JOURNAL OF MATERIALS SCIENCE **38** (2003) 275–278

Electrocatalytic properties of mechanically alloyed Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo alloy powders

ELSA M. ARCE-ESTRADA, VICTOR M. LOPEZ-HIRATA, LOBSANG MARTINEZ-LOPEZ, HECTOR J. DORANTES-ROSALES, MARIBEL L. SAUCEDO-MUÑOZ, FELIPE HERNÁNDEZ-SANTIAGO
Instituto Politecnico Nacional (ESIQIE), Apartado Postal 75-876, Mexico, D.F. 07300, Mexico
E-mail: elsa.arce@eudoramail.com

Mechanically alloyed Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo (nominal compositions) alloy powders were produced by milling of pure elemental powders. Mechanically alloyed powders were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. MA powder specimens were tested electrollitically in a 30% KOH aqueous solution at 298 K. X-ray diffraction analysis and transmission electron microscopy of milled powders showed the presence of two phases, an fcc solid solution and intermetallic compounds of Ni or Co with Mo. These phases showed a nanometric size. The linear sweep voltammograms confirmed also the presence of two phases in both mechanically alloyed alloy powders. The Co-20wt%Ni-10wt%Mo alloy powders showed the best electrocatalytic activity for hydrogen evolution reaction.

1. Introduction

One of the most interesting properties of nanocrystalline materials is their catalytic activity because of the large amount of active sites for catalysis in this type of materials [1].

In the last two decades, there has been a great interest in developing new electrocatalytic materials, which permit to obtain catalytic properties similar to those of platinum. For example, Ni–Mo, Ni–Zn, Ni–Co, Ni–Fe and Ni–Cr alloy were obtained by means of electrodeposition and then tested electrollitically in a 30% KOH aqueous solution at 70°C [2]. Ni–Mo alloys showed the best catalytic activity for the hydrogen evolution reaction (HER). Ni–Mo alloys were also prepared by mechanical alloying (MA) and evaluated at the same above conditions [3]. The results of this study showed a high catalytic activity for this MA Ni–Mo alloys.

Arul *et al.* [4] determined the electrocatalytic activity for different ternary Ni-base alloys, fabricated by electrodeposition, in HER. The electrocatalytic activity of these alloys decreased in the following order: Ni–Mo–Fe, Ni–Mo–Cu, Ni–Mo–Zn, Ni–Mo–Co, Ni–Mo–W and Ni–Mo–Cr.

Other works have also shown that Co–O, Co–Ni–Mo and Ni–Co–Mo alloys, obtained by electrodeposition, exhibited good electrocatalytic properties in HER [5, 6].

The goals of this work are to produce MA Co–Ni–Mo alloys and to evaluate their catalytic properties for the hydrogen evolution reaction.

2. Experimental procedure

Powder mixtures of the following compositions: Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo were prepared using pure elemental powders. These compositions were selected on the basis of results reported for electrodeposited alloys [5, 6].

These mixtures were milled in a low-energy ball mill of austenitic stainless steel under an argon gas atmosphere. A ball to powder weight ratio of 36 was used. Milling process was conducted at 100 rpm using austenitic stainless steel balls of about 12 mm.

Milled powders were characterized with an X-ray diffractometer using copper Kα radiation, scanning electron microscope and transmission electron microscope. These were also analyzed chemically by atomic absorption technique.

To study the electrocatalytic activity of MA powders, synthetic graphite powder, −200 mesh, high purity, 99.999%, was used to prepare the working electrode by mixing a total of 0.8 g graphite powder with 0.2 g of MA alloy powder in a agate mortar. A total of 0.8 ml silicon oil was added to the resulting powder and carefully mixed to obtain a homogeneous paste. The paste was placed in a 7 cm long, plastic tube (0.2 cm inner diameter); equipped with a plunger to eliminate reached paste (approximately 0.5 cm). The plunge manually ejected reacted paste onto an emery paper to renew the surface for each experiment.

A platinum wire, silver soldered to a copper wire, provided the electrical contact to the graphite paste. A pure platinum rod was used as a counter electrode and a saturated calomel electrode (SCE) as a reference. The potential given in the work refer to the SCE scale. Tests were carried out using 30% KOH aqueous solution as the electrolyte at room temperature. Pure milled nickel, molybdenum and cobalt powders were also prepared in the same way as indicated above and tested electrollitically for comparison with MA alloy powders.

A Pyrex electrochemical cell, designed to work at room temperature and under an inert atmosphere, was used. The cell employed the conventional three-electrode systems. The voltammetric response was obtained using a potentiostat coupled to a personal computer.

Calculation of current densities passing through the CPE-mechanical alloy electrodes requires estimation of the surface area of the electrode. However, several characteristics of the CPE-electroactive species make estimation of the geometric area unreliable, A more realistic estimation of surface area is the evaluation of the cross-sectional area of MA alloy particles, which depends on the weights of MA alloy and carbon added. The mechanical alloy carbon paste electrode in this work was completely homogeneous so that geometric areas calculated from the mechanical alloy carbon paste in contact with the electrolyte are directly proportional to the real active area. The current densities were calculated based on this geometric area (3.14×10^{-2} cm^2).

3. Results and discussion

3.1. Structural and microstructural characterization of MA alloy powders

The chemical composition of the MA alloy powders and milled pure powders is shown in Table I. The presence of a small iron content can be observed for all milled powders. Fig. 1a and b show the X-ray diffractogram of the MA alloy powders, nominally Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo, respectively. An fcc solid solution was identified to be present in both MA alloy powders Additionally, Co_3Mo and Ni_3Mo intermetallic compounds were identified to be present in the MA Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo alloy powders, respectively. The presence of these phases seems to be in agreement with the predicted phases, (Co–Ni) solid solution and intermetallic compounds of either Ni or Co with Mo, for these compositions in the equilibrium Co-Ni-Mo phase diagram [7]. The DF-TEM micrographs of the MA Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo alloy powders are shown in Fig. 2a and b, respectively, along with its corresponding electron diffraction patterns. Both micrographs indicated the presence of equiaxial grains with a size between 20 and 50 nm. The ring electron diffraction pattern for both alloys also confirmed the formation of an fcc solid solution. The presence of the intermetallic compound Ni_3Mo was detected in the MA Co-70wt%Ni-10wt%Mo alloy powders.

TABLE I Chemical composition for tested powders

Material	Ni (wt%)	Co (wt%)	Mo (wt%)	Fe (wt%)
Ni	99.37	—	—	0.63
Co	0.13	99.10	—	0.77
Mo	—	—	99.57	0.43
Co-70Ni-10Mo	61.03	29.15	6.02	0.82
Co-20Ni-10Mo	17.51	75.90	5.99	0.60

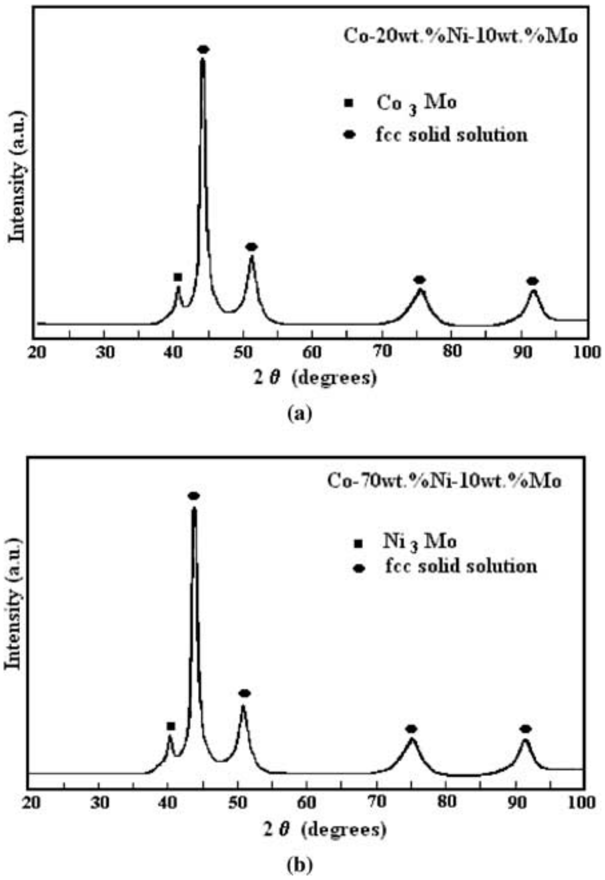

Figure 1 XRD pattern of MA (a) Co-20wt%Ni-10wt%Mo and (b) Co-70wt%Ni-10wt%Mo alloy powders. Cu Kα radiation ($\lambda =$ 0.154051 nm).

3.2. Electrochemical behavior of MA alloy powders

The corresponding linear sweep voltammogram (LSV) of the MA alloy powders, nominally Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo, tested in a 30% KOH solution at 298 K, are shown in Fig. 3a and b, respectively. These voltammograms also include the anodic curve for pure Co, Ni and Mo elements. Jovic *et al.* [8] found that only a dissolution peak is present in the LSV of alloys forming one solid solution. These authors also observed that the LSV of an alloy containing intermetallic compounds shows different dissolution peaks, corresponding to each intermetallic compound, located at potentials between that of the dissolution peaks for the pure components.

Fig 3a shows that the voltamperometric response of the MA Co-20wt%Ni-10wt%Mo alloy powders does not correspond to the addition of the voltamperometric responses corresponding to the pure components. The anodic curve for the MA alloy shows clearly the presence of three dissolution peaks, A_1, A_2 and A_3. The anodic peaks A_1 and A_2 are located between the

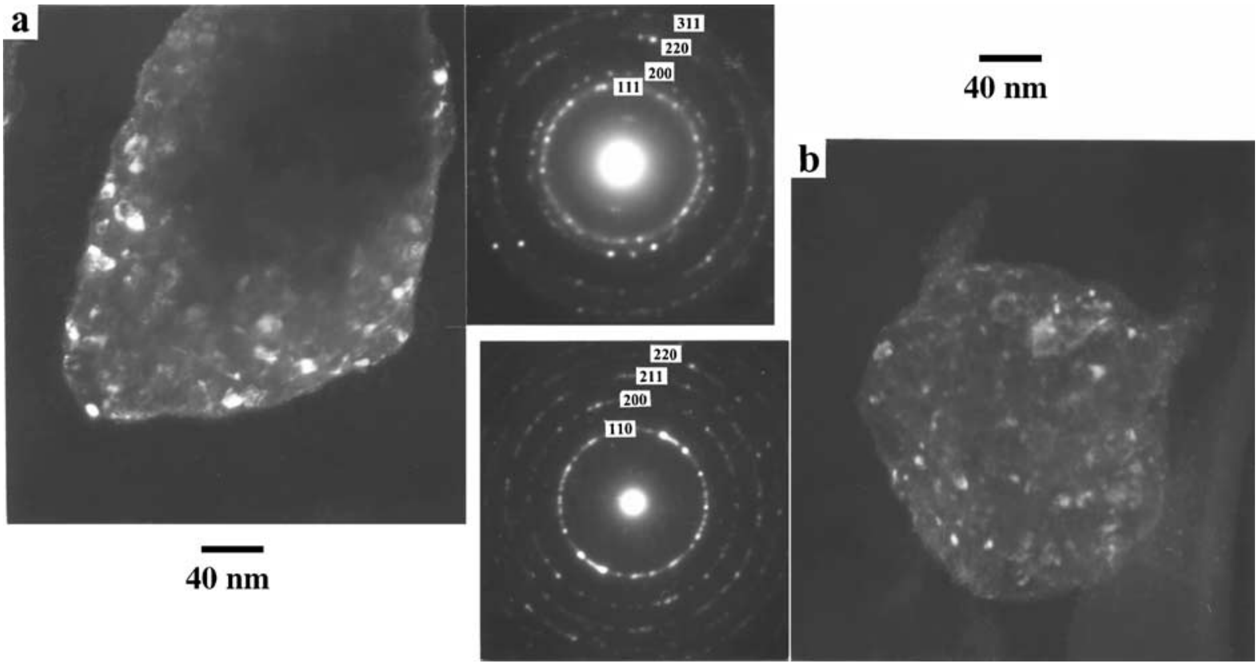

Figure 2 BF-MET micrographs of MA (a) Co-70wt%Ni-10wt%Mo and (b) Co-70wt%Ni-10wt%Mo alloy powders with its corresponding electron diffraction pattern.

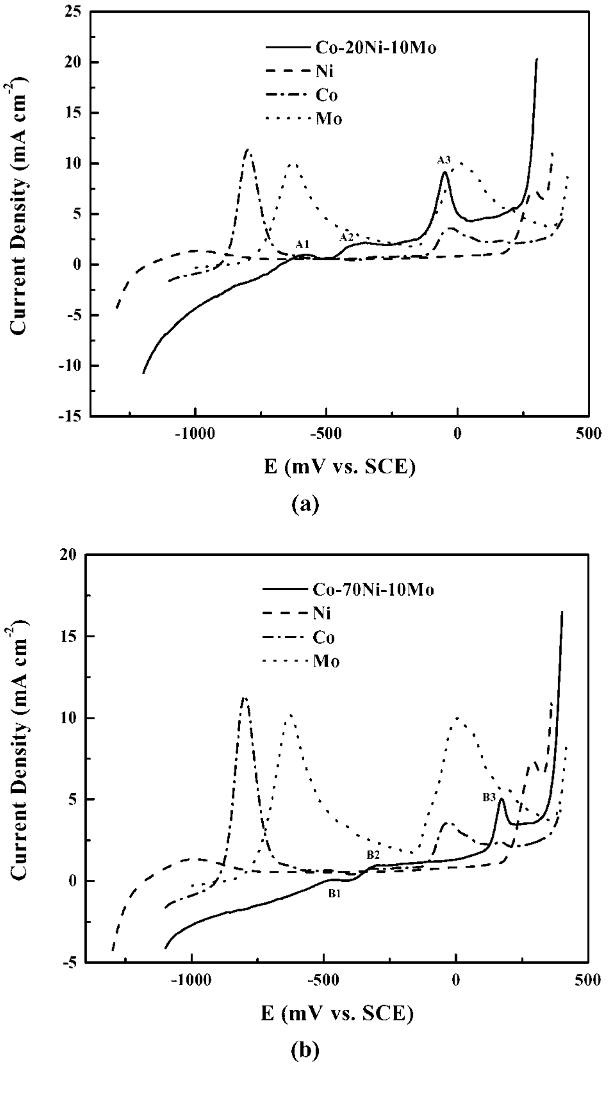

Figure 3 LSV of MA (a) Co-20wt%Ni-10wt%Mo and (b) Co-70wt%Ni-10wt%Mo alloy powders.

dissolution peak of pure Co and Mo. This suggests that these peaks may correspond to the dissolution of an intermetallic compound between Co and Mo. The anodic peak A_3 is shifted to a more positive potential than that of of pure Co and Mo, and located at a potential slightly more negative than that of pure Ni. We believed that this dissolution peak is related to the dissolution of the fcc solid solution.

In the case of LSV for MA Co-70wt%Ni-10wt%Mo alloy powders, three anodic peaks are again observed, B_1, B_2 and B_3. These dissolution peaks seem to be similar to those found in the LSV of MA Co-20wt%Ni-10wt%Mo alloy powders, but with a lower current density. The anodic peaks B_1 and B_2 are located at a more positive potential than that of peaks A_1 and A_2. That is closer to the Ni dissolution peak. Thus, they seem to be associated with the dissolution of intermetallic compound between Ni and Mo. The anodic peak B_3 might be also associated with the dissolution of the fcc solid solution.

Table II shows the values of current density for the hydrogen evolution reaction (HER) determined for the pure metal Co, Ni and Mo, as well as for the MA Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo

TABLE II Current densities of HER for tested powders

Material	i (mA cm^{-2}) $E = -1.3$ V	i (mA cm^{-2}) $E = -1.4$ V	i (mA cm^{-2}) $E = -1.5$ V	i (mA cm^{-2}) $E = -1.6$ V
Ni	6.36	11.60	16.63	23.06
Co	1.79	3.46	14.83	36.55
Mo	2.08	5.48	11.03	31.70
Co-70Ni-10Mo	7.17	18.54	28.49	58.70
Co-20Ni-10Mo	5.06	12.76	38.20	73.69

alloy powders at potentials of −1.3, −1.4, −1.5 and −1.6 V, after testing in a in a 30% KOH solution at 298 K. It is evident from these data that the highest electrocatalytic activity for HER at −1.6 V corresponds to the Co-20wt%Ni-10wt%Mo alloy powders, since the evolution of hydrogen increases as the current density increases for a given potential.

Fan *et al.* [5, 6] produced Ni-13.9Co-13.2Mo and Co-28.8Ni-14Mo alloys by the electrodeposition technique and studied their electrocatalytic activity for HER in a 30% KOH solution at 298 K. They determined a current density of about 100 mA cm^{-2} at 1.297 V for the Ni-base alloy and at −1.315 V for the Co-base alloy. On the other hand, the current density for the MA Co-20wt%Ni-10wt%Mo alloy powders was determined to be about 7.128 at −1.3 V. This large difference in current density can be attributed to the difficulty to determine precisely the area for the MA powder specimens.

4. Conclusions

An electrochemical and structural characterizations of the MA alloy powders, nominally Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo, was carried out and the following conclusions were drawn:

1. The MA Co-20wt%Ni-10wt%Mo and Co-70wt%Ni-10wt%Mo alloy powders showed the presence of two phases, an fcc solid solution and an intermetallic compound Co_3Mo and Ni_3Mo, respectively, with a nanometric size.
2. The anodic peaks of the linear sweep voltammograms confirmed the presence of two phases in both MA alloy powders.
3. The best electrocatalytic activity for the hydrogen evolution reaction was observed in the MA Co-20wt%Ni-10wt%Mo alloy powders.

Acknowledgements

The authors wish to thank the financial support from CEGEPI-IPN and CONACYT.

References

1. B. L. HUANG and J. E. LAVERNIA, *J. Mat. Synth. Process* **3** (1995) 1.
2. D. E. BROWN, M. N. MAHMOOD, M. C. MAN and A. K. TURNER, *Electrochim. Acta* **29** (1984) 1551.
3. R. I. ARUL and K. I. VASU, *J. Appl. Electrochem.* **20** (1990) 32.
4. *Idem.*, *ibid.* **22** (1992) 471.
5. C. FAN, D. L. PIRON and P. PARADIS, *Electrochim Acta* **39** (1994) 2715.
6. *Idem.*, *J. Electrochem. Soc.* **141** (1994) 382.
7. ASM, in ”Alloy Phase Diagrams” Vol. 3 (ASM, Material Park, Ohio, 1992) p. 2.
8. V. D. JOVIC, R. M. ZENILOVIC, A. R. DESPIC and J. S. STEVANOVIC, *J. Appl. Electrochem.* **18** (1988) 511.

Received 31 December 2001
and accepted 2 July 2002