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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. 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 current densities. 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 and Ni–Ti 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. Asoka-Kumar et al. 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 and PAS measurements.

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. 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 redshifted with the energy shift given by

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

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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100 sources have energies up to 546 keV, giving a typical im-

erial, the sample with a higher low-momentum fraction has a

ted, and subsequently quenched from a melt on water-cooled

copper block. The defect population may include point de-

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

\[ S = A \exp \left( -\frac{t}{\tau_D} \right) + S_e, \]  

where \( S \) is the low momentum fraction, \( t \) is time, \( \tau_D \) is the
rate of decay constant, \( A \) is a constant, and \( S_e \) is approxi-
imately equal to the low momentum fraction the system is
decaying to (i.e., equilibrium low momentum fraction). Fig-
ure 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, \( \tau_D \), 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 \( \tau_D \) 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 momen-
tum fraction versus time data (Fig. 1 and 2), with the resist-
ivity 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 con-
centration 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 nonequi-
librium defects (relaxation) at annealing temperature \( T \), for
annealing time \( t \), is expected to given by
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 $E_m = 1.36 \pm 0.1$ 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 Fe$_{61}$Al$_{39}$, Fe$_{66}$Al$_{2}$, and Fe$_3$Al, with reported values of $1.7 \pm 0.2$, $1.7 \pm 0.2$, and $1.3 \pm 0.1$ eV, respectively. 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$_3$Ti 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$_3$Ti, 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 Fe$_{60}$Al$_{40}$ system$^9$ 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 $\alpha$ sublattice mechanism.$^{23}$

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