AEM STUDY OF EARLY STAGE GROWTH OF THE

Ni₃Al INTERMEDIATE PHASE IN NiAl-Ni DIFFUSION COUPLES

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The early stage of growth of the Ni₃Al intermediate phase in NiAl-Ni diffusion couples, has been studied using a Philips EM400T analytical electron microscope. The high x-ray spatial resolution (≤ 50 nm) has permitted the measurement of concentration profiles across the Ni₃Al intermediate phase in couples heat treated for diffusion times as short as several seconds. Absorption and thickness corrected data taken across the diffusion interfaces appear consistent with interface concentrations predicted from phase equilibria.

The major experimental techniques used during the past decade to study the kinetics of interdiffusion and intermediate phase growth have been the optical microscope and the electron microprobe. Because both of these techniques have spatial resolution limits of the order of a micron, it has not been possible to examine early growth kinetics in most systems. For example, prior studies of Ni₃Al layer growth have concentrated on the later stages of growth and have used experimental times longer than three hours (1). Therefore, there is little or no information available on the kinetics and/or morphology of initial or early stage Ni₃Al layer growth. This paper deals with the growth kinetics and the intermediate phase microstructure developed during early stage growth of Ni₃Al layers in NiAl/Ni diffusion couples. The work reported here concerns results obtained using analytical electron microscopy (STEM and an energy dispersive x-ray detector) and TEM; parallel studies using optical microscopy have also been performed, and these results have been reported separately (2).

A serious problem related to the quantitative x-ray analysis of thin foil Ni-Al specimens is that significant x-ray absorption takes place in this system. For nonabsorbing systems the Cliff-Lorimer technique relates the concentration ratio of elements A and B (CA, C_B) to the intensity ratios of the elements (I_A, I_B) by a factor k_AB which is a constant for a given operating voltage independent of composition and thickness (3). If prefer-
ential absorption of one of the species occurs within the thin foil sample, the Cliff-Lorimer equation must be modified. The effect of specimen absorption on x-ray intensity ratios as x-rays are produced through a thin foil of thickness $t$ has been given by Goldstein et al. (4)

$$\frac{C_A}{C_B} = k_{AB} \left[ \frac{I_A}{I_B} \frac{\mu_A/\rho_{\text{spec}}}{\mu_B/\rho_{\text{spec}}} \frac{1-e^{-\mu_A/\rho_{\text{spec}}}}{1-e^{-\mu_B/\rho_{\text{spec}}}} \csc \alpha(\mu t) \right]$$

where $\mu_{\text{spec}}$ is the mass absorption coefficient of element A or B in the specimen, $\rho$ is the density of the foil at the point of analysis, and $t \csc \alpha$ is the path length of the exiting x-rays at a take-off angle $\alpha$. Certain precautions must be taken when Eq. (1) is applied to practical systems (5). For example, the quantities $\mu$ and $\rho$ are generally taken to be those at the point of analysis. Strictly speaking, these quantities must be representative of the material along the x-ray exit path. Care must be taken whenever possible to orient the foil in order to present an isocompositional path to the detected x-rays.

**Experimental**

Experimental details concerning materials, sample configuration and preparation, diffusion treatments, sectioning, layer thickness measurements, and thin foil preparation used in the present study have been previously published (2). End-member materials were a 99.99% pure polycrystalline Ni rod with a grain size of ~1 mm, and an NiAl (32.5 wt% Al) single crystal. Diffusion treatment was accomplished by rapidly heating the vacuum-encapsulated-clamped couple such that the specimen capsule was brought to temperature (1100°C) in 240 seconds or less. After the appropriate hold time, the capsules were quenched to below red heat within 15-30 seconds. Thin foils were prepared from sections cut parallel to the diffusion direction by first electro-jet polishing in a 15% HNO$_3$/H$_2$O solution, and then ion beam thinning in an argon beam. The thin foils were examined in a Philips EM400T electron microscope equipped with an EDAX x-ray detector. Foil thickness determinations were made at the points of analysis by the contamination spot separation technique (6). Thin foils taken from the NiAl single crystal were used for the determination of the $k_{\text{NiAl}}$ factor; details concerning these measurements have been published elsewhere (5). The Ni and Al-$K_x$ x-ray data were analyzed and the backgrounds stripped by use of an EDAX 9100 computer system. The major errors for STEM analysis arise primarily from the low x-ray counting rates, from the error in determination of the $k$ factor, and also from thickness measurement. For the present study, the error has been estimated to be ±10% and this is reflected in the error bars used for the profiles presented here.

**Results and Discussion**

A typical microstructure produced at 1100°C is presented in Fig. 1, and demonstrates the irregular nature of the interphase interfaces. In all instances, the protrusions and broadened regions of the Ni$_3$Al phase were found to be associated with the presence of grain boundaries in the Ni$_3$Al layer. The short time Ni$_3$Al layer growth data at 1100°C (2) is compared with longer time data from Janssen (1) in Fig. 2. The present short time data does appear parabolic, and a least squares fit gives a parabolic growth rate of $2.8 \times 10^{-22} \mu m^2/sec$. Extrapolation of this growth rate line shows that Janssen's data lie above it and have a somewhat faster growth rate. However, this is not surprising because Janssen indicated that the Ni-rich NiAl he used gave faster growth rates than stoichiometric
NiAl (as was used in the present investigation). The most significant feature of Fig. 2 is that the short time data do not extrapolate back to zero layer thickness. Because all the diffusion couples were brought to temperature in 240 seconds or less, the growth rate below 1100°C was apparently greater than at the hold temperature, 1100°C. The increased growth rate upon heating results from the fact that grain boundary diffusion significantly contributes to Ni₃Al layer growth below 1100°C (2). The fact that the number density of Ni₃Al layer protrusions decreased with increasing hold time at 1100°C suggests that grain boundary diffusion no longer strongly contributes to layer growth at 1100°C.

STEM profiles obtained across the diffusion interfaces are shown in Fig. 3a for a specimen held at 1100°C for 15 minutes. The corresponding thickness profile taken across the thin foil is shown in Fig. 3b. In order to obtain the final concentration profile (upper data set in Fig. 3a) the data were corrected both for thickness and absorption effects. The contamination spot thickness measurement appears to have a systematic error (7) which tends to overestimate the foil thickness; this error appears to relate to a combination of the presence of either amorphous or crystalline surface films and the actual topography of the carbon contamination spot which causes difficulty in the measurement. Stenton et al. (8) have reported that thickness measurements obtained by multiple beam interferometry...
were about 50% of the values obtained by contamination spot thickness measurements for Al thin foils. Michael and Williams (9) report a similar error in Cu foils. Both of these studies were performed in the identical microscope used in this study. Therefore, a corrected thickness of 0.6t was used to calculate concentration ratios as given in Eq. (1). In the model for x-ray absorption it is assumed that the depth distribution of x-ray production \( \varphi_R(p,t) \sim \varphi_B(p,t) \sim 1.0 \) (4). However, using Monte Carlo simulations Kyser has shown that \( \varphi(p,t) \) functions become thickness dependent with increasing density (10). Although \( \varphi(p,t) \) of Al is essentially constant, \( \varphi(p,t) \) of Cu increases as much as 3% relative from 0 to a 400 nm thick film. Recent experimental measurements have been reported by Stenton et al. (8) for nickel foils up to 380 nm thick, and these show that \( \varphi(p,t) \) increases by \( \sim 30\% \) over this thickness range. Therefore, Eq. (1) would tend to overcorrect for absorption in the Ni-Al system, because it does not account for the increased generated intensity for Ni.

The equilibrium concentrations as given by Hansen at the appropriate two-phase boundaries at 1100°C are shown in Fig. 3a. Within the error of the present technique, the data obtained at the NiAl/Ni3Al and Ni3Al/Ni interfaces after 1100°C for 15 minutes appears consistent with the interface concentrations predicted from phase equilibria. It has been proposed in the literature that non-equilibrium conditions may exist at short times at the interfaces in a diffusing system. A concentration profile obtained from a specimen (Fig. 1) heated to 1100°C and immediately quenched, i.e., zero time, is shown in Fig. 4. The foil thickness was fairly uniform across the specimen ranging from about 300 nm on the NiAl side to 260 nm on the Ni side. The Ni3Al layer in this specimen is less than one micron thick. Interfacial measurements at the Ni/Ni3Al interface are again in good agreement with phase equilibrium predictions. The concentration value on the Ni3Al side of the NiAl/Ni3Al boundary appears to be high but this could be caused either by slight tilting of the foil in the microscope, or by error in the thickness measurement which was particularly difficult in the inter-

Fig. 3: a) STEM and b) thickness profiles for specimen held at 1100°C for 15 mins. (left).

Fig. 4: STEM profile of thin foil couple 1100°C-zero time (above).
face region. It thus appears that within the error of the STEM method, interfacial equilibrium is established even at the shortest times studied during this investigation.

Conclusions

1. The high x-ray spatial resolution (≤ 50 nm) of the analytical electron microscope permits the measurement of concentration profiles during the early stage of growth of the Ni₃Al intermediate phase in NiAl-Ni diffusion couples. This is of considerable interest since the spatial resolution of the electron microscope, the instrument which has provided the large majority of experimental interdiffusion data during the last decade, is limited to ~1 micron.

2. Even at the shortest times studied during this investigation, absorption and thickness corrected data taken across the NiAl/Ni₃Al and Ni₃Al/Ni diffusion interfaces appear consistent with interface concentrations predicted from phase equilibria.

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References