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Electric current enhanced defect mobility in Ni₃Ti intermetallics

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The effect of the application of a dc current on the annealing of point defects in Ni₃Ti was investigated by positron annihilation spectroscopy. An increased defect annealing rate was observed under the influence of the current and was attributed to a 24% decrease in the activation energy of mobility. The results are interpreted in terms of the electron wind effect and the complex nature of diffusion in ordered intermetallic phases. They provide direct evidence for an increase in defect mobility in ordered intermetallics under the influence of a current. © 2004 American Institute of Physics. [DOI: 10.1063/1.1774268]

A considerable effect of high electric current fluxes on solid-state reactivity has been shown recently.^{1–5} However, several fundamental aspects of the role played by the current in reactivity enhancement are yet to be understood. In this letter we present evidence of the effect of the current on defect mobility in an intermetallic system.

Experiments have been conducted in which metal–metal diffusion couples are reacted isothermally but with varying dc current densities.^{1–3} Such experiments permit the study of current effects on phase formation kinetics which are unrelated to Joule heating effects. Significant current-enhanced reactivity was observed in the Au–Al^{2,3} and Ni–Ti¹ systems. In these studies, however, it was not possible to determine the role of the current; the general expectations of electromigration were not realized, as the enhancement was independent of current direction.

It was suggested that the current increases the concentration and/or mobility of point defects thus aiding mass transfer and enhancing intermetallic growth.^{1,3} Asoka-Kumar *et al.*⁶ found a significant increase in point defect concentration in the Al–Cu system when it was subjected to a current. In this letter we focus on the latter proposal—that an applied current enhances vacancy mobility in the Ni–Ti system. Our approach was to conduct defect relaxation experiments in which high-defect samples are annealed at different temperatures with and without an applied current and analyze the samples by positron annihilation spectroscopy (PAS). Isothermal annealing has been utilized to determine vacancy migration energies, through electrical resistivity^{7,8} and PAS measurements.⁹

PAS takes advantage of the fact that positively charged positrons tend to localize in open volume regions (e.g., free volume, vacancies, dislocations, voids, etc.), where there are missing positively charged atomic nuclei.¹⁰ Furthermore when a positron and an electron annihilate the resulting gamma rays yield information about the annihilation site, making PAS a sensitive probe for defects. A positron–electron annihilation produces primarily two 511 keV gamma rays traveling in opposite directions.

Coincidence Doppler broadening (CDB), a specific PAS technique, was used to characterize the defects in the specimens produced in this study. In CDB, the energies of the photons produced are measured simultaneously. Due to the momentum of the positron–electron pair prior to annihilation, the 511 keV photons may be blueshifted or redshifted¹¹ with the energy shift given by

$$\Delta E = \frac{1}{2} p_L c, \quad (1)$$

where p_L is the longitudinal component of the electron–positron momentum and c is the speed of light.

Two parameters are extracted from the CDB data; low momentum fraction, the normalized area under the central portion of the distribution (referred to as S in the positron literature), and high momentum fraction, the normalized area in a fixed interval under the high momentum tail of the distribution (referred to as W in the positron literature). The low momentum fraction parameter is due to positron annihilations with valence electrons, more likely to occur in regions with defects. The high momentum fraction parameter is due to positron annihilations with core electrons, more likely to occur when the positron not trapped in an open volume region annihilates in the bulk material. Low momentum fraction and high momentum fraction are not absolute param-

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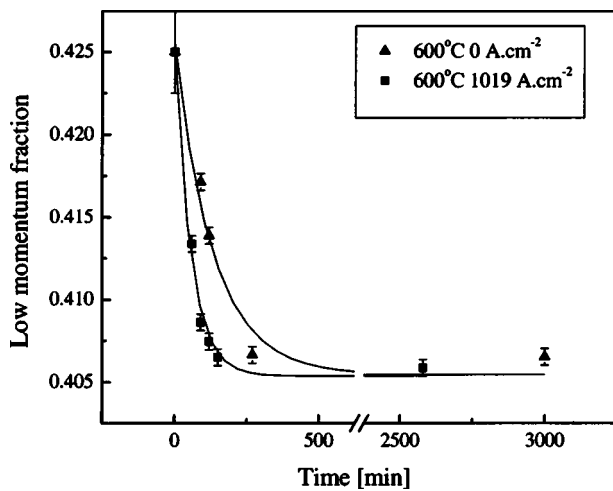


FIG. 1. Low momentum fraction, S , as a function of time for samples annealed at 600 °C with and without a dc current of 1019 A cm⁻². S parameter is evaluated using events with momentum values of up to 0.38 a.u.

eters. However the relative magnitudes of the low and high momentum fractions are good indicators of the defect concentration in a material, i.e., given the same bulk material, the sample with a higher low-momentum fraction has a higher defect concentration.

Ni₃Ti (99.99% purity) ingots were obtained from ACI Alloys (San Jose, CA). The 100-mm-long rods were sectioned perpendicularly to produce discs (6 mm diameter and 1 mm thick). The discs are polished using 1200 grit SiC metallographic paper and cleaned ultrasonically in acetone, to ensure good electrical and thermal contact with electrodes.

The ingots were then annealed in a system that allows the samples to be subjected to different dc current densities (ranging from 0 to 2546 A cm⁻²) at a constant temperature under a high vacuum (10⁻⁷ Torr). The system contains a large (16.5-cm-diameter and 6.5-cm-long) cylindrical W mesh furnace surrounding the dc electrodes. The temperature range in this study was from 600 to 700 °C, and the annealing time varied from 15 to 3000 min. Concerns regarding the validity of temperature measurements and other details of the experimental method are discussed in a previous publication.¹ After annealing, the samples were quenched by being dropped quickly from the furnace heat zone onto a water-cooled stainless steel plate.

CDB experiments were performed using a setup similar to the one described in previous works.^{10,11} With this setup, a 1 T magnetic field focuses positrons from a ²²Na source into a ~3-mm-diameter spot. Positrons emitted from ²²Na sources have energies up to 546 keV, giving a typical implantation depth of the positrons into materials of up to 30 to 100 μm.

Figure 1 shows the change of the low momentum fraction (for $p_L \leq 0.38$ a.u.) with annealing time for samples annealed at 600 °C without current and with an applied current density of 1019 A cm⁻². The zero-time data point is an average for the as-received (unannealed) material (0.425±0.0025), and the time scale, with a break, extends to 50 h. The as-received samples have a high low momentum fraction, indicative of high defect concentration, as is expected in a material which was synthesized by arc-melting and subsequently quenched from a melt on water-cooled copper block. The defect population may include point de-

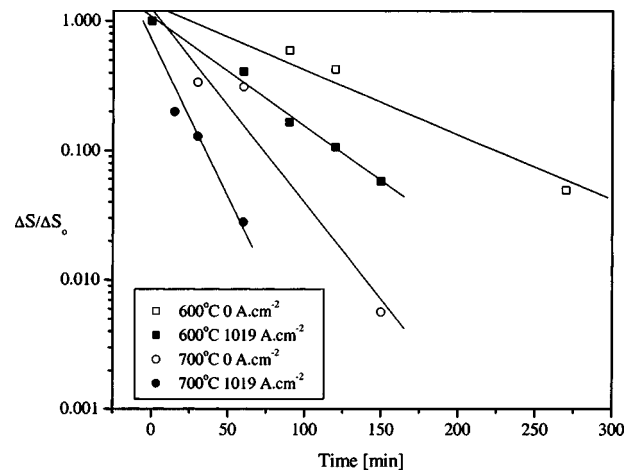


FIG. 2. Normalized change in low momentum fraction $\Delta S/\Delta S_0$ as a function of time for samples annealed at 600 and 700 °C under current densities of 0 and 1019 A cm⁻².

fects and their complexes and an S -parameter measurement alone cannot distinguish them. The solid lines in Fig. 1 are an exponential fit of the data, as given by

$$S = A \exp\left(\frac{-t}{\tau_D}\right) + S_e, \quad (2)$$

where S is the low momentum fraction, t is time, τ_D is the rate of decay constant, A is a constant, and S_e is approximately equal to the low momentum fraction the system is decaying to (i.e., equilibrium low momentum fraction). Figure 2 shows the normalized low momentum fraction data for 600 and 700 °C experiments with and without an applied current of 1019 A cm⁻². In this case $\Delta S = S - S_e$ and $\Delta S_0 = S_0 - S_e$ where S_0 is the low momentum value of the as-received sample. The fit to the data indicates that the low momentum fraction is decreasing exponentially with time with the decay constant, τ_D , providing a measure of the rate at which the defects are annealed out under the different conditions. The calculated values of this rate constant are 250.8, 52.5, 26.4, and 10.1 min for 600 °C—0 A cm⁻², 600 °C—1019 A cm⁻², 700 °C—0 A cm⁻², and 700 °C—1019 A cm⁻², respectively.

The τ_D values decrease significantly by the application of a current. At 600 °C it decreases from 250.8 to 52.5 min and at 700 °C from 26.4 to 10.1 min, a reduction by a factor of 4.7 and 2.6, respectively. Resistivity measurements were performed on the samples to corroborate the CDB results. These measurements show similar trends to the low momentum fraction versus time data (Fig. 1 and 2), with the resistivity decreasing exponentially with time.

When high momentum fraction is plotted versus low momentum fraction, the fit is linear,¹² suggesting that there is a single type of defect with varying concentrations in the samples observed by positrons.^{10,13} In this case the low momentum fraction is directly proportional to the defect concentration in the sample so that it can be used much like electrical resistivity^{7,14} to analyze defect migration kinetics.

In metallic systems the rate of disappearance of nonequilibrium defects (relaxation) at annealing temperature T , for annealing time t , is expected to given by

$$\frac{dC}{dt} = C_1 \exp\left(\frac{-E_m}{k_B T}\right), \quad (3)$$

where C is the point defect concentration, E_m is the defect migration energy, k_B is Boltzmann's constant, and C_1 is a constant. Thus dS/dt values (from data in Fig. 2) can be used to calculate a rough estimate of the migration energy, E_m , of the vacancies with and without an applied current. Since the defect population may involve more than one type of defect, we chose this simple approach (instead of a two-state trapping model) to estimate the defect migration energy. The calculated estimates are $E_m = 1.79 \pm 0.2$ eV without a current and $E_m^C = 1.36 \pm 0.1$ eV with an applied current; a decrease of 24% in the presence of the current. These calculated E_m values are similar to vacancy migration values in other intermetallics such as $\text{Fe}_{61}\text{Al}_{39}$, $\text{Fe}_{63}\text{Al}_{47}$, and Fe_3Al , with reported values of 1.7 ± 0.2 , 1.7 ± 0.2 , and 1.3 ± 0.1 eV, respectively.⁹ It should be noted that the values calculated here for the close-packed Ni–Ti intermetallics cannot be unambiguously attributed to monovacancy migration. Vacancy mobilities in close-packed intermetallics may differ substantially from those in more open-structures (such as the B2-type structure in Fe–Al intermetallics); the agreement in migration energies may be due to the migration of vacancies and additional larger open volume regions in the close-packed Ni–Ti intermetallic.

We believe that the increased defect mobility with the imposition of current in the Ni_3Ti intermetallic compound is a result of the electron wind effect. In metallic systems, the electron wind effect^{15–17} may be manifested by a directional dependence of mass transport and consequently phase growth with dc current direction. Experiments showing asymmetry in the growth of product layers with respect to the current direction have been observed in some cases but not in most, including in the work on the effect of current on the growth of intermetallic phases in the Ni–Ti system,¹ where no asymmetry was observed. A lack of asymmetry in metallic systems, in some cases, is a consequence of the complex nature of the diffusion process in ordered metallic compounds. For Ni_3Ti , the diffusion of either element is coupled with that of the other so as to maintain structure and stoichiometry. This is supported by the relatively high activation energy for mobility calculated for the case in the absence of a current, 1.79 eV. Similar conclusions of a complex jump mechanism were arrived at for the $\text{Fe}_{60}\text{Al}_{40}$

system⁹ on the basis of annealing experiments.¹⁸ Numerous complex jump mechanisms for ordered intermetallic compounds have also been proposed, including a six-jump cycle (Huntington–McCombie–Elock (HME) mechanism),^{19–21} the antistructure bridge mechanism,²² and the α sublattice mechanism.²³

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