Role of Iron-group Metals in the Induced Codeposition of Molybdenum from Aqueous Solution*

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Binary and ternary alloys of molybdenum with iron-group metals were electrodeposited from ammoniacal tartrate baths under galvanostatic conditions. The relationship between the composition of electrodeposited alloys and the cathode current efficiency indicated the two characteristic alloy compositions; the one appeared at a maximum partial current efficiency of molybdenum and the other corresponded to the limiting content of molybdenum. These characteristic alloy compositions were discussed in connection with the mechanism of the induced codeposition of molybdenum based on the electronic structure of the iron-group metals.

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I. Introduction

In the electrodeposition of Mo with iron-group metals, which is termed "induced codeposition" by Brenner⁽¹⁾, the cathodic behavior of individual metals seems to be so irregular that the complicated mechanism of alloy deposition should be reflected. The authors have been studying the mechanism of the induced codeposition of Mo with Ni, and reported the results suggesting the formation of the partly-reduced Mo oxide and subsequent reduction of this film by atomic hydrogen^{(2)~(4)}. Although many hypotheses⁽⁵⁾ assuming the existence of the intermediate Mo species have been proposed so far, no complete mechanism has been yet available.

In the present work, the relationships between the composition of binary and ternary Mo alloys with iron-group metals and the partial cathode current efficiencies of individual metals were examined in relation to the number of the holes, and hence the number of the unpaired 3d electrons, of iron-group metals, and the role of iron-group metals in the induced

codeposition of Mo was discussed.

II. Experimental

Five types of plating baths containing molybdic acid, metal(II) sulfate (Ni, Co, Fe, Zn), potassium sodium tartrate (as a complexing agent) and ammonium hydroxide (for adjusting pH of the solution to 10.5) were used for the electrodeposition of (Ni, Co, or Fe)-Mo, Ni-Co-Mo and Ni-Zn-Mo alloys. In each bath, concentrations of potassium sodium tartrate and total metal ions were kept constant (0.27 kmol/m³). Metal-percentage of Mo, which was defined by Brenner⁽⁶⁾ as (weight of metal Mo/total metal weight contained in bath) × 100, was varied in (Ni, Co, or Fe)-Mo baths and Ni-Co-Mo bath in which molar ratio of Ni to Co was kept constant, 0.26. In the Ni-Zn-Mo bath, the concentration ratio of Ni to Zn was varied at the fixed Mo concentrations of 0.014, 0.030 and 0.100 kmol/m³ to give metal-percentages of Mo of 8, 17 and 49, respectively. After the preparation, each solution was deaerated with nitrogen gas for more than 24 h prior to electrolysis.

A H-section cell of the sealed type contained a platinum anode in the smaller compartment and a 1 × 2 cm² copper cathode in the larger compartment which was separated from the anolyte by a sintered glass to minimize contamination by anodic oxidation products.

Electrolysis was carried out galvanostatically

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at 1 kA/m², at 30°C for 20 min. The deposited metals were dissolved from the cathode with aqua regia and quantitatively analyzed by atomic absorption spectrometry, and the composition of alloys and the cathode current efficiency were calculated.

Further, the empirical confirmation of the surface film was tried. In order to evaluate the film resistance due to the intermediate Mo lower oxide which might be formed during the electrodeposition of Mo alloys with iron-group metals⁽⁵⁾, the parameter $(R/R_0)/(\rho/\rho_0)$ was introduced. R and R_0 were the resistances across the cathode and the tip of the capillary bridge of the reference electrode during the electrodepositions of Mo alloys and iron-group single metals, respectively. ρ and ρ_0 were the specific resistances of bulk solutions for the alloy and the iron-group single metal depositions, respectively. In the absence of the surface film, and hence any additional resistance except the solution, the parameter $(R/R_0)/(\rho/\rho_0)$ approaches approximately unity when neglecting the change in specific resistance due to the variation of bath composition in the vicinity of the cathode. On the other hand, the parameter is anticipated to exceed unity under the conditions that there exists a significant ohmic contribution due to the surface film to the measured resistance.

Specific resistance of each solution was measured at 30°C using a digital conduct meter. R (or R_0) was determined by the interrupter method⁽⁷⁾. The constant current pulse of repetition frequency 18.3 ms, duty factor 96.42% and of current density 1 kA/m² was applied to the electrodes (the cylindrical platinum cathode of 0.136 cm² area and the platinum mesh anode), and the cathode potential (vs N.H.E.)—relaxation waveform was observed on the oscilloscope, from which the potential difference between the capillary tip and the electrode surface, i.e., the resistance overvoltage, was read off.

III. Results

Figures 1 and 2 showed the effect of metal-percentage of Mo in the bath on the cathode current efficiency and on the composition of

Fig. 1 Effect of metal-percentage of Mo in the bath on the electrodeposited alloy composition and on the cathode current efficiency in the electrodeposition of binary Mo alloys with iron-group metals. Metal-percentage of Mo = [wt. Mo/total wt. (Mo + iron-group metal)] $\times$ 100.

Fig. 2 Effect of metal-percentage of Mo in the bath on the electrodeposited alloy composition and on the cathode current efficiency in the electrodeposition of Ni-Co-Mo alloys.

binary and ternary Mo alloys with iron-group metals, respectively. The Mo content in the electrodeposited alloys increased gradually with increasing the metal-percentage of Mo in the bath. In all cases, a decreasing tendency of the cathode current efficiency for the alloy deposition was recognized with an increase of the Mo content in the alloys. Therefore, the relationship between the Mo content in the alloys and the partial cathode current efficiencies of individual metals were examined, and the results were summarized in Fig. 3. The partial cathode current efficiency of Mo

Fig. 3 Relationship between the composition of alloys and the cathode current efficiency during the electrodeposition of Mo-iron-group metal alloys.

was initially increased gradually with the increased Mo content of the alloys, and then decreased to zero after a maximum was achieved. This indicated that it was difficult to obtain the high-Mo content alloy because of its poor current efficiency, and that there existed an upper limit of Mo content. Further, according to Fig. 3, the existence of two characteristic alloy compositions was recognized with respect to the partial cathode current efficiency of Mo; the one appeared at a maximum partial current efficiency of Mo and the other corresponded to the limiting content of Mo.

Figure 4 shows the parameter $(R/R_0)/(\rho/\rho_0)$ measured at regular time intervals from the beginning of the electrodeposition of the alloys from the same baths as for the plating study shown in Fig. 1, plotted as a function of Mo content of the binary alloys. Through an alloy composition range in which the partial cathode current efficiency of Mo showed an increasing tendency in Fig. 3, $(R/R_0)/(\rho/\rho_0)$

Fig. 4 Relationship between the Mo content in deposit and $(R/R_0)/(\rho/\rho_0)$ in the electrodeposition of binary Mo alloys with iron-group metals at various amount of charge.

became approximately unity, indicating the ohmic contribution only due to the solution to the measured resistance overvoltage. On the other hand, $(R/R_0)/(\rho/\rho_0)$ exceeded unity after the Mo content in the alloys at the maximum partial cathode current efficiency of Mo in Fig. 3 was achieved.

IV. Discussion

1. Speculation of previously proposed mechanisms of the induced codeposition of molybdenum with iron-group metals

Many hypotheses⁽⁵⁾ have been proposed so far with respect to the mechanism of induced codeposition of Mo. One of the most plausible mechanisms assumed the formation of an oxide of the partly-reduced reluctant metals such as Mo or W, followed by the reduction of this film by atomic hydrogen. This has been called the catalytic reduction mechanism⁽⁸⁾⁽⁹⁾. Our experimental results presented in the previous papers^{(2)~(4)} also supported this mechanism. However, this mechanism has been left in an incomplete stage due to the lack of the detailed knowledges of the intermediate compound composition and its formation process. Thus, the mechanism proposed so far represents only an outline of the complicated mechanism of Mo codeposition. Then, the equational expression of this mechanism might be qualitatively given as follows:

where n : valence of Mo in the intermediate compound ($0 < n < 6$), M: inducing metal atom, H(M): atomic hydrogen held on the inducing metal, Mo(M): molybdenum deposited on the inducing metal.

Assuming that the alloy deposition occurs in accordance with the mechanism expressed by the above equations, the cathode current efficiency for the alloy deposition should be

controlled by the relative depositing rate of Mo^{n+} oxide and of inducing metal as described later in detail. Therefore, the inducing metal must have following properties in order to gain the alloy deposition with high current efficiency; the high ability of holding atomic hydrogen and the capability of being easily deposited from aqueous solutions. Table 1 showed the heats of atomic hydrogen adsorption on the various metals presented by Delahay *et al.*⁽¹⁰⁾ The asterisked elements represent the metals which can be electrodeposited from aqueous solutions with high current efficiency reported by Lyons Jr.⁽¹¹⁾ As is evident from Table 1, only iron-group metals satisfy the above mentioned two properties of the inducing metal. This is in good agreement with the fact that the iron-group metals appeared to be the only alloying elements that make possible the codeposition of substantial amount of reluctant metal.

In the catalytic reduction mechanism⁽⁸⁾⁽⁹⁾, the reason why the iron-group metals are the only effective inducing elements is attributed to their electronic structure. Figure 5, quoted from Kittel's work⁽¹²⁾, shows the change in the saturation magnetization of Ni alloys as a function of at. % of added elements. Since the saturation magnetization in Bohr magnetons per atom corresponds to the unequal distribution of the holes in the two sub-bands, the number of the holes, and hence the number of unpaired 3d electrons, can be seen from Fig. 5. The number of unpaired 3d electrons in Fig. 5 is, however, applicable only in the case that an atom exists in the bulk of the metal crystals. In other words, the iron-group metals are predicted by band theory to have the decimal number of unpaired electrons per atom only when they are in a metallic state (form a

Fig. 5 Saturation magnetization of Ni alloys in Bohr magnetons per atom as a function of the atomic percent of solute element. Quoted from Kittel's work⁽¹²⁾.

metallic bond). In the electrodeposition of alloys, however, the inducing iron-group metals no longer exist in the bulk crystal, but in the surface of the electrode. Further, the electronic structure of the iron-group metals may be changed by alloyed Mo, although band theory can not definitely conclude as yet whether the 3d band of the iron-group metals is filled with the 5s electrons of Mo. As mentioned above, the electronic structure of the iron-group metals in alloy deposition still remains in the incomplete stage. However, since the ferromagnetism in the iron surface has been confirmed recently⁽¹³⁾, it is assumed in the following discussion that the electronic structure of

Table 1 Heats of adsorption of atomic hydrogen on the metal (kJ/mol)⁽¹⁰⁾.

Ag*	Al	Au*	Be	Cd*	Cr	Cu*	Fe*	Ga*
240.6	242.7	248.2	243.6	225.6	251.5	244.8	253.2	236.5
Hg*	In*	Mg	Mn	Mo	Nb	Ni*	Pb*	Pd
221.4	236.5	228.9	240.6	275.4	283.3	251.9	232.7	249.0
Pt	Ta	Ti	Tl*	V	W	Zn*		
263.2	287.1	255.3	231.4	258.2	287.1	229.8		

* Metal which can be electrodeposited from aqueous solution with high cathode current efficiency⁽¹¹⁾.

the iron-group metals which exist in the cathode surface is the same as the one in bulk crystals.

2. Relationship between the number of unpaired electrons of iron-group metals and the characteristic alloy compositions

The catalytic reduction mechanism⁽⁸⁾⁽⁹⁾ implies that the iron-group metals are in order of the magnitude of the number of their unpaired electrons with respect to the ability of inducing Mo codeposition, since the atomic hydrogen held on the iron-group metals per atom is equal in number to their unpaired electrons. From Fig. 5, the number of unpaired 3d electrons of Ni, Co and Fe were 0.6, 1.6 and 2.2, respectively, and the degree of two characteristic compositions shown in Fig. 3 corresponded to the order of the magnitude of the number of unpaired electrons. This suggests that these characteristic compositions are closely related to the unpaired electrons of the iron-group metals.

As pointed out in the discussions about Figs. 3 and 4, the existence of the resistive components on the cathode was confirmed not in the alloy composition range of the increased partial cathode current efficiency of Mo, but in the range of the decreased one. According to the above mechanism, this indicates that although the continuous deposition of Mo can occur while the depositing rate of the iron-group metal is greater enough than that of Mo^{n+} oxide, the lag in the reduction of Mo^{n+} oxide occurs with further increase in the formation rate of Mo^{n+} oxide, permitting the accumulation of unreduced oxide on the cathode. Thus, the partial cathode current efficiency of Mo may be increased by increasing the formation rate of Mo^{n+} oxide while the reduction of Mo^{n+} oxide to metal occurs rapidly enough in the presence of freshly deposited iron-group metal. On the other hand, it may be decreased when unreduced Mo^{n+} oxide is left on the cathode, resulting in the formation of the surface film to make the deposition of the iron-group metals difficult due to the film resistance. Therefore, the maximum partial current efficiency of Mo seems to be attained when the formation rate of Mo^{n+} oxide is balanced by

the depositing rate of the iron-group metal. With regard to one atom of iron-group metals, alternatively, the above situation leads to the gradual increase in the frequency of participation of the unpaired electrons in the reduction of Mo^{n+} oxide with its increased formation rate. Then, let us consider the situation that the electrodeposition of alloys occurs, in which the unpaired electrons of the iron-group metal participate once in Mo deposition. It requires n hydrogen atoms to reduce one Mo^{n+} oxide molecule to pure Mo. Therefore, the number of Mo atoms deposited in the presence of one iron-group metal atom having N unpaired 3d electrons is N/n . The weight percentage of Mo in alloy is then given as follows:

$$\% \text{ of Mo} = [(95.94 N/n)/(W + 95.94 N/n)] \times 100,$$

where W is an atomic weight of the iron-group metal.

The relationship between the number of unpaired 3d electrons and the Mo content in the electrodeposited alloys was calculated using above eq. The results are shown in Fig. 6. In the calculation, the mean value of the atomic weights of the iron-group metals was used since they do not differ so much from each other, and $n(1, 2, \dots, 6)$ was taken as a parameter. The Mo content observed at the maximum partial current efficiency of Mo in Fig. 3 was plotted against the N value obtained from Fig. 5. As can be seen from Fig. 6, the Mo content in the alloys at the maximum partial current efficiency of Mo was in good agreement with the curve for $n=4$. The authors⁽³⁾⁽¹⁴⁾ have already reported that the cathode current efficiency of Ni-Mo alloys was closely related to the depositing rate of Mo lower oxide from the Mo single bath and that the spectroscopic analysis of this hydrated oxide revealed the composition of $\text{MoO}_{2-x}(\text{OH})_{2x}$ ($x: 0 \sim 2$). Consequently, the valence of Mo in the intermediate compound is 4, and the maximum partial current efficiency of Mo appears to be attained when the unpaired electrons of the iron-group metal participates once in the reduction of the Mo intermediate compound.

In case the Mo content of the alloys exceeded

Fig. 6 Relationship between the number of unpaired 3d electrons and the Mo content in deposit during the electrodeposition of Mo with iron-group metals. Solid lines: calculated relationship
○: Mo content in deposit observed at the maximum partial cathode current efficiency of Mo

the one at the maximum partial cathode current efficiency of Mo, the participation frequency of the iron-group metal in the reduction of Mo^{n+} oxide should be more than once. The alloy composition can then be expressed by the following eq. involving m , the frequency of participation of the iron-group metal in Mo deposition:

% of Mo

$$= [(95.94mN/n) / (W + 95.94mN/n)] \times 100.$$

Figure 7 was obtained by altering the result shown in Fig. 3 into the relationship between the cathode current efficiency and m , using the

Fig. 7 Relationship between the cathode current efficiency of alloy deposition and the frequency of participation of iron-group metals in Mo deposition.

above eq. for $n=4$. Within the region of $m \leq 1$, the cathode current efficiency for individual iron-group metal deposition was reflected in that of alloy deposition. When $m > 1$, i.e., a given iron-group metal atom must participate several times in Mo deposition, the current efficiency tended to be decreasing rapidly to zero at $m=3$. Thus, the maximum frequency of participation of the iron-group metal in Mo deposition seems to be 3, and the alloy composition at $m=3$ will give the limit of Mo deposition.

Table 2 shows the comparison of the alloy composition at the maximum partial current efficiency of Mo derived from Fig. 3 with that calculated under the assumption that the intermediate Mo^{4+} oxide was formed and the reduction of this lower oxide film was participated once by the iron-group metals. Table 2 also shows a comparison of the limit-

Table 2 Characteristic composition of Mo alloys containing Fe, Co and/or Ni.

Inducing metal	Cont. of Mo in alloy at the max. partial C.C.E. of Mo (wt %)		Limiting content of Mo in alloy (wt %)	
	experimental.	calculated.	experimental.*	calculated.
Ni	20.0	19.7	40~42	42.4
Co	38.0	39.4	61~68	66.1
Fe	47.5	48.6	78	73.9
Ni-Co	31.7	33.8	57~61	61.9

* estimated by extrapolation of C.C.E. to zero in Fig. 3.

ing Mo content estimated by extrapolation of current efficiency to zero in Fig. 3 with the alloy composition calculated assuming 3 times participations of the iron-group metals in Mo deposition. Two characteristic compositions which appeared in the electrodeposition of the iron-group metal-Mo alloys were in good agreement with the calculated ones based on the above assumptions, indicating that the holes in the 3d band, and hence the unpaired 3d electrons, of the iron-group metals played an essential role in the induced electrodeposition of Mo. This conclusion was also confirmed by the following experiment.

According to Fig. 5, the 3d bands of Ni are filled up with the 4s electrons of Zn in 30Zn-70Ni alloy i.e., the number of unpaired electrons of Ni is observed to go to zero at about 30 at. % Zn. Then, the electrodeposition of Mo-Ni-Zn alloys were carried out. The cathode current efficiencies of Mo and alloy are shown in Fig. 8 as a function of atomic ratio of Zn to Ni in the alloys. It is indicated that the cathode current efficiency is decreased to zero at the atomic ratio Zn/Ni of about 0.4, and hence about 30 at. % Zn, in the deposit.

V. Summary

Binary and ternary Mo alloys with iron-group metals were electrodeposited from the ammoniacal tartrate bath under galvanostatic conditions, and the relationships between the

composition of electrodeposited alloys and the cathode current efficiency were studied. With increased Mo content of the alloys, the partial current efficiency of Mo tended to increase initially and then decreased to nearly zero after the maximum was achieved. This showed the existence of two characteristic alloy compositions, the one appeared at a maximum partial current efficiency of Mo and the other corresponded to the limiting Mo content. These characteristic compositions were in good agreement with the calculated ones based on the number of unpaired 3d electrons of iron-group metals. Further studies on the electrodeposition of Ni-Zn-Mo alloys indicated that the electrodeposition of Mo ceased when the alloy composition was achieved, in which atomic ratio of Zn to Ni corresponded to the one that the positive holes in 3d band of Ni were filled up with 4s electrons of Zn. Thus, the unpaired 3d electrons of freshly deposited iron-group metals appeared to play an important role in the induced codeposition of Mo.

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Fig. 8 Relationship between the cathode current efficiency and the atomic ratio of Zn to Ni in the electrodeposited Mo-Ni-Zn alloys.