

# Growth kinetics of compound layers at the nickel–bismuth interface

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Received 7 July 1995; in final form 2 October 1995

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## Abstract

The  $\text{NiBi}_3$  compound layer formation at the Ni–Bi interface has been investigated at 150, 200 and 250 °C using metallography, X-rays and electron probe microanalysis. Its growth kinetics have been studied with the use of microhardness indentations as the markers. The growth process has been found to be diffusion controlled, with the Bi atoms being the main diffusing species. An increase in layer thickness took place entirely at the Ni– $\text{NiBi}_3$  interface. The layer thickness–time dependence in the 1 to 300 h time range obeys a parabolic equation,  $x^2 = 2k_1 t$ . Values of the reaction diffusion constant  $k_1$  have been calculated both from this equation and its differential form, yielding identical results. The temperature dependence of the  $\text{NiBi}_3$  reaction diffusion constant is well described by an equation of the Arrhenius type:  $k_1 = A \exp(-E/RT)$ , where  $A = (0.49 \pm 0.05) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and  $E = (67.1 \pm 0.7) \text{ kJ mol}^{-1}$ .

**Keywords:** Growth kinetics;  $\text{NiBi}_3$  compound layer; Nickel–bismuth interface; Reaction diffusion constants

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## 1. Introduction

While the nickel–bismuth phase diagram is well established [1–3], data on the growth kinetics of compound layers at the nickel–bismuth interface are lacking in the literature. This binary system seems, however, to be suitable as a model to investigate the main features of layered compound formation in reaction couples including the phase selection, i.e. which compound appears first between the initial phases.

Voss [1] found two intermetallic compounds,  $\text{NiBi}$  and  $\text{NiBi}_3$ , to exist in the nickel–bismuth binary system (see also Ref. [2]). Recently, Feschotte and Rosset [3] thoroughly reinvestigated this diagram and confirmed the existence of these two intermetallics. However, contrary to the expectations of Voss [1] and Hansen and Anderko [2], they have not revealed a wide range of homogeneity of the  $\text{NiBi}$  compound. The composition of this compound was found to be  $51.0 \pm 0.3$  at. % Bi. Thus, its range of homogeneity is very narrow, if any. The  $\text{NiBi}_3$  compound is stoichiometric [3]. Both compounds melt incongruently:  $\text{NiBi}$  at 646 °C and  $\text{NiBi}_3$  at 467 °C [3].

The aim of this work was to:

(a) establish which of the two compounds grows first

as a separate compact layer between nickel and bismuth at 150 to 250 °C;

- (b) study the layer growth kinetics;
- (c) reveal the main diffusing species during the layer formation;
- (d) determine the values of the reaction diffusion constants describing the growth process.

## 2. Experimental details

### 2.1. Materials and specimens

Electrolytic-grade nickel (99.98 mass% Ni) was used in the form of polished plates  $3 \times 9 \times 14 \text{ mm}^3$ . Their final treatment involved electrolytic polishing, both to remove the surface contaminations and to reduce mechanical stresses.

The plates were mounted into graphite crucibles, 11 mm inner diameter, and heated to 350 °C under a low-melting flux. The crucibles were then filled with molten bismuth (greater than 99.99 mass% Bi) and allowed to cool until its crystallization. A continuous, coherent  $\text{NiBi}_3$  layer, 2  $\mu\text{m}$  thick, was found to form during the specimen preparation. Hence, this technique ensured an intimate contact between the nickel and bismuth phases so that the reaction started simul-

taneously at all points of the Ni–Bi interface. This condition is clearly very essential in order to obtain reliable kinetic data.

Each bimetallic specimen was cut into two pieces using an electric-spark machine.

## 2.2. Experimental methods

The Ni–Bi specimens were annealed in sealed glass ampoules, filled with helium, at 150, 200 and 250 °C for 1 to 300 h. Each specimen was annealed successively a few times. After the first annealing, the specimen surface was ground mechanically and then polished electrolytically using the “Elypovist” apparatus.

The compound layer formed was examined metallographically, by X-rays and electron probe microanalysis (EPMA). X-ray patterns were taken both from the cross-sections and the powdered phases by standard techniques using Cu K $\alpha$  radiation. The nickel and bismuth contents of the phases and their concentration profiles within the Ni–Bi transition zone were found with the use of a JEOL Superprobe-733 microanalyser operating at 25 kV.

The compound layer thickness was measured using a microhardness tester and an optical microscope. The microhardness tester was also used to put the markers onto the surfaces of the phases involved in the interaction before each subsequent anneal. The microhardness indentation method was shown by van Loo [4] to possess advantages over other marker methods (inert wires, particles, etc.). The main advantage being that the microhardness indentations do not hinder the growth process. It should be noted, however, that in some systems a possible disadvantage of this method may arise from the surface effect.

Five to ten rows of microhardness indentations, typically at a load of 0.196 N (20 g), were put onto the surface of the Ni–Bi cross-section in the direction of diffusion at different places of the Ni–Bi interface. The layer thickness at each annealing time was thus taken as the average of five to ten measurements. The experimental results were treated using standard statistical methods.

## 3. Results and discussion

### 3.1. Phase selection

Only the NiBi<sub>3</sub> compound formed a compact layer between nickel and bismuth, Fig. 1. Its interplanar distances (d-spacings), found experimentally, coincided with those calculated using the lattice parameters reported by Glagoleva and Zhdanov [5]:  $a = 0.8875 \pm 0.0006$  nm,  $b = 0.4112 \pm 0.004$  nm,  $c = 1.1477 \pm$

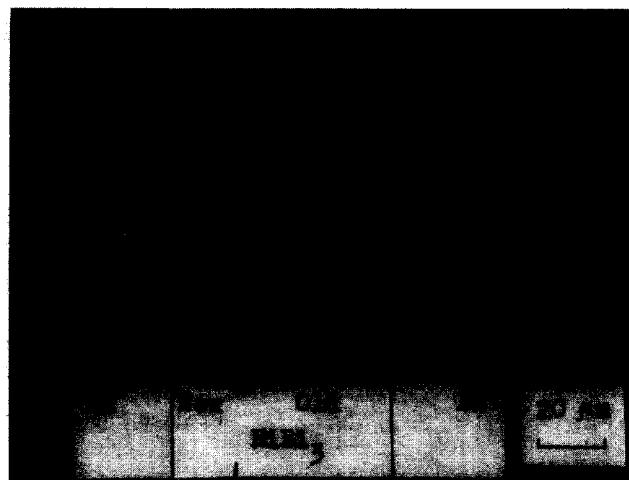


Fig. 1. Secondary electron image of the Ni–Bi transition zone with the Ni and Bi concentration profiles. Microhardness indentations were put onto the surface of the cross-section at a load of 0.196 N (20 g). Temperature 250 °C. The time of the first annealing is 4 h, while that of the second is 3.5 h (7.5 h in total).

0.0008 nm. The orthorhombic unit cell of this compound contains four NiBi<sub>3</sub> molecules.

The compositions of the compound layer and the adjacent phases measured by EPMA are presented in Table 1. From these data it follows that:

- (i) the composition of the layer corresponds well enough to the stoichiometry of the NiBi<sub>3</sub> compound;
- (ii) this compound has either very narrow or, rather, no range of homogeneity.

Note that, besides the results of Table 1, the electron probe measurements were also performed on three other specimens annealed under different conditions. In all the cases the scatter of experimental points was purely statistical whilst, in the case of existence of a noticeable homogeneity range, a gradual decrease of the Ni content and accordingly an increase of the Bi content in the layer from the Ni–NiBi<sub>3</sub> interface to the NiBi<sub>3</sub>–Bi interface could clearly be observed. It should be emphasised that, when investigating the Ni–Bi phase diagram, Feschotte and Rosset [3] also did not reveal the existence of an appreciable homogeneity range of the NiBi<sub>3</sub> compound.

The fact that the NiBi<sub>3</sub> compound layer grows first at the nickel–bismuth interface agrees with a general trend formulated by d’Heurle [6] as the ordered Cu<sub>3</sub>Au rule. In most cases, the first phase formed contains the highest proportion of the element with the lowest melting point.

It should be noted, however, that this rule is not of general validity, for example, Blanpain et al. [7] found Pd<sub>2</sub>Al<sub>3</sub>, not PdAl<sub>3</sub>, to form and grow first between palladium and aluminium. Exceptions to the rule are hardly predictable *a priori*, while in most cases they can be understood and explained *a posteriori* (for

Table 1

Electron probe microanalysis of the Ni–Bi transition zone. Temperature 250 °C, annealing time 90000 s

Phase	Place of measurement	Content			
		Ni		Bi	
		mass%	at.%	mass%	at.%
1	2	3	4	5	6
<i>At distance l away from the Ni–NiBi<sub>3</sub> interface</i>					
Ni	<i>l = 2.5 μm</i>	100.0	100.0	0.0	0.0
	10	100.0	100.0	0.0	0.0
	25	100.0	100.0	0.0	0.0
	50	100.0	100.0	0.0	0.0
NiBi <sub>3</sub>	<i>5</i>	8.6	25.1	91.4	74.9
	15	8.9	25.8	91.1	74.2
	25	8.3	24.4	91.7	74.6
	35	8.6	25.2	91.4	74.8
	45	8.2	24.2	91.8	75.8
	60	8.0	23.6	92.0	76.4
	75	8.1	23.8	91.9	76.2
	85	8.8	25.5	91.2	74.5
	95	8.5	24.9	91.5	75.1
	115	8.1	23.9	91.9	76.1
	<i>At distance l away from the NiBi<sub>3</sub>–Bi interface</i>				
Bi	<i>l = 2.5 μm</i>	0.0	0.0	100.0	100.0
	15	0.0	0.0	100.0	100.0
	30	0.0	0.0	100.0	100.0
	60	0.0	0.0	100.0	100.0
	100	0.1	0.3	99.9	99.7

more details see, for example, the work of d'Heurle and Gas [8]).

The NiBi layer is missing in the Ni–Bi couple for kinetic reasons. In a binary system with two and more compounds the first layer formed should usually reach a certain minimal thickness before the second can grow (for more details see Refs. [9,10]). Probably, this thickness was not reached under the conditions of this investigation due to insufficient annealing times.

The second part of the ordered Cu<sub>3</sub>Au rule states that, in the process of layer formation, the majority atoms constitute the dominant diffusing species. Marker experiments were performed to check whether this is the case in Ni–Bi couples.

### 3.2. The main diffusing component during the NiBi<sub>3</sub> layer growth

From a general viewpoint, the NiBi<sub>3</sub> compound layer growth (except at the very beginning of the Ni–Bi interaction) is due to two partial chemical reactions (see Refs. [9,10]). Firstly, the Bi atoms may diffuse across the layer bulk from interface 2 to interface 1 (Fig. 2) and then react with the surface Ni atoms to form NiBi<sub>3</sub> at the Ni–NiBi<sub>3</sub> interface:

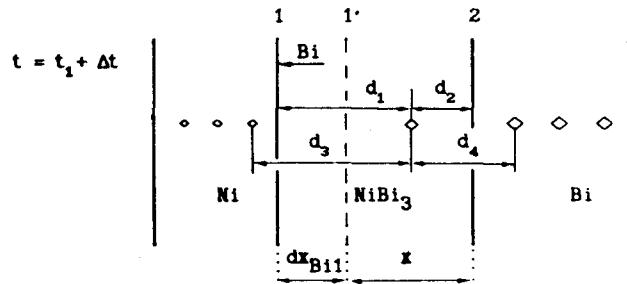
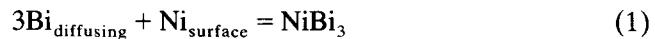
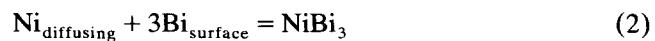


Fig. 2. Schematic illustration of the NiBi<sub>3</sub> growth process at the nickel–bismuth interface.



Secondly, the Ni atoms may diffuse across the layer bulk in the opposite direction and then react with the surface Bi atoms to form more NiBi<sub>3</sub> at the NiBi<sub>3</sub>–Bi interface:



Owing to the different sizes of the Ni and Bi atoms, and also to the great difference in melting points of the components, the contributions of these reactions to the layer growth process can hardly be expected to be equal. Microhardness indentation markers permit-

ted these contributions to be “visualised” (see Figs. 1 and 2).

The distances between the markers at the same place were measured three times:

(1) before each successive annealing, except the first of an as-received Ni–Bi specimen;

(2) after each annealing, without any polishing of the cross-section surface;

(3) after the electrolytic repolishing of the cross-section to remove some amount of the cross-section material from its surface so that the craters of the microhardness indentations remained visible under microscope.

In the latter two cases, only insignificant differences were observed in measured values of the distance between the corresponding markers (compare the numbers in the last two rows of Table 2). This means that, under the conditions of this investigation, the surface effect due to the difference in values of surface and volume diffusivities of the components was negligible, if any. Additional proof for the absence of significant surface effect was obtained by comparing the layer thickness existing, say, after the second annealing and before the third annealing. Namely, before the third annealing the Ni–Bi specimen was ground to remove 0.3–0.5 mm of its surface material and again polished electrolytically. Comparison of the layer thickness in both cases did not reveal significant differences.

The distance  $d_2$  between the microhardness indentations located initially in the middle part of the  $\text{NiBi}_3$  layer and interface 2 did not change during annealing. Hence, no appreciable diffusion of the Ni atoms across the growing  $\text{NiBi}_3$  layer took place.

In contrast, the distance  $d_1$  between this microhardness indentation and interface 1 was found to increase with increasing annealing time. Therefore, at 150 to 250 °C the layer growth is due to the partial chemical reaction (1), the contribution of the partial chemical reaction (2) being negligible, if any. Thus, the Bi atoms are predominant diffusing species in the course of layer formation, in agreement with the ordered  $\text{Cu}_3\text{Au}$  rule.

It should be mentioned that the sum of the distances

$d_3$  and  $d_4$  slightly diminished during annealing. This is due to a decrease in volume of the  $\text{Ni–NiBi}_3\text{–Bi}$  specimen connected with the formation of the  $\text{NiBi}_3$  compound. The ratio of the decrease in  $(d_3 + d_4)$  value to the corresponding increase in thickness of the  $\text{NiBi}_3$  layer was experimentally found to be  $0.20 \pm 0.05$ .

Note that the distances between the markers located in the Ni phase did not change in the course of annealing, indicative of no formation of a solid solution of bismuth in nickel. The distances between the markers located in the Bi phase remained unchanged as well. Also, no changes in size or configuration of the microhardness indentations were observed in either phases. Hence, the components are in fact mutually insoluble at 150 to 250 °C.

### 3.3. Layer growth kinetics

As only the Bi atoms are diffusing across the  $\text{NiBi}_3$  layer, its growth kinetics at the Ni–Bi interface can be described by the equation (see Refs. [9,10])

$$dt = \left( \frac{1}{k_0} + \frac{x}{k_1} \right) dx \quad (3)$$

where  $x$  is the total layer thickness at the time  $t$ ,  $k_0$  is a chemical constant and  $k_1$  is a physical (diffusional) constant.

If the layer thicknesses are large enough, the condition  $k_0 \gg k_1/x$  is satisfied. Therefore, Eq. (3) is simplified to

$$dt = \frac{x}{k_1} dx \quad (4)$$

By integrating this equation with initial condition  $x = 0$  at  $t = 0$ , the equation

$$x^2 = 2k_1 t \quad (5)$$

is obtained. It can also be rewritten as follows:

$$x = (2k_1 t)^{1/2} \quad (6)$$

If the layer thickness–time dependence is well described by this equation, then the growth process is considered to be diffusion controlled. A plot of the layer thickness against the square root of the anneal-

Table 2

Typical changes in distance between the indentation markers on the surface of the Ni–Bi cross-section (see also Fig. 2). Temperature 250°C. The time of the first annealing is 50 h, while that of the second is 25 h (75 h in total)

Measurements made	Distance ( $\mu\text{m}$ )											
	Between five markers in Ni phase				$d_1$	$d_2$	$d_3$	$d_4$	Between five markers in Bi phase			
Before second annealing	80	79	77	80	88	104	142	158	76	76	77	78
After second annealing without polishing	81	79	78	79	122	104	174	121	77	75	78	77
After second annealing with slight electrolytic polishing	80	78	77	79	121	105	174	120	76	75	77	78

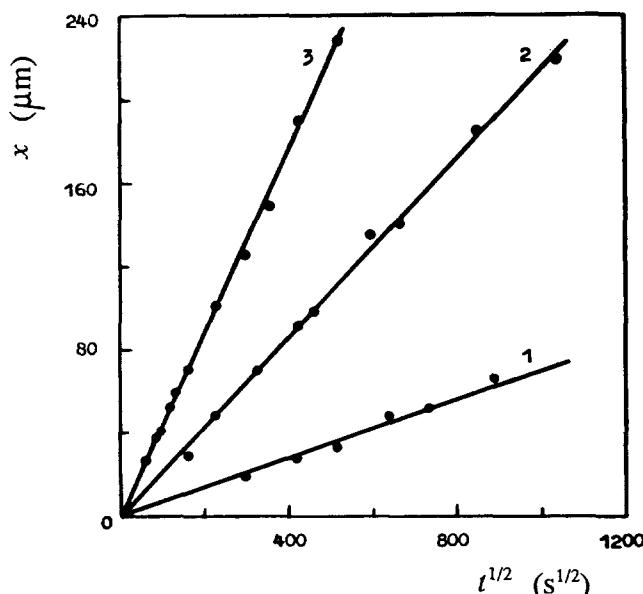


Fig. 3.  $\text{NiBi}_3$  layer thickness plotted against the square root of the annealing time. 1, 150 °C; 2, 200 °C; 3, 250 °C.

ing time is shown in Fig. 3. As seen in Fig. 3, the experimental points yield three straight lines. Thus, the  $\text{NiBi}_3$  layer growth is indeed diffusion controlled. The constant  $k_1$  may therefore be called the reaction diffusion constant.

The value of the reaction diffusion constant  $k_1^{(\text{int})}$  can be calculated using the integrated Eqs. (5) or (6). The superscript (int) is used to distinguish between the value of the constant calculated from the integrated equation and that found from the differential equation. The latter is denoted  $k_1^{(\text{dif})}$ .

The experimental values of  $k_1^{(\text{int})}$  at all three temperatures are listed in Table 3, together with their 0.95 confidence limits. These values represent the volume diffusivities of the Bi atoms in the  $\text{NiBi}_3$  lattice in the course of reaction diffusion. Note that, in general the reaction diffusion coefficient of any component in a compound is much greater than the self-diffusion coefficient of that component in the compound [11].

The value of the reaction diffusion constant can also be calculated from the differential Eq. (4):

$$k_1^{(\text{dif})} = x_{\text{mean}} \frac{\Delta x}{\Delta t} \quad (7)$$

where  $x_{\text{mean}} = (x_{i+1} + x_i)/2$ ,  $\Delta x = x_{i+1} - x_i$ , and  $\Delta t =$

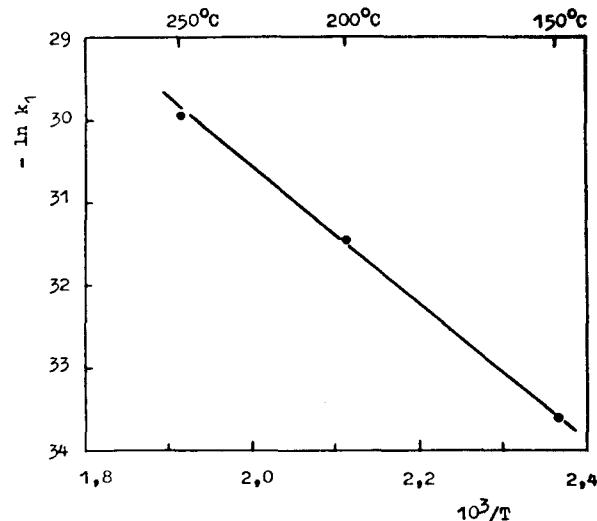


Fig. 4. Temperature dependence of the  $\text{NiBi}_3$  reaction diffusion constant.

$t_{i+1} - t_i$ ,  $x_{i+1}$  and  $x_i$  being the layer thickness at time  $t_{i+1}$  and  $t_i$  respectively. In this equation,  $\Delta t$  is the time range between two successive annealings.

The experimental values of  $k_1^{(\text{dif})}$  obtained are given in Table 3. If the  $\text{NiBi}_3$  layer growth is indeed diffusion controlled, and follows the parabolic law, then  $k_1^{(\text{int})}$  and  $k_1^{(\text{dif})}$  must clearly coincide at each annealing temperature. As seen in Table 3, this is in fact the case; the difference being practically only in the somewhat different scatter of the values of  $k_1^{(\text{int})}$  and  $k_1^{(\text{dif})}$ .

Note that  $k_1^{(\text{int})}$  coincides with  $k_1^{(\text{dif})}$  only in this particular case, where one component (bismuth) is diffusing across the growing layer. In the general case, where two components A and B are diffusing at comparable rates,  $k_1^{(\text{int})}$  is equal to the sum of  $k_1^{(\text{dif})}$  for A and  $k_1^{(\text{dif})}$  for B. The latter values should be determined from the partial increases in layer thickness at both interfaces with the initial phases [9].

#### 3.4. Temperature dependence of the reaction diffusion constant

The temperature dependence of reaction diffusion constants is usually described by the Arrhenius equation (see Ref. [12])

Table 3  
Values of the  $\text{NiBi}_3$  reaction diffusion constants

Temperature (°C)	$k_1^{(\text{int})}$ ( $\text{m}^2 \text{s}^{-1}$ )	0.95 confidence limits for $k_1^{(\text{int})}$ ( $\text{m}^2 \text{s}^{-1}$ )	$k_1^{(\text{dif})}$ ( $\text{m}^2 \text{s}^{-1}$ )	0.95 confidence limits for $k_1^{(\text{dif})}$ ( $\text{m}^2 \text{s}^{-1}$ )
150	$2.4 \times 10^{-15}$	$\pm 0.4 \times 10^{-15}$	$2.6 \times 10^{-15}$	$\pm 0.3 \times 10^{-15}$
200	$2.2 \times 10^{-14}$	$\pm 0.2 \times 10^{-14}$	$2.1 \times 10^{-14}$	$\pm 0.2 \times 10^{-14}$
250	$9.5 \times 10^{-14}$	$\pm 0.3 \times 10^{-14}$	$9.5 \times 10^{-14}$	$\pm 0.5 \times 10^{-14}$

Table 4

Temperature dependence of the  $\text{NiBi}_3$  reaction diffusion constant  $k_1 = A \exp(-E/RT)$ 

Temperature		$1/T$ ( $\times 10^{-3} \text{ K}^{-1}$ )	$k_1$ ( $\text{m}^2 \text{ s}^{-1}$ )	$\ln k_1$	$A$ ( $\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ )	$E$ ( $\text{kJ mol}^{-1}$ )
°C	K					
150	423	2.364	$2.5 \times 10^{-15}$	-33.622	$0.49 \pm 0.05$	$67.1 \pm 0.7$
200	473	2.114	$2.1 \times 10^{-14}$	-31.494		
250	523	1.912	$9.5 \times 10^{-14}$	-29.985		

$$k_1 = A \exp(-E/RT) \quad (8)$$

where  $A$  is the frequency factor,  $E$  is the activation energy of the process of reaction diffusion,  $R$  is the gas constant and  $T$  is the absolute temperature.

Eq. (8) can also be used in the form

$$\ln k_1 = \ln A - E/RT \quad (9)$$

It is seen that a graph of  $\ln k_1$  plotted against the reciprocal temperature  $1/T$  gives a straight line (Fig. 4), from whose slope and intercept the values of  $E$  and  $A$  can readily be determined.

The experimental data have been treated according to Eq. (9) using the least-squares fit method. To calculate the temperature dependence, the average values of the reaction diffusion constant  $k_1 = (k_1^{(\text{int})} + k_1^{(\text{dif})})/2$  were taken (Table 4). The constants of this equation are  $A = (0.49 \pm 0.05) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and  $E = (67.1 \pm 0.7) \text{ kJ mol}^{-1}$ .

#### 4. Conclusions

(1) The  $\text{NiBi}_3$  compound layer grows at the Ni–Bi interface at 150 to 250°C and annealing times up to 300 h.

(2) Its growth process is diffusion controlled.

(3) The Bi atoms constitute the main diffusing species during the layer formation, while the rate of diffusion of the Ni atoms is quite negligible.

(4) An increase in layer thickness takes place entirely at the Ni– $\text{NiBi}_3$  interface.

(5) The layer growth kinetics obey a parabolic equation  $x^2 = 2k_1 t$ .

(6) The temperature dependence of the reaction diffusion constant is well described by the Arrhenius

equation  $k_1 = A \exp(-E/RT)$ , with  $A = (0.49 \pm 0.05) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and  $E = (67.1 \pm 0.7) \text{ kJ mol}^{-1}$ .

#### Acknowledgements

The authors would like to thank A.V. Samelyuk for help with EPMA. One of the authors (V.I.D.) expresses his sincere gratitude to F.M. d'Heurle, F.J.J. van Loo, P. Gas, J. Philibert and B. Pieraggi for many helpful discussions of the problems of reaction kinetics. The research described in this publication was made possible in part by Grants No. UBR000 and UBR200 from the International Science Foundation and the Government of the Ukraine.

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