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Indium diffusion inside InBi during and after electrodeposition at various temperatures

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Abstract

The influence of temperature on indium galvanostatic electrodeposition from aqueous solutions on bismuth cathodes has been investigated, as well as the time evolution of the deposit composition. The formation of In–Bi intermetallic compounds was observed owing to indium diffusion into, and reaction inside, the bulk of the cathode. By considering the charge transfer and mass transport phenomena, we estimated the In diffusion coefficient into InBi at 30 to 70°C (from 0.79×10^{-15} to $3.77 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$) and from applying an Arrhenius-type relation, we estimated the activation energy (32.8 kJ mol^{-1}) and frequency factor ($3.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

Keywords: Electrodeposition; Indium; Bismuth; In–Bi intermetallic compound; Diffusion coefficient

1. Introduction

In previous papers [1–4], In electrodeposition on Bi cathodes at room temperature was investigated. Owing to In solid state diffusion and reaction inside the bulk of the electrode, the formation of three In–Bi intermetallic compounds (InBi, In_5Bi_3 , In_2Bi) was observed. Indeed, the composition of the deposits changed with time during and after electrodeposition until a unique InBi layer was formed. The mechanisms of In diffusion and reaction were analyzed and the diffusion coefficient into the three different In–Bi compounds was estimated. Exceptionally high values (from 10^{-15} to $10^{-16} \text{ m}^2 \text{ s}^{-1}$) were obtained, those of In_5Bi_3 and In_2Bi being about one order of magnitude smaller than that of InBi.

Owing to the interest of In–Bi intermetallic compounds for applications in electronics, we also aimed

to consider the influence of temperature on the process, in particular on InBi formation.

2. Experimental

The working electrode was Bi of 99.9995% purity (ground with silicon carbide paper) while the reference and counterelectrode were obtained from a 99.999% In bar. The electrolyte was 0.67 N InCl_3 . To avoid colloidal formation, the pH of the solution was adjusted to 1.3 with aqueous HCl. Electrodeposition was performed in galvanostatic conditions, at current densities from 5.0 to 14.3 A m^{-2} for 1.5 to 4.5 h. The measurements were carried out in a traditional PTFE cell at room temperature and in a special temperature-controlled glass cell at 30 to 70°C. The electrode was introduced in the cell already at the testing temperature. No parasitic hydrogen evolution occurred in these experimental conditions [1]. So, In electrodeposition from In^{3+} ions could be assumed to have a 100% efficiency. The coulometric thickness of the deposited In films ranged from 2.8 to 6.1 μm , assuming a density of 7.286 g cm^{-3} . For SEM-EDS in-

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vestigation, we prepared 12.6 μm thickness deposits both at room temperature and at 70°C, by electrodeposition at 21.4 A m^{-2} for 3 h.

For further details, reference should be made to our previous paper [1].

3. Results and discussion

3.1. Indium electrodeposition

Typical curves giving the potential vs. In of the Bi cathode as a function of time during In electrodeposition at two different temperatures but at the same current density are depicted in Fig. 1 (dashed curves). The circuit was periodically opened for 30 s during electrodeposition to monitor the cathode open-circuit potential vs. In. These values, indicative of the cathode surface composition, are shown as dots in Fig. 1. At the end of the deposition process, the electrode potential vs. In was continuously monitored to evidence the time evolution of the deposits (full curves of Fig. 1).

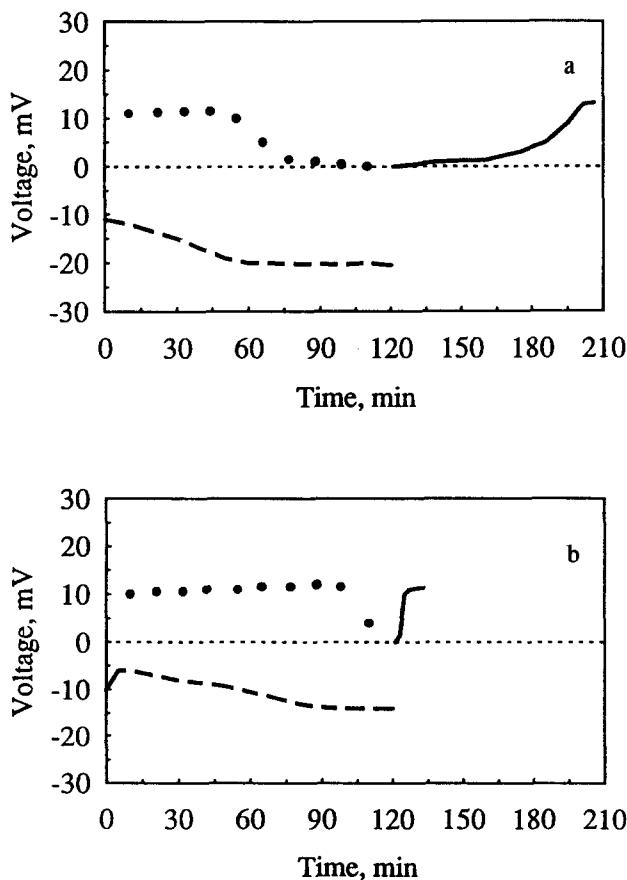


Fig. 1. Cathode potential vs. In of the Bi cathode in closed-circuit conditions (dashes) and after periodically opening the circuit for 30 s (dots) as a function of time during In electrodeposition at 10.6 A m^{-2} , at (a) 50°C and (b) 70°C. The full curves show the time evolution of the electrode potential after In electrodeposition.

Note that the dots in Fig. 1 form an initial plateau which is related to the formation of InBi, as shown by thermodynamic data and structural investigation. At higher electrodeposition temperatures, the plateau is more extended and is observed at slightly higher potentials. Indeed, the kinetics of the diffusion process with reaction is faster and the removed In quantity in the time unit is higher. Moreover, the absolute value of the standard free energy of InBi formation from the elements increases with temperature (see below). At the end of the plateau, the dotted curves gradually decrease to zero since metallic In accumulates on the electrode surface. No intermediate quasi-plateaus were observed in our experimental conditions, the In diffusion rate being so high that the two In–Bi compounds less stable than InBi could not be formed practically.

So, on the basis of experimental results, we expect to be able to evaluate the diffusion coefficient of In in InBi as a function of temperature and, consequently, the activation energy of the process.

3.2. Time evolution of the deposits

The voltage of the Bi electrode was continuously monitored after electrodeposition, as shown on the right (continuous line) of Figs. 1(a) and 1(b). Starting from the value of 0 V vs. In (the electrode surface was initially covered with an In film) the voltage increased up to the plateau due to InBi (the final product) in a much shorter time at 70°C than at 50°C, the deposited In quantity being the same in both cases. The shape of the curves is different, an extended quasi-plateau appearing at the lower temperature (Fig. 1(a)).

SEM and SEM-EDS pictures of the deposit surface and cross-section (obtained by cutting the sample after a short immersion in liquid nitrogen) during time evolution after electrodeposition at 21.4 A m^{-2} for 3 h, at room temperature and at 70°C are respectively shown in the first and second columns of Fig. 2. Note the different morphology of the deposits obtained at the two different temperatures (Fig. 2(a) vs. Fig. 2(b)) as well as the surface changes taking place at room temperature (Fig. 2(a) vs. Fig. 2(e)).

The deposits obtained at room temperature show the typical multilayered structure, see for example Fig. 2(c). From the right to the left we may distinguish Bi, an InBi layer of about 10 to 15 μm and an In_2Bi layer on the surface. The In-line profile is difficult to read because of the skewness of the surface. A single layer of InBi is present after 72 h (Fig. 2(g)). In contrast, only one layer due to InBi is present in the deposit obtained at 70°C (Figs. 2(d) and 2(h)), as also confirmed by X-ray analysis. Indeed, in agreement with electrochemical results, In diffusion with reaction was so fast at such a temperature that the formation of

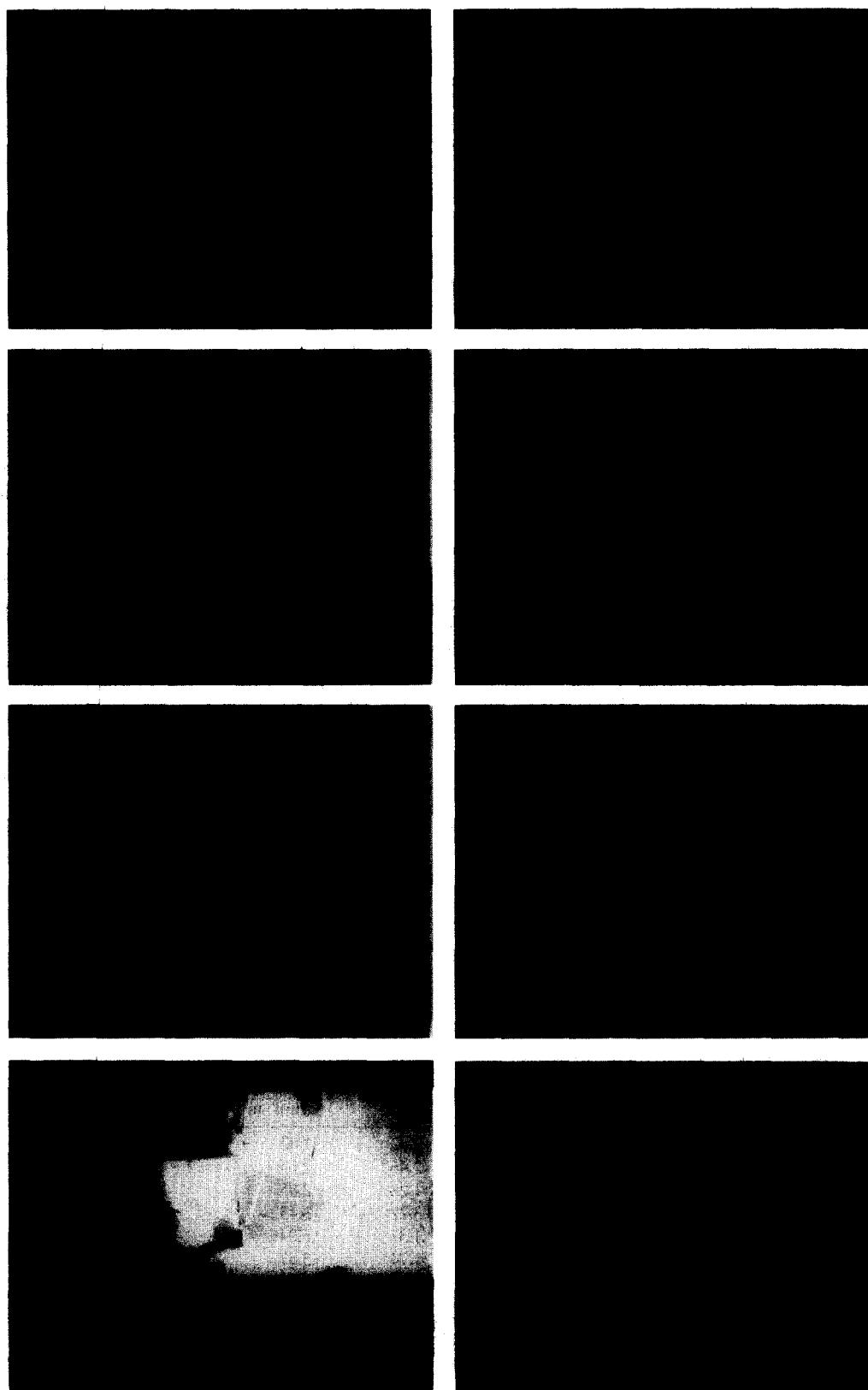


Fig. 2. SEM images of the surface and cross-section of a deposit (a) 20.2, (c) 24.5, (e) 74.03 and (g) 72 h after In electrodeposition at 21.4 A m^{-2} for 3 h, at room temperature; and of a deposit (b) and (d) 6.5, (f) 23.5 and (h) 24 h after In electrodeposition, at 70°C . The In-line profile (scanned along the white line in the micrographs) is reported below.

intermetallic compounds having a higher In/Bi ratio than InBi could not be observed.

3.3. Indium diffusion and reaction

In order to evaluate the In diffusion coefficient, we used the results obtained during electrodeposition by comparing the In moles deposited on, and removed from the unit surface area, m_{dep}^* and m_{rem}^* respectively.

The deposited In quantity depends on the (constant) current density i and linearly increases with deposition time t according to Faraday's law:

$$m_{\text{dep}}^* = \frac{it}{zF} \quad (1)$$

$z = 3$ being the charges transferred during the transfer reaction and F is the Faraday constant.

The removed In quantity may be evaluated from the thickness of the InBi reaction product layer Δx which follows a parabolic growth rate law. Indeed, according to the theory by Schmalzried [5], the dependence of Δx on time t is given by:

$$\Delta x^2 = 2D't, \quad \text{with } D' = -D_{\text{In}}(\text{InBi}) \frac{\Delta G_f^\circ}{RT} \quad (2)$$

where the proportionality constant D' depends on the average value of the In diffusion coefficient in InBi, $D_{\text{In}}(\text{InBi})$, and on the standard Gibbs free energy of formation of InBi from the elements, ΔG_f° . T is the absolute temperature and R the gas constant. So, m_{rem}^* finally results to be proportional to the square root of time:

$$m_{\text{rem}}^* = \frac{\rho}{M} \Delta x = \frac{\rho}{M} (2D't)^{1/2} = (D^* t)^{1/2} \quad (3)$$

Table 1
Evaluation of the D^* values according to Eq. (4) and of the average $D_{\text{In}}(\text{InBi})$ values (see text)

T (°C)	i (A m ⁻²)	t_{dep} (h)	t_{min}^* (h)	t_{max}^* (h)	t^* (h)	$D^* \times 10^6$ (mol ² m ⁻⁴ s ⁻¹)	$D_{\text{In}}(\text{InBi}) \times 10^{15}$ (m ² s ⁻¹)
30	7.2	2.70	0.73	0.90	0.82	1.82	0.79 ± 0.00
40	5.0	3.83	2.37	2.55	2.46	2.64	1.20 ± 0.06
	7.2	2.70	1.18	1.38	1.28	2.85	
50	5.0	4.50	3.13	3.30	3.22	3.45	2.05 ± 0.51
	7.2	2.00	1.27	1.47	1.37	3.04	
	7.2	2.70	1.65	1.82	1.74	3.87	
	10.6	1.83	1.01	1.18	1.10	5.31	
	11.9	1.80	0.90	1.07	0.98	5.98	
	11.9	2.16	0.80	0.92	0.86	5.22	
	14.3	1.50	0.53	0.72	0.63	5.49	
60	5.0	4.50	3.83	4.00	3.92	4.21	2.34 ± 0.40
	7.2	3.50	2.47	2.65	2.56	5.70	
	14.3	1.50	0.57	0.75	0.66	5.78	
70	7.2	4.33	3.20	3.38	3.29	7.33	3.77 ± 0.35
	10.6	1.83	1.63	1.82	1.73	8.33	
	10.6	2.50	1.82	2.00	1.91	9.21	
	11.9	1.80	1.33	1.43	1.38	8.42	

ρ and M being the InBi mass density (9.012 g cm⁻³) and molecular weight (323.80 g mol⁻¹) respectively.

At time t^* , $m_{\text{rem}}^* = m_{\text{dep}}^*$, and the open-circuit potential vs. In decreases towards zero (Figs. 1(a) and 1(b)). Table 1 collects the minimum and maximum times, t_{min}^* and t_{max}^* , (the experimental values are discontinuous), as well as the deposition time t_{dep} , and the average time t^* , at which a change in the potentiometric curve is observed. Several measurements were carried out, and the average values, only, are reported in Table 1. Equating Eqs. (1) and (3) results in

$$D^* = \left(\frac{i}{zF} \right)^2 t^* \quad (4)$$

which allows evaluation of D^* (also reported in the table) from the average time.

As shown in Table 1, D^* values increase with temperature, in agreement with its positive influence on the kinetics of the mass transport process. Moreover, contrary to what is expected on the basis of Eq. (3) where D^* is assumed independent of i , D^* also increases with the current density at constant temperature.

This result cannot be explained by taking into account the structure defects (e.g. grain, dislocation and twin boundaries), as they are well known to increase with the growth rate and to hinder the diffusion process. Instead, it may tentatively be explained by considering the change with the current density in the crystal size of the deposits. Indeed, at low current densities and temperatures, outward growth occurred and was preferred to lateral growth, and relatively thick In microcrystals were formed in correspondence with isolated active centers, i.e. crystal growth surpassed nucleation. At intermediate current

densities, the whole electrode surface was covered by a smooth deposit, whereas at higher current densities the surface became very rough. Hence, the area of the electrode surface in contact with In, and thus effectively working for In diffusion, was smaller, equal or even larger, respectively, than the geometric surface area. So, we expect that the more realistic D^* values for the determination of the diffusion coefficient are the average values at each temperature.

At the highest current density and temperature (14.3 A m⁻² and 70°C) uncontrolled, irregular and irreproducible results were obtained. Indeed, during some of the tests no InBi was formed, while during other tests, high t^* and consequently high D^* values were observed. Possibly, the initial state of the electrode surface is very critical in such extreme experimental conditions. These results were, therefore, not considered further.

Other information on the In diffusion and reaction process may be obtained as follows.

At the end of the evolution process after electrodeposition, i.e. when the deposit was a single layer of InBi, the removed In quantity was exactly the same as the deposited one. At this time t_{fin} we have

$$m_{dep}^* = \frac{it_{dep}}{zF}$$

and

$$m_{rem}^* = (D^* t_{fin})^{1/2}$$

Indeed, in all our experimental conditions, the electrode surface was covered with In after electrodeposition, and, therefore, the time evolution of the deposits was controlled by the In diffusion and reaction process.

By equating the two above quantities, and by introducing for D^* its value from Eq. (4), then

$$t_{fin} = \frac{t_{dep}^2}{t^*} \quad (6)$$

The values of t_{fin} , estimated according to Eq. (6) are compared with the experimental values in Table 2. The latter have been measured at the beginning of the last plateau of the experimental curves (see, for example, Figs. 1(a) and 1(b)). At this time, the electrode surface was already covered with InBi but In was still diffusing inside the bulk of the InBi layer, that is the process was not completed. Hence, the actual t_{fin} values are expected to be slightly larger than the experimental values reported in the last column of Table 2, as indicated by \geq .

The estimated and experimental values agree well, though we did not consider the possible formation of In₅Bi₃ and In₂Bi. These compounds have much smaller diffusion coefficients than InBi [2]. So, the very

Table 2

Evaluation of the t_{fin} values at different temperatures according to Eq. (6) and comparison with the experimental results (see text)

T (°C)	i (A m ⁻²)	t_{dep} (h)	t^* (h)	t_{fin}^* (estimated) (h)	t_{fin}^* (experimental) (h)
30	7.2	2.70	0.82	8.89	≥ 7.16
40	5.0	3.83	2.46	5.96	≥ 5.23
	7.2	2.70	1.28	5.70	≥ 4.42
50	5.0	4.50	3.22	6.29	≥ 5.56
	7.2	2.00	1.37	2.92	≥ 2.33
	7.2	2.70	1.74	4.19	≥ 3.64
	10.6	1.83	1.10	3.04	≥ 3.09
	11.9	1.80	0.98	3.31	≥ 2.96
	11.9	2.16	0.86	5.42	≥ 5.92
	14.3	1.50	0.63	3.57	≥ 2.90
60	5.0	4.50	3.92	5.16	≥ 5.30
	7.2	3.50	2.56	4.78	≥ 4.33
	14.3	1.50	0.66	3.41	≥ 2.96
70	7.2	4.33	3.29	5.70	≥ 5.15
	10.6	1.83	1.73	1.94	≥ 2.13
	10.6	2.50	1.91	3.27	≥ 3.13
	11.9	1.80	1.38	2.35	≥ 2.46

small difference between the two groups of values seems to indicate the negligible role played by the higher In–Bi intermetallic compounds even during deposit evolution.

3.4. Thermodynamic quantities

The determination of the In diffusion coefficient in InBi also requests the knowledge of the InBi standard free energy of formation from the elements at different temperatures, $\Delta G_f^\circ(T)$. The latter thermodynamic quantity may be evaluated from literature data [6–9] of ΔG_f° and ΔH_f° at 273 K, according to the Gibbs–Helmholtz equation, assuming a constant value for the enthalpy of formation. However, since there is a certain spread in the values of different authors, although in the range of the usual uncertainties in this type of determination, we preferred to utilize the equation

$$\Delta G_f^\circ(T) = -1464.4 - 7.58128 \times T \text{ J mol}^{-1} \quad (7)$$

given by Chevalier [10], who optimized the experimental data of other authors during his thermodynamic evaluation of the In–Bi phase diagram. The results are collected in Table 3, together with the values of the related plateau potentials vs. In, $E^\circ(T)$. The relatively small difference in the free energies at the different temperatures implies a very small difference in the plateau voltages, in the range of the experimental error.

3.5. Indium diffusion coefficient

From Eqs. (2) and (3), taking the average value of $D^*(T)$ (Table 1) and the value of $\Delta G_f^\circ(T)$ (Table 3) into

Table 3
Standard Gibbs free energy of formation of InBi at different temperatures from Eq. (7) and related plateau voltage

T (K)	$\Delta G_f^\circ(T)$ (kJ mol ⁻¹)	$E^\circ(T)$ (mV vs. In)
273.16	-3.535	12.21
298.16	-3.725	12.87
303.16	-3.763	13.00
313.16	-3.838	13.26
323.16	-3.914	13.52
333.16	-3.990	13.78
343.16	-4.066	14.04

account, and assuming the value at room temperature (i.e. 9.012 g cm⁻³ [11]) as the density for InBi, we estimated the average In diffusion coefficient from 30 to 70°C (Table 1).

Unusually high values (around 10⁻¹⁵ m² s⁻¹) were obtained, in comparison with those for many metals and semiconductors (and their alloys) which range from 10⁻²⁰ to 10⁻⁵⁰ m² s⁻¹, at room temperature [12]. With the exception of In in InSb, whose diffusion coefficient is around 10⁻¹⁶ m² s⁻¹ at 100°C [13], values comparable with that for In in InBi are only observed when very small atoms are diffusing (e.g. around 10⁻¹⁵ m² s⁻¹ for Li in Ge and Si, and 10⁻¹⁷ m² s⁻¹ for C in b.c.c. Fe at 70°C) or at high temperatures (e.g. around 10⁻¹⁵ m² s⁻¹ for Zn and Cu in Cu and 10⁻¹⁷ m² s⁻¹ for Fe in Fe at 727°C) [12].

The Arrhenius plot $\log D_{In}(InBi)$ as a function of $1/T$ is shown in Fig. 3, where the error bars are also reported. Such temperature dependence appears to be true in our case, so, from the slope and the y-axis intercept of the observed straight line, we estimated

the values of 32.8 kJ mol⁻¹ and 3.7 × 10⁻¹⁰ m² s⁻¹ for the activation energy and the frequency factor respectively.

The very small value of the activation energy (usually about 100 to 400 kJ mol⁻¹ for many materials of interest) is certainly at the origin of the high diffusion coefficient we found for In in InBi, notwithstanding the exceptionally small frequency factor (the theoretically predicted—and experimentally observed—values are between 10⁻⁵ and 10⁻⁷ m² s⁻¹ [12]).

4. Conclusions

Indium electrodeposition on Bi electrodes at current densities from 5.0 to 21.6 A m⁻² and at temperatures from 30 to 70°C has been investigated and the time evolution of the deposit composition also considered. The results show the predominant formation of InBi over that of the two other intermetallic compounds: In₅Bi₃ and In₂Bi. Furthermore, a regular increase of the rate of In diffusion and reaction inside InBi is observed both with temperature and current density. This last phenomenon has tentatively been explained on the basis of a change in the crystal size of the deposits with current density bringing about an increase of the effective area for diffusion. Instead, the structure defectiveness increases with current density and, therefore, the diffusion process is hindered. Very high values were obtained for the diffusion coefficient (from 0.79 × 10⁻¹⁵ to 3.77 × 10⁻¹⁵ m² s⁻¹) while the activation energy was 32.8 kJ mol⁻¹ and the frequency factor 3.7 × 10⁻¹⁰ m² s⁻¹.

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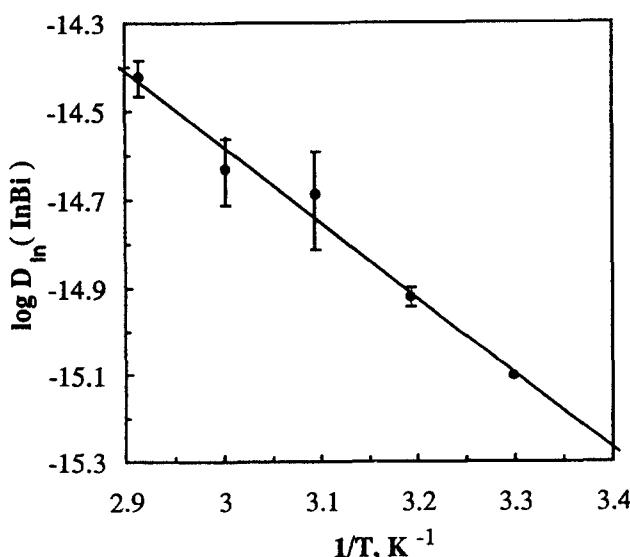


Fig. 3. Logarithm of the average In diffusion coefficient as a function of the reverse of the absolute temperature. The standard deviation from the mean value is also indicated.

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