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Correlation of microstructure and catalytic activity of crystalline Ni–Co–Y alloy electrode for the hydrogen evolution reaction in alkaline solution

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Abstract

The electrocatalytic activity of crystalline $Ni_{65}Co_{29}Y_6$ alloy with respect to the hydrogen evolution reaction (HER) was studied in relation to its microstructure examined by optical microscopy, scanning electron microscopy coupled with electron probe microanalysis, and XRD measurements. Kinetic parameters of the HER were evaluated on the basis of electrochemical impedance spectroscopy and steady-state polarization techniques in 1 M NaOH solution at room temperature. The results were compared with those obtained on polycrystalline Ni metal. The enhanced electrocatalytic activity observed for the HER on the investigated alloy was ascribed to a pronounced synergetic effect between the alloy constituents, i.e. $Ni_{63}Co_{37}$ and $(Ni,Co)_{17}Y_2$ intermetallic compounds.

Keywords: Ni–Co–Y alloy; Casting; X-ray diffraction; Electrochemical reactions

1. Introduction

The growing utilization of electrolytic hydrogen in different industries for the production of food, chemicals, fertilizers and also a nonpolluting fuel option is driving electrolysis research towards alternative materials and methods for the production of hydrogen at a lower cost.

Because of the importance of hydrogen evolution reaction (HER) in both fundamental and technological electrochemistry, the aim of many papers dealing with this reaction has been to understand the principles of its kinetics and mechanism, as well as to improve the electrocatalytic behaviour of electrode materials. The improvement consisted in targeting several fields of interest such as the intrinsic nature of the reaction [1], electrode composition [2–10], surface morphology [11–14], structural, chemical and electronic properties [15–23] physico-chemical and electrochemical activation treatment [24–26].

Two properties play an important role in selecting catalytically active materials for the HER. Firstly, the actual electrocatalytic effect of the material, which is directly dependent on the voltage used to operate the electrolyzer at significant current densities, and secondly, its long term stability. Thus, from an electrochemical point of view, the problem to be tackled in order to decrease the cost of electrolytic hydrogen is the reduction of overpotential, which can be achieved by choosing a highly catalytically active electrode material, or by increasing the active surface area of the electrode.

After three decades of intense development of activated electrode materials for alkaline water electrolysis [27,28], a careful revision of the literature shows that innovations are restricted to a small number of new systems [29–31]. Among them, Ni-based alloys either amorphous [32–34] or crystalline [35–37] have been successfully tested as efficient cathode materials. Moreover, the effects of replacement of one of the components with some other metals on the structural and hydrogen sorption properties have been studied and it was found that the hydrogen sorption properties are strongly influenced when nickel is partially substituted [38].

Some rare earth-based hydrogen storage alloys have presented interesting and potentially valid characteristics as cathodes for HER in alkaline media. Kitamura et al. [39,40] published that $LaNi_5$, $MmNi_5$ (Mm: mischmetal) and other combinations of rare earth metals and Co or Ni, used as cathodes, exhibited very high activity for the HER. Tanaka et al.

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[41] reported apparent exchange current density (log i_0, A 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 $LaNi_{4.7}Al_{0.3}$ and −1.8 for $MmNi_{3.4}Co_{0.8}Al_{0.8}$ in 25% KOH at 70 °C [42]. Moreover, a beneficial effect of lanthanides on the electrocatalytic properties of nickel and iron-based alloys towards the HER in alkaline solution has been evidenced [43,44].

In this paper, we report the results regarding the hydrogen evolution reaction on a crystalline Ni–Co–Y alloy electrode as well as on spectroscopically pure polycrystalline nickel electrode, in order to characterize alloy electrocatalytic efficiency. The material was studied in relation to its microstructure using steady-state polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. Literature data on the constitutional properties of the investigated alloy

Several Ni–Co–Y alloys in the (Ni,Co)-rich region were considered. As for the binary sub-systems, Co and Ni exhibit complete solid solution in the α (fcc) phase at a temperature between the solidus and the allotropic transformation temperature of α-Co and hcp ε-Co phase.

The richest metal transition (T) phases reported for the binary Y–T systems correspond to the R_2T_{17} (T = Ni and Co) stoichiometry. In both systems an eutectic reaction L (93.0) → Y_2Co_{17} + (α-Co) at 1340 °C and L (93.3) → Y_2Ni_{17} + (Ni) at 1285 °C were reported [45]. The Y_2Ni_{17} show a peritectic formation at 1330 °C and crystallize in the hexagonal hP38-Th_2Ni_{17} type. Carfagna and Wallace [46] postulated a composition range for Y_2Ni_{17}, based on lattice parameter and Curie temperature measurements. This range extends on the Y-rich side, but the extent was not determined.

Y_2Co_{17} melts congruently (1360 °C) and a homogemeity region was suggested at high temperature [47]. For Y_2Co_{17} phase, the two inter-related structures hR57-Th_2Zn_{17} and hP38-Th_2Ni_{17} have been described. A discussion about the temperature range of stability of the two forms for the different lanthanides has been given [48,49] and the hR57-Th_2Zn_{17} form was suggested as the probably room temperature phase.

A complete isothermal section of the Y–Co–Ni system was studied by Kharchenko et al. [50] at 873 K and by Xue et al. at 1273 and 1448 K [51]. In the Co–Ni rich region an extension of the Y_2Co_{17} phase up to about 32 at.% Ni and of the Y_2Ni_{17} up to about 22 at.% Co was determined by [50].

Recently a thermodynamic modelling of the Co–Ni–Y system has been performed by [52].

3. Experimental details

3.1. Alloy sample preparation

The samples were prepared in the composition range up to 11 at.% Y, starting from cobalt (99.98 mass%), nickel (99.9 mass%) and yttrium(99.9 mass%) rods. Calculated amounts of the elements were weighed to an accuracy of 0.01 mg and arc-melted on a water-cooled copper plate under an argon atmosphere. Zirconium was used as a getter material within the arc chamber. Several samples were synthesized by induction melting in alumina crucibles under argon atmosphere. The samples were re-melted two times for homogenisation, and possible mass losses were generally found to be negligible. The samples were used as-cast.

3.2. Microstructural characterization

Prior to electrochemical evaluation, the sample characterization was performed by optical microscopy and then analysed by EPMA in order to determine the composition of the different phases. SEM micrographs were taken with an OXFORD INCA Energy 300, which allowed chemical analysis by EDS. In order to compare the results obtained from the electrochemical measurements, binary Ni–Co samples having the $Ni_{63}Co_{37}$ composition, identical to the primary crystals composition determined in the ternary alloy and the binary $Y_2(Co,Ni)_{17}$ (22 at.% Co) phase were also prepared and investigated.

3.3. Electrochemical measurements

All the experiments were carried out at 298 K in deaerated 1 M NaOH aqueous solution, which was prepared from analytical reagent grade NaOH and Type I, 18 MΩ water. A conventional, three-electrode cell was used in the electrochemical investigations. A large area platinum foil served as the counter electrode and a saturated calomel electrode (sce) was used as the 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 paste down to 0.1 μm 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. Ten frequencies per decade were scanned using a sinusoidal potential of 10 mV peak-to-peak. In all cases triplicate experiments were carried out in order to ensure reproducibility.

4. Results and discussion

The SEM analysis confirmed the nominal composition of the samples. Fig. 1 shows the micrograph of the $Ni_{65}Co_{29}Y_6$ at.% as-cast alloy were the $Ni_{63}Co_{37}$ primary crystals are surrounded by a fine two-phase mixture having a $Ni_{66}Co_{26}Y_8$ global composition (formed by $Ni_{63}Co_{37}$ and $Y_{10.5}(Co,Ni)_{89.5}$ with 22 at.% Co). A divorced behaviour of the two-phase mixture around the $Ni_{63}Co_{37}$ primary crystals should be noticed. This micrographic aspect occurred in all samples, both prepared by induction and arc melting. Moreover, the same behaviour was observed in the ternary R–Ni–Co (R = Y, Ce, Pr) Ni-rich (6–7 at.% R and Ni content > 65 at.% Ni) and Co-rich (6–7 at.% R and Co content > 55 at.% Co) samples both as-cast and annealed few days at 800 °C and quenched in cold water. Besides, the microstructural feature observed studying binary R–Ni (R = Y, Ce, Pr, Sm, Tb) crystalline alloys [43], showed a similar divorced eutectic behaviour around the primary (Ni) crystals.

The cathodic polarization curves of the HER obtained for nickel, Ni–Co and Ni–Co–Y electrodes in the potential range between −1070 and −1500 mV versus sce, are displayed in Fig. 2. Tafel behaviour was observed during the HER polar-