

Equilibrium Defects and Concentrations in Nickel Aluminide

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ABSTRACT

Perturbed angular correlation of gamma rays was applied to determine properties of equilibrium defects in B2 NiAl near the stoichiometric composition. Point defects were detected through quadrupole interactions they induce at In probe atoms on the Al sublattice. Well-resolved signals were observed for probe atoms having zero, one or two Ni-vacancies (V_{Ni}) in the first neighbor shell. The fractions of probes in different sites are analyzed using a thermodynamic model to determine defect properties as follows. The equilibrium high-temperature defect is determined to be the triple defect combination (two V_{Ni} and one Ni-antisite atom) through the variation of the vacancy concentration with composition and not, for example, the Schottky vacancy pair. The binding enthalpy of V_{Ni} with a probe atom was determined to be in the range 0.18-0.24 eV. Site fractions were measured for three samples having 50.03, 50.14 and 50.91 at.% Ni at temperatures up to 1300 C. Vacancy concentrations were deduced from the site fractions and binding enthalpy. The equilibrium constant for formation of the triple defect was determined as a function of temperature from the vacancy concentrations and sample compositions. The formation enthalpy was found to be in the range 1.65-1.83 eV, depending on the binding enthalpy. The formation entropy was found to be $-3.2(4) k_B$. The large, negative value of the formation entropy probably cannot be explained in terms of a binding entropy, and we speculate that triple defects harden the B2 lattice, perhaps by disrupting the well-known $1/3 \langle 111 \rangle$ 'soft mode' lattice instability in B2 and bcc materials.

INTRODUCTION

NiAl is a highly ordered intermetallic structural material used in aerospace applications. Knowledge of its point defects is needed to understand phenomena such as diffusion and climb. Methods that resolve defects directly provide model-independent information about the defects. Perturbed angular correlation of gamma rays (PAC) is a microscopic method that provides excellent resolution of defects when using the sensitive PAC probe $^{111}\text{In}/\text{Cd}$. The defects are detected by local disturbances they produce in internal fields in solids. Of relevance for this study is the electric-field gradient (efg) disturbance produced by the screened Coulomb potential of the defect charge. Since the defect-induced efg falls off rapidly with distance, only defects in the first-neighbor shell of probe atoms produce high-frequency quadrupole interactions. For more information about methods, see ref. [1], [2], or [3].

NiAl has the B2 (CsCl) structure and a wide single-phase range made possible by structural point defects: Ni-vacancies (V_{Ni}) in Ni-poor alloys and Ni-antisite atoms (Ni_{Al}) in Ni-rich alloys. Because In is isovalent with Al and has a larger size, one can be certain that In PAC probes are sited on the Al-sublattice [4], surrounded by eight Ni atoms or defects in the first neighbor shell. Initial PAC studies of NiAl identified signals of structural defects in annealed samples and showed that signals of near-neighbor V_{Ni} could be clearly resolved [5]. Later, experiments on rapidly-quenched samples were used to determine properties of equilibrium defects [6,7]. More recently, we have been making PAC studies at high temperature to avoid complications that come from quenching experiments involving impurity probe atoms [8].

In the present paper we summarize PAC measurements of equilibrium defects at temperatures up to 1300°C. Observation of V_{Ni} and Ni_{Al} structural defects in Ni-poor and Ni-rich alloys suggests

that those are the lowest energy defects [9]. In an ordered single-phase alloy, the equilibrium defect must be some combination of elementary defects that preserves the local proportion of elements. Such a combination made out of the observed structural defects is the triple defect, $2V_{Ni} + Ni_{Al}$. This combination has *a priori* to be considered the most likely equilibrium defect combination. Indeed, the triple defect is confirmed below to be the dominant defect below 1200 C, and its properties are determined.

EXPERIMENTS

NiAl(^{111}In) samples were made by arc-melting high-purity metals (m5N) together with ^{111}In activity under argon. The ^{111}In probe fractional concentration was below 10^{-8} . Compositions were determined from the original Ni and Al masses after checking that there was negligible loss of mass during the melts. Since, as will be shown, there are great changes of vacancy concentrations with composition close to stoichiometry, special care was taken to determine compositions of such samples to better than 0.05 at.%. An oven was designed and built that uses resistive and electron-beam heating for PAC measurements to over 1300°C [10]. Measurements were made using a standard 4-detector PAC spectrometer and data were analyzed as described previously [1]. Each PAC spectrum was fitted to a superposition of quadrupole interaction signals described completely in ref. [6] or [10]. For purposes of this paper, the signals are grouped according to the number of Ni-vacancies in the closest atomic shell of probe sites: (1) a vacancy-free signal for probes with no vacancies in the first atomic shell, (2) a monovacancy signal for probes having one V_{Ni} in the first shell, and (3) a minor divacancy signal for probes with two neighboring V_{Ni} . Since no other signals were observed in these experiments, the site-fractions f_0 , f_1 and f_2 of the grouped signals sum to unity. To illustrate, in Fig. 1 are shown PAC spectra for a sample with 50.14 at.% Ni. The room-temperature spectrum at bottom exhibits the monovacancy signal (period ~ 50 ns) with a site fraction of about 20% after quenching from high temperature. The remaining low-frequency signal corresponds to probes with no V_{Ni} in the first shell. The top four spectra are in thermal equilibrium. As can be seen, the site fraction of the 1V signal increases with temperature up to 1457 K. The 1508 K spectrum exhibits damping attributed to jumping of vacancies at rates of order 10 MHz, described in ref. [11].

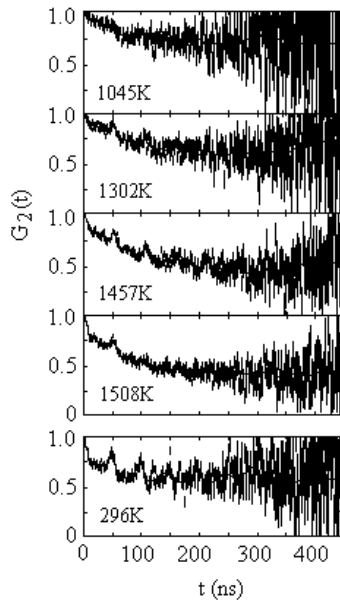


Figure 1. PAC spectra of a NiAl sample with 50.14 at.% Ni measured at the indicated temperatures. The 296K spectrum exhibits quenched-in vacancies.

ANALYSIS AND RESULTS

Thermodynamics of site fractions and defect concentrations

For a fractional concentration $[V]$ of vacancies on the Ni-sublattice, the site fraction for mono-vacancy complexes, f_1 , can be expressed in terms of the site fraction for vacancy-free probes, f_0 , as

$$f_1/f_0 = 8[V]\exp(E_{B1}/k_B T) \quad (1)$$

using the law of mass action. Here, E_{B1} is the binding enthalpy of the first vacancy to the probe and 8 is the number of equivalent ways in which a vacancy can be placed in the first shell. The vacancy concentration is governed by formation of the triple defect: $0 \rightarrow 2V_{Ni} + Ni_{Al}$, which has an equilibrium constant $K = [V]^2[Ni_{Al}] = \exp(S_F/k_B)\exp(-E_F/k_B T)$ according to the law of mass action, in which S_F and E_F are the formation entropy and enthalpy of the triple defect. Assuming negligible concentrations of defects other than V_{Ni} and Ni_{Al} , the fractional concentrations of elementary defects in an alloy of composition $Ni_{1+2x}Al_{1-2x}$ must obey the equation of constraint $[V] - 4x = 2[Ni_{Al}]$. Eliminating $[Ni_{Al}]$ between the last two equations yields a cubic equation for $[V]$ in terms of K and the deviation from stoichiometry x :

$$\frac{[V]^3}{2} + 2x[V]^2 = K = \exp(S_F/k_B)\exp(-E_F/k_B T). \quad (2)$$

The following approach is used below to determine properties of the triple defect. Given a measured value of the normalized monovacancy site fraction f_1/f_0 and a value for E_{B1} , first $[V]$ is determined using eq. 1 and then K using eq. 2. An Arrhenius plot of K then yields S_F and E_F .

Examination of eq. 2 reveals three thermodynamic regimes. (1) At stoichiometry. When $[V] \gg 4x$, then $[V] = (2K)^{1/3}$, and the effective formation enthalpy Q for V_{Ni} is $E_F/3$. (2) Off stoichiometry. When $[V] \ll x$, then $[V] = (K/2x)^{1/2}$, so that $Q = E_F/2$ and there is an inverse square-root power-law dependence of $[V]$ on the deviation from stoichiometry. (3) Crossover regime. When $[V] \approx 4x$, measurements on a single sample may show Q crossing over from $Q = E_F/2$ at lower temperature to $Q = E_F/3$ at higher temperature.

Vacancy-probe binding enthalpy

In experiments on quenched NiAl by Jiawen Fan [7,6], excess vacancies produced by quenching were observed to start trapping at PAC probes at 300°C in 15 minute anneals. However, annealing out of excess vacancies was found to be very sluggish and only occurred appreciably above 650°C in annealing times of about one hour. This means that there is a 300 degree range in which the concentration of vacancies remains largely constant while a local equilibrium can be established between trapped and untrapped vacancies [6]. From eq. 1, an Arrhenius plot of f_1/f_0 should then have a slope equal to E_{B1} . In this way Jiawen Fan determined a value of 0.22(1) eV [6,7]. More recently, Fan's data were reanalyzed, leading to a revised value of 0.18(1) eV [10], and one of us independently obtained a new measurement of 0.24(2) eV [10], although based on only two data points. For simplicity, we use the value 0.18 eV below, but quote results for 0.24 eV where appropriate.

Composition dependence of the vacancy concentration

Measurements were made at 1460 K on six samples having 50.03, 50.14, 50.44, 50.91, 51.15 and 52.17 at.% Ni. Vacancy concentrations $[V]$ calculated using eq. 1 with $E_{B1} = 0.18$ eV are shown in Fig. 2 in a double-logarithmic plot versus x . Excluding the datum at $x=0.0003$ for which $[V] > 4x$, a fit of the remaining five points to a straight line yielded the slope $d \ln[V] / d \ln x = -0.4(1)$. This slope is consistent with -0.5 expected off-stoichiometry when the equilibrium defect is the triple defect (see eq. 2 and discussion above). Other equilibrium defects appear to be ruled out, such as the Schottky vacan-

cy pair, for which the slope would have been -1. Thus, the dominant equilibrium defect appears to be the triple defect, at least near 1460 K [12].

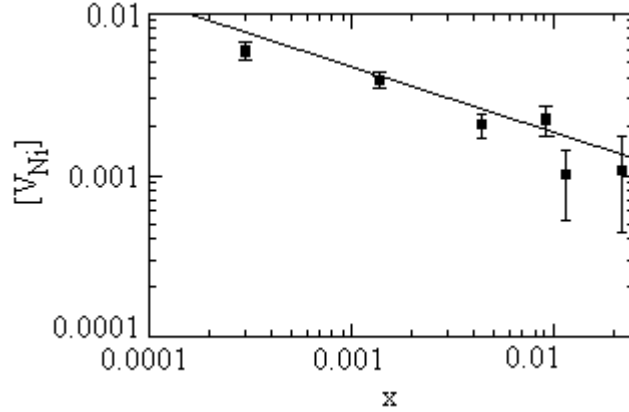


Figure 2. Concentration of Ni-vacancies at 1460K versus the deviation from stoichiometry, x . The straight line is a power-law fit to the five points with greater x . The slope, $-0.4(1)$, is consistent with the triple-defect model.

High-temperature equilibrium

Samples with 50.03, 50.14 and 50.91 at.% Ni were studied up to 1575 K. In Fig. 3 is an Arrhenius graph of monovacancy site fractions f_1/f_0 measured at temperatures below 1520 K [13]. Drawn on the figure are best fitted straight lines for data of the 50.03 and 50.91 at.% Ni samples, whose fitted slopes yield, respectively, activation enthalpies of $-0.36(2)$ eV and $-0.65(2)$ eV. The difference in slopes is explained as follows. From eq. 1, it can be seen that the slopes equal sums of an effective vacancy formation enthalpy Q and binding enthalpy E_{B1} . As it turns out, data for the 50.03 and 50.91 at.% Ni samples fall, respectively, in the “at-stoichiometry” and “off-stoichiometry” regimes, so that the activation enthalpies for f_1/f_0 are, respectively, $E_F/3 + E_{B1}$ and $E_F/2 + E_{B1}$. The 50.14 at.% sample is intermediate.

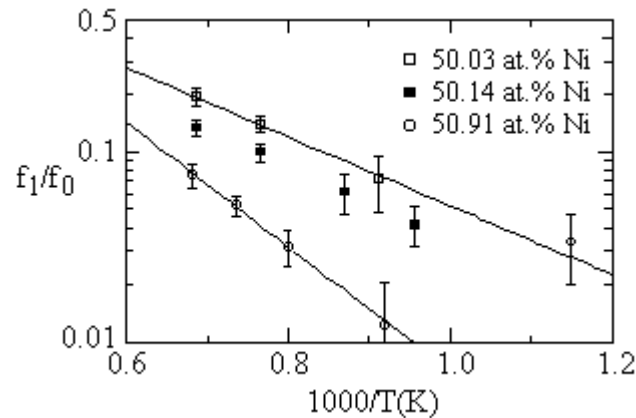


Figure 3. Equilibrium monovacancy site fractions, normalized to the vacancy-free site fraction, for three NiAl samples.

The equilibrium constant was calculated using the site fractions in Fig. 3. First, $[V]$ was obtained using eq. 1 with $E_{B1} = 0.18$ eV. Then, K was determined from $[V]$ and x using eq. 2. Fig. 4 shows an Arrhenius plot of K for all three samples. As can be seen, the data all collapse onto a single straight line (as they should), with a fitted activation enthalpy for formation $E_F = 1.64(23)$ eV shown by the straight line. Due to slight offsets among the sets of data for the three samples, fits of K for the individual sets yielded consistent values of E_F with smaller uncertainties. An average value of K for the three sets is $E_F = 1.65(4)$ eV, obtained using $E_{B1} = 0.18$ eV. Using the alternate value $E_{B1} = 0.24$ eV leads to $E_F = 1.83$ eV.

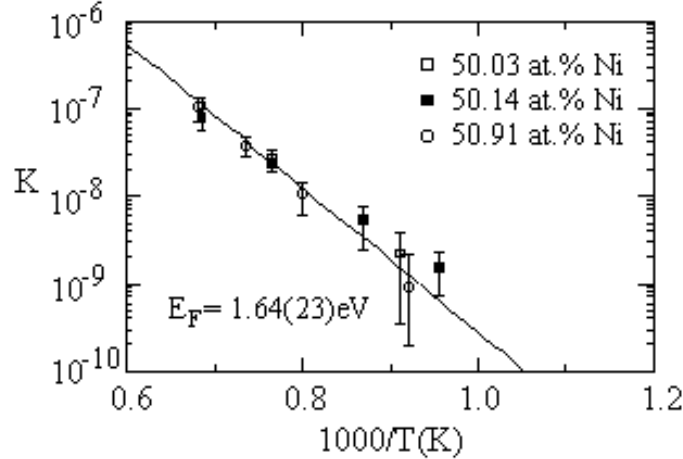


Figure 4. Equilibrium constant for formation of triple defects. Note the collapse of data for the vacancy site fractions in Fig. 3 onto a single line.

Formation entropy

The formation entropy S_F reflects the change in vibrational state of the crystal when a triple defect is formed. Using eq. 2, the fitted intercept in Fig. 4 yielded $S_F = -3.2(4) k_B$. This value is independent of the uncertainty in E_{B1} , but could be affected by an appreciable entropy of binding S_B , which was not considered in eq. 1. Binding entropy reflects the change in vibrational states of the crystal between situations in which a vacancy is and is not next to a PAC probe atom. Inclusion of binding entropy in the analysis would lead to the result that the fitted entropy, $-3.2 k_B$, is equal not to S_F alone but to $S_F + (2-3)S_B$, in which the variable coefficient 2-3 depends on whether data are from in the off-stoichiometric or at-stoichiometric regimes. Thus, a value $S_B = -1.3 k_B$ would be consistent with a formation entropy of about zero. Clearly, it would be very useful to have an estimate of the magnitude and sign of S_B . Our guess is that S_B is small, in which case $S_F = -3.2 k_B$. One naively expects the formation of each vacancy of the triple defect to contribute a positive formation entropy of about $+2 k_B$ due to “bond breaking”, as for vacancies in pure metals. Thus, one has to contrast the value $-3.2 k_B$ with the naïve expectation of $+4 k_B$ for the two vacancies formed. It is hard to conceive that a discrepancy as large as $7 k_B$ can be attributed to the binding entropy. We therefore believe that S_F is genuinely negative and that it can not be explained by simple changes to the vibrational spectrum of the lattice, such as obtained using an Einstein model. As one explanation, we propose that triple-defects may “harden” the lattice by interfering with the well-known $1/3 \langle 111 \rangle$ “soft mode” lattice instability in the B2 and bcc structures. A further discussion may be found in reference [14].

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