Time-Differential Length Change Measurements for Thermal Defect Investigations: Intermetallic *B*2-FeAl and *B*2-NiAl Compounds, a Case Study

H.-E. Schaefer,* K. Frenner, and R. Würschum

Universität Stuttgart, Institut für Theoretische und Angewandte Physik, Pfaffenwaldring 57, 70569 Stuttgart, Germany
(Received 24 September 1998)

Time-differential length change measurements after temperature changes were developed and applied to the study of high-temperature atomic defect in the case of intermetallic alloys. The enthalpies $H_1^F = 1.0 \pm 0.1$ eV or $H_1^E = 1.5 \pm 0.2$ eV derived for $B2$-Fe$_{55}$Al$_{45}$ from the temperature-dependent amplitudes and time constants of the length change, respectively, coincide with the vacancy formation and migration enthalpies H_V^F and H_V^M from earlier positron studies. This demonstrates the feasibility of the technique. By this technique, for the first time, the enthalpies $H_V^M = 1.8 \pm 0.1$ eV and $H_V^F = 1.5 \pm 0.25$ eV in $B2$-Ni$_{47}$Al$_{53}$ were determined. [S0031-9007(98)08324-0]

Atomic defects in thermal equilibrium at high temperatures in metals or intermetallic compounds are involved in a number of solid state processes such as structural order-disorder transition [1], self-diffusion [2], or mechanical creep [3]. For the investigation of thermal defects techniques are required which are specific for the detection of these defects, sensitive to low atomic concentrations, and applicable at high temperatures. Positron lifetime studies (see [4]) and concomitant *ab initio* calculations [5] have contributed substantial progress to the studies of thermal defect formation and migration in intermetallic compounds. Positron annihilation studies are, however, inappropriate for more complex systems with structural vacancies or free volumes so that more versatile techniques are desirable. Here, we demonstrate that time-differential length change measurements can be successfully employed as a sensitive technique for defect formation and migration studies. This method will be, in addition, of general and wide interest for sensitive studies of condensed matter kinetics.

A time-dependent length change $\Delta l(t, T_i, T_f)$ of a specimen is expected when the thermal defect concentrations equilibrate after a fast temperature change between the initial and final temperatures T_i and T_f (Fig. 1). The temperature variation of this behavior yields direct information on defect formation and migration as well as on the vacancy formation volume ΔV if the absolute values of atomic defect concentrations are available [6,7]. This technique is furthermore specific to the thermal formation of vacancies or interstitials which are expected to give rise to either an expansion or a contraction [8], respectively.

The length change kinetics after temperature changes were studied earlier [9] by a mechanical probe. For the present thermal defect studies by high-precision time-differential dilatometry [10] an incremental Michelson laser intereferometer was employed which permits contact-free length change measurements up to high temperatures without contamination. For the first time, defect formation as well as migration in the vicinity of thermal equilibrium could be studied by means of this technique.

The time dependence of the length change $\Delta l(t, T_i, T_f)$ after a temperature change (see Fig. 1) originates from the long-range migration of, e.g., thermally formed vacancies generated at sources in order to equilibrate the thermal equilibrium vacancy concentration at T_f. Because of its delay this effect can be separated from the anharmonic lattice expansion $\Delta l'$ which occurs simultaneously with the temperature change.

In the simple case of a regular array of defect sources or sinks [11] the time dependence of the specimen length

$$l = l_0 + \Delta l(t, T_i, T_f) = l_0(T_i) + \Delta l' + \Delta l(t, T_i, T_f)$$
$$= l_0 + \Delta l_s(T_i, T_f)[1 - \exp(-t/t_E(T_f))] \tag{1a}$$

with

$$\frac{1}{t_E} = \alpha^2 D_V = \frac{1}{t_{E,0}} \exp(-H_V^M/k_B T) \tag{1b}$$

after a fast temperature change is given by an exponential with the time constant t_E [Eq. (1a)]. This is determined by the vacancy diffusivity D_V or the vacancy migration enthalpy H_V^M and the preexponential factor $t_{E,0}$. α characterizes the density of vacancy sources or sinks. The length l_0 denotes the equilibrated state at T_i.
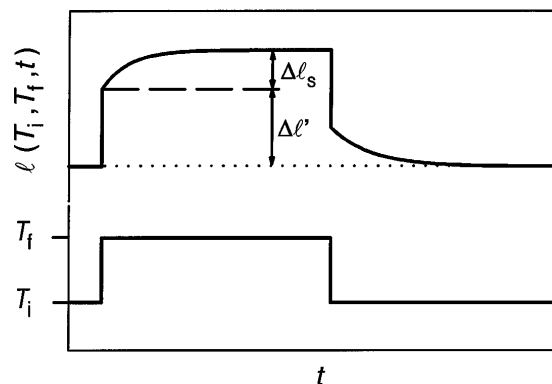

FIG. 1. Schematics of the time-differential length change Δl (T_i, T_f, t) due to the equilibration process of the thermal defect concentration after a temperature change from T_i to T_f.

From the temperature variation of the length change amplitude

$$3\frac{\Delta l_s(T_i, T_f)}{l_0} \simeq \frac{\Delta V}{V}[C_V(T_f) - C_i(T_i)] \qquad (2)$$

induced, e.g., by thermally formed vacancies the effective formation enthalpy H_V^F can be derived according to $C_V = \exp(S_V^F/k_B)\exp(-H_V^F/k_B T)$ if the vacancy concentration C_V at the lower temperature can be neglected. Here, S_V^F is the vacancy formation entropy and V the mean atomic volume. The defect induced length change may be more complex than sketched here due to more complex source/ sink structures [12] or a contribution of vacancies and antisite atoms on the various sublattices of intermetallic compounds [13].

The $Fe_{55}Al_{45}$ and $Ni_{47}Al_{53}$ specimens for the present studies were prepared by comelting the high-purity metals and zone melting [14]. From the ingots specimens with a ring-shaped ledge (see Fig. 2) were spark cut. The change in specimen length (20 mm) between the polished measuring planes (Fig. 2) could be measured by a two-beam Michelson laser interferometer (SP120D, SIOS Messtechnik, Germany) to an accuracy of about 20 nm corresponding to an atomic defect concentration of about 3×10^{-6}. The specimen temperature measured by two chromel-alumel thermocouples welded on the specimen was stable within 0.1 K with a gradient less than 20 K and a temperature setting time of 200 s after a temperature change which presently limits the time range of the equilibration studies. The specifications of the present length change setup are suitable for studying systems with high ratios of $H_V^M/H_V^F > 1$ as in $B2$ intermetallics but should be extended for, e.g., pure metals with $H_V^M/H_V^F \leq 1$ to shorter times.

In Fig. 3 the time-dependent isothermal contraction of a $Fe_{55}Al_{45}$ specimen after cooling from high to slightly lower temperatures is shown with an acceleration of the equilibration when T_f is raised (see Fig. 3a). A good fit of the isotherms can be obtained by two superimposed exponentials with the time constants t_{E1} and t_{E2} for the con- tributions with the higher (main) and smaller amplitudes, respectively. From their temperature variations (Fig. 4) the activation enthalpies and the preexponential factors

$$H_1^E = 1.5 \pm 0.2 \text{ eV}, \qquad t_{E,01}^{-1} = 4 \times 10^5 \text{ s}^{-1}; \quad (3a)$$

$$H_2^E = 0.6 \pm 0.1 \text{ eV}, \qquad t_{E,02}^{-1} = 0.8 \text{ s}^{-1} \qquad (3b)$$

are derived in analogy to Eq. (1b). The time constants t_{E1} (see Fig. 4) are very similar to the values determined by positron lifetime spectroscopy (see Fig. 4) for long-range vacancy migration from the equilibration process of the vacancy concentration [15]. In addition, the value of H_1^E in Eq. (3a) coincides within the experimental uncertainties with the vacancy migration enthalpy $H_V^M = 1.7$ eV in $B2$-FeAl [15] as deduced from positron lifetime studies after temperature changes. This coincidence demonstrates that thermal vacancies in $B2$ intermetallics can be specifically investigated by sensitive length change measurements. The rate constant $t_{E,01}^{-1}$ in Eq. (3a), which is much smaller than the Debye frequency relevant for a single jump, is attributed to a number of vacancy jumps of $\sim 10^7$ during the equilibration process [15] and corresponds to a reasonable density of dislocations of 2.2×10^9 m^{-2} as sources or sinks (see [16]).
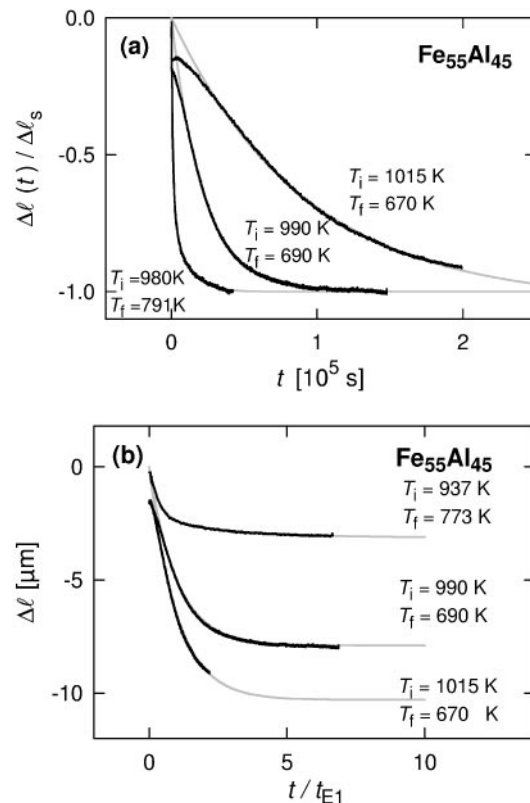
FIG. 3. Time dependence of the isothermal contraction Δl of a $Fe_{55}Al_{45}$ specimen after fast cooling to the final temperature T_f. Variation of (a) the equilibration rate with T_f and (b) the amplitude of the length change with the initial temperature T_i where the time scale is normalized to the relaxation time t_{E1} of the process with the higher amplitude. l_s denotes the length change amplitude. The gray lines denote model fits to the experimental data (see text).
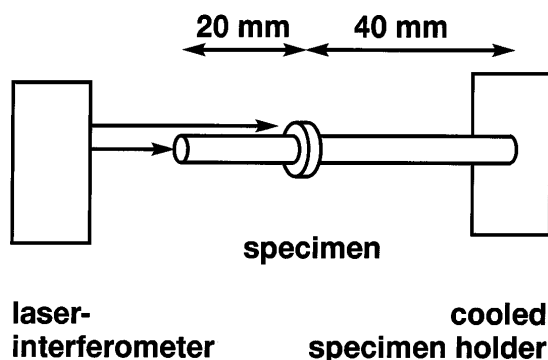
FIG. 2. Sketch of the experimental setup. The length of the specimen, which is suspended together with the furnace in a vacuum recipient, is measured by the two laser beams on the polished parallel planes on the specimen front and ledge.
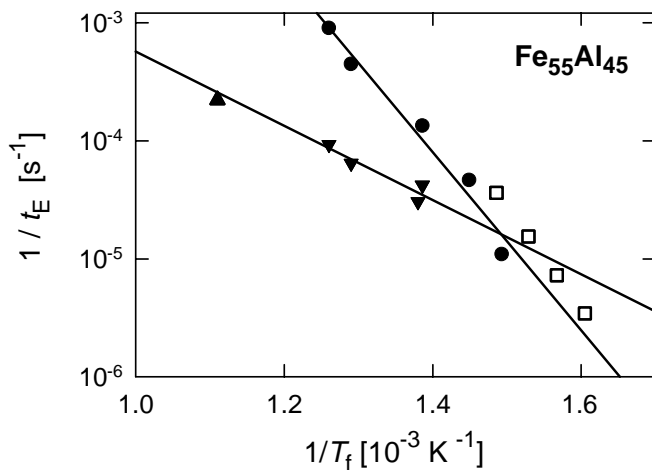
FIG. 4. Temperature variations of the time constants $t_{E,1}$ (●) and $t_{E,2}$ (▼: after cooling; ▲: after heating) of the isotherms in Fig. 3a together with the time constant (□) of the vacancy equilibration isotherms measured by positron lifetime experiments [15].

The second process in the length change studies on $Fe_{55}Al_{45}$ with the time constant t_{E2} (Fig. 4), which is also found in high-statistics positron lifetime measurements [17], exhibits an anomalously weak temperature dependence and an extremely small preexponential factor $1/t_{E,02}$ [see Eq. (3b)]. Small preexponential factors reported for atomic diffusion processes in relaxed metallic glasses or in *i*-AlPdMn quasicrystals have recently been ascribed to collective multiatom jump processes [18]. It should be noted that the isotherms in Fig. 3a may need, due to their initial incubationlike behavior, an even more complex description than discussed here as, e.g., characterized by a nucleation and growth process [19].

The temperature variations of the amplitudes $\Delta l_{s1}/l_0$ and $\Delta l_{s2}/l_0$ derived by means of two-exponential fits to the data in Fig. 3b are plotted in Fig. 5 together with the concentration of vacant lattice sites as derived from positron lifetime data [15]. The bending at high temperatures (Fig. 5) can be explained with the vacancy migration parameters of Eq. (3a) by defect losses during cooling.

From the $3\Delta l_s/l_0$ data for $Fe_{55}Al_{45}$ in Fig. 5 the activation enthalpies and the preexponential factors

$$H_1^F = 1.0 \pm 0.1 \text{ eV}, \qquad \ln \frac{\Delta V_1}{V} + S_1^F/k_B = 4.3;$$

(4a)

$$H_2^F = 0.9 \pm 0.1 \text{ eV}, \qquad \ln \frac{\Delta V_2}{V} + S_2^F/k_B = 2.7$$

(4b)

are derived. Both processes are attributed to vacancy formation because the activation enthalpies are similar to the vacancy formation enthalpy $H_V^F = 0.98$ eV [15] determined by positron lifetime spectroscopy. The vacancy formation volume $\Delta V/V = 0.53$ can be additionally de-
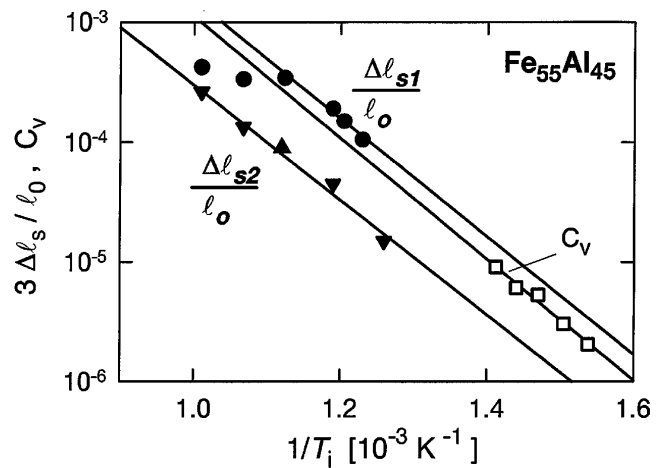
FIG. 5. Temperature variations of the length change amplitudes $\Delta l_{s1}/l_0$ (●) and $\Delta l_{s2}/l_0$ (▼: after cooling; ▲: after heating) of $Fe_{55}Al_{45}$ derived from two-exponential fits to the time-differential length changes after temperature changes (Fig. 3b) and of the concentration C_V (□) of vacant lattice sites determined from the positron trapping rates $\sigma C_V(T)$ in $Fe_{61}Al_{39}$ [15] and $\sigma = 1.3 \times 10^{15}$ s^{-1} deduced in conjunction with differential thermal expansion studies [7]. T_i is the temperature from which the cooling in the time-differential length change studies was started or at which the equilibrium studies of C_V were performed (for ▲: T_i denotes the final temperature after heating).

termined according to Eq. (2) from the presently measured total length change $(\Delta l_{s1} + \Delta l_{s2})/l_0$ and the atomic concentration of vacancies in Fig. 5. A vacancy formation volume $\Delta V/V = 0.7$ in this range was derived for Fe_3Al from the pressure variation of positron annihilation [20] whereas the higher value of $\Delta V/V = 1.42$ found for $B2$-FeAl was attributed to the formation of divacancies in this compound [21]. It should be mentioned that,
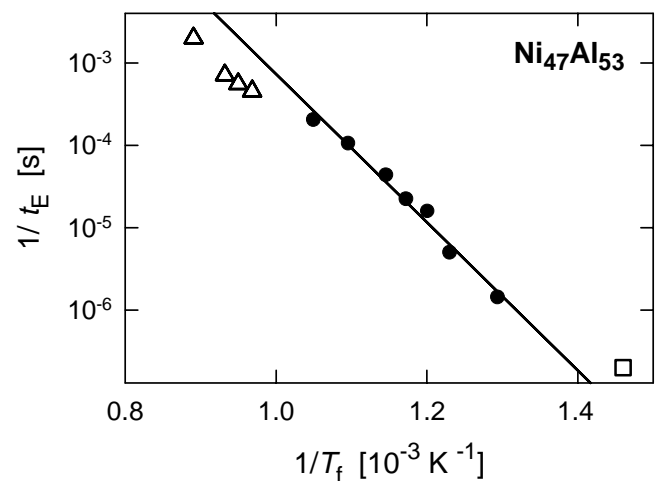

FIG. 6. Temperature variation of the equilibration rate $1/t_E$ in $B2$-$Ni_{47}Al_{53}$ determined from single exponential fits to the equilibration isotherms after cooling (●) or heating (△). An estimate of the rate constant $1/t_E$ from positron lifetime spectroscopy on $Ni_{52}Al_{48}$ in long-term low-temperature equilibration experiments (□) [24] is also indicated.
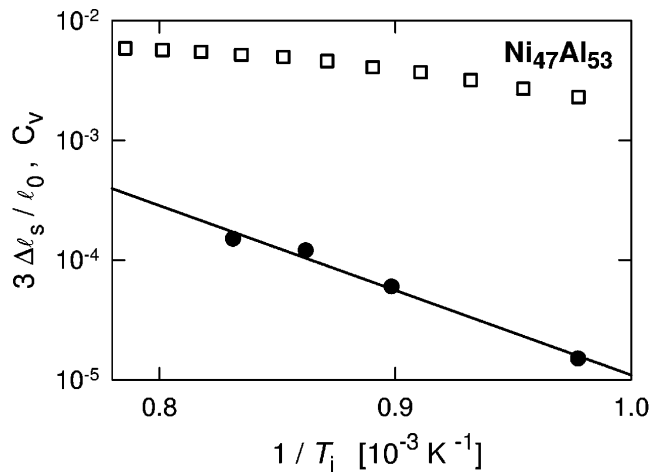
FIG. 7. Temperature variations of the length change amplitude $3\Delta l_s/l_0$ (●) and of the concentration of vacant lattice sites C_V (□) [23] in $Ni_{47}Al_{53}$ with T_i as defined in Fig. 5.

furthermore, high vacancy formation entropies $S^F > 3k_B$ are derived with $\Delta V/V = 0.53$ from Eq. (4).

Time-differential length change measurements may be of particular interest in the case of $B2$-NiAl where specific studies of thermal vacancies are scarce because their detection by means of specific positron annihilation studies is impeded due to positron saturation trapping at structural vacancies [4]. The results of first measurements on $B2$-$Ni_{47}Al_{53}$ are shown in Figs. 6 and 7 with the equilibration isotherms after cooling or heating fitted by a single exponential.

From the temperature dependence of $1/t_E$ (Fig. 6) for the first time the high vacancy migration enthalpy and the preexponential factor were deduced as

$$H_V^M = 1.8 \pm 0.1 \text{ eV} \quad \text{and} \quad t_{E,0}^{-1} = 6.7 \times 10^5 \text{ s}^{-1}.$$
$$(5)$$

The temperature variation of the length change amplitude $3\Delta l_s/l_0$ (Fig. 7) yields the values

$$H_V^F = 1.5 \pm 0.25 \text{ eV}, \qquad \ln\frac{\Delta V}{V} + S_V^F/k_B = 4.8.$$
$$(6)$$

This H_V^F value is higher than in $B2$-$Fe_{61}Al_{39}$ [15]. In addition, a high vacancy formation entropy S_V^F is observed as in other intermetallics [4]. The observation that the present H_V^F value for $Ni_{47}Al_{53}$ is higher than predicted by *ab initio* calculations (0.93 eV [22]) may raise the question as in how far antisite atom formation may contribute. The present H_V^F value is also higher than the value derived from initial differential thermal expansion data [23]. The concentration of vacant lattice sites C_V there (see Fig. 7), however, appears to be much too high because a value $\Delta V/V$ derived from a comparison of $3\Delta l_s/l_0$ and C_V is far too small.

*Email address: schaefer@itap.physik.uni-stuttgart.de

[1] O. Dimitrov, in *Intermetallic Compounds—Principles and Practice,* edited by J. H. Westbrook and R. L. Fleischer (John Wiley, Chichester, 1994), Vol. 1, p. 771.

[2] *Diffusion Mechanisms in Crystalline Materials,* edited by Y. Mishin, G. Vogl, N. E. B. Cowern, C. R. A. Catlow, and D. Farkas, MRS Symposia Proceedings No. 527 (Materials Research Society, Pittsburgh, 1998).

[3] G. Sauthoff, in *Diffusion in Ordered Alloys,* edited by B. Fultz, R. W. Cahn, and D. Gupta (TMS, Warrendale, 1993), p. 205.

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

[5] M. Fähnle, B. Meyer, J. Mayer, J. S. Oehrens, and G. Bester, in Ref. [2], p. 23.

[6] R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 1 (1960).

[7] R. Kerl, J. Wolff, and Th. Hehenkamp, Intermetallics (to be published).

[8] A. Seeger, Cryst. Lattice Defects **4**, 221 (1973).

[9] A. H. van Ommen and J. de Miranda, Philos. Mag. A **43**, 387 (1981).

[10] K. Frenner, Diploma thesis, Stuttgart University, 1998.

[11] D. N. Seidman and W. R. Balluffi, Phys. Rev. **139**, 1824 (1965).

[12] F. Heigl and R. Sizmann, Cryst. Lattice Defects **3**, 13 (1972).

[13] M. Fähnle and B. Mayer, Scr. Mater. **38**, 1131 (1998).

[14] U. Essmann, R. Henes, U. Holzwarth, F. Klopfer, and E. Büchler, Phys. Status Solidi (a) **160**, 487 (1997).

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

[16] H.-E. Schaefer and G. Schmid, J. Phys. Condens. Matter **1**, 49 (1989).

[17] M. Müller (private communication).

[18] W. Frank, P. Scharwaechter, and R. Blüher, in "Continuum Models and Discrete Systems," edited by E. Inan and K. Z. Markov (World Scientific, Singapore, to be published).

[19] J. Rieux and C. Goux, Mem. Sci. Rev. Metall. **66**, 869 (1969).

[20] M. Franz, J. Wolff, and Th. Hehenkamp, Mater. Sci. Forum **175–178**, 355 (1995).

[21] J. Wolff, A. Broska, M. Franz, B. Köhler, and Th. Hehenkamp, Mater. Sci. Forum **255–257**, 593 (1997).

[22] C. L. Fu, Y. Y. Ye, M. H. Yoo, and K. M. Ho, Phys. Rev. B **48**, 6712 (1993).

[23] F. Zobel, Dissertation, Technical University of Berlin, 1994.

[24] R. Würschum and H.-E. Schaefer, Mater. Sci. Forum **255–257**, 81 (1997).