

# Experimental determination of transformation enthalpies of metastable phase transitions in ion-irradiated NiAl<sub>3</sub>

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A novel experimental technique has been developed by which metastable phase transformations in thin films may be investigated. The technique is demonstrated by the determination of the enthalpies of transformation of two commonly observed metastable phases in the compound NiAl<sub>3</sub>; the vapor deposited, fcc extended solid solution phase, and the ion-induced amorphous phase. The measured transformation enthalpies are  $-4.16 \pm 0.35$  and  $-5.02 \pm 0.49$  kcal/mole, respectively. The latter compares with a calculated value of  $-5.83$  kcal/mole, determined using the embedded atom model. This technique demonstrates the feasibility of determining phase transformation enthalpies in ion-irradiated and vapor-deposited metastable phase thin films.

## 1. Introduction

Ion irradiation is a well established technique for the formation of metastable phase materials [1,2]. These materials, many of which were inaccessible prior to the application of ion beam processing, have for the most part been well characterized with regard to their physical and chemical properties. For example, hardness, corrosion and wear resistance, electrical conductivity, and residual stress are properties for which accurate measurement techniques have been developed. However, the thermodynamic parameters governing the formation and transformation of these materials are poorly understood at best, due to the difficulty in generating samples of sufficient mass to thermally analyze using existing techniques. Without such information, it is difficult to precisely control or reproduce the desired structure, or to understand the nature of its formation.

Limited work has been performed using differential scanning calorimetry (DSC), to characterize the amorphous-to-crystalline transformation in ion-irradiated silicon [3]. In this experiment, epitaxial (100) Si discs were irradiated with Xe<sup>+</sup> ions, at four energies up to 3 MeV, to form relatively thick (1.8 μm) amorphous layers. The transformation enthalpy was then measured in the DSC, yielding a value of  $11.9 \pm 0.7$  kJ/mole. This method is unique in that ion-induced amorphization of a pure element is a very rare phenomenon, and a

relatively large (thick), sample mass could be prepared for analysis without the need for removal of the supporting substrate. On the other hand, measurement of the transformation of ion-induced metastable *compounds* has not been successfully demonstrated. Therefore, the objective of the present study was 1) to develop a technique by which a variety of metastable phase transformations in thin films could be thermally analyzed, and 2) to apply this technique for characterization of two well documented phase transformations which occur in the compound NiAl<sub>3</sub>: ion irradiated amorphous → ordered orthorhombic (ε), and vapor deposited, f.c.c. extended solid solution → ε, and to compare the measured values with those computed using the “embedded atom” atomistic simulation model [4].

## 2. Experimental

Sample films of nominal composition Al-23Ni were vapor deposited directly onto pure Al DSC sample pans, using a multiple hearth, dual electron gun source, in a cryo-pumped chamber with a base vacuum of less than  $5.0 \times 10^{-7}$  Torr. The elements were coevaporated at independently controlled evaporation rates of 1.0 Å/s (Ni), and 4.3 Å/s (Al), to result in total film thicknesses of 0.8–0.9 μm. Monitoring of the individual evaporation rates and corresponding thicknesses was accomplished using water-cooled, Inficon quartz crystal thickness monitors which were isolated by means of a simple shield, arranged so that each monitor would only

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“see” the desired evaporation source. Evaporation rate control was achieved via a feedback loop which varied electron gun input power, based on the monitored rate of evaporation of the element. No substrate temperature control was attempted.

Chemical composition analysis was performed using Rutherford backscattering spectrometry (RBS), and RUMP spectrum simulation software [5]. Microstructure identification was achieved via selected area electron diffraction, using a JEOL 2000FX, 200 kV scanning transmission electron microscope (STEM). Sample pans were weighed prior to film deposition, and again just before thermal analysis, using a Perkin-Elmer AD-4 Microbalance, to obtain the net weights of the sample films.

Subsequent to deposition, the samples were separated into two groups. The first group was left as-is, to be directly analyzed in the DSC in the as-deposited (fcc, extended solid solution), condition. The second group was annealed at 500 °C for 2 h, in a Ti gettered, high purity Ar flow tube furnace. This treatment was sufficient to form the stable equilibrium NiAl<sub>3</sub> ( $\epsilon$ ) phase, the starting structure for ion irradiation.

After annealing, the samples in the second group were individually irradiated with 1.5 MeV Ni<sup>2+</sup> ions, to doses varying between 5 and 20 × 10<sup>15</sup> ions/cm<sup>2</sup>, at target current densities of ≤ 1.4 μA/cm<sup>2</sup>, to form the amorphous structure. Selected samples from the group were then core drilled to provide 3 mm diameter discs, and electrochemically back-thinned to the surface, using standard techniques, for TEM verification of sample amorphicity. Simulations performed using TRIM soft-

ware [6], indicated an ion-induced damage profile of 0.5–1.0 displacements (ion/Å) throughout the film thickness, with the minimum value (0.5) found at the surface. It was thus assumed that verification of an amorphous structure at the sample surface would indicate complete amorphization through the thickness of the film.

Transformation enthalpies for the metastable → stable reactions in both groups were measured using a Perkin-Elmer DSC-7 differential scanning calorimeter. A heating rate of 10 °C/min was used in a majority of the analyses, with the scanned temperature range being 50–275 °C. The DSC cells were flushed with dry nitrogen during the entire course of the scan. The reference cell was loaded with annealed samples of mass and composition identical to those loaded into the sample cell, to exactly duplicate all conditions in both cells, except for the metastability of the sample film contained in the sample cell. A second scan was run on each sample immediately following the first, then subtracted from the first to give the net heat released during the reaction. Selected samples were again removed and examined by TEM, as described above, to verify the stable equilibrium ( $\epsilon$ ) reaction product.

### 3. Results

#### 3.1. Fcc → $\epsilon$ transformation

The microstructure of the as-deposited films was found to be a face-centered cubic, extended solid solu-

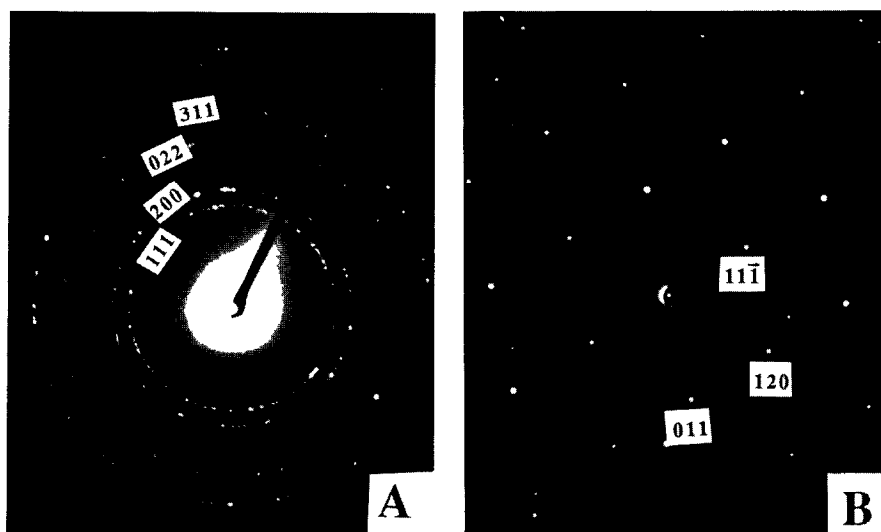


Fig. 1. (a) Electron diffraction pattern of as-deposited, 77Al–23Ni sample film. Structure is fcc; labelled indices correspond to Al {*hkl*} planes. (b) Electron diffraction pattern of DSC-transformed sample film from (a), revealing stable equilibrium, ordered orthorhombic  $\epsilon$  structure.

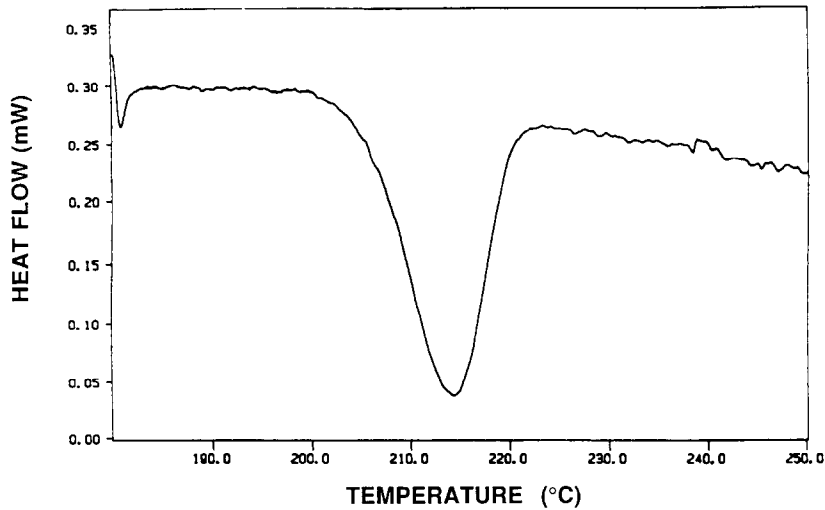


Fig. 2. Representative DSC trace for the fcc  $\rightarrow$   $\epsilon$  transformation, showing distinct exothermic reaction. Scanning rate was 10 °C/min, sample mass 0.09 mg.

tion of Ni in Al. Because the average film composition of samples used in this study exceeded the equilibrium room temperature solubility limit of Ni in Al by over 22 at.%, the fcc solid solution is a metastable phase. The fcc structure was identified using selected area electron diffraction patterns (SADP), as shown in fig. 1a. Ring indices shown in this figure are those of fcc Al. The absence of superlattice rings in the pattern indicates that the structure is a disordered mixture of Ni and Al.

Fig. 1b is the SADP of the post-transformation structure. This pattern corresponds to that of the ordered orthorhombic ( $\epsilon$ ) NiAl<sub>3</sub> phase.

Thermal analyses performed on a group of 23 such samples, with an average sample mass of 0.09 mg, resulted in a transformation enthalpy value of  $-4.16 \pm 0.35$  kcal/mole. A representative DSC thermogram for the reaction is presented in fig. 2. The average peak onset temperature for the transformation was found to

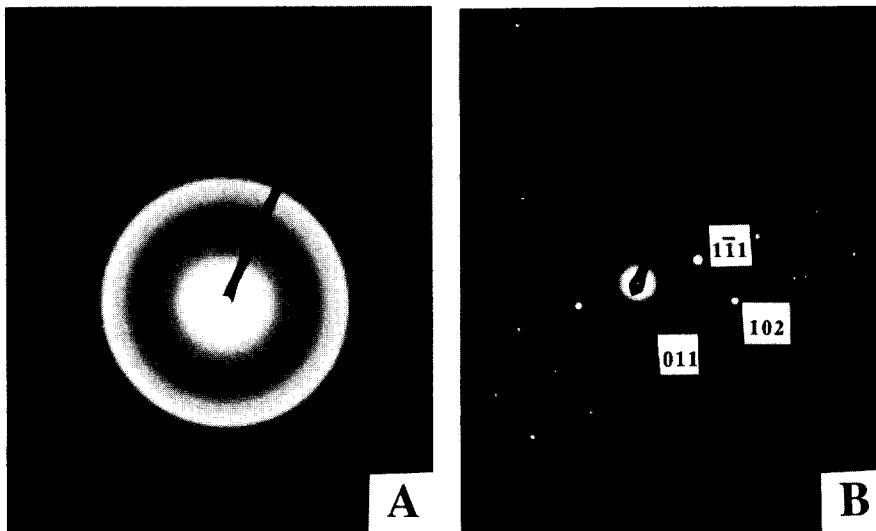


Fig. 3. (a) Electron diffraction pattern of as-irradiated, 77Al-23Ni sample film, showing ion-induced amorphous structure. (b) Electron diffraction pattern of DSC-transformed sample film, in the ordered orthorhombic  $\epsilon$  structure.

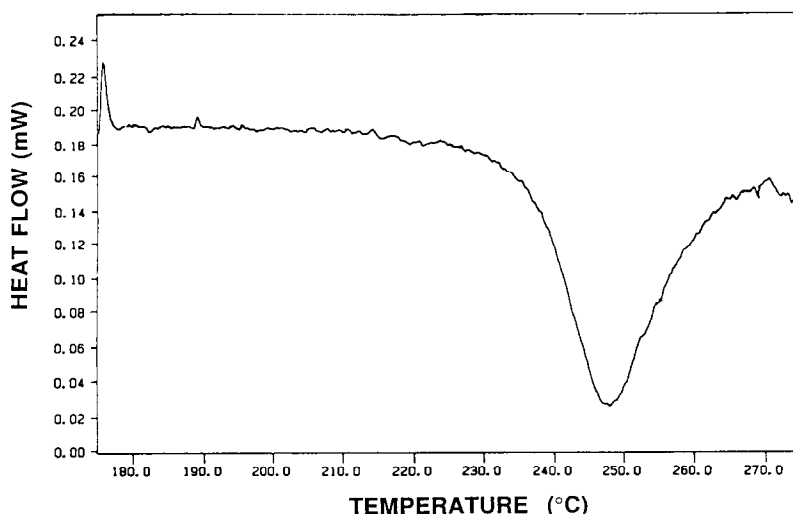


Fig. 4. Representative DSC trace for the amorphous  $\rightarrow$   $\epsilon$  transformation, showing distinct exothermic reaction. Scanning rate  $10^\circ\text{C}/\text{min}$ , sample mass 0.07 mg.

be  $198 \pm 2^\circ\text{C}$ , for the  $10^\circ\text{C}/\text{min}$  scanning rate used in the majority of measurements.

### 3.2. Amorphous $\rightarrow$ $\epsilon$ transformation

As-annealed sample films subject to ion doses of  $\geq 5 \times 10^{15}$  ions/cm<sup>2</sup> were found to completely transform to the amorphous structure, as indicated by the broad, diffuse diffraction rings observed in the electron diffraction pattern shown in fig. 3a. Fig. 3b shows the post-transformation structure, again the ordered, orthorhombic  $\epsilon$  phase.

Transformation enthalpy measurements performed on the 11 samples prepared in this fashion, with an average mass of 0.07 mg, resulted in a value of  $-5.02 \pm 0.489$  kcal/mole. No correlation could be found between ion dose and measured enthalpy. A representative DSC thermogram for this reaction is shown in fig.

4. Peak onset temperature was observed to vary substantially between samples, with a range of  $160$ – $228^\circ\text{C}$ .

### 4. Discussion

Results of the thermal analyses of both reactions investigated are presented in table 1. For purposes of comparison, enthalpy values computed using the embedded atom model [7], are also tabulated. Although a calculated value for the fcc  $\rightarrow$   $\epsilon$  transformation was not available, the measured enthalpy was found to be similar to that calculated for the disordered  $\epsilon(\text{DO}_{20}) \rightarrow$  ordered  $\epsilon(\text{DO}_{20})$  reaction. Hence, this calculated enthalpy was included in the table.

The calculated enthalpy values shown in the table were arrived at by first simulating both the stable and metastable structures, then calculating their formation heats based on the embedded atom model. The dif-

Table 1

Calculated and measured values for the amorphous  $\rightarrow$   $\epsilon$  and fcc  $\rightarrow$   $\epsilon$  transformation enthalpies; measured values presented are arithmetic means of all measurements performed per sample group

Transformation		$\Delta H$ [kcal/(g atom)]		No. of measurements	$\sigma_x$	$\sigma_x/\Delta H$ [%]
Starting structure	Ending structure	Calculated <sup>a</sup>	Measured			
amorphous	$\epsilon$	-5.83	-5.02	11	0.49	9.70
fcc solid solution	$\epsilon$	-4.31 <sup>b</sup>	-4.16	23	0.35	8.40

<sup>a</sup> Values calculated using the "embedded atom" model [4].

<sup>b</sup> This value represents  $\Delta H$  for the simulation transformation from disordered  $\text{DO}_{20} \rightarrow$  ordered  $\text{DO}_{20}$ .

ference in heats of formation between the metastable and stable states is then taken as the enthalpy of the transformation from one state to the other. The amorphous structure was modeled by first disordering the equilibrium orthorhombic structure, then displacing the atoms from their lattice positions in a random direction, by some small amount, given as  $\delta$ , which was allowed to vary between zero and the value of the half-width at half-maximum of the crystalline pair distribution function (PDF), of NiAl<sub>3</sub>. The displacement distance which resulted in a computed PDF most similar to that of an amorphous solid was then used to simulate the amorphous structure [7]. The value of the enthalpy of transformation between this "disordered amorphous" and the  $\epsilon$  phase,  $-5.83$  kcal/mole, compares favorably to the measured mean enthalpy value,  $-5.02 \pm 0.49$  kcal/mole, as seen in the table.

There are several factors inherent to the experimental process which can contribute to measurement error. The presence of residual Al, on average  $\approx 2$  at.%, would lead to a slightly lower (minus  $\approx 3\%$  in absolute value) measurement than would a purely stoichiometric sample. Imprecision in mass measurements, in this case  $\approx \pm 0.005$  mg, would also contribute to measurement error, to an extent of  $\approx \pm 2\%$  of the measured enthalpy for average sample masses of 0.070 mg. Inconsistencies in the sample pan/sample cell contact surface, due to sample pan distortion during processing, were found to have a marked effect on the recorded DSC curve, in some cases resulting in virtually indistinguishable transformation peaks. Operator error, such as inconsistent sample pan positioning and cell cover placement within

the DSC, as well as incorrect cursor positioning in defining the reaction peak area to be integrated by the thermal analysis software, can also have an effect on measured values. The first two sources mentioned are quantifiable, and the total from all sources of error falls below the statistically determined value of  $\sigma$ .

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