

# Determination of the diffusion coefficient of yttrium in the Ni<sub>2</sub>Y phase

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A uniform Ni<sub>2</sub>Y layer was formed on a nickel substrate by electrolysis of yttrium ions in molten LiCl–KCl–NaCl at 500 °C, and the diffusion coefficient of yttrium in Ni<sub>2</sub>Y was found to be  $(2.84 \pm 0.40) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  using an electrochemical transient technique.

## 1. Introduction

Ni<sub>2</sub>Y, Ni<sub>2</sub>Y<sub>3</sub> and NiY intermetallic compounds can be produced on a nickel substrate by electrolysis of yttrium ions in molten LiCl–KCl–NaCl at various temperatures (from 450 to 700 °C) over a wide current density range (from 30 to 200 mA cm<sup>-2</sup>), and an adhesive uniform Ni<sub>2</sub>Y deposit can be obtained in a temperature range from 500 to 700 °C at the above current densities [1]. Considering the effective catalytic characteristics of rare earth metals, there may be a possibility of such Ni–Y intermetallic compounds as surface functional materials. On the other hand, quantitative knowledge of transport kinetics in solids is of importance both for understanding of transport mechanisms and for the technological application of many solid-state reactions, especially in high power density battery research. However, there is very little information on fundamental properties of these intermetallic compounds [2]. The aim of this study is to determine the diffusion coefficient of yttrium in Ni<sub>2</sub>Y at 500 °C. As well as conventional metallurgical and radiotracer methods, electrochemical techniques have also come into use for determination of transport kinetics. The important advantage of this approach is that the voltage of a suitable galvanic cell is directly related to appropriate thermodynamic quantities, and the current can provide easily measurable kinetic information at the same time. So far, several methods of measurement of solid-state diffusivities have been developed [3–6]. In this paper a new approach is proposed in which a galvanostatic transient technique was employed and the influence of the moving boundary due to interdiffusion of two phases was taken into account.

## 2. Theoretical consideration

The simple electron transfer reaction,  $O + ne^- = R$ , is considered. A planar working electrode and an unstirred solution are assumed, with only species O initially present in the electrolyte at a concentration  $C_0^*$ . The initial locus of solution–electrode interface is taken as  $x = 0$ . The locus of solution–electrode

interface,  $x_s$ , moves in the opposite direction to the diffusion of R because of the entrance of R into the electrode. A schematic illustration of such a system is shown in Fig. 1. Assuming the movement of the interface is proportional to the total amount of R diffusing into the electrode,

$$x_s = -k \int_0^t i(t) dt \quad (1)$$

where  $k$  is a proportionality constant. The diffusion equation and boundary conditions can be written as follows

$$\frac{\partial C_0(x, t)}{\partial t} = D_0 \left[ \frac{\partial^2 C_0(x, t)}{\partial x^2} \right] \quad -\infty < x < x_s \quad (2)$$

$$\frac{\partial C_R(x, t)}{\partial t} = D_R \left[ \frac{\partial^2 C_{mR}(x, t)}{\partial x^2} \right] \quad x_s \leq x < \infty \quad (3)$$

where the values of  $C_0(x, t)$  at  $x > x_s$  and  $C_R(x, t)$  at  $x < x_s$  have no physical significance.

$$\text{At } t = 0 \text{ or } x \longrightarrow \infty \quad C_R(x, t) = 0 \quad (4)$$

$$-D_0 \left[ \frac{\partial C_0(x, t)}{\partial x} \right]_{x=x_s} = \frac{i(t)}{nF} \quad (5)$$

If pure R does not accumulate on the surface of the electrode or dissolve into the electrolyte, that is, R only diffuses into the electrode, then

$$-D_0 \left[ \frac{\partial C_0(x, t)}{\partial x} \right]_{x=x_s} = -D_R \left[ \frac{\partial C_R(x, t)}{\partial x} \right]_{x=x_s} - C_R(x_s, t) dx_s/dt \quad (6)$$

where  $D_0$  is the diffusion coefficient of O in the electrolyte and  $D_R$  is the diffusion coefficient of R in the electrode.

Laplace transformation of Equation 3 on the variable  $t$  gives

$$\frac{d^2 \mathcal{C}_R(x, s)}{dx^2} - \frac{s \mathcal{C}_R(x, s)}{D_R} = 0 \quad (7)$$

solving Equation 7 gives

$$\mathcal{C}_R(x, s) = A(s) \exp \left[ - \left( \frac{s}{D_R} \right)^{0.5} x \right] + B(s) \exp \left[ \left( \frac{s}{D_R} \right)^{0.5} x \right] \quad (8)$$

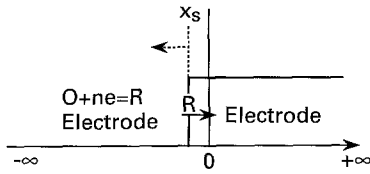


Fig. 1. Schematic illustration of the interface of the electrolyte and the electrode.

Equation 4 (the semi-infinite limit) can be transformed to

$$\mathcal{C}_R(x, s)_{x \rightarrow \infty} = 0 \quad (9)$$

Comparing Equation 8 with Equation 9 it is known that  $B(s)$  must be zero to make Equation 8 converge. Therefore,

$$\mathcal{C}_R(x, s) = A(s) \exp \left[ - \left( \frac{s}{D_R} \right)^{0.5} x \right] \quad (10)$$

The evaluation of  $A(s)$  is based on another boundary condition. From Equations 5 and 6, another boundary condition of Equation 3 can be stated as

$$-D_R \left[ \frac{\partial C_R(x, t)}{\partial x} \right]_{x=x_s} - \frac{C_R(x_s, t) dx_s}{dt} = \frac{i(t)}{nF} \quad (11)$$

If the electrolysis current is constant, i.e.  $i(t) = i$ , Equation 11 can be transformed to

$$\frac{d\mathcal{C}_R(x_s, s)}{dx} - \left( \frac{ki}{D_R} \right) \mathcal{C}_R(x_s, s) = \frac{-i}{snFD_R} \quad (12)$$

By differentiating Equation 10 with respect to  $x$ , at  $x = x_s$ , we obtain

$$\left[ \frac{d\mathcal{C}_R(x, s)}{dx} \right]_{x=x_s} = - \left( \frac{s}{D_R} \right)^{0.5} A(s) \exp \left[ - \left( \frac{s}{D_R} \right)^{0.5} x_s \right] \quad (13)$$

Substituting Equation 13 and 10 into Equation 12,  $A(s)$  then can be evaluated as

$$A(s) = \left( \frac{i}{nFD_R} \right) \left\{ \frac{1}{s^{0.5}} \left[ \frac{ki}{D_R^{0.5}} + s^{0.5} \right] \right\} \times \left( \frac{s}{D_R} \right)^{-0.5} \exp \left[ \left( \frac{s}{D_R} \right)^{0.5} x_s \right] \quad (14)$$

Thus Equation 10 can be rewritten as

$$\mathcal{C}_R(x, s) = \frac{i}{nFD_R} \left\{ \frac{1}{s^{0.5}} \left[ \frac{ki}{D_R^{0.5}} + s^{0.5} \right] \right\} \left( \frac{s}{D_R} \right)^{-0.5} \times \exp \left[ - \left( \frac{s}{D_R} \right)^{0.5} (x - x_s) \right] \quad (15)$$

Using the convolution integral, the inverse transform of this equation then yields the following expression for  $C_R(x, t)$

$$C_R(x, t) = \frac{i}{nFD_R} \int_0^t \exp \left( \frac{k^2 i^2 \tau}{D_R} \right) \operatorname{erfc} \left( \frac{ki\tau^{0.5}}{D_R^{0.5}} \right) \times \left[ \frac{D_R}{\pi(t - \tau)} \right]^{0.5} \exp \left[ \frac{-(x - x_s)^2}{4D_R(t - \tau)} \right] d\tau \quad (16)$$

At the surface of the electrode ( $x = x_s$ ), the concentration of R is

$$C_R(x_s, t) = \frac{i}{nFD_R} \int_0^t \exp \left( \frac{k^2 i^2 \tau}{D_R} \right) \operatorname{erfc} \left( \frac{ki\tau^{0.5}}{D_R^{0.5}} \right) \times \left[ \frac{D_R}{\pi(t - \tau)} \right]^{0.5} d\tau \quad (17)$$

Finally, rearranging Equation 17 gives

$$C_R(x_s, t) = \left( \frac{1}{nFk} \right) \operatorname{erf} \left( \frac{kit^{0.5}}{D_R^{0.5}} \right) \exp \left( \frac{k^2 i^2 t}{D_R} \right) \quad (18)$$

In this case, the electron transfer reaction is:  $Y(\text{III}) + 3e^- = Y(\text{O})$ , so that  $O = Y(\text{III})$  and  $R = Y$ . The growth rate of the  $\text{Ni}_2\text{Y}$  layer results from competition between the electrolysis rate of yttrium  $J_E (= i/nF)$  and the diffusion flux of yttrium  $J_D (= -D_Y [\partial C_Y(x, t)/\partial x]_{x=x_s})$ . At the beginning of the electrolysis, the diffusion flux of yttrium is equal to the electrolysis rate  $J_E$ , i.e.  $J_D = J_E = i/nF$ . The concentration of yttrium at the surface increases with increase of electrolysis time according to Equation 18. At a certain time  $t_s$ ,  $C_Y(x_s, t_s) = C_Y$  (concentration of pure yttrium:  $5.03 \times 10^{-2} \text{ mol cm}^{-3}$ ). After this time  $t_s$ , pure yttrium then accumulates at the surface, this means that  $C_Y(x_s, t)$  remains constant and the Equation 6 will no longer hold.

### 3. Experimental details

55 LiCl–36KCl–9NaCl (mol %) eutectic mixture was used as a solvent electrolyte. LiCl, KCl and NaCl were all of reagent grade (Wako Chemical Co.). The eutectic mixture was vacuum dried for at least 48 h at 200°C. The anhydrous  $\text{YCl}_3$  was obtained by slowly heating a mixture of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$  under vacuum. Nickel discs 7 mm in diameter were used as working electrodes. A stabilized zirconia–air electrode was used as a quasi-reference electrode [1, 7]. A glassy-carbon rod of 5 mm in diameter was used as a counter electrode. The salt mixture was contained in a high purity alumina crucible (SSA–S, 99.5%  $\text{Al}_2\text{O}_3$ , Nippon Kagaku Tokyo Co.) and was melted under dry argon atmosphere. After anhydrous  $\text{YCl}_3$  was added to the eutectic, dry HCl gas was flowed through the eutectic for 2 h. The concentration of  $Y(\text{III})$  ion was 1.2 mol %. Finally, the cell pressure was kept slightly higher than atmospheric by dry argon gas to exclude atmospheric moisture.

Samples for measurement of the diffusion coefficient of yttrium were prepared by galvanostatic electrolysis at various current densities at 500°C. After electrolysis, the samples were taken from the bath, washed with distilled water and cleaned in ethanol using an ultrasonic cleaner. The weight increases of these samples were measured, and the current efficiencies were calculated as the ratio of electrode weight increase during the electrolysis to the theoretical weight increase corresponding to the charge passed

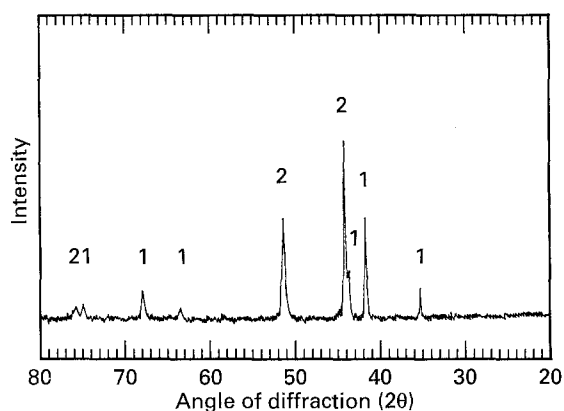


Fig. 2. XRD spectrum for sample prepared at 22.5 mA cm<sup>-2</sup> (using CuK<sub>α</sub>), (1.2 mol % YCl<sub>3</sub>, 500 °C). Key: (1) Ni<sub>2</sub>Y; (2) holder (Monel).

through the electrodes. The surfaces were analyzed by X-ray diffraction (XRD), and the cross-sections by electron probe microanalysis (EPMA) with atomic number (Z)-adsorption-fluorescence(ZAF) correction. Three series of samples were prepared at

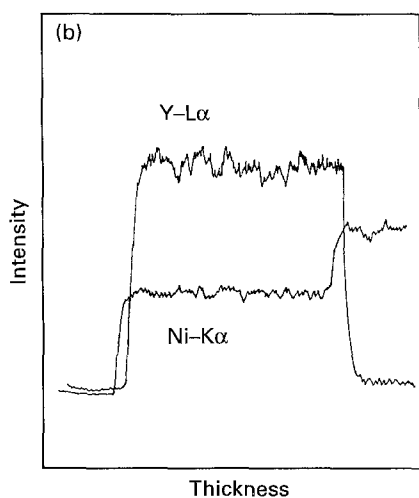
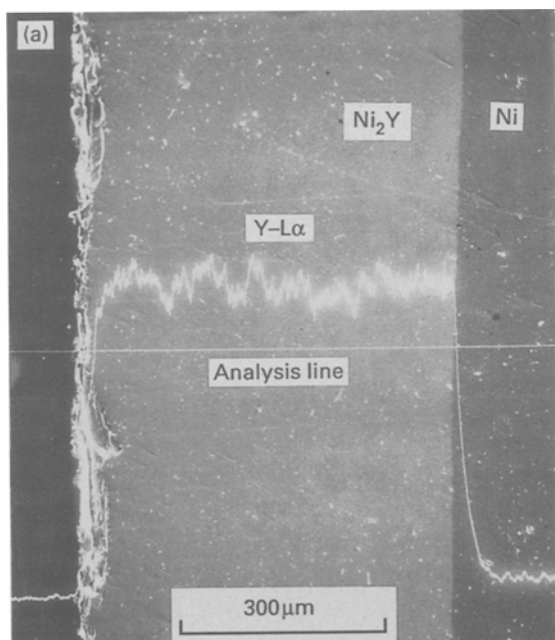


Fig. 3. (a) SEM image of the cross-section of sample prepared at 22.5 mA cm<sup>-2</sup>. (b). Concentration profiles of Y and Ni of the cross-section. (1.2 mol % YCl<sub>3</sub>, 500 °C).

Table 1. Condition and results

Sample No.	Current density/ mAcm <sup>-2</sup>	Electrolysis time/s	Electricity quantity/C	Ni <sub>2</sub> Y thickness μm
1	22.5	7200	65.2	50
2	22.5	14400	125.2	100
3	22.5	21600	192.7	150
4	22.5	28800	250.4	185
5	22.5	72000	643.4	400
6	45	4620	80.6	25
7	45	8100	140.5	65
8	45	14400	251.4	110
9	45	28800	502.7	120
10	45	46200	803.7	210
11	100	1320	50.8	37.5
12	100	2880	111.3	40
13	100	7800	301.2	55
14	100	20100	776.3	60

electrolysis current densities of 22.5, 45 and 100 mA cm<sup>-2</sup>, respectively. All samples were produced at identical current densities but for various electrolysis periods. The relation between electrolysis period and the thickness of Ni<sub>2</sub>Y layers grown during electrolysis of these samples were determined using SEM.

4. Results and discussion

Figure 2 shows the XRD pattern of the sample prepared at 22.5 mA cm<sup>-2</sup> for 41 hours. The result reveals that the product is Ni<sub>2</sub>Y. The SEM image of a cross-section of the sample prepared at 22.5 mA cm<sup>-2</sup> for 41 h is shown in Fig. 3. It can be seen that an adhesive uniform layer is formed. Quantitative EPMA analysis with ZAF correction shows that the bulk product is Ni<sub>2</sub>Y. Line analysis of the cross-section was implemented to identify the existence of a uniform Ni<sub>2</sub>Y layer. The concentration profiles of Y and Ni are also shown in Fig. 3. The result of line analysis also proves that the Ni<sub>2</sub>Y layer formed is uniform.

The conditions of preparation and the results for the samples are summarized in Table 1. The relation-

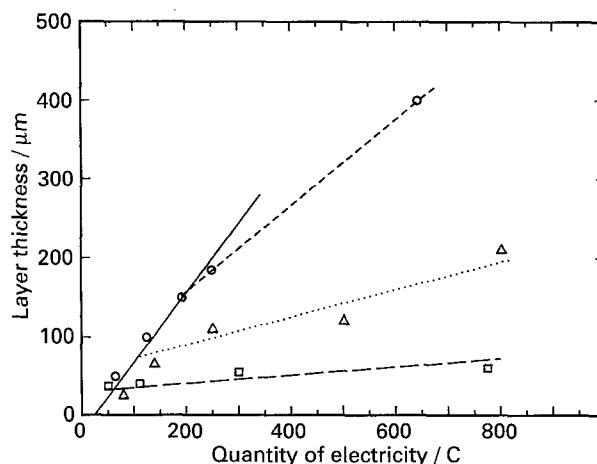


Fig. 4. Relationship between the thickness of Ni<sub>2</sub>Y layer and the quantity of electricity for various current densities. (1.2 mol % YCl<sub>3</sub>, 500 °C). Current density: (○) 22.5, (△) 45 and (□) 100 mA cm<sup>-2</sup>.

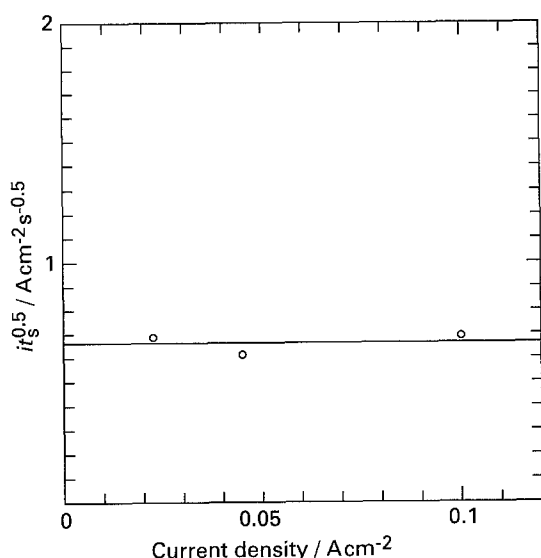


Fig. 5. Relationship between  $i_s^{0.5}$  and  $i$ .

ship between the thickness of the  $\text{Ni}_2\text{Y}$  layer and the quantity of electricity  $Q$  (instead of electrolysis period) is shown in Fig. 4. It can be seen that beyond a certain value of  $Q$  (or a certain electrolysis time  $t_s$ ) the slope of the straight line decreases drastically. The value of  $Q$  (or  $t_s$ ) depends on current density, that is  $t_s$  decreases with the increase in current density. At this point, the surface concentration  $C_Y(x_s, t)$  becomes saturated.

It is impossible to solve Equation 18 to obtain a direct relation between the current density and the electrolysis time,  $t$ . The solution of Equation 18 has been carried out numerically by computer to give a table of values of  $C_R(x_s, t)$  as a function of  $k i t^{0.5} / D_R^{0.5}$ . When  $C_Y(x_s, t_s) = C_Y$ , the corresponding  $k i t_s^{0.5} / D_Y^{0.5}$  has a certain value,  $b$ , which can be known from the table. Thus

$$i t_s^{0.5} = b D_Y^{0.5} / k \quad (19)$$

This means that although  $t_s$  decreases with increase of electrolysis current density  $i$ , the product of  $t_s^{0.5}$  and  $i$  remains constant, so a horizontal line is obtained when plotting  $i t_s^{0.5}$  against  $i$ . From its intercept  $\epsilon$ , the diffusion coefficient,  $D_Y$ , can be deduced:

$$D_Y = (\epsilon k / b)^2 \quad (20)$$

Numerical calculation of Equation 18 gives the value of  $b$  as  $3.76 \times 10^{-1} \text{ cm}^{-2}$ . From Fig. 4 a series of  $Q$  values are read, so  $t_s$  is known. The  $i t_s^{0.5}$  against  $i$  plot is represented in Fig. 5. The value  $\epsilon$  was found to be  $(6.64 \pm 0.25) \times 10^{-1} \text{ A cm}^{-2} \text{ s}^{0.5}$ . The value of the proportionality constant,  $k$ , is estimated as  $9.63 \times 10^{-5} \text{ cm C}^{-1}$  from the result of the previous study [1]. From this the diffusion coefficient,  $D_Y$ , was calculated to be  $(2.84 \pm 0.40) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ .

There is no further literature concerning the diffusion coefficient of yttrium in  $\text{Ni}_2\text{Y}$  and comparison is therefore impossible.

## 5. Conclusion

A uniform  $\text{Ni}_2\text{Y}$  layer was formed on a nickel substrate by electrolysis of yttrium ions in molten  $\text{LiCl-KCl-NaCl}$  at  $500^\circ\text{C}$ , and the diffusion coefficient of yttrium in  $\text{Ni}_2\text{Y}$  was found to be  $(2.84 \pm 0.40) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ .

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