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Grain boundary diffusion of Ni in NiTi shape-memory alloy

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Abstract. Ni grain boundary diffusion was measured in slightly Ti rich polycrystalline NiTi shape-memory alloy in the temperature range of 428-678K. Grain boundary tail in the penetration plots could only be detected below 700 K. The temperature dependence of the grain boundary triple product P ($P = \delta D_b k$, δ : grain boundary width, D_b : grain boundary diffusion coefficient, k : segregation factor) can be represented by the following Arrhenius parameters: preexponential factor: $P_0 = 2.6 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$, activation energy: $Q_b = 90 \text{ kJmol}^{-1}$. The order of magnitude of the triple product NiTi at a reduced temperature scale is similar to that of the grain boundary diffusivity measured in other B2 systems, but the detection of it is difficult, because there is not enough contrast between the volume and the grain boundary diffusion.

Introduction

Shape memory alloys (SMAs) attract permanently considerable attention because of their wide range of practical applications. From technological point of view, NiTi alloys may be considered to be the most important SMAs, for the reason of their superior shape-memory properties, superelasticity and biocompatibility as well [1, 2]. The NiTi phase shows peculiar volume diffusion properties: Ni atoms move very fast, the activation energy is rather low (155 kJ/mol) as it was measured recently by Bernardini *et al.* [3]. The experimental studies of the diffusion properties of the constituents may help to reveal the defect structure and the diffusion mechanisms in the system.

The aim of the present GB diffusion studies in NiTi was twofold. First, we intended to provide the missing experimental GB diffusion data; second, we wanted to check our preliminary experiences which implied suppressed Ni grain boundary diffusion in this system.

Experimental

Samples with nearly equiatomic composition (50.07 at% Ti) were used in our tracer experiments. The grain size of samples was about 150 μm . The parallelepiped-shaped samples were cut from same ingot as it was used for volume diffusion experiments carried out by Bernardini *et al.* [3]. One side of the samples was polished using successive grade of SiC and alumina suspension down to 1 μm . ⁶³Ni tracer was electrodeposited onto the flat surface. Radioactive samples were encapsulated in quartz ampoule under high purity argon. After diffusion anneals successive thin sections parallel to the active ⁶³Ni layers were removed with a precision grinding machine on glass sheets using SiC suspension. The specimen was cleaned in an ultrasonic cleaner, weighed on a microbalance, and the penetration depth (x) was calculated. After each section, the surface activity (I) was measured by means of a windowless PIN silicon photodiode device combined with a pulse height analyzer. Gruzin's residual activity method was applied for establishing the penetration profiles.

Results and discussion

In order to check the reliability of our experimental method, at first we carried out a volume diffusion experiment at 1073 K. The diffusion coefficient we deduced $D=6.9 \times 10^{-16} \text{ m}^2\text{s}^{-1}$ is in good agreement with the coefficient ($D=5.1 \times 10^{-16} \text{ m}^2\text{s}^{-1}$) calculated from the Arrhenius parameters published by Bernardini *et al.* [3]. We reduced the volume penetration depth, however detectable grain boundary tail appeared when the volume penetration depth was about $1 \mu\text{m}$. Grain boundary diffusion experiments could only be carried out below 700 K, at reduced temperature scale it corresponds to $T \approx 0.4 T_m$, where T_m is the melting temperature.

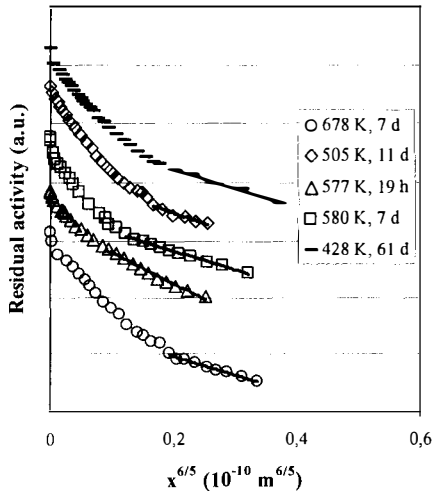


Fig. 1. Penetration profiles of Ni grain boundary diffusion in NiTi. The annealing parameters are indicated in the legend.

The last parts of the penetration curves were fitted by straight lines and the triple product was evaluated from the slope of them according to the Suzuoka's solution [4]:

$$k\delta D_b = 2\sqrt{\frac{D}{t} \left(\frac{\partial \ln \bar{c}}{\partial x^{6/5}} \right)^{-5/3}} (0.775)^{5/3} \quad (1)$$

where t is the annealing time, \bar{c} is the mean tracer concentration in a section. The dimensionless β and η parameters defined by the expressions:

$$\beta = \frac{\delta D_b}{2D\sqrt{Dt}} ; \quad \eta = \frac{x}{\sqrt{Dt}} \quad (2)$$

permit to choose the optimal experimental conditions. In the case of type-B regime, the following conditions must be fulfilled [5]:

$$\beta > 10 \text{ and } \eta\beta^{-1/2} > 2 \quad (3)$$

The numerical factor in Eq.(1) depends slightly on the value of β , this was taken into consideration when evaluated the triple products.

| T (K) | $time$ | P (m ³ /s) | β | $\eta \beta^{-1/2}$ |
|---------|--------|-------------------------|-------------------|---------------------|
| 428 | 61 d | 3.1×10^{-29} | 6.6×10^7 | 5.71 |
| 505 | 11 d | 1.5×10^{-27} | 1.5×10^5 | 3.88 |
| 578 | 19 h | 2.8×10^{-26} | 2.4×10^4 | 7.47 |
| 578 | 7 d | 2.53×10^{-26} | 5.9×10^3 | 5.93 |
| 678 | 7 d | 2.51×10^{-25} | 61 | 4.64 |

Table 1.

The annealing parameters, and the results of the grain boundary diffusion experiments.

We carried out two experiments at the same temperature ($T=578$ K) with different annealing time (19 hours and 7 days), the GB diffusivity was found to be time independent. Plotting the logarithm of P against the reciprocal temperature, the data can be fitted an Arrhenius line which is described by (see also Fig.2):

$$P = 2.6 \cdot 10^{-18} \exp\left[-\frac{90000 \text{ kJ} \cdot \text{mol}^{-1}}{RT}\right] \text{ m}^3/\text{s} \quad (4)$$

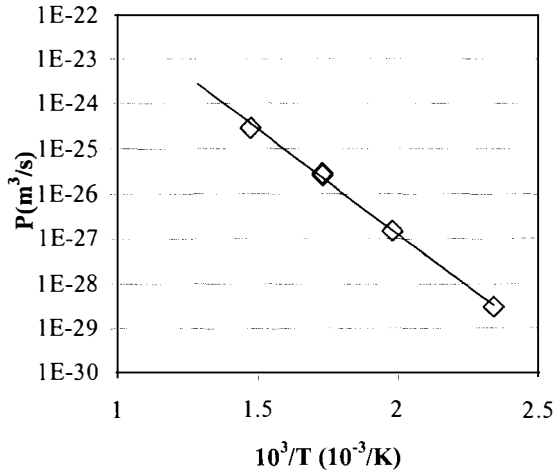


Fig.2 Arrhenius plot of grain boundary self-diffusion of ⁶³Ni in NiTi.

| System | Diffusant | P_0 (m ³ /s) | Q_b | Ref. |
|--------|-----------|---------------------------|-------|-----------|
| FeCo | Co | 1.5×10^{-13} | 156 | [5] |
| FeCo | Fe | 1.2×10^{-11} | 191 | [5] |
| NiAl | Ni | 9×10^{-15} | 152 | [6] |
| NiTi | Ni | 2.6×10^{-18} | 90 | this work |
| Ni | Ni | 4.4×10^{-11} | 187 | [7] |

Table 2
Comparison of grain boundary diffusion data in some B2 systems, GB data in Ni are also included

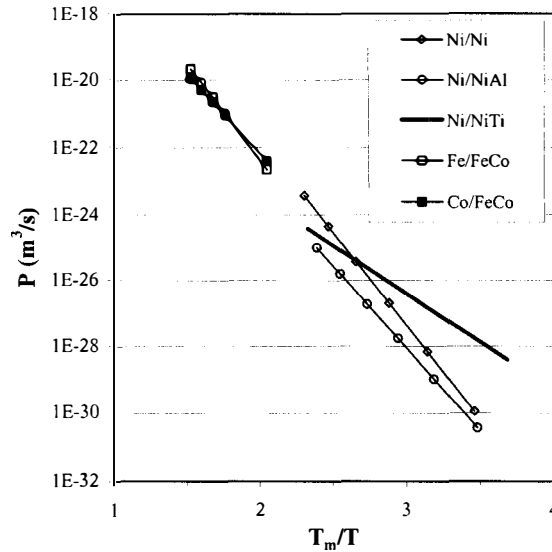


Fig.3. Grain boundary diffusivity vs. reduced reciprocal temperature in some B2 phase and in pure Ni

It is obvious from Fig.3 that the order of magnitude of the grain boundary diffusivity in NiTi in a reduced temperature scale is similar to that of the GB diffusivity measured in other B2 systems. It means that diffusion in grain boundaries is not suppressed by segregated impurities or other phases occurring in GBs, (for example oxides). However, the detection of the process is difficult because there is not enough contrast between D and D_b : at $T=678$ K for example $D_b/D=104$! This is the consequence of the low activation energy of the volume diffusion (155 kJ/mol), i.e. the volume diffusion coefficient is rather high even at low temperatures, which hampers the separation of different diffusion contributions.

In order to clarify the origin of the unusual form of the first part of penetration plots, we carried out a short time annealing at 350 K. At that temperature the sample was transformed into the high temperature phase, but the grain boundary penetration was negligible. The extension of the penetration was about 1.5 μm (extension and form is similar to that of visible in Fig.1.), but the last tail was missing. On the basis of that experiment, we concluded that the first part of the penetration

plots is a consequence of macroscopic deformations and surface roughness of the samples ($\sim 0.5 \mu\text{m}$) developed during the phase transformation.

On the basis of the equation [8,9]

$$D_{eff} = D + \frac{4\delta D_b}{3d} \quad (5)$$

we can check to what extent are the volume diffusion data measured by Bernardini *et al* affected by grain boundary diffusion at low temperatures. At the lowest temperature (i.e. at 783 K) they used, the GB contribution was estimated to be about only 3.5 %, so the experimental volume diffusion data do not need correction.

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