2 (c) 6 A/ dm^2
(d) 7 A/ dm^2 (e) 8 A/ dm^2

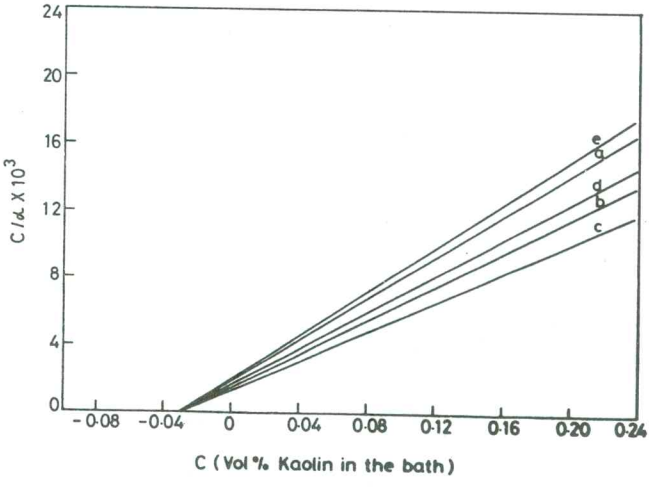

Fig. 2: Variation of (C/ α) as a function of (C) for Zn-Kaolin composite
(a) 4 A/ dm^2 (b) 5 A/ dm^2 (c) 6 A/ dm^2
(d) 7 A/ dm^2 (e) 8 A/ dm^2

Fig. 2 is the plot of the results from Fig. 1 according to equation 1. The experimental points can be satisfactorily grouped on a sheaf of straight line converging at a negative point on the abscissa. At $C/\alpha = 0$, the common intersection of the sheaf of straight lines (1/k) is equal to -0.034, which is purely a dimensionless number. However, some of the points do not fit exactly, possibly due to experimental errors similar to that indicated by other researchers [8-10] for their systems of study. Agreement of these results indicate that the electrodeposition of Zn-Kaolin follows the Guglielmi's adsorption model.

Zinc-molybdenum disulphide codeposition

From Fig. 3 it can be seen that the codeposition of MoS_2 is maximum (20.5%) at a current density 6 $A.dm^{-2}$ with about 1 Vol% of MoS_2 in the suspension.

In Fig. 4, the plot is obtained between the ratio C/α vs C, the Vol% of MoS_2 particles in suspension according to equation (1). The intercept on 'C' axis (1/k) has a value -0.28 and gave 3.5 for adsorption constant k. As in Zn-Kaolin system, the experimental points are satisfactorily grouped on a sheaf of straight lines converging at a negative point on the abscissa. These results follow that the codeposition of Zn-MoS_2 also agrees with the model proposed by Guglielmi. This indicate that in both cases of codeposition, adsorption mechanism is followed irrespective of the particle even though the values are different due to the difference in physical constants namely density, particle size, etc.

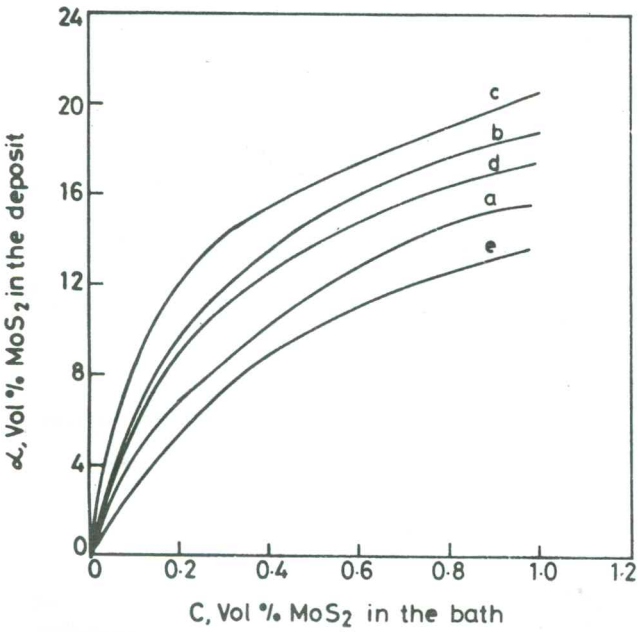

Fig. 3: Variation of Vol% MoS_2 codeposited (α) as a function of Vol% MoS_2 in the bath (C)
(a) 4 A/ dm^2 (b) 5 A/ dm^2 (c) 6 A/ dm^2
(d) 7 A/ dm^2 (e) 8 A/ dm^2

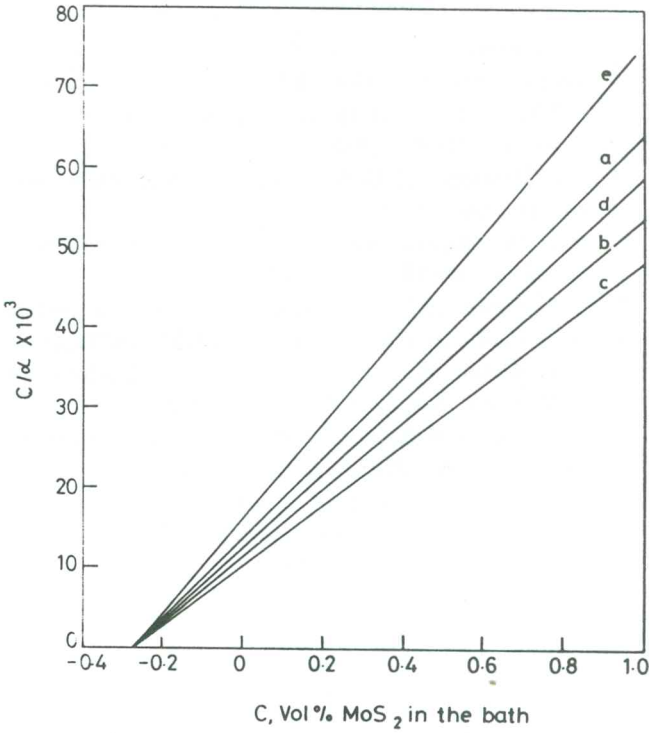

Fig. 4: Variation of (C/α) as a function of (C) for Zn –MoS_2 composite
(a) 4 A/ dm^2 (b) 5 A/ dm^2 (c) 6 A/ dm^2
(d) 7 A/ dm^2 (e) 8 A/ dm^2

CONCLUSIONS

It is concluded that Guglielmi's model is valid for the codeposition of inert particles, Kaolin and molybdenum disulfide from zinc sulphate plating baths. The experimental results are well agreed for the two step adsorption process and the rate determining step is second adsorption step. In this step, the layer of adsorbed ions on the inert particles is broken and a real contact occurs between the particle and the cathode.

REFERENCES

1. R Narayanan and B H Narayana, *Reviews in coatings and corrosion,* **4(2)** (1981)
2. J P Celis and J R Roos, *Reviews in coatings and corrosion,* **5(1-4)** (1982)
3. B J Hwang and C S Hwang, *J Electrochem Soc,* **140(4)** (1993) 979
4. W A Donakowski and J R Morgan, *Plat and Surf Finishing,* **70(11)** (1983) 48
5. M Hiramatsu, H Kawasaki, Y Nakayama and T Omi, *Plat and Surf Finishing,* **74(7)** (1987) 48
6. J P Celis, J R Roos and C J Buelens, *J Electrochem Soc,* **134(6)** (1987) 1402
7. J P Celis, J R Roos, C J Buelens and J Fransaer, *Trans Inst met Finish,* **69(4)** (1991) 133
8. R V Williams and P W Martin, *Proceedings 6th International Conference on Electrodeposition and Metal Finishing,* (1964) 182
9. C A Brandes and D Goldthorpe, *Metallurgia,* **76** (1967) 195
10. A M J Kariapper and J Foster, *Trans Inst Met Finish,* **52** (1974) 87
11. R Bazzsard and P J Boden, *Trans Inst Met Finish,* **50** (1972) 63
12. J L Valdes and H Y Cheh, *J Electrochem Soc,* **134(4)** (1987) 223c
13. J P Celis and J R Roos, *Trans Inst of Met Finish,* **75(3)** (1997) 118
14. N Guglielmi, *J Electrochem Soc,* **119(8)** (1972) 1009
15. J P Celis and J R Roos, *J Electrochem Soc,* **124(10)** (1977) 1508
16. A K Bhargava, A N Tiwari and D Kumar, *Trans Indian Inst Metals,* **33(6)** (1980) 451
17. M K Totlani and S N Athavale, *J Electrochem Soc India,* **31** (1982) 119
18. G N K Ramesh Bapu and M Mohammed Yusuf, *Materials Chemistry and Physics,* **36** (1993) 134