DIFFUSION OF GALIUM IN POLYCRYSTALLINE Ni$_3$Ga

Petr Mareček
Tomáš Fous
Jiří Čermák

Institute of Physics of Materials AS CR, Žižkova 22, CZ-616 62 Brno, Czech Republic,
cermak@ipm.cz

Abstract
The diffusion of $^{67}$Ga radiotracer in polycrystals of Ni$_3$Ga intermetallic was studied by residual activity method. Both volume- and grain boundary diffusivity was investigated and quantitatively described. Obtained diffusivities of Ga in Ni$_3$Ga lattice show the increasing dependence on increasing Ga concentration.

1. INTRODUCTION

Intermetallic alloys are materials that show a series of very promising characteristics [1]. A number of investigations have been done in recent years that were devoted before all to their mechanical behavior. Since some of high-temperature characteristics are controlled by diffusion, it is clear that these materials are also very often a subject of diffusion studies. Due to atomic ordering of the intermetallic alloys, the study of diffusion processes is – besides its technological importance – interesting also from the theoretical viewpoint. A couple of sophisticated mechanisms have been proposed in recent years [1-4] that can explain diffusion coefficients measured in ordered structures. There are, however, open questions in the field and the state of art is far from being well understood.

Under the wide variety of compounds, the transition-metal aluminides attract the greatest attention of both basic and applied research. One of the prominent compounds lying at the focus of interest is Ni$_3$Al, which is a material of superior structural stability, it has very good high-temperature strength and it resists to chemical degradation. This material, however, suffers from low temperature brittleness, which may be suppressed considerably by (micro)alloying, e.g., by boron [5], nevertheless, the elimination of brittleness of Ni$_3$Al-based alloys still remains a hot topic.

It is known that the brittleness of these materials in polycrystalline form is related to grain boundaries (GB) [1]. Since GBs are places, where the alloying elements may segregate [6], it implies that the data on grain boundary chemistry and thermal changes of concentration controlled by grain boundary diffusion (GBD) of chemical components may be useful for the assessment of behavior of intermetallic polycrystals with strong impact into practice.

Diffusion measurements provide a complete information on diffusion mechanisms in those instances only, where it is possible to measure the diffusivities of both (all) chemical components. It is not the case of Ni$_3$Al, because there is no proper radioisotope of Al for the diffusion measurement. Therefore, it is inevitable, to model this intermetallic by another ones that have radioisotopes of alloying elements and that
would scale the diffusion properties of Ni$_3$Al. One of the candidates is Ni$_3$Ga, which has the same structure (L1$_2$ - it is derived from FCC structure; the Ni atoms occupy the centers of faces, Ga atoms are in cubes corners) as Ni$_3$Al.

### 2. EXPERIMENTAL

#### 2.1. Experimental alloys

Six experimental alloys were prepared by induction melting from pure components (4N Ga and 3N7 Ni) under the protective Ar atmosphere and cast into copper mould. Ingots (cylinders of diameter x length = 12 mm x 80 mm) were homogenization annealed at 1000°C for 5 days. The chemical homogeneity after the annealing was checked by line X-ray chemical microanalysis at SEM/EDAX/WEDAX. Chemical composition of alloys is shown in Table 1. Mean grain size of experimental alloys after thermal treatment was about 200 µm.

#### Table 1

Chemical composition of experimental alloys in at.%.  

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>c$_{Ga}$</th>
<th>c$_{Ni}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.4</td>
<td>bal.</td>
</tr>
<tr>
<td>2</td>
<td>23.9</td>
<td>“</td>
</tr>
<tr>
<td>3</td>
<td>25.2</td>
<td>“</td>
</tr>
<tr>
<td>4</td>
<td>26.3</td>
<td>“</td>
</tr>
<tr>
<td>5</td>
<td>27.5</td>
<td>“</td>
</tr>
<tr>
<td>6</td>
<td>28.3</td>
<td>“</td>
</tr>
</tbody>
</table>

#### 2.2. Measurement

The diffusion samples were machined from the thermally treated ingots in the form of small cylinders diameter x height = 10 mm x 3 mm and the welded planes were ground flat with metallographic papers (last grade 2400). The flat front planes of cylindrical samples were mechanically polished with diamond paste after grinding, so the mirror-like surface smoothness was achieved.

The tracer was deposited on the polished surface by vacuum-evaporation technique. The aqueous solution of gallium citricum was used as a source that was dropped-and-dried on the tungsten boat. The compound was thermally decomposed in vacuum chamber into gaseous phase and Ga, which was evaporated from the shock-heated boat onto the cold polished samples (thickness of the radioactive layer was of the order 10$^2$ nm). The edges of the samples were masked to prevent the lateral diffusion along the sample surface.

The samples were wrapped-up in Ni foil and sealed together with a piece of Ti foil (getter) into quartz ampoules filled with 6N Ar to about 10$^4$ Pa. This should prevent the evaporation of Ga (both $^{67}$Ga from the surface and the Ga from the near-surface region of the samples).

Diffusion anneals of sealed samples were carried out in a horizontal tube furnace CLASSIC with controlled temperature. Fluctuation and absolute accuracy of chosen temperature was within ±1 K. The penetration – depth curves were measured by residual activity method [7]. The individual layers were taken-off by fine grinding and
their thickness was obtained by precise weighing. Concentration of $^{67}$Ga in layers was measured by $\alpha/\beta/\gamma$ Low-Level Counter CANBERRA 2400.

3. RESULTS

3.1. Volume diffusion

The experimental arrangement of the present diffusion measurement realizes the diffusion from thin surface source into a half-space, which is described by initial – boundary conditions

\[
c(0, 0) = M \\
c(x, 0) = 0 \\
\int_0^\infty c(x, t) \, dx = M.
\]

(1)

Analytical, so-called thin film solution of diffusion equation with the conditions (1) is

\[
c(x, t) = \frac{M}{\sqrt{\pi D t}} \exp \left( -\frac{x^2}{4Dt} \right).
\]

(2)

Coefficient of volume diffusion $D$ can be obtained by fitting Eq.(2) to measured penetration curves $c(x, t)$. An example of measured concentration – depth curve $c(x, t)$ for annealing 1240 K / 2hrs is illustrated in Fig.1.

Fig. 1 An example of penetration curves measured for the diffusion anneal carried out at 1240 K for 2 hrs. Solid lines - fitted equation (2).
It can be seen that the concentration curves can be well approximated by the known solution in a certain near-surface region. At greater depth $x$ there is a considerable upward curvature caused by the rapid diffusion along the GBs.

Concentration and temperature dependence of all obtained $D$ values is shown in Figs. 2 and 3.

Fig. 2 Measured volume diffusion coefficients of Ga, $D$, in dependence on Ga concentration.

Fig. 3 Temperature and concentration dependence of $D$. The plane – Eq.(5).
3.2. GBD

As it was mentioned above, obtained penetration curves have shown an upward curvature at greater depth \( x \). This makes possible to evaluate the GB diffusivity.

LeClaire [8] analyzed numerically Suzuoka’s exact solution for the case defined by conditions (1) [9], and derived simple approximate relation for evaluation of triple product \( P = \delta D_b \) which is called GB diffusivity and characterizes quantitatively the rate of diffusion transport of given component along GB. \( s \), \( \delta \) and \( D_b \) stand for segregation factor (ratio of diffusant concentration in GB to that in the grain next to GB), GB width (conventionally taken to be about 0.5 nm) and diffusion coefficient in GB respectively. Having the dependence of average diffusant concentration \( c \) on penetration depth \( x \), the LeClaire’s theory says that – as sufficiently great \( x \) where the volume diffusion flux contributes negligibly only to overall flux – the logarithm of \( c \) is a linear function of \( x^{1.2} \) with relatively high numerical accuracy. The theory also gives the relation that can be used for numerical estimation of \( P \)

\[
P = \alpha A^t t^\eta D^\eta
\]  

(3)

In Eq.(3), \( A \) is the slope of great-depth linear segment of ln \( c \) vs. \( x^{1.2} \) curve, \( t, D \) are diffusion time and coefficient of volume diffusion respectively and constants \( \alpha \) through \( \eta \) are known from the theory for various diffusion kinetics. The latter are characterized by the value of parameter \( \beta \)

\[
\beta = \frac{P}{2D^{1.5}t^{0.5}}
\]  

(4)

In Fig. 4 one can see examples of measured penetration curves in co-ordinates log \( c \) vs. \( x^{1.2} \) illustrating the existence of linear tails.

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**Fig. 4** Examples of penetration profiles.
4. DISCUSSION

It can be seen in Fig. 2 that the volume diffusion coefficients show a slight increase with increasing content of Ga. This is in agreement with known literature data [2] and it supports the idea that the diffusion of minority component, Ga, may run by Ga-antisite-assisted mechanism [2-4]. Comparison of present results (obtained for alloy 3 that is close to stoichiometry A3B) with literature data on both Ga and Ni [10,11] volume diffusion in Ni3Ga can be seen in Fig.5.

![Fig. 5](image)

**Fig. 5** Comparison of present results with literature data on Ga and Ni volume diffusion in Ni3Ga close to stoichiometry A3B. ($T_m = 1473$ K)

It is obvious that present results agree well with the literature and that there is no significant difference between the Ni and Ga diffusivity. This means that Ga does most likely not diffuse via so called six-jump mechanism.

Since neither expressive concentration dependence of activation energy $Q$ nor temperature dependence of slopes in Fig.2 were observed, for the concentration - temperature dependence of $D$ can be taken simple empiric relation

$$\ln D = \ln D_o + B x_{Ga} - \frac{Q}{R T}. \quad (5)$$

Eq.(5) was fitted to measured $D$’s (see the plane in Fig. 3) with the result: $\ln D_o = -(18.6 \pm 1.1)$ (m$^2$/s), $B = (0.312 \pm 0.036)$ (at.% Ga)$^{-1}$ and $\phi = (236.9 \pm 5.1)$ kJ/mol.

GB diffusivities $P$ were calculated from Eq.(3) using measured slopes $A$, $D$’s calculated from Eq.(5), diffusion times $t$ and constants $\alpha = 0.258$, $\varepsilon = -1.7182$, $\phi =$...
- 0.5309 and $\eta = 0.4691$ (values recommended in [13] for $\beta < 100$). In contrary to volume diffusion, GB diffusivity $P$ of Ga does not depend significantly on $x_{Ga}$. The temperature dependence of $P$ is shown in Fig. 6.

**Fig. 6** Arrhenius diagram of GB diffusivity $P$ of Ga in Ni$_{3-x}$Ga$_x$. Points – measured values, full line – Arrhenius equation fitted to points, dashed line – GB diffusivity $P$ of Ni GBD [12].

It can be seen that $P$’s for Ga GBD are slightly lower than those for Ni GBD, however, obtained Arrhenius parameters equal, in the frame of errors, ones to another ($P_o$ in m$^3$/s):

GBD of Ga - present paper : $Q_P = (201.4 \pm 8.1)$ kJ/mol, $\log P_o = - (10.31 \pm 0.41)$

GBD of Ni [12]: $Q_P = (192.8 \pm 4.1)$ kJ/mol, $\log P_o = - (10.48 \pm 0.19)$

**5. SUMMARY**

The volume diffusion of minority component in Ni$_3$Ga intermetallic runs most likely via Ga-antisite-assisted mechanism. The GBD of both components, Ga and Ni runs via the same mechanism.
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REFERENCES