SHORT COMMUNICATION

ELECTROLYTIC PREPARATION AND CHARACTERIZATION OF Ni–Fe–Mo ALLOYS: CATHODE MATERIALS FOR ALKALINE WATER ELECTROLYSIS

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SUMMARY

Ni–Fe–Mo alloys have been electroplated by using suitable bath solution and plating conditions. SEM and XRD analysis showed that the deposited alloys are partially amorphous. Polarization studies indicated a dependence of the hydrogen evolution mechanism on temperature and current density. The alloys exhibited sufficiently low hydrogen over voltage even on prolonged electrolysis in 30% KOH. Electrokinetic parameters are evaluated for hydrogen evolution reaction on Ni–Fe–Mo alloys. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: Ni–Fe–Mo alloys; cathode materials; anomalous codeposition; hydrogen overvoltage; water electrolysis; Tafel slope

1. INTRODUCTION

Alkaline water electrolysis has become a prominent method of producing hydrogen for H₂–O₂ fuel cells. Extensive work has been done on this process (Bockris and Srinivasan, 1969; Trasatti, 1990; Tilak *et al.*, 1981). Ni–Zn porous electrodes show low hydrogen overvoltage and their catalytic activity depends on the morphology of the surface and the design of catalytic particles (Santos *et al.*, 1992; Wendt, 1994). Catalytic activity is enhanced by adding oxides of iron and cobalt to the electrolytic cell (Schmidt and Wendt, 1994). Electrolytically prepared Ni–P (*P* ~ 3%) electrodes are used as a cathode material for alkaline water electrolysis (Ivo, 1995). Surface modification by foreign elements have been shown to enhance the catalytic activity (Yoshida and Morimoto, 1994). Sufficiently low hydrogen overvoltage has been observed on Fe–Co–W alloys during alkaline water electrolysis (Ramesh *et al.*, 1998). Despite many developments in fuel cell technology over the past four and a half decades, the basic understanding of the technology is still in its infancy. The coated materials lose their catalytic activities during operation because of the surface contamination of solution components. Hence, it is aimed to develop ternary alloys of Ni, Fe and Mo by electroplating techniques with the idea of using them as effective cathode materials for production of hydrogen for H₂–O₂ fuel cells.

2. EXPERIMENTAL

The deposition of alloys was carried out on copper foils (99.9%). The copper surface was mechanically polished by 4/0 emery paper with ethanol as lubricant and electropolished in 60% (v/v) H₃PO₄ at a cell

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potential of 1.2 V for 30 min with a large copper foil as cathode (Jacquet, 1949). The surface was washed with 10% H_3PO_4 solution and finally rinsed with distilled water and used for deposition. Constant temperature and pH were maintained during each experiment. Polarization experiments were carried out under galvanostatic condition by using a potentiostat/galvanostat (EG & G PAR 273A). A saturated calomel electrode and a platinum flag were used as reference and counter electrodes, respectively. Deposition potentials were recorded at regular intervals of time using a digital voltmeter with an accuracy of ± 2 mV.

The deposited samples were stripped in HNO_3 solution (1:3) and the composition of the coatings was obtained by using atomic absorption spectrophotometer (Varian Spectra AA320). Surface and structural characteristics of the samples were obtained by using scanning electron microscopic (Jeol JSM) and X-ray diffraction (Philips PW 1142) techniques respectively. Experiments were repeated to ensure reproducibility.

3. RESULTS AND DISCUSSION

Many organic compounds were advantageously used as complexing agents in the plating bath solution. Triammonium citrate (TAC) was found to be more suitable to complex metal ions in alkaline condition. Detailed studies were carried out by varying bath composition and plating conditions and a workable procedure (Table 1) was developed to get good quality deposits with appreciable catalytic activity.

3.1. Plating variables

Experiments were carried out to study the effect of plating variables, viz., metals ion ratio in the bath solution, pH, cd, temperature and the concentration of the complexing agents on the composition of the alloy. The pH of the bath solution was maintained as constant (pH 9) by using NaOH and boric acid.

Ni-Fe-Mo alloys were electroplated at a current density of 1.5 A dm^{-2} to a constant thickness ($20 \mu\text{m}$) at 303 K and pH 9 from a bath solution containing various metal ratios in the presence of 0.32 mol l^{-1} TAC. Under these plating conditions, preferential deposition of nickel over iron was noticed (Figure 1). TAC as a complexing agent reduced the anomalous co-deposition of iron over nickel (Brenner, 1969).

Experiments were also carried out at different cds using bath solution containing definite metal ion ratio and 0.32 mol l^{-1} TAC at 303 K and pH 9. The % of nickel in the deposit increased, whereas iron and molybdenum contents decreased with increase in cd (Figure 1). The alloys were electroplated at various temperatures (303–343 K) keeping other variables as constant. There was no significant change in the alloy composition with increase in temperature. The current efficiency was found to increase with increase in pH and temperature, but decreased with increase in current density.

Table 1. Bath composition and operating conditions

Bath composition	mol dm^{-3}	Operating conditions	
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.28	pH	9.0
FAS	0.08	Temperature	303 K
Triammonium citrate	0.32	Current density	15 mA cm^{-2}
Ammonium chloride	0.30	Agitation	180 rpm
Boric acid	0.28	Cathode	Copper foil
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.08	Anode	SS 316
		Time	60 min

Figure 1. Dependence of alloy composition on bath composition and current density

Figure 2. SEM photograph of FeNiMo (24:64:12) alloy obtained at 303 K

3.2. Surface and structural analysis

Ni-Fe-Mo alloys electroplated under various plating conditions were examined under a metallurgical microscope. In a range of temperature, pH and cd studied, the alloy deposits appeared to be amorphous and mat in texture. SEM photograph of the alloy obtained at 303 K for 60 min at 1.5 A dm^{-2} is shown in Figure 2. The alloy deposits obtained under optimum conditions (Table 1) were subjected to X-ray

diffraction analysis to characterize the phases present. The X-ray data is given in Table 2. These results show the presence of multiphases in the deposit. However, the peak intensities were slightly broadened indicating partial amorphous nature of the deposit.

3.3. Catalytic activity

Thirty percent KOH (wt%) is extensively used in electrolytic cell to produce hydrogen for H_2 - O_2 fuel cell (Dobos, 1975). To understand the electrocatalytic activities of the deposited alloys for hydrogen evolution reaction, detailed galvanostatic polarization experiments were carried out on electroplated alloys having different compositions in 30% KOH at different temperatures (303–343 K). Among all the alloys deposited, only Fe–Ni–Mo (24:64:12) with high nickel content was found to be a better catalyst for the hydrogen evolution reaction. Hence, the alloy with the above composition was used for detailed investigation. Some of the results obtained with Ni–Fe–Mo alloys are shown in Figure 3. The Tafel diagram consists of two Tafel regions with different reaction mechanisms for hydrogen evolution reaction in the cd range chosen. Electrochemical parameters were evaluated and summarized in Table 3.

Table 2. XRD data of Fe–Ni–Mo codeposits

Observed <i>d</i> (Å)	Std ASTM <i>d</i> (Å)	Phase
2·083	2·086	Cu(110)
2·002	2·000	Fe(100)
1·983	1·980	Ni(111)
1·826	1·822	Fe(104)
1·639	1·640	Fe(201)
1·428	1·428	MoO ₃ (110)
1·232	1·232	Fe(103)
1·012	1·016	Ni(302)

Co K_α radiation

Figure 3. Tafel plots obtained on FeNiMo (24:64:12) alloy deposit in 30% KOH at various temperatures

Table 3. Electrochemical parameters for hydrogen evolution reaction on Fe–Ni–Mo (24:64:12) codeposits at different temperatures

Temp. (K)	β_{low} (mV deg ⁻¹)	β_{high} (mV deg ⁻¹)	α_{low}	α_{high}	i_0 low (mA cm ⁻²)	i_0 high (mA cm ⁻²)	η_{100} (mV)
303	43	163	1.39	0.37	1.0	11.2	148
323	43	163	1.49	0.40	1.15	13.4	126
343	44	164	1.54	0.43	1.90	15.2	104

Figure 4. Arrhenius plots under (a) low (b) high polarization region with FeNiMo (24:64:12) alloy in 30% KOH

The exchange current density (i_0) value for hydrogen evolution with Ni–Fe–Mo alloy was much higher compared to the values obtained on Ni or Ni–Zn or Ni–Fe–Zn (Conway *et al.*, 1987) alloys. The high values of i_0 indicated increased surface activity of the electrodes for hydrogen evolution reaction. The observed two Tafel slopes in the present system did not agree with Ni–Zn or Ni–Co–Zn alloys. However, they agreed very well with the system developed by Arul Raj and Vasu (1990).

Temperature has slight effect on Tafel slope (Table 3). This fact contradicts the classical theories on the subject and is accounted by Conway *et al.* (1989). However, the transfer coefficient (α) varied with temperature. The values of activation energy, (E_a) for hydrogen evolution reaction were evaluated from the Arrhenius plots (Figure 4) for both low and high Tafel regions.

Continuous operation test up to 40 h were conducted using the deposited alloys in 30% KOH at 343 K at a cd of 10 A dm⁻² (Figure 5). The electrode exhibited almost steady overpotential of –104 mV upto 40 h which is much lower than the values observed with mild steel (–380 mV) or Ni–Zn or Ni–Co–Zn alloys. This indicates the stability of cathode material for prolonged electrolysis for electrolytic production of hydrogen.

4. CONCLUSION

Triammonium citrate (TAC) in the plating bath solution has reduced the extent of anomalous codeposition of iron over nickel. Bath composition and plating conditions were optimized to get Ni–Fe–Mo alloys with

Figure 5. Variation of overpotential on FeNiMo alloy (24:64:12) with time in 30% KOH at 100 mA cm^{-2} and 343 K

good catalytic activity for cathodic evolution of hydrogen from alkaline water electrolysis. The alloys were partially amorphous and exhibit sufficiently low hydrogen overpotential in alkaline solution. The mechanism of hydrogen evolution reaction depends on the current density range investigated.

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