GRAIN BOUNDARY DIFFUSION OF Al-SUBSTITUTING ELEMENTS IN Ni₃Al

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Abstract

The grain boundary diffusion of ⁶⁷Ga and ⁶⁸Ge as Al-simulating elements in the Ni-rich Ni₃Al alloys has been investigated using the serial sectioning method. The effect of stoichiometry and temperature on the ⁶⁷Ga grain boundary diffusivity was measured for three compositions between 22.4 and 24.8 at.% Al in pure (not boronized) Ni₃Al alloys in temperature region from 500 to 900 ºC. It was found that the grain boundary diffusivity increases with increasing concentration of Ni. Activation energies for ⁶⁷Ga grain boundary diffusivity in all three experimental alloys are equal.

⁶⁸Ge grain boundary diffusivity was measured at temperatures from interval 600 - 975 ºC. In contrast to almost equal volume diffusivity of ⁶⁸Ge and ⁶⁷Ga, grain boundary diffusivity of ⁶⁸Ge is significantly lower than that of ⁶⁷Ga. It may be due to higher grain boundary segregation of the ⁶⁸Ge in Ni₃Al, which tends to reduce the GB diffusion rate.

1. INTRODUCTION

Intermetallic compound Ni₃Al belongs to the most frequently studied hi-tech materials in recent years. This is due mainly to its excellent mechanical parameters and high corrosion resistance. The crystallographic structure of Ni₃Al (L1₂) is derived from the FCC lattice. Larger Al atoms occupy the corners of the unit cell, Ni atoms reside in the centers of faces. Atomic order of Ni₃Al, which is the principal reason for a series of outstanding material properties of Ni₃Al, is preserved up to the melting point.

The greatest disadvantageous feature of this compound – more or less common to many other intermetallics – is its brittleness connected with the presence of grain boundaries (GB’s). It had been known years ago that the singlecrystals of Ni₃Al suffer from brittleness in a considerable less extent. Knowledge of these facts together with extraordinary high potential of Ni₃Al for the engineering practice have started an intensive study of GB characteristics in this compound. Contrary to numerous theoretical and experimental works published in the field up to now, a number of issues remain to be solved.

Quantitative data on grain boundary diffusivity (GBD) of alloy’s components are needed for an aimed design of new materials since the stability of desired structures depends on kinetics of diffusion-controlled processes running in the material during the service. Let us just remind that the GB’s act as high-diffusivity paths that promote significantly the redistribution of atoms in solid matter.

One of the components in Ni₃Al, namely aluminum, plays an extraordinary important role in oxidation processes due to its high affinity to oxygen. The oxidation may by an unwanted process at GB’s where it leads to decreased fracture ductility at high temperatures
but, on the other hand, it is beneficial by surface, where it contributes to the protective layer formation [2]. Bearing in mind these facts, it is clear that the knowledge of Al diffusivity in Ni₃Al is of a great interest. Unfortunately, Al has no radioisotope that would be suitable for tracer diffusion measurements. Therefore, a number of papers have been devoted to an indirect evaluation of Al bulk diffusivity (BD) from interdiffusion measurements [3]. There are also data on BD of Al-substituents in Ni₃Al, which are believed to simulate the diffusion of Al itself [4]. Temperature dependence of GBD of Al or its substituents in Ni₃Al was not measured as yet (GBD of Ge was reported for a single temperature only in [5]).

The aim of this work is to make an attempt to assess the Al GBD in Ni₃Al with the help of Ga and Ge as Al-simulating elements.

2. EXPERIMENTAL

Three experimental alloys were prepared by induction melting from pure components (5N Al and 3N7 Ni) in Ar protective atmosphere and cast into Cu mould. Ingots (cylinders of diameter ? length = 12 mm ? 80 mm) were sealed into silica tubes (6N Ar at ca 10⁴ Pa) and homogenised at 1523 K for 5.5 h. After the treatment, the mean grain size of all three Ni₃Al alloys was about 300 μm. The composition of the alloys was checked by X-ray chemical microanalysis by SEM/EDAX using Ni₃Al standard as a reference. The accuracy was about 0.4 at. %. The annealed ingots were machined down to diameter 10 mm and diffusion samples of length about 3 mm were spark-cut. Their surfaces were ground with metallographic papers and polished using diamond paste (2 μm).

Thin radioactive layer was deposited by vacuum evaporation technique on Ni₃Al samples. A water solution containing the respective radioisotope (⁶⁷Ga or ⁶⁸Ge) was dropped and dried on the tungsten boat. After the thermo decomposition of the carrier (moderate heating of the boat with the carrier in vacuum) the radioisotope was evaporated by a short thermal shock from the boat on the cold polished samples.

For the diffusion anneals, the samples were wrapped into Ta foil that acted as oxygen getter and, at the same time, it held mechanically the samples in the fixed position. Then the wrapped samples were sealed into silica tubes with pure (6N) Ar under the pressure of about 10⁴ Pa. Following diffusion anneals were carried out in horizontal furnaces at chosen temperatures kept constant within ±1 K.

The diffusion measurement was made by the residual activity method using the low-level counter CANBERRA 2400 for relative residual sample activity measurement and precise grinding with subsequent sample weighting for the penetration depth calculation.

3. EVALUATION PROCEDURE

3.1 Penetration profiles

Examples of measured penetration profiles, i.e., the relative residual activity, I(x,t), in dependence on total thickness of the taken-off layer x are shown in Fig. 1. It can be seen that the profiles consist of two segments, as it is a common case for GB diffusion in type-B kinetics [6]. The steep near surface segment is given, before all, by the BD from the free surface, the deeper one is due to diffusion along grain boundaries [7].

For the measured residual activity I(x,t) it can be written

\[
I(x,t) \sim \phi c(x,t) \exp \left( -\frac{D_B}{x} \right),
\]
where \( c(x,t) \) is concentration in the depth \( x \) under the original surface after the diffusion annealing of duration \( t \), \( \gamma \) and \( \mu \) are the proportionality constants and the attenuation coefficient of the radiation in the matter of the sample, respectively. Values of attenuation coefficients were taken from [8].

### 3.2 Bulk diffusion in Ni\(_3\)Al

Variation of BD \( D \) with composition of Ni\(_3\)Al was studied. Near-surface parts of measured penetration curves were fitted by Eq. (1) (solid line in Fig. 1) using known thin-film solution

\[
c(?,t) = \frac{M}{\sqrt{?Dt}} \exp\left(\frac{?^2}{4Dt}\right),
\]

In Eq. (2), \( M \) and \( D \) stand for initial surface concentration and BD coefficient, respectively. Both the constants were obtained as fit parameters.

### 3.3 Grain boundary diffusion

Dependence of GBD on composition of Ni\(_3\)Al was measured. The rate of diffusion in grain boundaries is quantitatively described by the triple product \( P = s ? D_b \) (\( s \) – segregation factor, \( ? \) – GB thickness and \( D_b \) – diffusion coefficient in grain boundary). According to the LeClaire’s theory [7], the tail of the penetration curve \( c(x,t) \) is linear in co-ordinates \( \ln c \) vs \( x^{6/5} \) and the product \( P \) can be estimated from its slope. It was calculated from the relation

\[
P \approx p D^q t^r \ln c(x,t) x^{6/5},
\]

where the recommended values of constants \( p, q, r \) and \( u \) vary with the value of parameter \( \gamma \), defined by equation [7]
\[ \frac{D_b}{2D} \frac{\partial c}{\partial t} \] .

With respect to linearity of the concentration tail in co-ordinates \( \ln c(x,t) \) vs. \( x^{6/5} \), the concentration \( c(x,t) \) at great depths \( x \) can be taken in the form

\[ c(x,t) \sim A \exp\left[\frac{B}{x^{6/5}}\right]. \tag{5} \]

Fitting Eq. (1) with \( c(x, y) \) according to Eq. (5) to concentration tail (dashed line in Fig.1) gives fit parameters \( A \) and \( B \). Hence, the product \( P \) can be calculated from Eq. (3) using parameters \( p, q, r, u \) from [7] and the value of \( B \) for partial derivative in the right-hand side of Eq. (3).

4. RESULTS AND DISCUSSION

4.1 Bulk diffusion

It can be seen in Fig. 2 that our results on Ga diffusion measured at higher temperatures with alloy close to stoichiometry (Ni-24.8Al) agree well with literature data reported by Divinski [4] for Ni-24.1Al and, at the same time, they fit reasonably also with literature data on other Al-substituents in Ni\( _3 \)Al [9-14] (Fig. 3).

Moreover, it is obvious that there is a significant decrease in \( D \) with increasing Al concentration \( c_{Al} \). Relation

\[ D(T, c_{Al}) \sim D(T) \exp\left[\frac{25}{c_{Al}}\right]. \tag{6} \]
expresses well the concentration dependence of $D$ in the composition region studied, as it can be seen in Fig. 4. For the temperature term $D(T)$, Arrhenius relation can be taken

$$D(T) = D_0 \exp \left( \frac{Q}{RT} \right).$$

Using 3D optimization for both variables, $T$ and $c_{Al}$, parameters $\beta = (0.42 \pm 0.04)$ (at.%)$^{-1}$, $D_0 = (0.05 \pm 0.004)$ m$^2$ s$^{-1}$ and $Q = (356 \pm 6)$ kJ mol$^{-1}$ were obtained.

**Fig. 3** Comparison of our $^{67}$Ga BD coefficients with the literature.

**Fig. 4** Concentration dependence of $^{67}$Ga BD coefficients in Ni$_3$Al.
At lower temperatures, the diffusion coefficients $D$ obtained by procedure described above showed an up-ward curvature (see Fig. 2), which is caused by contribution from GB diffusion.

Coefficient of Ge BD needed for evaluation of Ge GBD was taken from [4].

4.2 Grain boundary diffusion

The measurement of Ga GBD was done in type-B kinetics. Arrhenius diagram of $^{67}$Ga grain boundary diffusivity $P$ can be seen in Fig. 5.

![Arrhenius diagram of Ga GBD’s in Ni$_3$Al.](image)

It was found that relevant activation enthalpies does not depend significantly on alloy composition ( (198 ? 13) kJ mol$^{-1}$ for $^{67}$Ga GBD in Ni – 24.8Al, (202 ? 4) kJ mol$^{-1}$ in Ni – 23.8Al and (201 ? 12) kJ mol$^{-1}$ in Ni – 22.4Al) and, therefore, the concentration dependence of $P$ can be ascribed to variation of the entropy term only represented by frequency factor $P_0$.

Fitting the measured values of $^{67}$Ga GBD $P$ by equations analogous to Eqns. (6, 7), one can obtain following fit parameters

$$P_0 = (2.3 \pm 1.9) \times 10^{11} \text{ m}^3 \text{ s}^{-1},$$

$$Q_P = (200 \pm 5) \text{ kJ mol}^{-1} \text{ and}$$

$$\gamma_P = (0.54 \pm 0.07) \text{ (at.\%)}^{-1}. \quad (8)$$

Positive value of $\gamma_P$ agree with an increase in $P$ with increasing Ni content for Ni, Ge and Co GB diffusion in Ni-rich Ni$_3$Al reported in papers [5,15] – see in Fig. 6.
Fig. 6 Comparison of concentration dependence of $^{67}\text{Ga}$ GBD with the literature data.

Authors of the paper [15] show that the Ni GBD increases with Ni content and for Ni – 22.4Al alloy the Arrhenius parameters approach those for Ni GB self-diffusivity. They argue that it is caused by the changing GB structure, which is in Ni-rich Ni$_3$Al close to that in pure nickel [16].

It can be seen that also in the present case, Ga GBD increases with increasing concentration of Ni in Ni$_3$Al towards the Ni GB self-diffusion. However in the present case, the activation enthalpy of Ga GBD in Ni$_3$Al remains higher compared to that of Ni GB self-diffusion, which may be caused by difficult diffusion of Ga in slightly oxidized GB’s in Ni$_3$Al (the oxidation of GB’s may not be rate determining factor for the GB diffusion of Ni atoms in Ni$_3$Al studied in [15]) .

Grain boundary diffusivity of Ge was measured in alloy Ni-24.8Al only. Comparison of Ga and Ge GB diffusivities is shown in Fig.7. The lower GB diffusivity is, most likely caused by the stronger segregation of Ge to GB’s. Unfortunately, there are no reliable data on Ga and Ge segregation to GB’s in Ni$_3$Al, which could enable the separation of the influence of segregation and comparison of the Ge and Ge diffusion coefficients $D_b$ itself. Therefore, thought both Ga and Ge seem to be good simulating elements that well scale the values for Al BD coefficients that are inaccessible by direct tracer diffusion measurement (Fig.3), they fail as for Al GBD simulation in Ni$_3$Al.
**Fig. 7** Comparison of $^{67}$Ga and $^{68}$Ge GBD in Ni$_3$Al.

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