ELSEVIER

Journal of Alloys and Compounds 434–435 (2007) 522–524

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Oxygen reduction reaction on cobalt–nickel alloys prepared by mechanical alloying

M.A. García-Contreras [a,b], S.M. Fernández-Valverde [a], J.R. Vargas-García [b,*]

[a] *Instituto Nacional de Investigaciones Nucleares, Depto. de Química, Apdo. Postal 18-1027 Col. Escandon, C.P. 11801 México D.F., Mexico*
[b] *Instituto Politécnico Nacional, Depto. de Ing. Metalúrgica, 07300 México D.F., Mexico*

Available online 27 September 2006

Abstract

Mechanical alloying technique was used to prepare several Co–Ni alloys in a high-energy SPEX 8000 mill. The initial ratios of elemental Co–Ni powders were 30:70, 40:60, 50:50, 60:40 and 70:30 wt.%. Elemental cobalt and nickel powders were milled separately during 20 h as a reference. XRD results indicated that crystalline solid solutions were achieved after 5 h of milling. TEM observations revealed that mechanical alloys consist of agglomerated fine particles of about 10 nm in size. Electrochemical measurements showed that the Co–Ni 30:70 wt.%, in particular, exhibited the highest current density for the oxygen reduction reaction (ORR) via four electrons.

Keywords: Nanostructured materials; Mechanical alloying; Electrochemical reactions; X-ray diffraction

1. Introduction

Mechanical alloying is an alternative process useful to prepare electrocatalysts. This process was developed in the 1970s [1] and has been shown to be useful to prepare nanometric materials, so, it has been utilized to produce alloys for hydrogen storage. Low temperature fuel cells require electrocatalysts to accelerate cathodic and anodic reactions, oxygen reduction and hydrogen oxidation, respectively. Electrodes for oxygen reduction have been prepared with transition metals by different techniques. Electrocatalytic activity of these materials strongly depends on their morphology, surface area and structure, which in turn depend on the preparation methods. Cobalt and nickel, being transition elements, with their electronic layer *d* incomplete, have shown good electrocatalytic properties for the oxygen reduction reaction (ORR) when combined with platinum [2–7] or as macrocycles [8–10]. Recently, there have been proposals of cobalt combined with Pd, Ag, Ni or Au for the ORR [11]. The purpose of this work is to explore the mechanical alloying technique to prepare cobalt–nickel alloys and to evaluate their performance for the oxygen reduction reaction in alkaline media.

2. Experimental

2.1. Mechanical alloying

Mechanical alloying was performed using commercial cobalt and nickel powders supplied by Merck, in a SPEX 8000 mill. An argon atmosphere was used to avoid oxidation and methanol (1 ml) was employed as the control agent process. Under these conditions, cobalt and nickel powders were milled for 2, 5, 10, 15 and 20 h. Cobalt–nickel alloys were prepared varying the composition from 30 to 70 wt.% of cobalt. Elemental cobalt and nickel powders were milled separately as a reference. The ball to powder weight ratio was about 10:1. Evolution of solid solutions was followed by X-ray diffraction (XRD) using a diffractometer SIEMENS D5000 with Cu Kα radiation. Morphology and particle size were analysed using a JEOL JSM-6300 scanning and a JEOL JEM 2000 FXII transmission electron microscopes, respectively. Chemical composition of alloys was investigated by EDS.

2.2. Electrochemical measurements

Electrochemical measurements were performed employing an electrochemical cell of three electrodes coupled to a Potentiostat/Galvanostat EG&G Model 273A. A unit for speed control (EG&G Model 636) was used in linear voltammetry measurements with a rotating disk electrode. The working electrodes consisted of Teflon cylinders as holders (1.4 cm in diameter and 1.2 cm height) having a concentric hole of 0.8 cm in diameter. The lower half of the hole was filled with a mixture paste of graphite and liquid paraffin (Aldrich), the upper half was filled with a paste consisting of Vulcan XC-72 (Cabot), liquid paraf-

* Corresponding author. Tel.: +52 55 5729 6000x55270; fax: +52 55 5729 6000x55270.
E-mail addresses: magc@nuclear.inin.mx (M.A. García-Contreras), smfv@nuclear.inin.mx (S.M. Fernández-Valverde), rvargasga@ipn.mx (J.R. Vargas-García).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.147

fin and the mechanically alloyed powders. An Hg/HgO homemade electrode was used as reference electrode and a platinum mesh as the counter electrode. The oxygen reduction reaction of mechanical alloys was investigated in a 0.5 M KOH solution at 298 K. Prior to electrochemical measurements, the electrolyte solution was deoxygenated by bubbling nitrogen during 30 min. Then, the working electrodes were cycled at 50 mV s^{-1} between 0 and 1.2 V versus NHE until reproducible cyclic voltammograms were obtained. To proceed with the ORR, oxygen was bubbled to saturate the electrolyte solution.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1 shows the typical change of the XRD pattern of Co–Ni samples 50:50 wt.% during the milling. The XRD pattern at $t = 0$ h corresponds to the mixture of the elemental cobalt and nickel powders. After milling for 2 h, reflections of hexagonal cobalt phase decrease drastically and completely disappear at 5 h. A shift in angle position to lower values is observed from 5 h of milling suggesting the formation of a cobalt–nickel fcc solid solution. A particle size of about 10–15 nm was estimated by the Scherrer equation using the (2 0 0) and (2 2 0) XRD reflections of the solid solution after milling for 20 h. Chemical analysis by EDS revealed a composition approximately of 48 wt.% Co, 48 wt.% Ni and 4 wt.% Fe. The iron contamination arouse from the steel container and balls. Fig. 2 shows the variation of the lattice parameter of Co–Ni 50:50 wt.% as a function of the milling time. The lattice parameter increases from that of pure Ni (0.3521 nm) suggesting that the fcc solid solution is being formed by incorporation of Co atoms into the Ni fcc lattice. Fig. 3 depicts the bright field TEM image of Co–Ni 50:50 wt.% after milling for 20 h. Fine agglomerated particles of about 10 nm in size can be observed consistently with the Scherrer estimation. The inset in Fig. 3 shows a typical ring diffraction pattern supporting the small particle size. Miller indexes of the diffraction spots match well with the XRD pattern shown in Fig. 1.

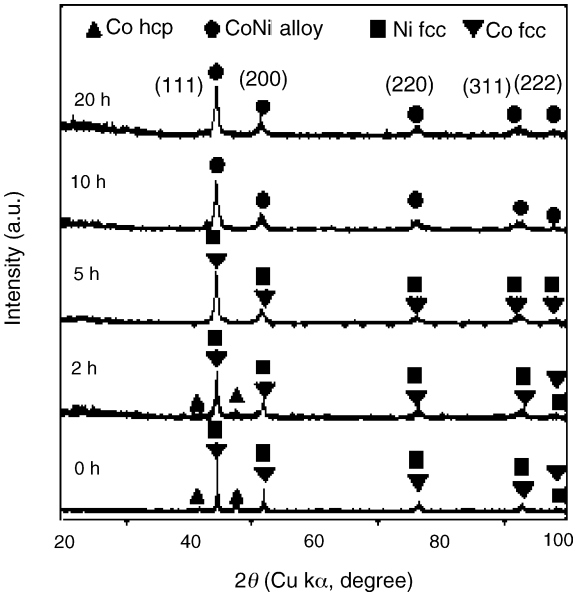

Fig. 1. Typical change of the XRD pattern of Co:Ni samples 50:50 wt.% during the milling.

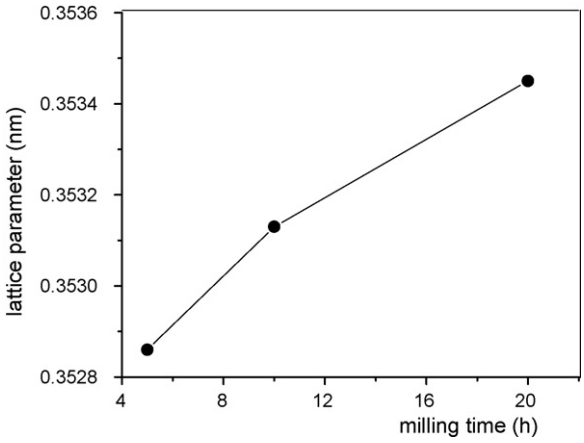

Fig. 2. Variation of the lattice parameter of Co–Ni 50:50 wt.% as a function of the milling time.

3.2. Oxygen reduction reaction (ORR)

Linear voltammograms displaying the ORR results for mechanically alloyed cobalt–nickel powders as well as those for elemental milled Co and Ni in KOH 0.5 M at 1600 rpm are shown in Fig. 4. It is noticeable that Co–Ni 30:70 wt.% exhibits the highest current density for the ORR most probably due to a synergistic effect. The composition of Co–Ni 30:70 wt.% was estimated to be about 29 wt.% Co, 67 wt.% Ni and 4% wt.% Fe. The current density was calculated by considering the effective electrode surface area [12]. Fig. 5 shows a Koutecky–Levich plot, which was derived from the linear voltammograms for the Co–Ni 30:70 wt.% after milling for 20 h. Straight lines marked with symbols represent experimental data, whereas the other two lines, $n = 2e$ and $n = 4e$ indicate the theoretical path for the ORR via two or four electrons, respectively. The slope of experimental data shows close proximity to that of the theoretical straight line $n = 4e$ implying that the ORR proceeds mainly via four electrons on Co–Ni 30:70 wt.% in alkaline media.

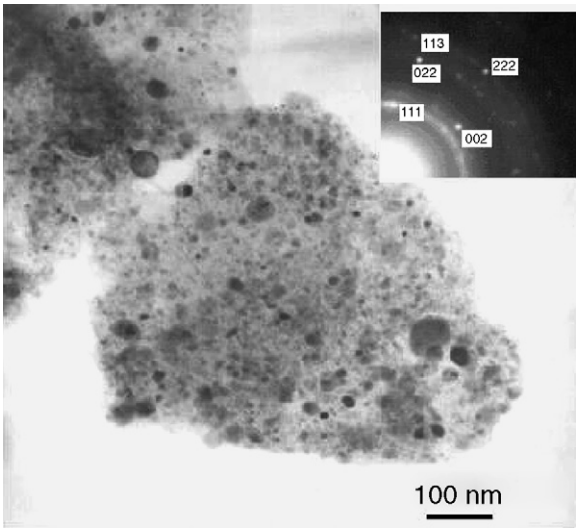

Fig. 3. Bright field TEM image of Co:Ni 50:50 wt.% after milling for 20 h.

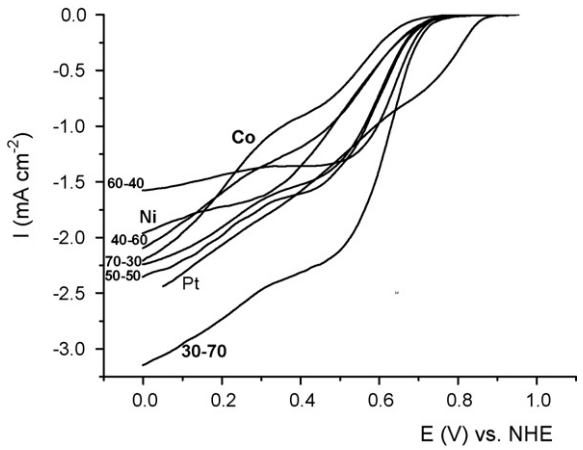

Fig. 4. Linear voltammograms displaying the ORR results of mechanically alloyed cobalt–nickel powders in KOH 0.5 M at 1600 rpm.

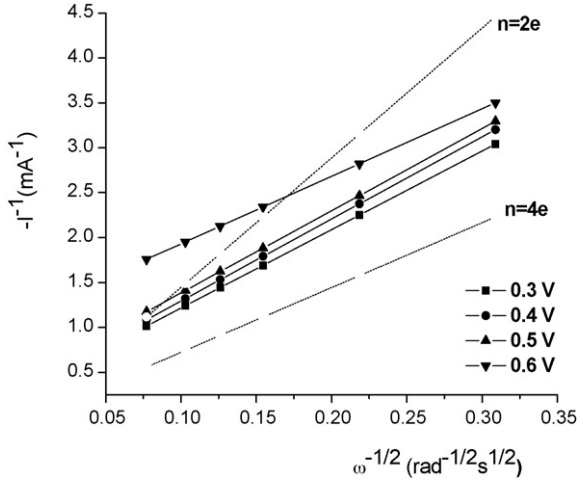

Fig. 5. Koutecky–Levich plot for Co:Ni 30:70 wt.% after milling for 20 h.

4. Conclusions

In this work, it has been demonstrated that mechanical alloying of elemental cobalt and nickel powders produces solid solutions after milling for 5 h. Particle size of the solid solutions was about 10 nm. In particular, the Co–Ni 30:70 wt.% exhibited the highest current density for the ORR via 4 electrons. The higher current density associated to the cobalt–nickel alloys was attributed to a synergistic effect.

Acknowledgments

This study was supported by ININ and IPN through the projects ININ-CB-606 and IPN-CGPI- 20051130, respectively. One of the authors (M.A. Garcia Contreras) would like to acknowledge the financial support from CONACYT.

References

[1] J.S. Benjamín, Sci. Am. 40 (1976) 234.
[2] S. Mukerjee, S. Srinivasan, M.P. Soriaga, J. Electrochem. Soc. 142 (1995) 1409.
[3] U.A. Paulus, A. Wokaun, G.G. Scherrer, T.J. Schmidt, V. Stamenkovic, N.M. Markovic, P.N. Ross, Electrochim. Acta 47 (2002) 3787.
[4] S. Mukerjee, S. Srinivasan, M.P. Noriega, J. McBreen, J. Phys. Chem. 99 (1995) 4577.
[5] T. Toda, H. Igarashi, H. Uchida, M. Watanabe, J. Electrochem. Soc. 146 (1999) 3750.
[6] U.A. Paulus, A. Wokaun, G.G. Scherer, J. Phys. Chem. B 106 (2002) 4181.
[7] L. Xiong, A.M. Kannan, A. Manthiram, Electrochem. Commun. 4 (2002) 898.
[8] G. Lalande, R. Coté, G. Tamizhamani, D. Guay, J.P. Dodelet, L. Dignard-Bailey, L.T. Wengs, P. Bertrand, Electrochim. Acta 40 (1995) 2635.
[9] M. Ladoucer, G. Lalande, D. Guay, J.P. Dodelet, J. Electrochem. Soc. 140 (1993) 1974.
[10] E. Claude, T. Addou, J.M. Latour, P. Aldebert, J. Appl. Electrochem. 28 (1998) 57.
[11] J.L. Fernandez, D.A. Walsh, A.J. Bard, J. Am. Chem. Soc. 127 (2004) 357.
[12] S. Treimer, A. Tang, D.C. Johnson, Electroanalysis 14 (2002) 165.