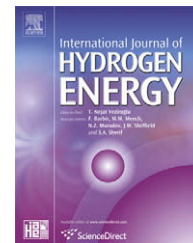


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Electrocatalytic behaviour of Co–Ni–R (R = Rare earth metal) crystalline alloys as electrode materials for hydrogen evolution reaction in alkaline medium

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ABSTRACT

Ternary Co–Ni–R (R = Y, Ce, Pr, and Er) crystalline alloys have been characterized by means of microstructural and electrochemical techniques in view of their possible applications as electrocatalytic materials for hydrogen evolution reaction (HER). The electrochemical efficiency of the electrodes has been studied on the basis of electrochemical data obtained from steady-state polarization and electrochemical impedance spectroscopy (EIS) techniques in 1 M NaOH solution at 298 K. The results were compared with those obtained on a Co–Ni commercial alloy. The microstructural features play a fundamental role in determining the electrocatalytic activity of the investigated alloys. The overall experimental data indicate that alloying Co–Ni with rare earth metals leads to an increase of electrocatalytic activity in hydrogen evolution with respect to the Co–Ni alloy. High catalytic efficiencies were achieved on Co_{57.5}Ni₃₆Y_{6.5} and Co₅₇Ni₃₅Ce₈ electrodes, the latter being the best electrocatalyst for the HER.

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1. Introduction

Hydrogen evolution reaction (HER) in aqueous solution is one of the most widely studied electrode reactions. The HER has received much attention because of its importance in both fundamental and technological electrochemistry. From a fundamental point of view, the HER has been treated as a prototype in electrochemical kinetic and electrocatalytic studies, although it is quite complex. Moreover, from an electrochemical point of view, the cost of hydrogen can be cut by reducing the electrode reaction overpotential. Even though water electrolysis is not the cheapest method of hydrogen production, it supplies hydrogen of very high purity. Therefore, the electrocatalytic HER on various

electrode materials has been studied at length, to reduce overpotential (η) for the HER at reasonably acceptable cathodic current density. The subject has been properly reviewed recently [1–5].

The most widely studied electrode material is Ni, its alloys and compounds. Nickel exhibits a high initial electrocatalytic activity towards the HER. However, it experiences extensive deactivation as a cathode during alkaline water electrolysis. Enhancement of cathodic activity of nickel for electrolytic hydrogen evolution has been carried out by increasing the real surface area (e.g. Raney-type alloys) or by increasing the intrinsic (real) activity of the material using alloys or composites [6–11]. In this context, Co–Ni alloys have been identified as efficient electrocatalysts for alkaline water

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electrolysis, as their catalytic activity is comparable to that of noble metals [12–14].

Some rare earth-based hydrogen storage alloys have presented interesting and potentially valid characteristics as cathodes for HER in alkaline media. Kitamura et al. [15,16] published that LaNi_5 , MmNi_5 (Mm: mischmetal) and other combinations of rare earth metals and Co or Ni, when used as cathodes, exhibited very high activity for the HER. Tanaka et al. [17] reported apparent exchange current density ($\log i_0/A \text{ cm}^{-2}$) equal to -3.5 for LaNi_5 and -3.7 for MmNi_5 , which are similar to the values obtained for Pd (-3.9) and Pt (-3.5). More recently, Bocutti et al. reported studies performed with HER on La–Ni alloys in alkaline solution. The experimental results produced $\log i_0$ as high as -1.3 for $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and -1.8 for $\text{MmNi}_{3.4}\text{Co}_{0.8}\text{Al}_{0.8}$ in 25% KOH at 70°C [18]. Moreover, our previous results [19–23] have shown a beneficial effect of lanthanides on the electrocatalytic properties of nickel and iron-based alloys towards the HER in alkaline solution.

The aim of this study was to investigate the activities of Co–Ni–R (R = Y, Ce, Pr, and Er) crystalline alloys towards the electrolytic HER, determine kinetic parameters by electrochemical methods and find the source of the electrode activity. Experimental data were obtained in 1 M NaOH solution at 298 K by using steady-state polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental details

2.1. Alloy sample preparation

The samples were prepared in the composition range up to 8 at% of rare earth (R = Y, Ce, Pr and Er), starting from cobalt (99.98 mass%), nickel (99.9 mass%) and rare earths (99.9 mass%) rods. Calculated amounts of the elements were weighed to an accuracy of 0.01 mg and synthesized using both arc-melting on a water-cooled copper plate (Zirconium was used as a getter material within the arc chamber) and induction melting in alumina crucibles under Ar atmosphere. The samples were re-melted twice for homogenisation, and possible mass losses were generally found to be negligible. The samples were used as-cast.

2.2. Microstructural characterization

Prior to electrochemical evaluation, the microstructures of the alloys were systematically investigated by light optical microscopy (LOM), scanning electron microscopy (SEM) and quantitative data were collected by EPMA (electron probe microanalysis). An electron microscope (Zeiss EVO-40) equipped with an OXFORD INCA Energy 300, which allowed chemical analysis by EDS, was used. Cobalt standard was used for calibration and the X-ray intensities were considered for ZAF effects using pure elements as standards; the compositional values derived were usually accurate to ± 1 at%.

2.3. Electrochemical measurements

All the experiments were carried out at 298 K in de-aerated 1 M NaOH aqueous solution. A conventional, three-

electrode cell was used in the electrochemical investigations. A large area platinum foil served as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. With these experimental conditions, the equilibrium potential for hydrogen was -1070 mV. Oxygen was removed from the solution by bubbling nitrogen gas for 60 min before each test. The geometrical area of all electrodes tested was 0.20 cm^2 . The experimental results refer to this geometric surface area. Before the experiments, the electrodes were mechanically polished with diamond pasted down to $0.1 \mu\text{m}$ and finally rinsed with distilled water. Steady-state polarization curves were recorded using a Solartron model 1286 Electrochemical interface at the scan rate of 0.1 mV s^{-1} . In order to correct the polarization data for IR drop effects, the uncompensated solution resistance values were calculated using the data acquired from the EIS measurements. Impedance measurements were performed in the potentiostatic mode using EG&G PAR system Model 2263 for measurements from 50 kHz to 10 Hz, and a Fast Fourier Transform (FFT) technique for frequencies from 10 Hz to 50 mHz. Seven frequencies per decade were scanned using a sinusoidal potential of 10 mV peak-to-peak. Impedance spectra were recorded at selected overpotentials mainly located in the linear portion of polarization curves.

3. Results and discussion

The EDS analysis confirmed the nominal composition of the samples; in Table 1 a brief summary of the investigated samples is presented. Their micrographic aspect is recurrent: primary crystals of $\sim\text{Co}_{70}\text{Ni}_{30}$ and the matrix composed of a two-phase mixture of the same phase and the richest-(Ni,Co) phase existing for the systems under investigation, which is $\text{R}(\text{Ni,Co})_5$ for R = Pr and Ce and $\text{R}_2(\text{Ni,Co})_{17}$ for R = Y and Er. To be noted is the “divorced” [24] behaviour of the two-phase mixture around the $\sim\text{Co}_{70}\text{Ni}_{30}$ primary crystals, which can be considered as a typical feature in these alloys. This kind of micrographic appearance was also observed in the ternary R–Ni–Co (R = Y, Ce, Pr, and Er) Ni-rich (6–7 at% R and Ni content > 65 at% Ni) samples both as cast and annealed for a few days at 800°C and quenched in cold water [21], as well as in the study of binary R–Ni (R = Y, Ce, Pr, Sm, and Tb) crystalline alloys that showed a divorced eutectic behaviour around the primary Ni crystals [19].

Fig. 1 shows the micrograph of the $\text{Ce}_8\text{Co}_{57.5}\text{Ni}_{35}$ at% as cast alloy, where the $\text{Co}_{71}\text{Ni}_{29}$ primary crystals are surrounded by a fine two-phase mixture formed by $\text{Co}_{71}\text{Ni}_{29}$ and $\text{Ce}_{16.5}(\text{Co,Ni})_{83.5}$ with 39.5 at% Co. The phase with composition $\text{Ce}_{16.5}(\text{Co,Ni})_{83.5}$ is the extension of the CeNi_5 phase in the Ce–Co–Ni system.

Fig. 2 shows the micrograph of the $\text{Y}_{6.5}\text{Co}_{57.5}\text{Ni}_{36}$ at% as cast alloy. The appearance is similar to that of the Ce–Co–Ni alloy: primary crystals of $\text{Co}_{69}\text{Ni}_{31}$ surrounded by a two-phase mixture of $\text{Co}_{69}\text{Ni}_{31}$ and $\text{Y}_{10.5}(\text{Co,Ni})_{89.5}$ with 41 at% Ni. In this case, the $\text{Y}_{10.5}\text{Co}_{48.5}\text{Ni}_{41}$ phase can be the solid solution of Ni in Y_2Co_{17} . As mentioned above, the divorced aspect of the two-phase mixture around the primary crystals is peculiar to these alloys.

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