

Thermal formation of vacancies in TiAl

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The formation of thermal vacancies, which is a key issue with respect to the high-temperature properties of ordered intermetallic compounds, was studied in γ -TiAl by means of positron lifetime spectroscopy between ambient temperature and 1400 K. An estimate of the atomic concentration of thermal vacancies yields a value similar as in pure fcc metals and an effective vacancy formation enthalpy of 1.41 ± 0.06 eV in good agreement with nearest-neighbor-bond model calculations. A comparison of these data with the results of recent self-diffusion studies suggests a low mobility of vacancies as typical for ordered intermetallic compounds. No evidence for structural vacancies at ambient temperature could be observed.

I. INTRODUCTION

Intermetallic aluminides, e.g., TiAl and Ni₃Al, have attracted considerable interest because of their potentials as high-temperature structural materials particularly in turbines and aerospace applications.^{1,2} They combine favorable mechanical properties as high yield strength at elevated temperatures with good corrosion resistance and low mass density.

The high-temperature properties of these materials, as creep, sintering, oxidation, and diffusion are influenced or determined by thermal vacancies and, therefore, a study of the thermal vacancy formation is of crucial interest. Compared to pure metals this process is more complex in binary ordered intermetallic compounds with the thermal formation of vacancies on the two sublattices, concomitant thermal formation of antisite defects on both sublattices, and the coexistence of point defects due to deviations from the stoichiometric composition. In the open B2 structure of FeAl,³ where triple defects are suggested to be formed,⁴ the concentration of thermal vacancies is found to be as high as several atomic percent. In the closed-packed L1₂ structure of Ni₃Al (Ref. 5), much lower thermal defect concentrations ($\approx 10^{-4}$) similar to those in pure metals were observed.

This work aims at a positron lifetime study of the thermal vacancy formation in γ -TiAl, which is of particular interest due to the application potentials of α_2 -Ti₃Al/ γ -TiAl alloys.⁶ The γ -TiAl alloy is ordered up to the solidus-liquidus transition at $T_M = 1726$ K with a $L1_0$ structure which is tetragonally distorted by 1.5% compared to the fcc lattice. Calculations of the thermal defect pattern in γ -TiAl using a nearest-neighbor-bond model were presented recently.⁷

The technique of positron lifetime spectroscopy, as described in detail elsewhere,⁸ represents a powerful technique for the study of vacancies, particularly in metals⁹ and alloys, and was applied earlier to the study of the thermal vacancy formation in the intermetallic compounds Fe₃Al (Ref. 10) and Ni₃Al (Ref. 5). In the simplest case of the applicability of a two-state trapping

model,¹¹ the positron trapping rate σC_V at vacancies with the atomic concentration C_V and the specific trapping rate σ is given by

$$\sigma C = I_1 \left[\frac{1}{\tau_0} - \frac{1}{\tau_1} \right]. \quad (1)$$

The time constants τ_0 and τ_1 with the relative intensities I_0 and $I_1 = 1 - I_0$ can be determined from the numerical analyses of the positron lifetime spectra (see Schaefer⁹ and references therein). The mean positron lifetime is given by $\bar{\tau} = I_0 \tau_0 + I_1 \tau_1$.

II. EXPERIMENTAL PROCEDURE

A polycrystalline γ -Ti_{48.5}Al_{51.5} alloy was prepared by comelting high-purity Ti and Al metals under an inert gas atmosphere. According to ¹⁶O (*d,p*) ¹⁷O nuclear reaction analysis (NRA) the oxygen content of the specimen was below 0.1 at. %.

For the positron lifetime studies at high temperatures a cylindrical specimen (5 mm in diameter, 14 mm in length) with an axial bore hole and a cover were prepared by spark erosion with subsequent chemical etching in a solution of HF (15%), H₂O₂ (15%), and H₂O (70%). After deposition of the positron emitter (7×10^5 Bq of ²²NaCl) into the bore hole the specimen was sealed by electron-beam welding (for Ref. see Schaefer *et al.*¹⁰). This specimen was enclosed in an Nb container (see Fig. 1) in order to suppress the selective evaporation of Al at high temperatures and to improve the temperature homogeneity. An additional Cu sample in a separate chamber of the container was used for *in situ* temperature calibration at the Cu melting temperature. The specimen container was electron-beam heated in a high vacuum chamber (2×10^{-4} Pa).¹² The temperature was measured and controlled (± 3 K) by means of Pt-Pt₈₇Rh₁₃ thermocouples and at temperatures above 1200 K, in addition, by optical pyrometry.

As evidenced by energy dispersive analysis of x-rays after heat treatment of test specimens at 1470 K (6 h un-

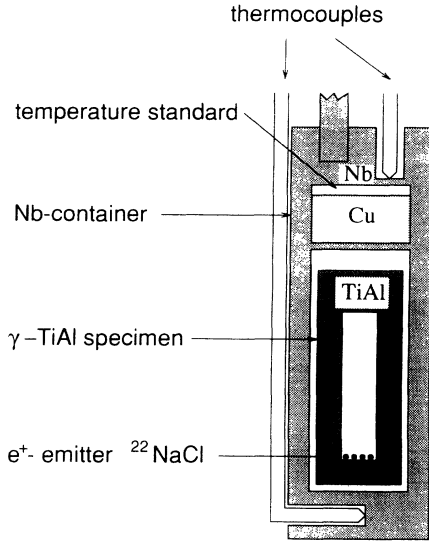


FIG. 1. Schematic setup of the γ -TiAl specimen with a sealed $^{22}\text{NaCl}$ positron source used for the high-temperature measurements. The specimen enclosed in an Nb container and fixed by spacers of the specimen material as diffusion barrier is electron-beam heated in an HV chamber, with the temperature measured by means of two Pt-Pt₈₇Rh₁₃ thermocouples and calibrated at the melting temperature of the Cu reference specimen.

der high vacuum), no significant compositional change (± 0.2 at. % uncertainty), e.g., due to Al evaporation, is expected during the high-temperature positron annihilation measurements.

The positron lifetime spectra were measured with a coincidence count rate of 25 cps and a total number of 2×10^6 coincidence counts by means of a fast-slow time spectrometer with BaF₂ scintillators yielding a time resolution full width at half maximum of 260 ps. After subtraction of a source correction (intensity $I_s = 1.3\%$, time constant $\tau_s = 363$ ps) the spectra were evaluated by two-component analyses (see Schaefer⁹ and references therein) for the determination of the positron lifetime components τ_i and the relative intensities I_i ($i = 0, 1$).

In order to compare the positron lifetime in thermal vacancies with that in irradiation-induced vacancies, supplementary positron lifetime measurements were performed after irradiation of TiAl specimens at 90 K with 2.5 MeV electrons of a total dose of $5.6 \times 10^{22} \text{ e}^- \text{ m}^{-2}$ (for experimental details see Würschum *et al.*¹³).

III. EXPERIMENTAL RESULTS AND DISCUSSION

In γ -TiAl a reversible increase of the mean positron lifetime $\bar{\tau} = I_0\tau_0 + I_1\tau_1$ from 142 ps up to 182 ps is observed between ambient temperature and 1400 K [Figs. 2 and 3(a)]. The nonlinear increase of $\bar{\tau}$ above 1100 K is due to an intensity increase [see I_1 , Fig. 3(b)] of the positron lifetime $\tau_1 \approx 211$ ps as deduced from numerical analysis of the positron lifetime spectra. The increase is typical for positron trapping and annihilation at thermally formed vacancies.

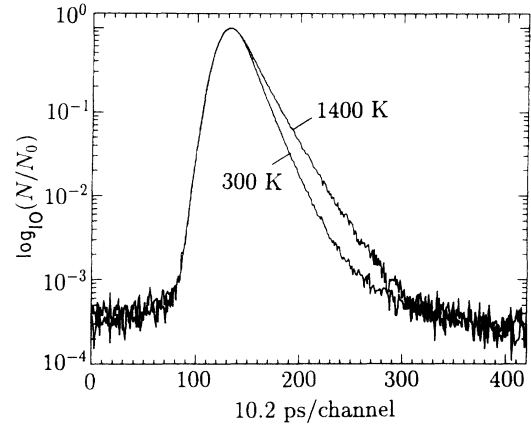


FIG. 2. Positron lifetime spectra measured on γ -TiAl in thermal equilibrium at two temperatures.

A. Characteristics of the positron lifetimes in γ -TiAl

The positron lifetime $\bar{\tau} \approx \tau_f = 143$ ps at ambient temperature is attributed to the free delocalized state because within the experimental uncertainties this value is equal to or even lower than the free positron lifetime τ_f in both pure Ti (Ref. 14) or pure Al (Ref. 15) (Table I). This implies that no structural vacancies (detection limit $\approx 10^{-6}$) exist in γ -TiAl, which is in agreement with theoretical considerations (see Refs. 7 and 16 and below) and with earlier positron lifetime studies.¹⁷ Disregarding the de-

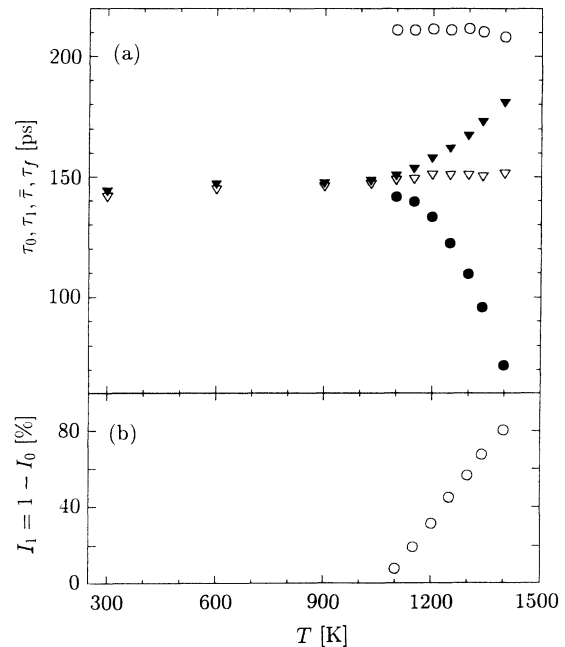


FIG. 3. (a) Mean positron lifetime $\bar{\tau}$ ($\blacktriangledown \blacktriangledown \blacktriangledown$) measured in γ -TiAl (numerical uncertainty ± 2 ps), the positron lifetime components τ_0 ($\bullet \bullet \bullet$) and τ_1 ($\circ \circ \circ$) with (b) the relative intensities I_1 ($\circ \circ \circ$) $= 1 - I_0$ as well as the free positron lifetime $\tau_f = (I_0/\tau_0 + I_1/\tau_1)^{-1}$ determined according to the simple trapping model ($\nabla \nabla \nabla$). The values given for 1100 and 1150 K were calculated with τ_1 fixed at 211 ps.

tails of the electron-density distribution, the very similar τ_f values in Ti and γ -TiAl might be understood with their similar averaged electron densities (Table I). The linear temperature variation of $\tau_f(T) = \tau_f(0) \times (1 + \alpha T)$ in γ -TiAl between 300 K and 1340 K [Fig. 3(a)] yields a value $\alpha = 5 \times 10^{-5} \text{ K}^{-1}$ slightly lower than in most pure metals.⁹

The positron lifetime $\tau_1 = 211 \text{ ps}$ attributed to the vacancy-trapped state at high temperatures appears to be slightly lower than the positron lifetime $\tau_1 = 225 \text{ ps}$ in vacancies induced by low-temperature electron irradiation (Table I). This difference is found to be significant because a numerical analysis of the high-temperature positron lifetime spectra with a fixed time constant $\tau_1 = 225 \text{ ps}$ yields a poor fit. The reduced value of τ_1 at high temperatures may be explained, as in some pure metals,¹⁸ with a partial detrapping of positrons from thermal vacancies at high temperatures or with a strong temperature dependence of the positron lifetime in vacancies. Additionally, one could take into consideration that the different lifetime values may originate from different types of lattice vacancies: Low-temperature irradiation with 2.5-MeV electrons induces vacancies on both the Ti and Al sublattice, whereas theoretical studies provide evidence for a formation of thermal vacancies predominantly on the Ti sublattice⁷ (see below).

As in the cases of the free positron lifetimes τ_f the positron lifetime τ_1 in vacancies in γ -TiAl is similar or slightly lower than that in Ti vacancies but significantly lower than that in Al vacancies (Table I).

B. Thermal vacancy formation

According to the present positron lifetime studies positron trapping at thermal vacancies sets in at $T_t = 1100 \text{ K}$. The ratio $T_t/T_M = 0.64$ (melting temperature $T_M = 1726 \text{ K}$) for γ -TiAl lies in between that of pure fcc metals ($T_t/T_M = 0.60$) and bcc metals [$T_t/T_M = 0.68$ (Refs. 9 and 19)]. This suggests a concentration C_V of thermal vacancies in γ -TiAl of the same order of magnitude as in pure metals with the reasonable assumption of a specific positron trapping rate $\sigma = 4 \times 10^{14} \text{ s}^{-1}$ in vacancies as derived for Al.⁹

The positron trapping rate σC (Fig. 4) can be determined from the experimental data according to Eq. (1) using the values of τ_0 , τ_1 , and I_1 (Fig. 3) obtained from numerical analyses (see above). The application of the

TABLE I. Free positron lifetime τ_f at ambient temperature, positron lifetime in vacancies in thermal equilibrium at high temperatures (τ_1^{eq}) or after low-temperature electron irradiation (τ_1^{irr} at 90 K) and valence electron density ρ_{val} in TiAl and its pure components assuming a valency of 4 for Ti and 3 for Al.

	τ_f [ps]	τ_1^{eq} [ps]	τ_1^{irr} [ps]	ρ_{val} [10^{29} m^{-3}]
TiAl	143	211 ± 3	225 ± 3	2.26
Ti	145 ^a		230 ± 6	2.16
Al ^b	163	248	251	1.81

^aReference 14.

^bReference 15.

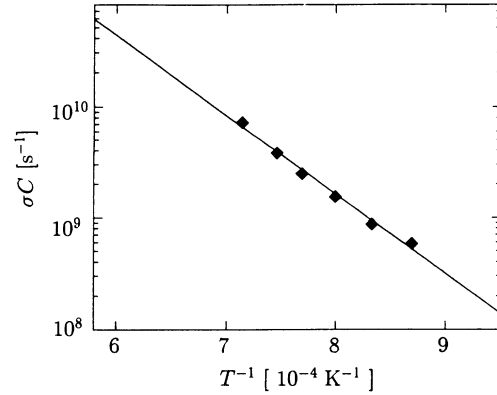


FIG. 4. Arrhenius plot of the positron trapping rate σC in γ -TiAl at high temperatures.

simple two-state trapping model appears to be justified because the free positron lifetime above T_t determined according to $\tau_f = (I_0/\tau_0 + I_1/\tau_1)^{-1}$ is within the uncertainty limits in agreement with a linear temperature variation of τ_f extrapolated from temperatures below T_t [see Fig. 3(a)].

With a temperature variation (Fig. 4)

$$\sigma C_V(T) = \sigma \exp(S_V^{F,\text{eff}}/k_B) \exp(H_V^{F,\text{eff}}/k_B T) \quad (2)$$

of the thermal vacancy concentration $C_V(T)$, an apparent enthalpy of vacancy formation

$$H_V^{F,\text{eff}} = 1.41 \pm 0.06 \text{ eV} \quad (3)$$

with a pre-exponential factor

$$\sigma \exp(S_V^{F,\text{eff}}/k_B) = 7.9 \times 10^{14} \text{ s}^{-1}, \quad (4)$$

can be derived making use of Eq. (1). From Eq. (4) an apparent entropy of vacancy formation

$$S_V^{F,\text{eff}} = 0.7 k_B \quad (5)$$

is obtained assuming $\sigma = 4 \times 10^{14} \text{ s}^{-1}$.

According to these values of $H_V^{F,\text{eff}}$ and $S_V^{F,\text{eff}}$ the extrapolated concentration $C_V = 1.5 \times 10^{-4}$ of thermal vacancies at the melting temperature, T_M , in γ -TiAl is similar as in pure metals and in the intermetallic compound Ni_3Al ,⁵ whereas much higher thermal vacancy concentrations were found, e.g., in the intermetallic compound Fe_3Al (Ref. 10) (Table II). We note that the formation enthalpy as given in Eq. (3) has to be considered as an effective value valid for the limited temperature range studied in this work.

The experimental results regarding the vacancy properties in γ -TiAl may be compared with recent theoretical studies. Calculations within a nearest-neighbor-bond model⁷ yield concentrations of thermal vacancies similar to the results from the present positron lifetime studies. According to these semiempirical calculations, thermal vacancies predominantly exist on the Ti sublattice together with a high concentration of antisite atoms on both sublattices.

On the other hand, first-principle calculations¹⁶ based on a local-density functional approach predict a thermal

TABLE II. Vacancy formation enthalpy H_V^F and extrapolated concentration C_V of thermal vacancies at the melting temperature T_M .

	Structure	T_M [K]	$H_V^{F,eff}$ [eV]	C_V^{eq}
Ti	hcp	1940		
TiAl	$L1_0$	1726	1.41 ± 0.06	1.5×10^{-4}
Al ^a	fcc	933	0.68	2.6×10^{-4}
Ni ₃ Al ^b	$L1_2$	1663	1.60 ± 0.06	3×10^{-4}
Fe ₃ Al ^c	DO_3	1773	1.18 ± 0.04	4×10^{-2}

^aReference 15.

^bReference 5.

^cReference 10.

vacancy concentration on the Ti sublattice below 10^{-6} at 1500 K (with $S_V^{F,eff} = 0.7k_B$). This is considered to be much too low for understanding the presently observed positron trapping at thermal vacancies. A comparison with the positron trapping rate given in Fig. 4 would require in this case a specific positron trapping rate above 10^{16} s^{-1} , which is higher than the value of about $4 \times 10^{14} \text{ s}^{-1}$ determined for monovacancies in metals.⁹

Recent results of perturbed angular correlation (PAC) studies after quenching of TiAl from high temperatures²⁰ were interpreted by thermal vacancy formation postulating a thermal vacancy concentration of 3.4×10^{-3} at 1500 K. This must be considered to be too high. In comparison with the data in Fig. 4, this value of C_V would lead to a specific trapping rate $\sigma = 4 \times 10^{12} \text{ s}^{-1}$ of positrons in vacancies far below the value known for metals (see above). The high fraction of vacancy-occupied sites around PAC probe atoms, which is attributed to a high thermal vacancy concentration by Collins and Fan,²⁰ may originate from capturing of vacancies during quenching.

We point out that the concept of a triple defect⁴ is inadequate for the thermal defect pattern in γ -TiAl because the measured or calculated thermal vacancy concentrations C_V are both much lower than the predicted concentration of thermally formed antisite defects.^{7,16}

In this context a few comments with respect to the possibility of positron trapping at antisite atoms will be made. For the compound semiconductor GaAs there is some evidence for positron trapping at negatively charged Ga antisite atoms.²¹ Positron trapping at antisite defects similarly as at small precipitates in metallic alloys might be caused by different positron affinities of the pure constituent metals (see Puska *et al.*²² and references therein). In the above-mentioned calculations⁷ on thermal defect formation in TiAl, high concentrations of antisite atoms were suggested at temperatures far below the onset of thermal vacancy detection at T_i . We conclude from the only slight linear increase of $\bar{\tau}$ below T_i [see Fig. 3(a)] that there is no evidence of a lifetime change due to thermal formation of antisite atoms. If, however, thermally formed antisite atoms gave rise to positron trapping without a measurable change of the positron lifetime this could be investigated by positron

diffusivity studies.²³

According to the theoretical approaches no significant concentrations of *structural* vacancies should be available in γ -TiAl at ambient temperature in agreement with the present results (see Sec. III A) and the results of differential expansion studies.²⁴

Finally, we may compare the results for the thermal vacancy formation with diffusion studies. Recent measurements of the ⁴⁴Ti self-diffusion in γ -TiAl show close similarities with the self-diffusion characteristics in fcc metals.²⁵ An activation enthalpy of $Q^{SD} = 3.1 \text{ eV}$ for self-diffusion was derived which is similar to values resulting from creep resistance studies.²⁶ If we apply the simple relationship

$$Q^{SD} = H_V^F + H_V^M \quad (6)$$

for self-diffusion processes mediated by thermal vacancies as in pure metals a vacancy migration enthalpy $H_V^M = 1.6 \text{ eV} > H_V^F$ may be estimated. The ratio $H_V^M/H_V^F > 1$, observed in ordered intermetallic compounds [Fe₃Al, (Ref. 10) B2-FeAl (Ref. 3)] in contrast to the situation in pure metals, reflects the more complicated jump process in ordered binary crystals.

From the annealing stage at 250 K observed in TiAl after electron irradiation¹⁷ an activation enthalpy below the vacancy migration enthalpy estimated above is suggested. This may indicate either considerable deviations from the simple relationship given by Eq. (6) or that the recovery after electron irradiation originates from the migration of defects different from the defects, e.g., vacancies on the Ti sublattice, which are formed in thermal equilibrium at high temperatures.

C. Summary

The results of the present vacancy study in γ -TiAl by means of positron lifetime spectroscopy can be summarized as follows:

A concentration level of thermal vacancies with an extrapolated value $C_V(T_m) = 1.5 \times 10^{-4}$ at the melting temperature similar as in pure fcc metals is observed. This is in good agreement with the results of calculations based on a nearest-neighbor-bond model which predict vacancy formation predominantly on the Ti sublattice.⁷

A comparison of the effective enthalpy of vacancy formation $H_V^{F,eff} = 1.41 \pm 0.06 \text{ eV}$ with a ⁴⁴Ti self-diffusion enthalpy of $Q^{SD} = 3.01 \text{ eV}$ suggests a low vacancy diffusivity as typical for intermetallic compounds.

No indication for structural vacancies was found above the experimental detection limit of $C_V \approx 10^{-6}$.

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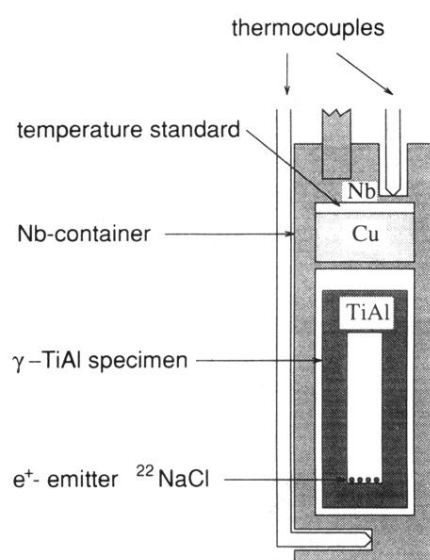


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