X-ray diffraction investigation of nickel hydride formation in alkaline solution

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Investigations of nickel hydride formation during cathodic charging of Ni in 3 mol dm^{-3} KOH solution with and without AsO_2^- were carried out using *in situ* and *ex situ* X-ray diffraction (XRD). A bulk β-NiH$_x$ phase was found to form in the nickel cathode during hydrogen evolution in the alkaline solution with AsO_2^- as well as in an acid one. The volume fraction of the β-NiH$_x$ phase reached up to 35% after ~70 minutes from the beginning of cathodic charging, and further it began to decrease, although the charging current was not switched off. The decrease of the volume fraction of the hydride phase was caused by exhaustion of AsO_2^- in the solution. The quantity of the β-NiH$_x$ phase formed during hydrogen evolution at nickel in the alkaline media was always less than in the acid one. It has been suggested that different hydrogen evolution reaction (HER) mechanisms in alkaline and acid media are responsible for the above result.

Key words: nickel, hydride, alkaline, X-ray diffraction

INTRODUCTION

It has long been known that nickel hydride forms during electrochemical hydrogen evolution at nickel electrode in acid solution [1–9]. A β-NiH$_x$ phase is also believed to form electrochemically in alkaline media [10–13]. The nickel hydride formation in acid solution was confirmed by X-ray diffraction (XRD) method *ex situ* [5, 6, 14–16] as well as *in situ* [7–9]. There is only one paper [11] giving the XRD evidence that the β-NiH$_x$ phase forms in the alkaline media. Recently Baranowski [17] claimed that the electrochemical formation of the bulk nickel hydride is impossible in alkaline solution. According to Baranowski, only traces of the bulk nickel hydride were confirmed by the XRD in Ref. [11]. Furthermore, these traces there formed using current densities greater than one order of magnitude and charging time much higher than in acid solutions [1].

The results of the XRD *in situ* and *ex situ* study of electrochemical β-NiH$_x$ formation in alkaline solution are presented here. Results obtained in alkaline media were compared with those in acid. It was tried to find the reason for a less amount of the nickel hydride formed in alkaline media than in acid one under the same hydrogen current density.

EXPERIMENTAL

Hydride formation was studied in 3 mol dm^{-3} KOH solution with 2.0 or 4.0 g dm^{-3} of As_2O_3. The solutions were prepared from analytical grade KOH and triply-distilled water. A copper electrode with a previously electroplated 10 µm thick nickel coating was used as a cathode. The nickel coating was electrodeposited from the Watts-type solution: $NiSO_4 \cdot 7H_2O$ – 240 g dm^{-3}, $NiCl_2 \cdot 6H_2O$ – 45 g dm^{-3}, H_3BO_3 – 30 g dm^{-3}, pH = = 4.8, t = 50 ± 1 °C, i_d = 20 mA cm^{-2}. The geometrical area of the Ni cathode surface was 1 cm^2 and that of the Pt anode ~6.5 cm^2. In some experiments 6 µm thick nickel foil was used as a cathode. The foil processing was described in [9]. Electrochemical hydrogen evolution was performed under galvanostatic conditions. The temperature of the solution was 20 ± 1 °C in a conventional electrolytic cell, but it was not maintained constant during XRD investigations *in situ*.

The frame of the electrolytic cell for the XRD investigations *in situ* was the same as in [9], and it schematic presentation is shown on Fig. 1. One of the cell walls was made of a thin (8 µm) X-ray transparent polyethyleneterefta late (PETF) film. The Ni cathode surface was approached to the film as close as possible only when *in situ* XRD measurement was carried out (cathode position presented by dashed line on Fig. 1). The electrolytic cell capacity was about 10 ml.

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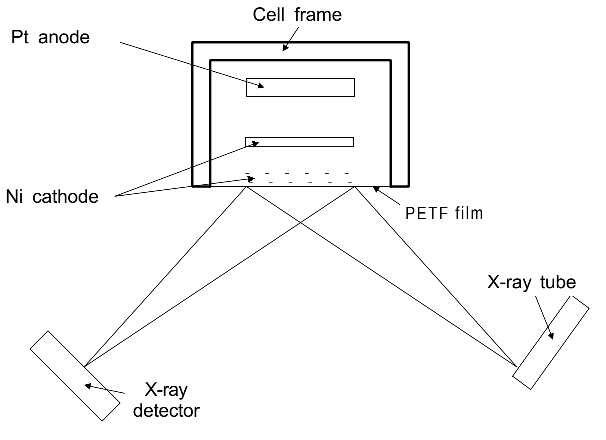

Fig. 1. Schematic presentation of the electrolytic cell for XRD investigations *in situ*

The cell was mounted on a horizontal goniometer of a DRON-2.0 X-ray diffractometer. The window with PETF film and the approached nickel cathode was attached to a sample holder in such a manner that the goniometer Θ axis lay actually on the plane of the nickel cathode. The XRD investigations were carried out using Mo K_α radiation selected by a secondary graphite monochromator. The step scan mode with a step size Δ2Θ of 0.05° and a counting time of 5–10 s per step was used in the range of $35° \le 2\Theta \le 40°$. The intensity profiles of the XRD peaks Ni (311), and β-NiH_x (311) were measured in this 2Θ range. Cu K_α radiation was used when the XRD method presented in [9] was employed. In the latter case XRD peaks Ni (200), and β-NiH_x (200) were measured.

The volume fraction of the β-NiH_x phase in the charged Ni electrode was calculated by the modified formula proposed in [5]:

$$V_{NiH} = (I_{NiH} / (I_{Ni} + I_{NiH})) \cdot 100, \qquad (1)$$

where V_{NiH} is the part by volume occupied by the β-NiH_x phase in the nickel electrode (in %), I_{NiH} is the integral intensity of β-NiH_x (311) peak, and I_{Ni} is the integral intensity of the Ni (311) peak.

RESULTS AND DISCUSSION

We began with attempts to use the same XRD *in situ* method as we did in the case of acid solution [9], *i.e.* to study the hydride formation in the nickel foil which served as one of the electrolytic cell walls at the same time. The nickel foil was charged with hydrogen in alkaline solution with AsO_2^- at a constant current density of 300 mA cm^{-2}. The intensity of the XRD peak β-NiH_x (200) increased during the first 4–5 minutes after cathodic polarization was applied, and then it began to decrease (Fig. 2). The XRD peak intensity dropped to the X-ray background level after some 10 minutes from the beginning of hydrogenation. Such a kind of variation of the intensity of hydride phase XRD peak was always observed in the alkaline solution with AsO_2^- regardless of hydrogen current density i_H (300–800 mA cm^{-2}) used. A maximum volume fraction of the β-NiH_x phase detected by this method was less than 1% in the alkaline media, while it reached more than 70% in the acid one [9]. The lesser amount of hydride phase formed in the alkaline solution could be caused by at least three reasons: 1) exhaustion of the promoter; 2) increase in solution temperature; 3) different mechanisms of HER in alkaline and acid solution.

To prove the first reason, V_{NiH} dependence on the quantity of electric charge, *Q*, passed through the alkaline solution with AsO_2^- at the given value of i_H was studied. Some copper electrodes with electroplated nickel coating one by one were charged with hydrogen in the alkaline solution with 2.0 g dm^{-3} of As_2O_3 at a constant current density of 150 mA cm^{-2} for 0.5 h each. When removed, the electrode was rinsed in distilled water, dried and placed immediately in a conventional sample holder of the XRD goniometer. The XRD pattern measurement started after 3–5 minutes from the moment when the electrode hydrogenation was stopped. Part of the XRD pattern shown in Fig. 3 evidenced an appreciable amount of hydride phase to have been formed. The $V_{NiH} \sim f(Q)$ dependence is presented in Fig. 4. It could be pointed out that the volume fraction of the β-NiH_x phase reached up to

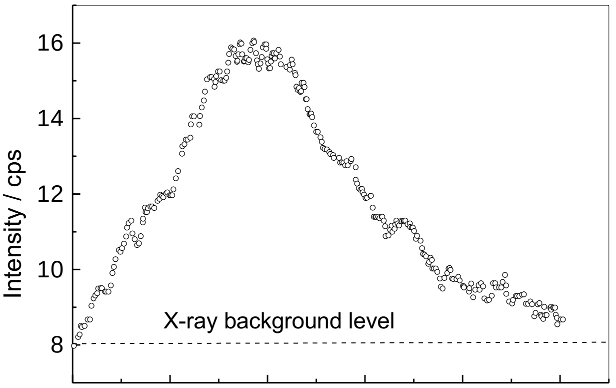

Fig. 2. Variations of intensity at the maximum of the X-ray diffraction peak β-NiH_x (200) as a function of the nickel cathode charging time in alkaline solution with 2 g dm^{-3} As_2O_3 at a constant current density of 300 mA cm^{-2}

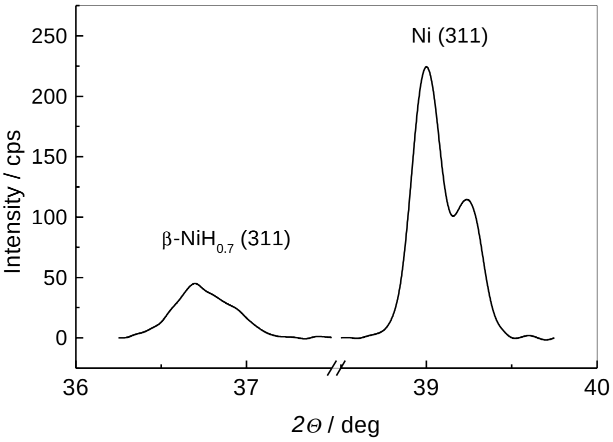

Fig. 3. The fragment of the XRD pattern measured from copper electrode with electroplated nickel coating charged with hydrogen in alkaline solution with 2 g dm^{-3} As_2O_3 at a constant current density of 150 mA cm^{-2} for 0.5 h

35% of the nickel coating 10 µm thick. Such an amount of the nickel hydride β phase may be treated as the bulk hydride rather than surface or sub-surface ones.

The V_{NiH} value decreases to zero when a certain charge, which could be signed as Q_z, passes through the alkaline solution containing AsO^-_2. The decrease in the V_{NiH} value may be caused by exhaustion of AsO^-_2 in the solution, because the temperature of the solution was maintained constant.

The X-ray fluorescence spectroscopy was used in an attempt to determine the quantity of As, c_{As} at the surface of the nickel cathode charged with hydrogen. The results obtained are presented in Fig. 4. The surface concentration of As shows a remarkable decrease for the first three samples charged in the solution (Q < 600 C), and later on c_{As} changes slightly. The β-NiH$_x$ phase becomes undeterminable by the XRD technique when c_{As} drops off to zero. Figure 4 shows that an increase in the amount of As_2O_3 added to the solution from 2.0 to 4.0 g dm^{-3} changes Q_z insignificantly. On the other hand, increasing the working solution volume from 25 to 50 ml causes a significant increase of the Q_z (Fig. 5). These results can be explained by diffusion limitations of the active species AsO^-_2 to the surface of the nickel electrode. A small capacity (10 ml) of the electrolytic cell for the XRD *in situ* investigations may be responsible for the short period of time during which the β hydride phase is detectable in the nickel foil cathode (Fig. 2).

The small quantity of the β phase formed at the beginning of electrolysis (Fig. 4, Q < 600 C) may be caused by codeposition of the impurities that were present in the arsenic oxide used.

According to the results presented above, the bulk β-NiH$_x$ phase arises in the Ni cathode during electrochemical hydrogen evolution in the alkaline solution with AsO^-_2. The β-NiH$_x$ phase quantity and its stability are high enough for nickel hydride to be detected by the XRD *ex situ* technique. On the other hand, the small amount of this phase discovered by XRD *in situ* may be explained (besides the low capacity of the cell) by the difference in the hydrogen absorption-desorption conditions in the conventional electrolytic cell and that for the XRD investigation *in situ*. The nickel hydride forms in nickel foil, which serves as one of

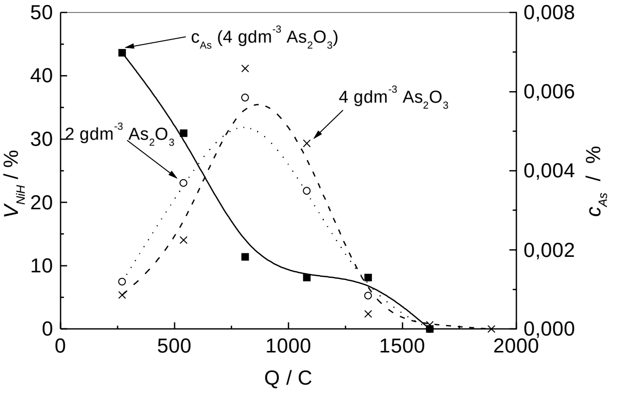

Fig. 4. Fraction by volume of the β-NiH$_x$ phase formed in the Ni cathode at a constant current density of 150 mA cm^{-2} for 0.5 h as a function of the electric charge passed through the alkaline solution with 2 and 4 g dm^{-3} of As_2O_3. Dependence of the surface content of As, c_{As}, on the electric charge passed through the alkaline solution with 4 g dm^{-3} of As_2O_3

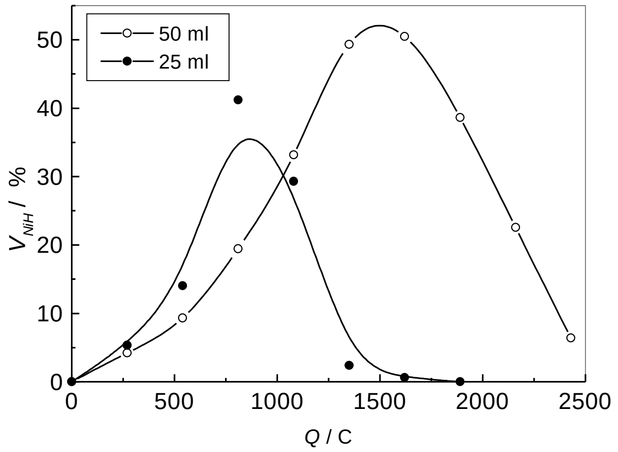

Fig. 5. Fraction by volume of the β-NiH$_x$ phase formed in the Ni cathode at a constant current density of 150 mA cm^{-2} for 0.5 h as a function of the electric charge passed through various volumes of alkaline solution with 4 g dm^{-3} of As_2O_3

the walls of the electrolytic cell for XRD investigation *in situ*. The nickel foil behaves as a membrane in this cell, and some part of the hydrogen flows out through the outer surface of the foil. Due to this feature of the cell, the concentration of atomic hydrogen in the Ni foil could never reach the value high enough to form the bulk β-NiH_x, if the concentration of the intermediate (NiH_{ads}) of the HER was low at the inner surface of the foil. When the conventional electrolytic cell is used, hydrogen evolution proceeds at the Ni deposited on the copper substrate, which prevents the outflow of the hydrogen. According to [18], the volume of the hydrogen gas absorbed by one volume of copper reaches 0.6–4.8 while that of nickel equals 18.0. To prove this hypothesis, we provided nickel foil with a thin X-ray transparent layer of copper, which was at the outer surface the foil only. The β-NiH_x phase was observed in the alkaline solution by the XRD *in situ* technique presented in [9] as long as polarisation was applied when a foil like this was used. The nickel hydride was detected by this method, if the hydrogen current density, i_H, was ≥ 150 mA cm^{-2}. The V_{NiH} value never exceeded 5% in the alkaline solution even when i_H = 800 mA cm^{-2} and charging time t = 120 min. We thought that a not continuous copper thin layer at the outer surface of the nickel foil and heating of solution caused by a high current density used were responsible for a small amount of the β-NiH_x phase observed by the XRD *in situ* technique presented in [9]. To prove the second reason for a small amount of the hydride phase formed, V_{NiH} dependence on the temperature of the alkaline solution was studied in a conventional electrolytic cell. The results are presented in Fig. 6. The amount of the β-NiH_x phase formed during 0.5 h of hydrogenation under a current density of 100 mA cm^{-2} decreased linearly with the solution temperature. The hydride phase would be undeterminable if the temperature of the solution reached ~60 °C. The solution in the electrolytic cell for XRD investigations *in situ* heated up to ~40 °C, while hydrogenation of the nickel foil was provided during 15 min under a current density of 300 mA cm^{-2}. Consequently, heating of the solution has a considerable influence on the amount of the hydride phase.

A larger amount of the β-NiH_x phase formed in the alkaline solution was observed by the XRD *in situ* technique presented in the experimental part of this paper. The V_{NiH} reaches up to 35% when i_H = = 150 mA cm^{-2} (Fig. 7). The V_{NiH}~$f(Q)$ dependence still has a sharp maximum for the alkaline solution, contrary to the acid one. The quantity of the β-NiH_x phase formed during hydrogen evolution at nickel in alkaline media is always smaller than in the acid one, regardless of the XRD method used. The promoter exhaustion period is much longer during HER in the acid than in the alkaline solution. These features of hydride formation could be caused by differences in HER mechanism in alkaline and acid media. The rate constant of the rate determining step (r.d.s.) of the HER is thought to be responsible for the different amount of the β-NiH_x phase formed in alkaline and acid solutions.

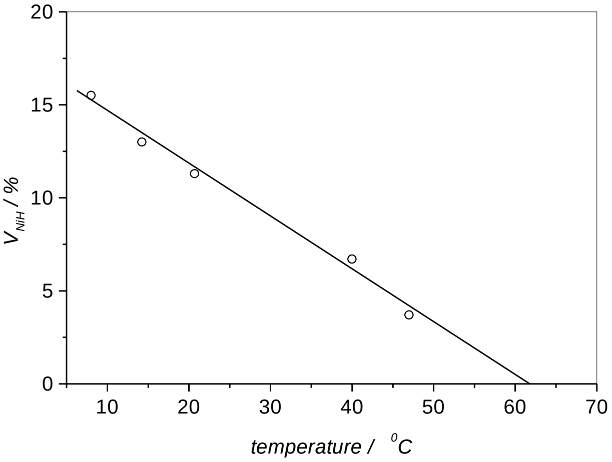

Fig. 6. Fraction by volume of the β-NiH_x phase formed in the Ni cathode during 0.5 h of hydrogen evolution at a current density of 100 mA cm^{-2} as a function of the temperature of the alkaline solution with 2 g dm^{-3} of As_2O_3

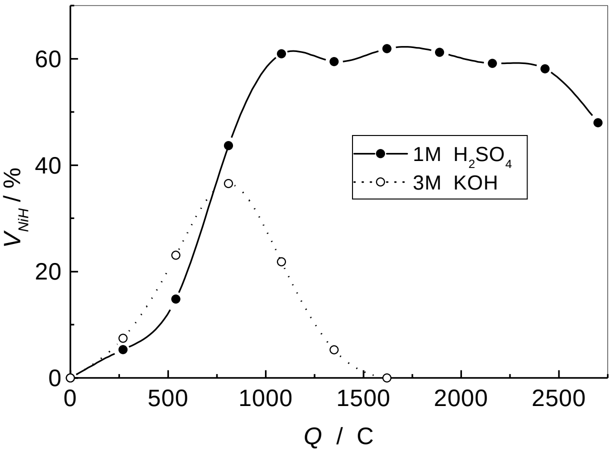

Fig. 7. Fraction by volume of the β-NiH_x phase formed in the Ni cathode during 0.5 h of hydrogen evolution at a current density of 150 mA cm^{-2} as a function of the electric charge passed through the alkaline and acid solutions with 2 g dm^{-3} of As_2O_3.

The HER at the nickel cathode proceeds through the Volmer–Heyrovsky mechanism, the Heyrovsky (3) reaction being r.d.s. [19–21]:

$$\mathrm{Ni} + \mathrm{H_2O} + e \xrightarrow{k_1}\xleftarrow{k_{-1}} \mathrm{NiH_{ads}} + \mathrm{OH^-} , \qquad (2)$$

$$\mathrm{NiH_{ads}} + \mathrm{H_2O} + e \xrightarrow{k_2}\xleftarrow{k_{-2}} \mathrm{H_2} + \mathrm{Ni} + \mathrm{OH^-} . (3)$$

It is essential that the Heyrovsky (3) reaction is the r.d.s. for the bulk β-NiH_x phase to form as it could be seen from the β-NiH_x formation mechanism [22]:

$$\mathrm{NiH_{ads}} \leftrightarrow \mathrm{NiH_{abs(surface)}} , \qquad (4)$$

$$\mathrm{NiH_{abs(surface)}} \rightarrow \mathrm{NiH_{abs(bulk,\alpha)}} , \qquad (5)$$

$$\mathrm{NiH_{abs(bulk,\alpha)}} \rightarrow \mathrm{NiH_{abs(bulk,\beta)}} . \qquad (6)$$

The amount of the β-NiH_x phase formed in the nickel cathode could be correlated with the ratio of the Volmer (2) and Heyrovsky (3) reaction rates, v_1/v_2: the faster is step (2) and the slower is step (3), the greater amount of the β-NiH_x phase could be expected to form. Thus, v_1/v_2 should be greater for acid than that for alkaline solution: $(v_1/v_2)_{acid} > (v_1/v_2)_{alkaline}$, because the V_{NiH} value reaches approximately 60% for the acid solution and only 35% for the alkaline one (Fig. 6).

The β-NiH_x phase has never been detected when nickel charging was provided in alkaline solution without AsO^-_2, which could be cathodically reduced at the surface of the Ni cathode. Depending on the value of the cathodic current density, it is possible to obtain arsenic alone or As with AsH_3 [23]. Consequently, As and/or AsH_3 hinders reaction (3), *i.e.* the ratio v_1/v_2 for the solution containing AsO^-_2 is greater than for that without AsO^-_2.

The mechanism for the enhancement of H sorption into host metals by adsorbed promoters remains still uncertain. The promotion of hydride formation was explained by an increase in the chemical potential of H, μ_H at the surface caused by coadsorption of a poison [24]. It is unclear if all poisons that increase μ_H would promote hydride formation, because equation (25) in ref. [24] has no term which would take into account special peculiarities of a poison acting as promoter.

CONCLUSION

Our XRD investigations evidence the bulk β-NiH_x phase to form in the nickel cathode in alkaline solution with AsO^-_2 as well as in an acid one. A higher content of nickel hydride is detected when there is no possibility for the hydrogen to flow out from the nickel cathode, *i.e.* when hydrogen evolution proceeds at the nickel coating on the copper substrate or on both sides of the nickel foil. Exhaustion of arsenic in the course of hydrogen evolution at nickel is faster in alkaline solution than in acid one and it causes a decrease in V_{NiH}. The quantity of the β-NiH_x phase formed during hydrogen evolution at nickel in alkaline media is always less than that in acid one. The rate of the Heyrovsky reaction, v_2, may be responsible for the quantity of the β-NiH_x phase formed at the nickel cathode.

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RENTGENO DIFRAKCINIAI NIKELIO HIDRIDO SUSIDARYMO ŠARMINIUOSE TIRPALUOSE TYRIMAI

Santrauka

Atlikti nikelio hidrido susidarymo katodinio Ni įvandenilinimo metu 3 mol dm^{-3} KOH tirpale su AsO_2^- tyrimai, naudojant Rentgeno spindulių difrakciją *in situ* ir *ex situ*. Nustatyta, kad, besiskiriant vandeniliui ant nikelio katodo, tūrinė β-NiH$_x$ fazė susidaro šarminiame tirpale su AsO_2^- taip, kaip ir rūgštiniame. Tūrinė β-NiH$_x$ fazės dalis šarminiame tirpale pasiekia apie 35% praėjus ~70 minučių nuo poliarizacijos įjungimo momento, vėliau ji pradeda mažėti nors poliarizacija ir neišjungiama. Hidridinės fazės tūrinės dalies mažėjimas buvo sukeltas AsO_2^- išsinaudojimo tirpale. β-NiH$_x$ fazės kiekis, susidarantis vandeniliui besiskiriant ant nikelio, šarminiame tirpale visada būdavo mažesnis negu rūgštiniame. Daroma prielaida, kad šio rezultato priežastis yra skirtingi vandenilio skyrimosi reakcijos mechanizmai šarminiame ir rūgštiniame tirpaluose.