# Design of Electrocatalyst for CO<sub>2</sub> Reduction

V. Effect of the Microcrystalline Structures of Cu-Sn and Cu-Zn Alloys on the Electrocatalysis of CO<sub>2</sub> Reduction

## Akihiro Katoh, Hiroyuki Uchida, Masami Shibata, and Masahiro Watanabe\*

Laboratory of Electrochemical Energy Conversion, Faculty of Engineering, Yamanashi University, Takeda 4-3, Kofu 400, Japan

## ABSTRACT

Electrocatalytic activities of Cu-Sn and Cu-Zn alloys for  $CO_2$  reduction were examined in 0.05M KHCO<sub>3</sub> aqueous solution at 2°C. It was found that the selectivity, the reversibility, and the reactivity for CO or HCOOH production strongly depended on the microcrystalline phase rather than the gross composition of alloys. The crystallites of the intermetallic compounds of  $Cu_{5,6}Sn$  and  $Cu_5Zn_8$  were effective phases for the selective formation of CO with a high reaction rate.

Electrochemical reduction of CO<sub>2</sub> is a promising approach for reducing the accumulation of  $CO_2$ , an origin of the global greenhouse effect or acid rain. Many studies on the electroreduction of CO<sub>2</sub> using various metal electrodes in aqueous or nonaqueous solutions have shown that selective (high faradaic efficiency) reduction has been per-formed, *e.g.*, formic acid on Hg, <sup>1-5</sup> Pb, <sup>4,5</sup> In, and Zn, <sup>4-6</sup> CO on Ag and Au, <sup>4</sup> methane and ethylene on Cu, <sup>4,7,8</sup> and some hydrocarbons on various transition metals.9 However, almost all the electrode reactions require a large overpotential for the electroreduction; they are not reversible. While several reports are available for reversible production of methanol on Ru, <sup>10</sup> RuO<sub>2</sub>-TiO<sub>2</sub>, <sup>11</sup> RuO<sub>2</sub>, <sup>12</sup> Ni, <sup>12</sup> Cu, <sup>12</sup> Mo, <sup>13</sup> and an oxidized Cu, <sup>14</sup> the current densities are very low; their reactivities are not high.

To reduce CO<sub>2</sub> with high selectivity, high energy efficiency, and high reactivity, it is essential to develop novel electrocatalysts. The reduction rate can be accelerated further by applying the electrocatalysts to a CO<sub>2</sub>-gas diffusion electrode.  $^{\rm 15-17}$  We have proposed a new concept  $^{\rm 18}$  for the design of such alloy-electrocatalysts which can satisfy either one or all of three requirements mentioned above for CO<sub>2</sub> reduction, and found their interesting electrocatalytic activities,<sup>18-21</sup> which are distinct from those of elemental metals.

We focus here on the effects of the microcrystalline phases in the Cu-Sn and Cu-Zn alloys on the selectivity, the reversibility, and the reactivity of the electroreduction of  $CO_2$ .

### Experimental

Electrodes of Cu-Sn and Cu-Zn alloys or the elemental metals were prepared on a gold flag electrode  $(1.5 \times 1.5 \text{ cm})$ 2.25 cm<sup>2</sup>, purity 99.9%) by electroplating from conven-tional plating baths<sup>22-24</sup> with a 10 C charge. The gold electrode was exposed to the electrolyte on one side by masking the other side with an epoxy resin Torr Seal. The alloy compositions were controlled by changing the bath compositions and/or the current densities at a constant plating temperature. The bath compositions and the plating conditions are listed in Table I. Very smooth electrode surfaces thus obtained were protected from formation of the oxides or dissolution of the components as follows.<sup>20</sup> The electrode potential was kept less positive than the rest potential of each electrode by blanketing the surface with hydrogen gas during the replacement of electrolytes, washing the electrode surface, and then saturating the electrolyte with CO<sub>2</sub> gas.

The procedures of the electroreduction experiments of CO<sub>2</sub> were the same as in Ref. 19 and 20. Potentiostatic electrolysis was carried out at 2°C in CO<sub>2</sub> saturated 0.05M KHCO3 aqueous solution (pH ca. 6.4). The electrolytic solution was prepared by dissolving reagent grade KHCO3 in pure water distilled from permanganate solution and purified further by pre-electrolysis in a similar manner to that

\* Electrochemical Society Active Member.

2054

J. Electrochem. Soc., Vol. 141, No. 8, August 1994 © The Electrochemical Society, Inc.

described previously.<sup>25</sup> A gastight H-type Pyrex cell was used, and the cathode and anode compartments were separated by an ion exchange membrane (Nafion® 117). A platinized platinum gauze and an Ag/AgCl [ $E^{\circ} = 0.199$  V vs. standard hydrogen electrode (SHE)] were used as a counterelectrode and a reference electrode, respectively. All the electrode potentials shown here are referenced to the SHE. During electrolysis, the gas pressure was maintained equal to atmospheric pressure,<sup>9</sup> and the catholyte (volume = ca. 60 cm<sup>3</sup>) was magnetically stirred. The charge passed during electrolysis was approximately 10 C.

Analyses of the reduction products in both the gas and liquid phases were carried out by using a gas chromatograph (Shimadzu GC-4C) and a liquid chromatograph (JASCO 875-UV), or a steam gas chromatograph (Ohkura Riken GC103). After electrolysis, the crystallite structures of the alloy electrode surfaces were analyzed in ambient air by grazing-angle x-ray diffraction (XRD) for thin film (MAC Science, MXP<sup>3</sup>), which gives the crystallite structures of a region of within 15 to 20 Å from the surface. Since, during electrolysis, the electrode was polarized at the potential of  $-0.5 \sim -1.5$  V vs. SHE negative enough compared with the potential for the electroplating of these alloys, no oxides were detected on the surface. To determine the gross composition of the electroplated alloy, the alloy was dissolved with aqua regia followed by analysis

Table I. Electroplating conditions for Cu-Sn and Cu-Zn alloy electrodes.

	Bat		-			
(a) Cu-Sn	$Cu(CN)_2$	$Na_2SnO_3$	NaCN	NaOH	$j/\mathrm{A}~\mathrm{m}^{-2}$	(°C)
Cu(95)Sn(5)	12	36	15	_	200	60
Cu(90)Sn(10)	12	36	15	15	200	60
Cu(86)Sn(14)	12	36	15	10	200	60
Cu(72)Sn(28)	12	36	15	5	200	60
Cu(69)Sn(31)	12	36	15	1	200	60
Cu(50)Sn(50)	6	36	15		200	60
Cu(26)Sn(74)	3	36	15		200	60
pure Cu CuSO	100	30				
pure Sn Sn(BI	100	30				

Cu(57)Sn(43) [pyrophosphate bath]; Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub> · 3H<sub>2</sub>O: 28, Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> · H<sub>2</sub>O: 47, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> · 10 H<sub>2</sub>O: 410, (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>: 20, j = 300 A m<sup>-2</sup>, 45°C.

	Bat	h composi		m		
(b) Cu-Zn	Cu(CN) <sub>2</sub>	Zn(CN) <sub>2</sub>	KCN	KOH	$j/\mathrm{A}~\mathrm{m}^{-2}$	Temp. (°C)
Cu(77)Zn(23)	50	30	80	60	222	40
Cu(50)Zn(50)	30	30	80	60	222	40
Cu(42)Zn(58)	17	60	80	60	222	40
Cu(25)Zn(75)	10	60	80	60	222	<b>40</b>
Cu(4)Źn(96)	1	60	80	60	222	<b>40</b>
pure Cu CuSC	100	30				
pure Zn ZnCl	200	30				

pure Zn ZnCl<sub>2</sub>: 150, NaCl: 25 (pH 3.7)

Downloaded on 2014-03-27 to IP 140.120.135.222 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms use) unless CC License in place (see abstract).



Fig. 1. Effect of the electroplating baths on the faradaic efficiencies for CO  $(\bigcirc, \bullet)$  and HCOOH  $(\triangle, \blacktriangle)$  formation on Cu-Sn alloy electrodes. Open symbols; Cu-Sn alloy (Sn a/o = 43) prepared from pyrophosphate bath, closed symbols; Cu-Sn alloy (Sn a/o = 50) prepared from cyanide bath.

with inductively coupled plasma (ICP) spectroscopy (Shi-madzu ICPS-500).

Faradaic efficiencies  $\epsilon$  for CO, HCOOH, and H<sub>2</sub> production were determined as functions of the electrolysis potential for various electrodes. As a measure of the reversibility of the electroreduction, we evaluated an approximate overpotential, the difference between the standard potential  $E^{\circ}$ and an onset potential  $E_{\text{onset}}$  for each reduction product.  $E_{\text{onset}}$  was determined by an extrapolation of the faradaic efficiency vs. potential relation to zero efficiency.  $\epsilon$  and  $E_{\text{onset}}$  are represented with the reduction product (CO or HCOOH) which is put in brackets. The values of  $E^{\circ}$  under our experimental conditions (2°C, pH 6.4) were -0.551 V vs. SHE for HCOOH and -0.475 V vs. SHE for CO formation, respectively. As a measure of the reactivity, the partial current density for each product was calculated by multiplication of the total steady current density by the value of  $\epsilon$  at a potential where the maximum  $\epsilon$  was obtained on each alloy electrode.

### **Results and Discussion**

As is well known, while CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are produced on a pure Cu electrode in the electroreduction of CO<sub>2</sub> in a potential region more negative than *ca.* -1.2 V *vs.* SHE, the predominant reduction products are HCOOH and CO at *ca.* -1.0 V.<sup>7,8,20</sup> The maximum faradaic efficiencies obtained on the electroplated pure Cu electrode were about 32% for HCOOH (-1.5 V) and 8% for CO (-1.2 V). Therefore, the pure Cu electrode is neither selective nor reversible for the formation of HCOOH and CO. By alloying Cu with Ni, Sn, Pb, Zn, Cd, or Ag, either the selectivities or reversibilities, or both for CH<sub>2</sub>OH, HCOOH, or CO were dramatically increased.<sup>18-20</sup>

Although their selectivity, reversibility, and reactivity strongly depend on the alloy composition, two kinds of Cu-Sn alloy electrodes which were prepared from a pyrophosphate bath and a cyanide bath so as to give almost the same gross composition showed considerably different selectivities and reversibilities as shown in Fig. 1.<sup>21</sup> The major reduction product was HCOOH on the former alloy (43% Sn,  $\epsilon$ [HCOOH] = 60% at -1.25 V) and CO on the latter (50% Sn,  $\epsilon$ [CO] = 35% at -1.25 V). Also, the 43% Sn alloy showed excellent reversibilities for CO and HCOOH production ( $E_{onset} = -0.5$  V for HCOOH and CO), but the 50% Sn alloy required a much larger overpotential. XRD of the electrodes indicates that two electrodes consist of different

microcrystalline structures;  $(Cu + Cu_6Sn_5 + Sn)$  for the 43% Sn alloy prepared from the pyrophosphate bath and  $(Cu_{5,6}Sn + Cu_3Sn)$  for the 50% Sn alloy from the cyanide bath. Then, we studied the effects of the alloy crystalline phase on the electrocatalytic properties for some Cu-based alloy electrodes.

Changes in the crystalline phases of Cu-Sn alloys with the gross composition.—Figure 2 shows the XRD patterns for the surfaces of a series of Cu-Sn alloys with various gross compositions, which were electroplated from cyanide baths. Unfortunately, it was impossible to control the crystalline phases of Cu-Sn alloys with use of pyrophosphate baths. Pure Cu deposited from the sulfate bath showed a face-centered cubic (fcc) structure in agreement with the crystallographic data (a = 3.615 Å).<sup>26</sup> For the alloys containing a small amount of Sn by 5 or 9 atom percent (a/o) (Fig: 2b and c), only the solid solution of (Cu + Sn) (fcc) was observed. The lattice constant, a, of the solid solution increased with increasing Sn content; a = 3.63 Å for 5 a/o Sn and a = 3.68 Å for 9 a/o.

On the surface of the alloy with 14 a/o of Sn (Fig. 2d), a single phase of the intermetallic compound  $Cu_{5.6}Sn$  (tetragonal structure,<sup>27</sup> reported as a high temperature phase,<sup>28</sup> Sn a/o = 15.2) appeared, indicating that the arrangement of Sn atoms in the alloy changed from the disordered form (fcc) of the solid solution at lower Sn content to an ordered one (tetragonal).



Fig. 2. XRD patterns for the surfaces of Cu-Sn alloys with various gross compositions. Sn a/o; a) 0 (pure Cu), b) 5, c) 9, d) 14, e) 28, f) 32, g) 57, h) 86, and i) 100 (pure Sn).  $\Box$ , Cu (fcc);  $\bigcirc$ , (Cu + Sn) solid solution (fcc);  $\triangle$ , Cu<sub>5.6</sub>Sn (tetragonal);  $\blacksquare$ , Cu<sub>3</sub>Sn (orthorhombic);  $\spadesuit$ , Cu<sub>6</sub>Sn<sub>5</sub> (hexagonal); and  $\blacktriangle$ , Sn (tetragonal).



Fig. 3. Effect of Cu-Sn alloy composition on the faradaic efficiencies for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation at -1.25 V vs. SHE. Region A) (Cu + Sn) solid solution; B) Cu<sub>5.6</sub>Sn; C) Cu<sub>5.6</sub>Sn + Cu<sub>3</sub>Sn; and D) Cu<sub>6</sub>Sn<sub>5</sub> + Sn.

With further increase of the Sn content (28 or 32 a/o), a new crystal phase Cu<sub>3</sub>Sn (orthorhombic, <sup>29</sup> Sn a/o = 25) was recognized in addition to the strong diffraction peaks assigned to Cu<sub>5.6</sub>Sn, as shown in Fig. 2e, f. Since the identified intermetallic compounds contain less Sn than the gross composition, pure Sn or some kind of compound with higher Sn content, which was not detected by XRD, may be produced in these alloys.

Further increase in the Sn content to more than 57 a/o resulted in a mixture containing pure Sn (tetragonal, a = 5.831 Å, c = 3.182 Å)<sup>30</sup> and Cu<sub>6</sub>Sn<sub>5</sub> (hexagonal).<sup>31</sup>

Effects of crystal structures of Cu-Sn alloys on the selectivity, reversibility, and reactivity for the electroreduction of  $CO_2$ .—Figure 3 shows the relationship between the faradaic efficiency  $\epsilon$  (selectivity) for the reduction products at -1.25 V vs. SHE and the gross composition of Cu-Sn alloys prepared from cyanide baths, together with crystalline structures (region A, B, C, and D) determined above. The addition of 14 a/o of Sn to Cu improved the faradaic efficiency for production of carbon monoxide and resulted in a maximum efficiency of 67%, which was much higher than that of elemental Cu or Sn. Comparing the  $\epsilon$ [CO] with the crystal structure exposed, it becomes clear that the intermetallic compound Cu<sub>5.6</sub>Sn, whose composition is close to the gross one of the electrode, is the most effective phase for the selective formation of CO when polarized with a relatively large overpotential (ca. 0.7 V). On the other hand, the  $\epsilon$ [HCOOH] was about 20% over the whole composition range, suggesting that the selectivity for formation of formic acid is insensitive to both the crystal structures and the gross compositions in Cu-Sn alloys.

Similar relationships are seen in Fig. 4, which shows the dependence of the partial current density (reactivity) for CO and HCOOH formation at -1.25 V on the composition (or crystal phase). The highest reactivity for CO production was obtained for Cu<sub>5.6</sub>Sn (Sn a/o = 14).

Figure 5 shows the relationship between the onset potential  $E_{\text{onset}}$  and the composition of Cu-Sn alloys. The  $E_{\text{onset}}$ [CO] shifted to positive potential with increasing the Sn content and reached the most positive value of -0.85 V at 14 a/o of Sn, the region B where the highest  $\epsilon$ [CO] was obtained. In contrast, alloying with Sn made  $E_{\text{onset}}$ [HCOOH] more negative than that of pure Cu.

Hence, the intermetallic compound  $Cu_{5.6}Sn$  exhibits prominent electrocatalytic properties for the reduction of



Fig. 4. Dependence of the partial current densities,  $j_{part}$ , for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation at -1.25 V vs. SHE on the composition of Cu-Sn alloys. Region A) (Cu + Sn) solid solution; B) Cu<sub>5.6</sub>Sn; C) Cu<sub>5.6</sub>Sn + Cu<sub>3</sub>Sn; and D) Cu<sub>6</sub>Sn<sub>5</sub> + Sn.

 $\rm CO_2$  into CO with respect to the selectivity, reversibility, and reactivity. However, strictly speaking, the positive shift of  $E_{onset}$  [CO] is only 50 mV compared with that of pure Cu. Since much larger shifts in  $E_{onset}$  [CO] were confirmed for the Cu-Sn alloy prepared from pyrophosphate bath (Cu<sub>6</sub>Sn<sub>5</sub> phase, see Fig. 1) and Cu-Pb (Pb a/o = 54),<sup>20</sup> Cu<sub>5.6</sub>Sn is a relatively less active electrocatalyst with respect to reversibility for CO production in spite of showing very high selectivity and reactivity.

Changes in the crystalline phases of Cu-Zn alloys with the gross composition.—Figure 6 shows the XRD patterns for the surfaces of a series of Cu-Zn alloys with various gross compositions. The alloy containing 25 a/o Zn gave the diffraction peaks corresponding to the solid solution of (Cu + Zn) (fcc, a = 3.63 Å) and the intermetallic compound Cu<sub>61</sub>Zn<sub>39</sub> (orthorhombic)<sup>32</sup> (Fig. 6b), which is not recognized



Fig. 5. Onset potentials,  $E_{onset}$  for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation as a function of Cu-Sn alloy compositions. Region A) (Cu + Sn) solid solution; B) Cu<sub>5,6</sub>Sn; C) Cu<sub>5,6</sub>Sn + Cu<sub>3</sub>Sn; and (D) Cu<sub>6</sub>Sn<sub>5</sub> + Sn.



Fig. 6. XRD patterns for the surfaces of Cu-Zn alloys with various gross compositions. Zn a/o; a) 0 (pure Cu); b) 25; c) 30; d) 50; e) 58; f) 75; g) 88; and h) 100 (pure Zn).  $\Box$ , Cu (fcc);  $\bigcirc$ , (Cu + Zn) solid solution (fcc);  $\triangle$ , Cu<sub>61</sub>Zn<sub>39</sub> (orthorhombic);  $\blacksquare$ , Cu<sub>5</sub>Zn<sub>8</sub> (cubic);  $\bullet$ , CuZn<sub>2</sub> (cubic); and  $\blacktriangle$ , Zn (hcp).

in the alloy phase diagram.<sup>28</sup> The  $Cu_{61}Zn_{39}$  disappeared at Zn content of 30 a/o (Fig. 6c), and a single phase of the solid solution with the lattice constant of 3.69 Å was identified.

The intermetallic compound  $Cu_5Zn_8$  (cubic,<sup>33</sup> Zn a/o = 61.5) was the predominant phase for the alloy with 50 a/o of Zn (Fig. 6d). For a Zn content between 58 and 75 a/o (Fig. 6e, f), diffraction peaks assigned to  $CuZn_2$  (cubic)<sup>34</sup> grew accompanied with a decrease of those for  $Cu_5Zn_8$ , although the  $CuZn_2$  is not reported in the alloy phase diagram.<sup>28</sup> Although two small but distinct peaks ( $2\theta = 23^{\circ}$  and  $31^{\circ}$ ) in Fig. 6e could not be assigned to any crystalline phases in the alloy phase diagram<sup>28</sup> or JCPDS data, they may be ascribed to a superlattice structure of cubic  $Cu_5Zn_8$ . Pure Zn (hcp)<sup>35</sup> was produced besides the  $CuZn_2$  at Zn content more than 88 a/o.

Effects of crystal structures of Cu-Zn alloys on the selectivity, reversibility, and reactivity for the electroreduction of  $CO_2$ .—Figure 7 shows the dependence of the faradaic efficiency  $\epsilon$  for the reduction products at -1.50 V vs. SHE on the gross composition of Cu-Zn alloys. The crystalline structures determined above are shown also as regions A to E in this figure. Due to a cooperative action between Cu and Zn, considerably high  $\epsilon$  [CO] of ca. 80% was obtained for the alloy with Zn a/o = 58% (region D). Snce  $\epsilon$  [CO] sharply increases in region C (Cu<sub>5</sub>Zn<sub>8</sub>) and decreases with increase in the amount of CuZn<sub>2</sub>, the most active crystalline phase for CO production must be Cu<sub>5</sub>Zn<sub>8</sub> when polarized at ca. -1.50 V. A diluting action by Zn was observed for HCOOH production.

As shown in Fig. 8, the effects of the crystalline structure on the reactivity (partial current density) for CO and



Fig. 7. Effect of Cu-Zn alloy composition on the faradaic efficiencies for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation at -1.50 V vs. SHE. Region A) (Cu + Zn) solid solution + Cu<sub>61</sub>Zn<sub>39</sub>; B) (Cu + Zn) solid solution; C) Cu<sub>5</sub>Zn<sub>8</sub>; D) Cu<sub>5</sub>Zn<sub>8</sub> + CuZn<sub>2</sub>; and E) CuZn<sub>2</sub> + Zn.

HCOOH production at -1.50 V are the same as those on the selectivity. The maximum partial current density for CO production on the Cu<sub>5</sub>Zn<sub>8</sub> (Zn a/o = 58) was about 1.0 mA/cm<sup>2</sup>, which is about one order of magnitude higher than that for pure Cu or pure Zn at the same potential.

Figure 9 shows the relationship between the onset potential  $E_{\text{onset}}$  and the composition of Cu-Zn alloys. Both  $E_{\text{onset}}$ [CO] and  $E_{\text{onset}}$  [HCOOH] shifted to negative potential with increasing Zn content and leveled off at almost same potential as for pure Zn. Thus, the reversibilities for CO and HCOOH production became worse than those for pure Cu and seemed to be controlled by the property of Zn. It is therefore clarified that the intermetallic compound Cu<sub>5</sub>Zn<sub>8</sub> (Zn a/o = 58) exhibits excellent selectivity and reactivity



Fig. 8. Plots of the partial current densities,  $j_{partr}$  for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation at -1.50 V vs. SHE as a function of Cu-Zn alloy compositions. Region A) (Cu + Zn) solid solution + Cu<sub>61</sub>Zn<sub>39</sub>; B) (Cu + Zn) solid solution; C) Cu<sub>5</sub>Zn<sub>8</sub>; D) Cu<sub>5</sub>Zn<sub>8</sub> + CuZn<sub>2</sub>; and E) CuZn<sub>2</sub> + Zn.



Fig. 9. Onset potentials,  $E_{onset}$ , for CO ( $\bullet$ ) and HCOOH ( $\blacktriangle$ ) formation as a function of Cu-Zn alloy compositions. Region A) (Cu + Zn) solid solution + Cu<sub>61</sub>Zn<sub>39</sub>; B) (Cu + Zn) solid solution; C) Cu<sub>5</sub>Zn<sub>8</sub>; D) Cu<sub>5</sub>Zn<sub>8</sub> + CuZn<sub>2</sub>; and E) CuZn<sub>2</sub> + Zn.

for CO production but requires a large overpotential of ca. 1 V owing to a low reversibility for the reaction.

## Conclusion

The electrocatalytic properties of alloys for CO<sub>2</sub> reduction can be controlled by the combination of alloy component, the microcrystalline structure on the surface and the electrolysis potential. Especially, the importance of the microcrystalline structures on the alloy surface was demonstrated for the Cu-Sn and Cu-Zn alloys. Both the selectivity and reactivity for CO production were greatly enhanced on the Cu<sub>5</sub>Zn<sub>8</sub> and Cu<sub>5.6</sub>Sn crystals although their reversibility was not good. The evaluation of electrocatalytic activities on the well-defined surfaces of alloys is very important, and better performance may be achieved by an enrichment of the catalytically effective crystalline phase on the electrode surface. Detailed studies on other alloy systems are currently in progress.

#### Acknowledgment

This work was supported in part by a Grant-in-Aid on Priority-Area Research No. 04241213 from the Ministry of Education, Science and Culture, Japan.

Manuscript submitted Dec. 6, 1993; revised manuscript received March 30, 1994.

Yamanashi University assisted in meeting the publication costs of this article.

#### REFERENCES

1. K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, Electrochim. Acta, 16, 1593 (1971).

- 2. P. G. Russell, N. Kovac, S. Srinivasan, and M. Steinberg, This Journal, 124, 1329 (1977).
- Y. Hori and S. Suzuki, Bull. Chem. Soc. Japan, 55, 660 (1982).
- 4. Y. Hori, K. Kikuchi, and S. Suzuki, Chem. Lett., 1695 (1985).
- 5. S. Ikeda, T. Takagi, and K. Ito, Bull. Chem. Soc. Japan, **60,** 2517 (1987).
- 6. S. Kapusta and N. Hackerman, This Journal, 130, 607  $(19\hat{8}3).$
- 7. Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, Chem. Lett., 897 (1986).
- 8. R. L. Cook, R. C. MacDuff, and A. F. Sammells, This Journal, 134, 2375 (1987); 135, 1320 (1988)
- 9. M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, and T. Sakata, ibid., 137, 1772 (1990).
- 10. K. W. Frese, Jr., and S. Leach, ibid., 132, 259 (1985).
- A. Bandi, *ibid.*, **137**, 2157 (1990); A. Bandi and H. M. Kühne, *ibid.*, **139**, 1605 (1992).
- 12. Y. Nakato, Chemistry and Chemical Industry (The Chem. Soc. Japan), **46**, 1417 (1993). 13. D. P. Summers, S. Leach, and K. W. Frese, Jr., *J. Elec*-
- troanal. Chem., 205, 219 (1986).
- 14. K. W. Frese, Jr., This Journal, 138, 3338 (1991).
- 15. N. Furuya, K. Matsui, and S. Motoo, Denki Kagaku, 55, 787 (1987); ibid., 56, 980 (1988); N. Furuya and K. Matsui, This Journal, 271, 181 (1989).
- 16. R. L. Cook, R. C. MacDuff, and A. F. Sammells, ibid., 137, 607 (1990); M. Schwartz, R. L. Cook, V. M. Kehoe, R. C. MacDuff, J. Patel, and A. F. Sammells, ibid., 140, 614 (1993)
- 17. M. N. Mahmood, D. Masheder, and C. J. Harty, J. Appl. Electrochem., 17, 1159 (1987); ibid., 17, 1223 (1987).
- 18. M. Watanabe, M. Shibata, A. Katoh, M. Azuma, and T. Sakata, Denki Kagaku, 59, 508 (1991).
- 19. M. Watanabe, M. Shibata, A. Katoh, M. Azuma, and T. Sakata, J. Electroanal. Chem., 305, 319 (1991)
- 20. M. Watanabe, M. Shibata, A. Katoh, M. Azuma, and T. Sakata, This Journal, 138, 3382 (1991).
- 21. A. Katoh, M. Shibata, and M. Watanabe, Denki Kagaku, 61, 805 (1993).
- 22. P. M. Vyacheslavov, New Electrochemical Coatings (in Russian 1972), translated into Japanese, Japan-Soviet News Agency (1980).
- 23. T. Kase, Electroplating Handbook for Engineers, Sangyo Tosyo (Tokyo, 1960).
- 24. Handbook of Electrochemistry, 4th ed., Electrochem. Soc. Japan, Maruzen, Tokyo (1985).
- M. Watanabe and S. Motoo, J. Electroanal. Chem., 60, 275 (1975); ibid., 98, 203 (1979); ibid., 110, 103 (1980); ibid., 187, 161 (1985); ibid., 194, 275 (1985); ibid., 202, 125 (1986); *ibid.*, **263**, 97 (1989). 26. JCPDS International Center for Diffraction Data,
- No. 4-836.
- 27. Ibid., No. 31-487.
- 28. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York (1958).
- 29. JCPDS International Center for Diffraction Data, No. 1-1240
- 30. Ibid., No. 4-673.
- 31. Ibid., No. 2-713.
- 32. Ibid., No. 19-179.
- 33. Ibid., No. 25-1228. 34. Ibid., No. 39-400.
- 35. Ibid., No. 4-831.