PHYSICAL REVIEW B **68**, 224102 (2003)

Slow removal of vacancies in $B2$-$\mathrm{Ni}_{52}\mathrm{Al}_{48}$ upon long-term low-temperature annealing

X. Y. Zhang,[1,2,*] W. Sprengel,[2] K. J. Reichle,[2] K. Blaurock,[2] R. Henes,[3]
and H.-E. Schaefer[2]
[1]*College of Materials Science and Engineering, Yanshan University, 066004 Qinhuangdao, China*
[2]*Institut für Theoretische und Angewandte Physik, Stuttgart University, D-70550 Stuttgart, Germany*
[3]*Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany*

(Received 2 December 2002; revised manuscript received 11 July 2003; published 9 December 2003)

Due to the high concentration and low diffusivities of thermal vacancies in $B2$-NiAl, these vacancies are thought to be only then fully removed when long-term annealing at low temperatures is employed [H.-E. Schaefer *et al.*, Intermetallics **7**, 277 (1999)]. In the present paper the annealing of vacancies in $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ in the temperature range from 635 K to 685 K on a one-year time scale is specifically studied by positron annihilation spectroscopy. The positron lifetime $\tau_V = (179 \pm 1)$ ps in as-prepared $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ demonstrates the presence of remnant single vacancies. The decrease of the concentration of these vacancies with annealing time demonstrates that they can be removed by low-temperature long-term annealing leading to vacancy clusters. From the annealing a vacancy migration enthalpy of $H_V^M = (2.0 \pm 0.1)$ eV has been determined for $\mathrm{Ni}_{52}\mathrm{Al}_{48}$. The remnant single vacancies are detected to be located on the Ni sublattice of ordered NiAl. The present results are expected to be of interest as an exemplary case that removal of vacancies and therefore thermal equilibrium in complex solids may be achieved only after long times.

DOI: 10.1103/PhysRevB.68.2241XX PACS number(s): 61.72.Ji, 71.20.Lp, 78.70.Bj

I. INTRODUCTION

The intermetallic compound $B2$-NiAl is a candidate for high-temperature structural components due to its high melting temperature, advantageous high-temperature mechanical properties, excellent corrosion resistance, and low mass density.[1–3] The nature of structural vacancies, which are introduced, e.g., into $B2$-NiAl (CsCl structure) upon deviations from stoichiometry, is often discussed[4–7] since it may substantially affect the diffusional and mechanical properties of the compound.[8,9] *Ab initio* calculations show that antisite atoms rather than structural vacancies are expected for the Ni-rich compound $\mathrm{Ni}_{52}\mathrm{Al}_{48}$.[6] In this compound, however, vacancies are available in high concentrations at ambient temperature after casting.[10] The nature of these vacancies (structural or thermal vacancy) should be further elucidated since no efficient removal of the vacancies is observed by annealing at high temperatures.[11,12] A high vacancy migration enthalpy $H_V^M = 1.8$ eV and a low vacancy formation enthalpy $H_V^F = 1.5$ eV in NiAl were determined by measurements of the time-differential length change after fast temperature changes.[13] From the high ratio $H_V^M/H_V^F > 1$ it is anticipated that due to their high equilibrium concentration and low diffusivities thermal vacancies in $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ can only be fully removed by long-term annealing at low temperatures. For testifying this conjecture application of specific local probes such as positrons is of interest. By positron lifetime spectroscopy vacancy-type atomic defects can be identified[14] and by coincident measurements of the Doppler broadening of the positron-electron annihilation photons the sublattice in an ordered binary compound can be determined[15] on which the vacancies are located. For the latter technique the chemical environment of the annihilation site—e.g., a vacancy—can be analyzed on an atomic level by considering the high-momentum part of the electron momentum distribution.[16]

In the present paper remnant vacancies in $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ are studied by positron lifetime spectroscopy during annealing over months at low temperatures. Coincident Doppler broadening measurements of the positron-electron annihilation radiation are employed for specifically identifying the sublattice on which these vacancies are formed.

II. EXPERIMENT

The $B2$-$\mathrm{Ni}_{52}\mathrm{Al}_{48}$ specimens were prepared by melting of pure Ni and Al in an induction furnace. The alloy was homogenized at 1573 K for 48 h and then cooled to room temperature at a rate of 50 K/h. The low-temperature annealing of $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ was carried out at temperatures between 635 and 685 K over months under vacuum ($p < 2 \times 10^{-3}$ Pa).

The positron lifetime spectrum of as-prepared and annealed $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ was measured at room temperature by a fast-slow $\gamma\gamma$ spectrometer with a time resolution of 210 ps [full width at half maximum (FWHM)] using a sandwiched ^{22}NaCl positron source. The time constants τ_i and their relative intensities I_i were numerically determined from positron lifetime spectra with $2 \times 10^6 - 6 \times 10^6$ coincidence counts by means of standard techniques.[17] By this procedure the time constants and intensities of the positron lifetime components could be derived with low uncertainty limits even in the case when three-component fitting is applied as demonstrated in Table I. This is due to the narrow time resolution of the spectrometer, the good statistics, and the wide separation of the time constants.

The measurements of the Doppler broadening of the positron-electron annihilation γ spectra up to the high momenta of the chemically characteristic core electrons were carried out at room temperature by measurements of the two annihilation photons with the energies E_1 and E_2 by means of two high-resolution Ge detectors. The high peak-to-background ratio of $> 5 \times 10^5$ was achieved by diagonal cuts of the $E_1 - E_2$-Doppler spectra along the $E_1 + E_2 = (1022$

TABLE I. Positron lifetime parameters τ_0, τ_V, and τ_c with the relative intensities I_0, I_V, and I_c and the lifetime τ_f of positron annihilation in the delocalized free state as well as the mean positron lifetime $\overline{\tau}$ measured on as-prepared $Ni_{52}Al_{48}$ and after annealing at temperatures between 635 K and 685 K for 60 days.

Specimen	τ_0 (ps)	I_0 (%)	τ_V (ps)	I_V (%)	τ_c (ps)	I_c (%)	τ_f (ps)	$\overline{\tau}$ (ps)
As-prepared			179±1	100				179±1
635 K			177±1	100				177±1
660 K	23±7	6.6±1	178±1	88.5±1	522±8	4.9±1	125±10	184±4
685 K	30±5	11.2±1	177±1	80.2±1	530±7	8.5±1	118±9	191±4

±1.5) keV energy conservation line. Each of these spectra contains more than 10^7 coincidence counts for achieving good statistics in the core electron region above $\Delta E = E - 511\ \mathrm{keV} = 5\ \mathrm{keV}$, which corresponds to $p_L \geqslant 19.6 \times 10^{-3} m_0 c$ for the core electron momenta. For demonstrating the details of the high-momentum tails, the Doppler broadening spectra measured on NiAl, defect-free pure Ni, and pure Al were normalized to the Ni Doppler broadening spectrum (see Fig. 4) so that the Ni spectrum is represented by a straight horizontal line.

III. RESULTS AND DISCUSSIONS

A positron lifetime $\tau_V = (179 \pm 1)$ ps determined in as-prepared $Ni_{52}Al_{48}$ (see Table I) is much longer than the value of $\tau_f = (120 \pm 5)$ ps expected for the lifetime of free delocalized positrons in defect-free NiAl as estimated from the mean valence electron density $\rho_{el} = 542\ \mathrm{nm}^{-3}$ derived from a comparison with the free positron lifetimes and valence electron densities of pure metals and other intermetallic compounds[11,18] (see Fig. 1). The experimentally determined positron lifetime ($\tau_V = 179$ ps) indicates positron saturation trapping at single vacancies in $Ni_{52}Al_{48}$ (see Fig. 1). Since in Ni-rich NiAl antisite atoms rather than structural vacancies are expected for compensating the Ni surplus,[6] the vacancies detected in $Ni_{52}Al_{48}$ are regarded as remnant thermal vacancies.

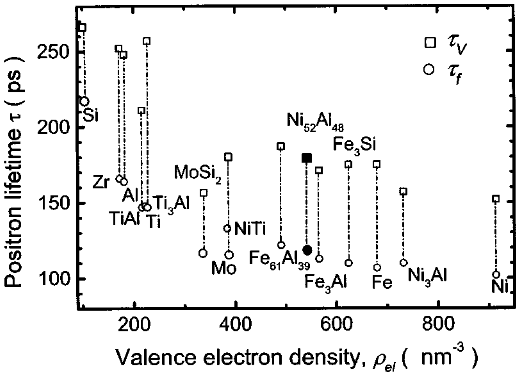

FIG. 1. Relationship between the experimentally determined positron lifetimes in the delocalized free state (τ_f) or the trapped state at single vacancies (τ_V) (Refs. 11 and 17) and the valence electron density (ρ_{el}) for pure metals and intermetallic compounds. The valence electron density $\rho_{el} = (n \times N_{el})/V$ is given by the number N_{el} of outer s, p, or d electrons and the volume V of the formula unit. The lifetime $\tau_f = (118 \pm 9)$ ps derived for the free delocalized positron state in $Ni_{52}Al_{48}$ from positron lifetime studies of the specimen annealed at 685 K (see Table I) is in good agreement with the data of free positron lifetimes in other systems. The positron lifetime $\tau_V = 179$ ps in as-prepared $Ni_{52}Al_{48}$ indicates positron saturation trapping at remnant single vacancies in the intermetallic compound.

During long-term annealing at the relatively low temperatures $T_a = 660$ K and $T_a = 685$ K, a long positron lifetime component appears, indicating the formation of vacancy clusters consisting of more than 20 single vacancies according to the lifetime of $\tau_c = (520-530)$ ps (see Table I).[19] Formation of the vacancy clusters occurs at the expense of the concentration of single vacancies which decreases according to the decrease of the relative intensity I_V (see Table I) of the positron lifetime component with the time constant τ_V attributed to vacancies. At the same time a short-lived component with the time constant τ_0 appears (see Table I) which is characteristic for partial annihilation of positrons in the free state because the vacancy concentration is now below the value required for positron saturation trapping. In this state the free positron lifetime $\tau_f = 1/(I_0/\tau_0 + I_V/\tau_V + I_c/\tau_c) = (120 \pm 5)$ ps can be derived (see Table I) making use of the parameters deduced from the positron lifetime spectra, where $I_0 = 1 - I_V - I_c$ is the relative intensity of the short-lived time constant τ_0. The quantities τ_V and I_V as well as τ_c and I_c are the lifetimes and relative intensities of positrons annihilated in the single-vacancy state and in the cluster state, respectively. The value of τ_f determined here for NiAl coincides well with the value expected from a comparison with the data of other metals and intermetallics (see Fig. 1).

Making use of the data derived from the positron lifetime spectra the evolution of the concentration of the single vacancies C_V with the concomitant formation of vacancy clusters can be determined according to[20]

$$\sigma_V C_V(t) = \frac{\tau_c - \overline{\tau}}{\tau_c - \tau_V} \left(\frac{I_V + I_c}{\tau_0} - \frac{\tau_c I_V + \tau_V I_c}{\tau_V \tau_c} \right) - \frac{\overline{\tau} - \tau_f}{\tau_f(\tau_c - \tau_V)}, \tag{1}$$

where $\overline{\tau}$ is the mean positron lifetime and $\sigma_V = 10^{15}\ \mathrm{s}^{-1}$ (see Ref. 21) the specific positron trapping rate.

In Fig. 2 the isothermal annealing data for the vacancy concentration C_V are given for various annealing temperatures T_a as derived from the positron trapping rates according to Eq. (1). Unfortunately the initial value of $C_{V,0}$ cannot be determined directly because it is so high that positron saturation trapping occurs. If we, however, fit a model isotherm

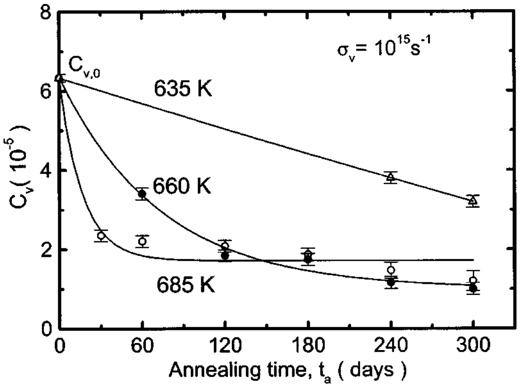

FIG. 2. Isothermal annealing of the concentration $C_V(t_a)$ of single vacancies in $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ annealed at low temperatures. The concentration C_V is determined from the positron trapping rate $\sigma_V C_V$ [see Eq. (1)] making use of $\sigma_V = 10^{15}\ \mathrm{s}^{-1}$ (see Ref. 21). The initial vacancy concentration $C_{V,0} = 6.3\times 10^{-5}$ was determined by fitting an exponential to the isothermal annealing data at $T_a = 660$ K. Curves are the fitting results according to Eq. (2) by taking use of the value of the determined $C_{V,0}$. The value of C_V after long-term annealing at $T = 660$ K lower than that upon annealing at 685 K indicates the lower equilibrium vacancy concentration at the lower annealing temperature.

$$C_V(t_a) = C_{V,0}\exp\left(-\frac{t_a}{t_E}\right), \qquad (2)$$

where t_E is the equilibration time constant, according to a first-order reaction to the isothermal data for $T_a = 660$ K (see Fig. 2), then the value $C_{V,0} = 6.3\times 10^{-5}$ can be determined. Making use of this value for the other isotherms the temperature variation of the equilibration rate

$$t_E^{-1} = t_{E,0}^{-1}\exp\left(-\frac{H_V^M}{k_B T_a}\right) \qquad (3)$$

can be determined, yielding the vacancy migration enthalpy $H_V^M = (2.0\pm 0.1)$ eV (see Fig. 3), which is similar to the value of 1.8 eV derived from earlier time-differential length change measurements of $\mathrm{Ni}_{47}\mathrm{Al}_{53}$ under thermal equilibrium conditions.[13]

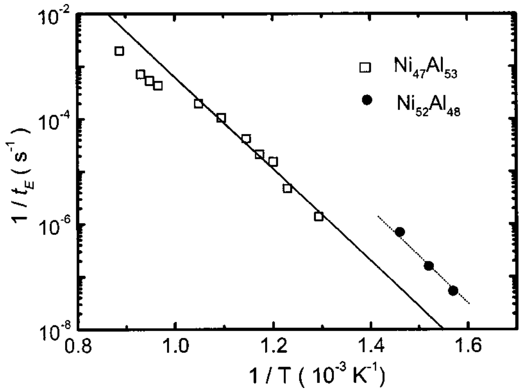

FIG. 3. Temperature variation of the equilibration rate t_E^{-1} in $B2$-$\mathrm{Ni}_{52}\mathrm{Al}_{48}$ determined by long-term low-temperature equilibration experiments (●). The vacancy migration enthalpy $H_V^M = 2.0$ eV is determined according to Eq. (3). The t_E^{-1} values determined by time-differential length change measurements in $B2$-$\mathrm{Ni}_{47}\mathrm{Al}_{53}$ are indicated in addition (□, Ref. 13).

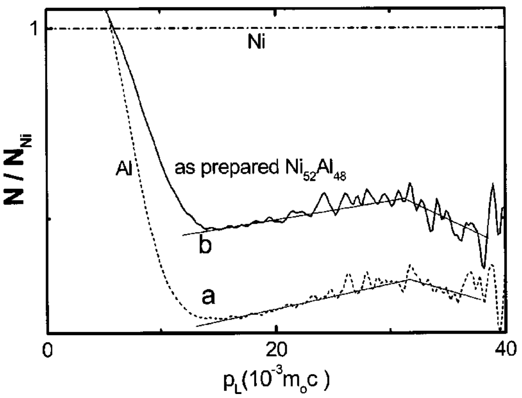

FIG. 4. The ratio curves of the area-normalized coincident Doppler broadening spectra of the positron-electron annihilation photon line measured on defect-free pure Ni and on pure Al, as well as on as-prepared $\mathrm{Ni}_{52}\mathrm{Al}_{48}$. The spectra are normalized to the Ni spectrum, which in this presentation yields a straight line. The similar slope of the ratio curves of pure Al and as-prepared NiAl in the range of $p_L > 20\times 10^{-3} m_0 c$ (see slopes a and b) demonstrates that positrons are annihilated in vacancies surrounded by Al atoms—i.e., in these vacancies are located on the Ni sublattice.

For a specific identification of the sublattice on which the remnant thermal vacancies in $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ are located the technique of the coincident Doppler broadening measurement[16,22] is employed here (see Fig. 4). The chemical surrounding of the positron annihilation site can be specifically characterized by the slope of a Doppler broadening ratio curve in the high-momentum core electron regime.[15,18] This has been demonstrated by *ab initio* calculations for SiC and vacancies therein.[23] The ratio curve of the as-prepared $\mathrm{Ni}_{52}\mathrm{Al}_{48}$ in the core electron momentum range $20-40 \times 10^{-3} m_0 c$ exhibits a slope (marked as b) quite similar to that of pure Al (marked as a) and is entirely different from that of Ni (horizontal line; see Fig. 4). From this we conclude that positrons are predominantly annihilated in vacancies with Al atoms in their nearest neighborhood, i.e., in single vacancies on the Ni sublattice. This is in agreement with theoretical predictions[24] of the vacancy formation enthalpy on the Ni sublattice in NiAl which is reported to be much lower than that of Al vacancies.

IV. CONCLUSIONS

In $B2$-$\mathrm{Ni}_{52}\mathrm{Al}_{48}$ vacancies are specifically detected after conventional preparation by positron lifetime measurements. We demonstrate that these vacancies with a high ratio $H_V^M / H_V^F > 1$ can only be removed by low-temperature long-term (over months) annealing. Under these conditions the migrating vacancies form clusters. The vacancy migration enthalpy is determined to $H_V^M = (2.0\pm 0.1)$ eV in agreement with earlier studies of time-differential length change measurements.[13] Coincident Doppler broadening measurements yield direct evidence that the remnant vacancies available at ambient temperature are located on the Ni sublattice.

ACKNOWLEDGMENTS

X.Y.Z. gratefully acknowledges the award of an Alexander von Humboldt research grant. We appreciate financial support by Deutsche Forschungsgemeinschaft (Grant Nos. Scha 428/17-3 and 428/22). We are indebted to W. Maisch, Max-Planck-Institut für Metallforschung, Stuttgart for technical support in specimen preparation and the long-term low-temperature annealing experiments.

---

*Corresponding author. Electronic address: xiangyi@itap.physik.uni-stuttgart.de; xyzh66@yahoo.com.cn

[1] J. H. Westbrook, in *Structural Intermetallics*, edited by R. Darolia, J. J. Lewandowski, C. T. Liu, P. L. Martin, D. B. Miracle, and M. V. Nathal (The Minerals, Metals and Materials Society, Warrendale, PA, 1993), p. 1.

[2] *Intermetallic Compounds—Principles and Practice*, edited by J. H. Westbrook and R. L. Fleischer (Wiley, Chichester, 1994), Vols. 1 and 2.

[3] G. Sauthoff, *Intermetallics* (VCH Verlagsgesellschaft, Weinheim, 1995).

[4] A. J. Bradley and A. Taylor, Proc. R. Soc. London, Ser. A **159**, 56 (1937).

[5] Y. A. Chang and J. P. Neumann, Prog. Solid State Chem. **14**, 221 (1982).

[6] B. Meyer and M. Fähnle, Phys. Rev. B **59**, 6072 (1999).

[7] W. Sprengel, M. A. Müller, and H.-E. Schaefer, in *Intermetallic Compounds—Principles and Practice*, edited by J. H. Westbrook and R. L. Fleischer (Wiley, Chichester, 2002), Vol. 3, p. 275.

[8] R. D. Noebe, R. R. Bowman, and M. V. Nathal, Int. Mater. Rev. **38**, 193 (1993).

[9] Y. A. Chang, L. M. Pike, C. T. Liu, A. R. Bilbrey, and D. S. Stone, Intermetallics **1**, 107 (1993).

[10] H.-E. Schaefer and K. Badura-Gergen, Defect Diffus. Forum **143–147**, 193 (1997).

[11] R. Würschum, K. Badura-Gergen, E. A. Kümmerle, C. Grupp, and H.-E. Schaefer, Phys. Rev. B **54**, 849 (1996).

[12] W. Puff, B. Logar, and A. G. Balogh, Acta Mater. **47**, 101 (1999).

[13] H.-E. Schaefer, K. Frenner, and R. Würschum, Phys. Rev. Lett. **82**, 948 (1999).

[14] R. Würschum, C. Grupp, and H.-E. Schaefer, Phys. Rev. Lett. **75**, 97 (1995).

[15] A. A. Rempel, K. Blaurock, K. J. Reichle, W. Sprengel, J. Major, and H.-E. Schaefer, Phys. Rev. Lett. **89**, 185501 (2002).

[16] P. A. Kumar, M. Alatalo, V. J. Ghosh, A. C. Kruseman, B. Nielsen, and K. G. Lynn, Phys. Rev. Lett. **77**, 2097 (1996).

[17] H.-E. Schaefer, Phys. Status Solidi A **102**, 47 (1987).

[18] X. Y. Zhang, W. Sprengel, K. Blaurock, A. A. Rempel, K. J. Reichle, K. Reimann, H. Inui, and H.-E. Schaefer, Phys. Rev. B **66**, 144105 (2002).

[19] M. Eldrup and B. N. Singh, J. Nucl. Mater. **251**, 132 (1997).

[20] H.-E. Schaefer and F. Banhart, Phys. Status Solidi A **104**, 263 (1987).

[21] H.-E. Schaefer, K. Frenner, and R. Würschum, Intermetallics **7**, 277 (1999).

[22] K. G. Lynn, J. R. MacDonald, R. A. Boie, L. C. Feldman, J. D. Gabbe, M. F. Robbins, E. Bonderup, and J. Golovchenko, Phys. Rev. Lett. **38**, 241 (1977).

[23] T. E. M. Staab, L. M. Torpo, M. J. Puska, and R. M. Nieminen, Mater. Sci. Forum **353–356**, 533 (2001).

[24] M. Fähnle, J. Mayer, and B. Meyer, Intermetallics **7**, 315 (1999).