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Pressure dependence of Ni self-diffusion in NiTi

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The volume diffusion of Ni was studied in a nearly equiatomic $B2$ NiTi compound at 1285 K in the pressure range of 0–0.91 GPa. Our measurements, carried out by the tracer technique, proved that the volume diffusion coefficient is independent of the external pressure, and the evaluated activation volume is close to zero. Results may refer either to the interstitial diffusion mechanism or vacancy-mediated diffusion, indicating that in the latter case the vacancy concentration is pressure independent in the investigated pressure range.

I. INTRODUCTION

It is well known that the intermetallic compound type $A_{0.5-x}B_{0.5+x}$ with a $B2$ structure can exhibit very different vacancy concentrations with a rather different temperature dependence and this behavior is also sensitive to the parameter x which designates the deviation from stoichiometry.[1–6] This is a consequence of the competition between two possible defect production processes [antisite defect (ASD) and vacancy formation]. Thus some of these compounds may have a very high vacancy concentration even at room temperature (''structural vacancies'') with a slight temperature dependence (i.e., with a low effective vacancy formation energy); some contain ASDs and thermal vacancies with a ''normal'' temperature dependence, while some of them show an intermediate defect structure (hybrid type behavior).[3,7] According to recent calculations[3,8] the transition between the above-mentioned categories is strongly affected by the off-stoichiometry as well. In the light of their important applications as shape memory alloys it is surprising that until now experimental diffusivity data in the NiTi system were extracted either from chemical diffusion[9] ($D_0=2\times10^{-7}$ m^2/s, $Q=142$ kJ/mol, where D_0 and Q are the pre-exponential factor and the activation energy, respectively) or from solid-state amorphization experiments[10] ($Q=126$ kJ/mol) only. These activation energies are close to that for the volume diffusion of Ni in crystalline β-Ti ($Q=139$ kJ/mol).[11,12] It is worth mentioning that Ni atoms move a few tens times faster in pure β-Ti than Ti atoms themselves and Ni atoms move probably through interstitial positions.[10,13] Very recently tracer measurements were carried out by Bernardini *et al.*[14] for^{63}Ni volume diffusion in NiTi. The following Arrhenius parameters were deduced from these experiments: $Q=155.6$ kJ/mol, $D_0=2.1\times10^{-8}$ m^2/s, in the temperature range of 783–1288 K. The microstructure of the samples used in the diffusion experiments was carefully controlled and investigated by transmission electron microscopy (TEM), so it was concluded that the obtained low activation energy cannot be affected by grain or phase boundary diffusion effects.[14]

In order to compare the volume diffusion parameters in different $B2$ intermetallics, the Q/RT_m ratios are shown for some nearly equiatomic $B2$ phases (Table I), where Q is the volume self-diffusion activation energies of the constituents A of the AB compounds, R is the universal gas constant, and T_m is the melting point. As for comparison, the same parameter for Ni impurity diffusion in β-Ti (Ref. 11) is also included in the table. According to the well-known empirical rule, the Q/RT_m ratios should be approximately constant for diffusion in different phases having similar structure, provided the operating mechanisms are the same.[15] As can be seen the dimensionless parameter Q/RT_m is the lowest one for NiTi and CoTi, somewhat higher for NiGa, and for other $B2$ phases the values of Q/RT_m are definitely higher.

In the case of CoTi only results of interdiffusion experiments are shown because tracer data are not available (Refs. 17 and 18). It is worth mentioning that according to Sprengel *et al.*,[17] the difference between the activation energies determined from multiphase chemical diffusion[18] and single-phase interdiffusion experiments in CoTi system[17] can be due to short-circuit effects. A similar effect is very unlikely in NiTi since different measurement techniques yield nearly identical, small activation energies (see Refs. 10 and 14).

TABLE I. The Q/RT_m ratios for different $B2$ systems; tracer data measured in intermetallics are taken from Ref. 16.

Phase	Composition	at. %	Q/T_m
β-Ti	-	-	8.34
CuZn	Zn	46.7–48	16.5
AgMg	Mg	52	17.5
AuZn	Zn	50	16.2
FeAl	Al	51.2	19.1
NiAl	Al	50.8	17.4
NiGa	Ga	50.67	12.6
PdIn	In	50	17.8
CoGa	Ga	52	24.2
FeCo	Co	50.8	26.8
CoTi	-	-	20
CoTi	-	-	13
NiTi	Ti	50.07	11.8

Until now in spite of theoretical and experimental efforts,

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the prevailing defect structures and diffusion mechanisms have not been unambiguously revealed in $B2$ structures. Nowadays it is almost generally accepted that in NiTi the deviation from stoichiometry is accommodated by antisite atoms,[19] i.e., a normal effective vacancy formation energy, and thus not a small value of the Q/RT_m ratio would be expected. Furthermore, positron lifetime measurements have not revealed a high vacancy concentration in nearly equiatomic NiTi alloys.[20] Calculations carried out in NiAl show that the vacancy concentration on the Al sublattice is negligible;[8,21] diffusion on the other sublattice is probably dominated by the mechanism of next-nearest-neighbor (NNN) vacancy jumps;[21] more complicated cycled mechanisms [antistructural bridge mechanism (ASB) and six-jump cycle mechanism (6JC)] may dominate the diffusion of Al (6JC mechanism) or may give a contribution to Ni diffusion in Ni-reach compositions[21] (ASB mechanism). A computer simulation study confirmed that in the NiTi system the vacancy formation on the Ti sublattice is unfavorable; the removal of a Ti atom resulted in a vacant Ni site and an ASD. In the same work the Ni-vacancy formation energy was estimated to be 142.8 kJ/mol, while for the energy of vacancy migration by the 6JC mechanism 123 kJ/mol was given.[22]

The activation volume of a diffusion process can be derived from diffusion experiments carried out at constant temperature at various hydrostatic pressures according to the expression

$$V = -kT\frac{\partial \ln D}{\partial p}\bigg|_T + kT\frac{\partial \ln D_0}{\partial p}\bigg|_T = V_f + V_m,$$

where T is the absolute temperature, k is the Boltzmann constant, and V_f and V_m are the defect formation and migration volumes, respectively. The second term in metals is estimated to be 1–5 % of the atomic volume and it is generally neglected. However, in ordered compounds the situation is more complicated because the effective formation volume of vacancies created, for example, on the α sublattice may be influenced by antisite defect formation (triple-defect formation) as was pointed out by Mayer and Fähnle.[5] Depending on the sign of the relaxation volumes of an α vacancy and an ASD on the β sublattice, it may occur that the experimentally obtained effective vacancy formation volume of an AB compound is considerable higher (or lower) than Ω (here Ω denotes the average atomic volume of the constituents). Recent molecular statics calculations forecast essentially different activation volumes relating to different diffusion mechanisms.[21] The calculated activation volumes vary from 0.44 Ω (ASB mechanism) to 3.14 Ω (6JC mechanism). Until now the pressure dependence of self-diffusion was studied experimentally only in one AB-type $B2$ system, in AuZn.[23] Despite the large error in the data, the following trends can be observed: the activation volumes of both constituents show a sharp maximum at $x=0$ ($V=0.9\ \Omega$), and they decrease on both sides of the stoichiometry; at the composition $x=0.01$ the measured activation volume is $V=0.35\ \Omega$.[23]

II. EXPERIMENT

Our samples applied in the high-pressure experiments and samples used by Bernardini *et al.* (see Ref. 14) were identical regarding composition (49.93 at. % Ni and 50.07 at. % Ti) and microstructure. The average grain size was about 150 μm, with a relatively wide range of size distribution. TEM investigations revealed secondary particles with low (1%) volume density in the $B2$ structure parent phase. Electron diffraction patterns showed that the precipitates are $Ti_4Ni_2O_x$ phase which was probably formed during the processing due to oxygen contamination (this means that the composition of the matrix has less Ti reach than the nominal composition). Samples were polished using successive grades of SiC and alumina suspension down to 0.3 μm. Samples were preannealed in an Ar-filled quartz ampoule at 1283 K for 28 h. The ^{63}Ni diffusion layer was electrochemically deposited, and the sample was placed into a stainless steel container. The container protected the high-pressure cell from radioactive contamination and in the bottom of it we placed the thermocouple in a good thermal contact with the sample. The high hydrostatic pressure was generated by means of a three-stage gas compressor (UNIPRESS IF-012A) using 99.999% purity Ar as the pressure transmitting medium. The samples were heated by a resistance furnace located inside the pressure cell. In order to remove residual gases released from the inner walls, we heated up the furnace and the inside wall of the cell ($T \leqslant 450$ K) and evacuated and refilled the chamber many times with fresh high-purity argon. Visible oxidation of the polished surface of the sample after diffusion anneals was not observed. Both temperature and pressure were controlled and recorded during the high-pressure heat treatment. Heat-up and cool-down corrections were calculated and taken into account. Before sectioning $\approx 10\sqrt{Dt}$ was removed from those surfaces of the sample which were not electroplated with ^{63}Ni in order to avoid surface diffusion effects. Successive thin sections parallel to the electroplated ^{63}Ni layer were removed using a precision grinding machine which allows reproducible removal of parallel layers. The specimen was weighed on a microbalance, to control the amount of material removed and to calculate the section thickness and penetration depth. After each section, the surface β activity was measured by means of a windowless p-i-n silicon photodiode device combined with a pulse height analyzer. A residual activity method was applied for establishing the penetration profiles. In all diffusion runs the same specimen was used. Taking into account the low energy of the β radiation ($E_{max} = 67$ keV), the surface activity I can be taken to be proportional to the average concentration of the tracer at the given depth. In Fig. 1 the ln(I) versus squared penetration depth functions are plotted at different pressures. Our D values measured at ambient pressures (1.4×10^{-14} m^2 s^{-1} at 1285 K) agree well with those measured by Bernardini *et al.*[14] at the nominally same temperature (9.83×10^{-15} m^2 s^{-1}). The evaluated volume diffusion coefficients measured at 1285 K as a function of pressure are plotted in Fig. 2. The estimated errors of the diffusivities were in the range of 9–19 %. The diffusion coefficient proved to be practically independent of the external pressure; a least-squares fit—assuming the validity of the $\ln D \propto p$ relation—yields the following activation volume: $V = -(0.01 \pm 0.13)\ \Omega$, where the error is the error of the least-squares fitting.

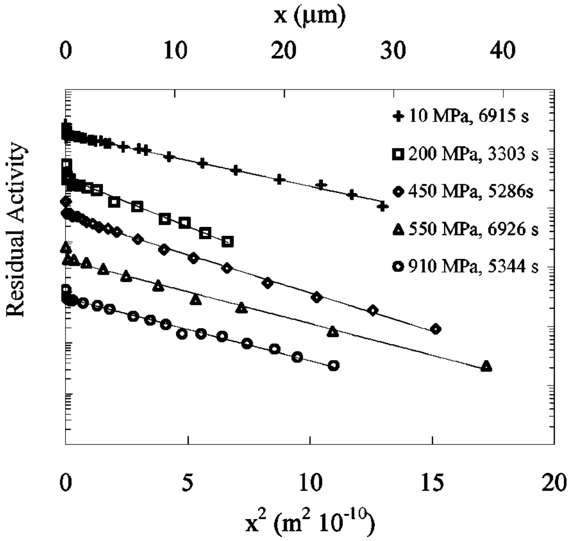

FIG. 1. Penetration plots measured at 1285 K; pressures and annealing times are displayed in the figure.

III. DISCUSSION

There are at least three opportunities to interpret the nearly zero activation volume.

(i) The diffusion process is not vacancy-mediated, Ni tracer jumps using interstitial positions. Theoretical calculations do not exclude this option, although the interstitial configurations are relatively complicated[22] (Ni-Ni dumbell, oriented in the $\langle 111 \rangle$ direction and centered on a Ti site, which has one or two adjacent antisite defects, Ti atoms on the Ni sublattice) and the mobility of Ni interstitials was not investigated.[22] Taking into account that the nearest neighbors of Ni atoms are Ti atoms in $B2$ structure, it is rather interesting to compare our result with the activation volume of Ni diffusion in β-Ti, $V = 0.21\ \Omega$.[13]

(ii) Theoretical calculations showed that in NiAl the ASB mechanism has the lowest activation volume.[21] Supposing a similarity between NiAl and NiTi systems, this option in our case (Ti surplus) seems to be unlikely because the *activation energy* related to the ASB mechanism in the Ti reach composition is very *high*, expressing that the vacancy and Ni ASD creation on the Ti sublattice is energetically unfavorable. Atomistic simulation found the ASB mechanism to be effective in Ni-reach compositions only.[21]

(iii) The activation volume refers to the pressure dependence of the defect concentration mediating the elementary diffusion steps. Supposing that Ni vacancies take place in the diffusion process, our experimental finding means that the vacancy concentration is not pressure dependent in our pressure range. According to some recent theoretical studies[3,6,24] the vacancy concentration does not follow an Arrhenius-type temperature dependence. It was also shown using a semiempirical model that the vacancy concentration on one of the sublattices can be much higher than in metals, even in phases which were earlier considered to be typical substitutional (ASD) compounds.[3] In compounds which tend to form a high concentration of vacancies, the vacancy concentration depends slightly on temperature; i.e., the ''effective formation energy'' can be rather low (structural or constitutional vacancies). In that case only the migration energy has to be supplied for diffusion to take place and thus the activation energy of diffusion—in accordance with the results of Bernardini *et al.* (Ref. 14)—has to be small. Using similar arguments, one can qualitatively explain the near-zero activation volume in an analogous way; i.e., only the migration volume has to be taken into account when an elementary diffusion step takes place.

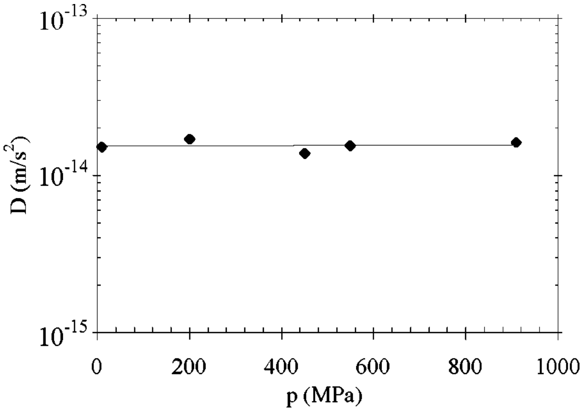

FIG. 2. Pressure dependence of the diffusion coefficient measured at 1285 K.

In conclusion, we have shown that the activation volume for Ni diffusion in NiTi $B2$ compounds is close to zero. This result together with the recently obtained small activation energy of diffusion[14] indicates that the experimental findings cannot be explained on the basis of the generally supposed 6JC diffusion mechanism and defect structure. The first and third options discussed above could be consistent with the experimental data, i.e., with the low activation energy and with the near-zero activation volume. However, the defect structure and mechanism of the atomic movement cannot be revealed by diffusion experiments only; further and theoretical investigations are inevitable to solve the problem of defect formation and to identify the mechanism of diffusion.

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