Intermetallic phase formation during annealing of Al/Ni multilayers

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(Received 2 May 1994; accepted for publication 26 August 1994)

The phase evolution during annealing of Al/Ni multilayer samples prepared by ion-beam sputtering with composition modulation wavelengths Λ between 10 and 400 nm was determined using x-ray diffraction and differential scanning calorimeter measurements. Samples with average compositions of $\text{Al}_{0.40}\text{Ni}_{0.60}$ and $\text{Al}_{0.75}\text{Ni}_{0.25}$ were investigated. For the $\text{Al}_{0.40}\text{Ni}_{0.60}$ samples the following results were obtained. A measure of the degree of periodicity and the sharpness of the interfaces in a sample with $\Lambda=80$ nm was the large number (over 20) of peaks observed in small-angle x-ray scattering measurements. A sample with $\Lambda=10$ nm was transformed by heat treatment directly to the AlNi phase. In the $\Lambda=80$ nm sample, the first phase formed after annealing was the metastable η phase. The η phase was identified as Al_9Ni_2 . In the 400 nm wavelength sample, both the metastable η phase and the stable Al_3Ni formed after the first exothermic reaction. For the $\text{Al}_{0.75}\text{Ni}_{0.25}$ samples two results were obtained. A $\Lambda=11.4$ nm sample transformed directly on annealing into Al_3Ni . The η phase was the first phase formed on annealing a $\Lambda=100$ nm sample. The difference in the component diffusivities and the concentration gradient play an important role in controlling phase formation and evolution. © 1994 American Institute of Physics.

I. INTRODUCTION

Intermetallic phases, formed by solid state reactions,¹⁻³ are important in technologies ranging from metallization layers in microelectronics to corrosion and oxidation coatings for bulk materials. Although the formation of intermetallics in composites during reactions between the matrix and reinforcement is generally detrimental, these reactions can be beneficial. For example, with proper control they may be utilized to create *in situ* interfacial debonding layers. The reactions producing the intermetallics are a result of an interplay between diffusion, and phase nucleation and growth. The phase sequencing depends on the temperature, reaction time, composition gradients, interfacial surface energies, Gibbs free energies, and other phases already present.

It is especially important to identify the first phase to form because this phase can strongly influence the subsequent phase evolution. Different sample geometries allow one to focus on different aspects of the phase evolution. For example, using bulk diffusion couples, in which there is an essentially infinite supply of the constituents, facilitates the study of the entire phase diagram. Much of the available information on the growth of intermetallic phases has been developed from classical, bulk diffusion couple studies. The nucleation of the first intermediate phase and the sequencing of subsequent phase formation have been investigated using bilayer film samples, in which there is a finite supply of the reactants. Annealing thin-film samples typically produces fewer coexisting phases than result from annealing bulk diffusion couples.⁴ Multilayer thin-film samples, with precisely repeated composition modulations, permit studies that focus on the interfacial region and are thus well suited for investigating the early stages of phase nucleation and growth.⁵⁻⁷ In multilayer samples, the new phases usually form in or near each interface, and because there are so many similar inter-

faces, the new phase comprises a relatively large fraction of the sample.

During the early stages of annealing, multilayer systems may form metastable structures such as amorphous phases. For example, it has been suggested that Au/La and Ni/Zr multilayers^{5,7} form amorphous alloys before they form intermetallic compounds. In other cases, such as the Al/Ni system, the formation of intermetallic compounds is preceded only by the formation of a solid solution.⁴

In the current work, the phase evolution during annealing has been investigated using Al/Ni multilayer samples prepared by ion-beam deposition with average compositions $\langle c \rangle$ of $\text{Al}_{0.40}\text{Ni}_{0.60}$ (equal thickness Al and Ni layers) and $\text{Al}_{0.75}\text{Ni}_{0.25}$. The samples had composition modulation wavelengths Λ between 10 and 400 nm. Previously, Ma, Thompson, and Clevenger⁸ studied Al/Ni multilayers prepared by electron-beam (*e*-beam) evaporation, in which $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$. In their work, only the Al_3Ni phase formed. No metastable phases were observed. We find the first phase formed is a function of $\langle c \rangle$ and Λ . For example, for equal thickness Al and Ni layers with $\Lambda=10$ nm, the AlNi phase is formed, while for $\Lambda=80$ nm, the first phase to form is a metastable phase, the η phase. Finally, for $\Lambda=400$ nm, two phases are initially detected, the η phase and the Al_3Ni phase. The η phase was also formed in a sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$ and $\Lambda=100$ nm, but in a sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda=11.4$ nm, Al_3Ni develops. Previously, the η phase of the Al/Ni system had only been observed in rapidly solidified microstructures.⁹⁻¹¹

II. Al/Ni SYSTEM

The Al/Ni system was chosen for this investigation because it is well characterized by previous studies,^{4,12} the phases that form are technologically relevant, and it offers

some experimental advantages. For example, the large charge difference between Ni and Al increases the amplitude of small-angle x-ray scattering peaks. Both Ni and Al have fcc structures but the lattice constant of Ni is 13% smaller than that of Al. With such a large lattice constant difference it is very difficult to produce coherent interfaces with each phase having the same structure and orientation. High-resolution electron microscopy on Ag/Ni films,¹³ which have a similarly large lattice constant difference, determined that the difference is accommodated by misfit dislocations at the interfaces.

The phase diagram for this system^{14,15} exhibits two solid solutions (0.1 at. % solubility of Ni in Al, and approximately 7 at. % solubility of Al in Ni at 400 °C), and five stable compounds, Al₃Ni, Al₃Ni₂, AlNi, Al₃Ni₅, and AlNi₃. Rapid liquid¹⁵ and vapor quenching¹⁶ may extend the Al-rich solid solution as high as 7.7 and 20 at. %, respectively. The Al₃Ni phase forms with only 3:1 stoichiometry. This phase was the initial phase formed in earlier investigations of Al/Ni bilayers.^{17,18} For Ni concentrations between 45 and 59 at. % at temperatures of 400 °C and below, the equilibrium phase is the AlNi phase. In addition, there is at least one metastable compound, usually formed by rapid quenching of aluminum alloys containing 2–12 at. % Ni, which has been identified as the η phase.^{9–11} From a comparison of the x-ray data, we suggest that the η phase is the metastable phase, Al₉Ni₂, reported by Perepezko and Furrer.¹⁹

Colgan⁴ has reviewed the thin-film investigations of nickel aluminide intermetallic formation. His review reports the following findings. First, the Al₃Ni phase has been identified as the initial phase to form between 250 and 275 °C. This phase was also the initial phase formed in earlier investigations of Al/Ni bilayers.^{20,21} Second, phase formation appeared to be governed more by the kinetics of the dominant moving species rather than by the thermodynamic driving forces. Parabolic growth of Al₃Ni indicated diffusion-limited kinetics with Al as the fastest diffusing species.²⁰ Third, the growth may be either laterally uniform (usually with diffusion-limited growth and well-defined kinetics) or irregular (proceeding preferentially along grain boundaries). The former is predominant except in cases of contamination when irregular growth is observed.⁴

III. EXPERIMENTAL AND ANALYSIS PROCEDURES

Multilayer samples were prepared in a computer-controlled, ion-beam sputtering system that has been described previously.^{22,23} The base pressure before sputtering was 10⁻⁷ Torr. In each run, multilayers were usually deposited on both NaCl and Si polished, single crystals. The substrate temperature was nominally at room temperature. With an argon-ion beam of 55 mA accelerated by 1000 eV at a chamber pressure of 3.4×10⁻⁴ Torr, the deposition rates were 0.323 nm/s for the Al and 0.167 nm/s for the Ni. These rates were determined from weight measurements and film thickness measurements made using a surface profilometer. The deposition times were chosen to produce samples with average compositions $\langle c \rangle$ of either Al_{0.40}Ni_{0.60} (equal thickness layers) or Al_{0.75}Ni_{0.25}. Multilayers samples were fabricated with Λ between 10 and 500 nm, but most of the mea-

surements were made on equal-layer thickness samples with $\Lambda=10, 80$, or 400 nm. The total film thicknesses were approximately 2000 nm.

The temperatures at which phase transitions occur were determined by differential scanning calorimeter (DSC) measurements performed with a Perkin-Elmer 7 Series thermal analysis system. Free-standing film samples for the DSC measurements were obtained by exposing the films deposited on the single-crystal NaCl to moist air. Calibration of the DSC system consisted of first establishing a straight base line for the desired temperature range and heating rate with the cell empty. A 99.9999% pure Pb standard was then used to calibrate the phase change onset temperature and enthalpy change ΔH at the heating rate used in all the DSC measurements, 20 °C/min.

All other measurements were made on films that had been deposited on single crystals of Si. The samples were prepared for annealing by putting them in sealed quartz tubes which had been thoroughly flushed with He and then evacuated to less than 50 mTorr. The encapsulated samples were heat treated using the same heating rate as in the DSC measurements, i.e., at 20 °C/min, to temperatures selected based upon the DSC measurements. To facilitate phase identification, the heat treatment temperatures were chosen to be near the high-temperature end of the DSC exotherms. When the chosen temperature was reached, the tube containing the sample was immediately quenched in water.

The layer-to-layer repeatability of the multilayer samples and the phases formed were investigated by x-ray scattering measurements performed using CuK α radiation in several instruments, including a rotating anode system. The different types of x-ray measurements performed were θ -2 θ scans, small-angle x-ray scattering (SAXS) and Read camera studies. The Read camera studies permit the detection of diffraction maxima that might be missed in θ -2 θ scans because of preferred orientation in the films.

The SAXS measurements exhibit interference maxima which provide information on the periodicity and the sharpness of the interfaces. The angle θ_m of the m th-order diffraction peak, uncorrected for refraction, is given²⁴ by

$$\sin \theta_m = \frac{\lambda}{2\Lambda} m. \quad (1)$$

Diffusion increases the width of the interface region and decreases the amplitude of the higher-order reflectance peaks. The amplitude of the m th-order reflectance peak R_m is given by²⁵

$$R_m \approx R_m^0 \exp[-(2\pi m\sigma/\Lambda)^2], \quad (2)$$

where R_m^0 is the value of R_m for perfectly sharp interfaces. In deriving Eq. (2), it was assumed that the gradient across the boundary can be represented by a Gaussian distribution of half-width σ . Deviations from periodicity also decrease the amplitude of high-order peaks.

The x-ray peak intensities and widths of the SAXS spectra were also fitted to model calculations^{26,27} to make further estimates about the microstructure. Because multilayers of fcc systems often are textured with the $\langle 111 \rangle$ direction normal to the plane of the film, it was assumed in the modeling

that both Ni and Al had this orientation. Bulk values were used for the interplanar spacings and atom densities on the planes. The relative scattering intensities were calculated using different values for the number of Ni and Al planes, N_{Ni} and N_{Al} , respectively, and the number of bilayers that coherently scatter, N_r . The calculated curves were labeled as follows: $(N_{\text{Ni}}, N_{\text{Al}}, N_r, \sigma)$. The model calculations for a bilayer are sensitive to the thicknesses of the two layers. The thickness of each layer is the product of the atomic interplanar spacing in that layer and the corresponding number of planes in the layer. The calculated curves are not sensitive to the individual atomic interplanar spacings. Thus, one cannot use comparisons between the calculated and experimental spectra to determine the interplanar spacings.

IV. EXPERIMENTAL RESULTS, $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$

X-ray-diffraction spectra of as-deposited, equal thickness Al/Ni multilayers with $\Lambda = 10, 80$, and 400 nm only show peaks corresponding to crystalline Ni, Al, and the Si substrate. Large-angle satellite peaks were not present because of the incoherent interfaces. The crystalline peaks of the 10 nm sample were broad and the (111) Al peak was missing. A Read camera photograph on a sample with $\Lambda = 10$ nm showed the Ni layers are textured with the $\langle 111 \rangle$ direction normal to the plane of the Si substrate but gave no clear evidence of a (111) Al reflection. Nevertheless, glancing angle x-ray scattering measurements provided firm evidence for the presence of the Al phase. The absence of the (111) Al reflection may be due to texturing. The broadening at $\Lambda = 10$ nm may be due to interfacial strains. In the limit of $\Lambda \rightarrow 0$, the strain is likely to become so large that the film is either amorphous or crystallizes into the AlNi phase. In this connection it is noteworthy that our as-deposited, sputtered films of AlNi are amorphous.

Scanning tunneling microscopy measurements, shown in Fig. 1, were made to investigate whether the large lattice mismatch roughened or otherwise distorted the film. These measurements showed that the surface features of the films did not change appreciably as a function of wavelength. Though these features resemble the top view of a columnar growth film, it is not clear whether the size of these surface features is correlated with the crystalline grain size. For the areas studied, the maximum height excursions for most of the top surface of the film are less than 16 nm.

Figure 2 shows the DSC spectra of samples with $\Lambda = 10, 80$, and 400 nm. The heat released per mg of sample is plotted as a function of temperature. The masses of the $\Lambda = 10, 80, 400$ nm samples were $3.970, 1.610$, and 3.350 mg, respectively. In general the phase transformations are exothermic and shift to higher temperatures with increasing Λ . The data shown in Fig. 2 differ in several respects from those of Ma and co-workers.⁸ In their work, double-peak structures in the DSC spectra were observed for all Λ . The two peaks tended to merge into a single peak with decreasing Λ . The first peak was modeled as due to the nucleation and lateral growth of the Al_3Ni phase at the interface and the second was associated with the thickening of this phase. In contrast, the number of peaks in the DSC spectra shown in Fig. 2 depends on Λ . For $\Lambda = 10$ nm, there is either a very broad

FIG. 1. Scanning tunneling microscope images of (a), (b) a $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 10$ nm Al/Ni multilayer sample and (c), (d) a $\Lambda = 400$ nm Al/Ni multilayer sample. The total height scale from the white to black scale is $11.8, 15.6, 4.7$, and 7.6 nm for (a), (b), (c), and (d), respectively.

single peak or a superposition of two peaks, while for $\Lambda = 400$ nm there are five peaks. The small Λ DSC peak from Ref. 8 is much narrower than the one or two peaks for the $\Lambda = 10$ nm sample shown in Fig. 2. One reason for some of these differences between our results and those of Ma and co-workers is that in our samples phases other than Al_3Ni are formed. The phase identifications are discussed below and listed in Table I. Further analysis of the reactions in Fig. 2 would require assumptions because: (1) Some mixing has occurred at the interface during fabrication; (2) there are enthalpy changes due to diffusion; (3) due to peak overlap, one cannot always uniquely associate a given feature in the DSC spectra to a specific phase transformation; and (4) after the reactions the samples usually contained unknown amounts of

FIG. 2. Heat released during DSC temperature scans of Al/Ni multilayer samples with $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$ and $\Lambda = 10, 80$, and 400 nm.

TABLE I. Summary of phases present after annealing in samples with $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$.

	10 nm	80 nm	400 nm
As-deposited	Ni, Al	Ni, Al	Ni, Al
First HT	175 °C	250 °C	335 °C
	NiAl	Ni, η	Ni, Al, Al_3Ni , η
Second HT	275 °C	310 °C	375 °C
	NiAl	Ni, η	Ni, Al_3Ni
Third HT		370 °C	
		Al_3Ni_2 , Ni	

several phases. Specifically, one cannot determine the energy given off per gram of material during a specific reaction from the data presented in Fig. 2 since one does not know the amount of mass that has reacted. Nevertheless, from the small enthalpy changes for the $\Lambda=400$ nm sample it is clear that this sample is further from equilibrium than the 80 nm sample.

A. $\Lambda=10$ nm sample

Figure 3 shows x-ray spectra from a θ - 2θ scan taken on samples with $\Lambda=10$ nm before and after they had been annealed to 175 and 275 °C at 20 °C/min. After annealing, only peaks corresponding to the AlNi phase are observed. Figure 4 shows experimental spectra for an as-fabricated sample, a sample annealed to 175 °C, and the calculated SAXS spectra. Values for Λ of 9.4 and 10.0 nm were obtained using Eq. (1) and the angular positions θ_m of the sharp peaks of the spectrum for the as-fabricated and 175 °C annealed samples, respectively. The values of Λ were determined from the slopes of the lines that result from plotting the values of θ_m vs m ($m=1,2,3,4$). The compound formation that has occurred by 175 °C has attenuated the sharp structure associated with periodicity but it has not totally removed it. The amplitude of the sharp features as a function of m were fitted to Eq. (2). This fit was used to determine the thickness of the interfacial

FIG. 3. Comparison of AlNi standard with the x-ray spectra of the $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=10$ nm, multilayer samples as-fabricated and after anneals to 170 and 275 °C at 20 °C/min. Additional peaks are due to the Si substrate.

FIG. 4. SAXS spectra of the as-fabricated and 175 °C annealed, $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=10$ nm, multilayer samples. The periodicity of the sharp peaks yields a calculated wavelength of 9.4 nm.

width which we define as $t_I=2\sigma$. Using this procedure we found t_I equal to 1.1 and 2.1 nm for the as-fabricated and 175 °C annealed samples, respectively. The remaining periodicity can either be attributed to some residual unreacted Ni or to composition gradients within the AlNi layer.

Both experimental spectra in Fig. 4 are more complicated than the spectra one expects for a multilayer with perfect square-wave modulation. If the square-wave modulation were perfect, then the amplitude of the even-integer, sharp peaks should be zero. This property, which is a consequence of the symmetry and the fact that the amplitudes are weighted Fourier transforms, is seen to be approximately satisfied for the calculated curve labeled (18, 21, 10, 0.5). The amplitudes and sharpness of the calculated peaks increase if one increases the number of bilayers. To obtain the correct half-width of the sharp features in the modeling, one must assume that the film contains segments of approximately ten or more 9.4 nm bilayers which scatter coherently.

In addition to the sharp features, broad features were also observed at $2\theta=0.8, 1.4$, and 2.1 . These broad features may result from scattering off a smaller number of planes which scatter coherently. Because the broad features seem to occur at more closely spaced values of 2θ , the basic scattering units within the segments appear to be larger than 10 nm and may be the result of diffusion. The sharp features, which are associated with the sharp interfaces of the as-fabricated sample, are attenuated in the sample annealed to 175 °C. The broad features are at least as pronounced in the as-prepared sample. The fact that the broad features are not attenuated is consistent with their being independent of the sharp interfaces. The sum of the two model curves qualitatively reproduces most of the features of the experimental spectra.

B. $\Lambda=80$ nm sample

Figure 5 shows x-ray spectra taken on the samples with $\Lambda=80$ nm after they had been heated to 250, 310, and 370 °C at 20 °C/min. The Read camera microgram of the

FIG. 5. X-ray spectra of the as-fabricated and annealed $(c)=\text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=80$ nm multilayer samples provide evidence for the formation of the Al_3Ni_2 phase at 370 °C.

sample annealed to 250 °C showed more diffraction maxima than the spectra shown in Fig. 5. The additional maxima are probably due to texturing. After the 250 °C anneal, no diffraction lines associated with the fcc Al phase were observed. The absence of these lines suggests complete reaction of the Al. After the 370 °C anneal, the x-ray spectrum shows the Al_3Ni_2 phase. Magnetization data²⁸ and the x-ray data shown in Fig. 5 indicate that not all the Ni has reacted even after the 370 °C anneal, however, the Ni peak at $2\theta \approx 98^\circ$ had broadened considerably.

Figure 6 shows an expanded view of the data shown in Fig. 5. After the 250 °C anneal, there are ten peaks that correspond to peaks previously assigned to the η phase.⁹ Of these peaks, seven cannot be attributed to the Al_3Ni phase. This is rather convincing evidence that the η phase has formed. In addition there are two peaks that could be assigned to the Al_3Ni phase but, alternatively, these peaks

FIG. 6. Comparison of the x-ray spectra of the annealed $(c)=\text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=80$ nm, multilayer samples and the average reported 2θ positions for the metastable η -phase peaks. The positions of the major peaks for the Al_3Ni phase are also shown.

FIG. 7. (a) A comparison of observed and calculated SAXS spectra of the as-fabricated, $(c)=\text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=80$ nm, multilayer. (b) SAXS spectra of the as-fabricated and annealed $(c)=\text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda=80$ nm, multilayer samples show intermixing in the annealed samples.

could belong to the η phase. Calculations¹⁹ have predicted many peaks which have not yet been observed. At 310 °C, the η phase is still present, but the evidence for the formation of Al_3Ni is not substantially stronger. Thus, the evidence for the formation of the Al_3Ni phase at either 250 or 310 °C is, at best, inconclusive.

Figure 7(a) shows a comparison of a SAXS spectrum taken on an as-fabricated $\Lambda=80$ nm sample with model calculations. The large number of observed higher-order diffraction peaks indicates that interfaces are abrupt relative to the modulation wavelength and that the periodicity is good. The agreement between the calculated values and experiment is good for $2\theta < 2.6^\circ$. Again both even and odd m modes are seen. Figure 7(b) shows SAXS data taken after different heat treatments. After the 310 °C anneal, diffusion has removed all but the lowest-order angle peaks. Even these are removed after the 370 °C anneal. Values of Λ of 75.9 and 78.8 nm were obtained using Eq. (1) and the angular positions θ_m of the sharp peaks of the spectra for the as-fabricated and 310 °C annealed samples, respectively. Fitting the m dependence of the amplitudes of the peaks of Eq. (2), t_l was determined to be 1.2 and 2.1 nm for the as-fabricated and

FIG. 8. X-ray spectra of the as-fabricated and annealed, $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 400$ nm multilayer samples indicating the formation of the Al_3Ni phase at 335 °C followed by dissolution at 375 °C.

310 °C annealed samples, respectively. It should be noted that t_f of the as-fabricated $\Lambda = 10$ and 80 nm samples were 1.1 and 1.2 nm, respectively, i.e., the interfacial widths or region with a large composition gradient are small and approximately independent of Λ .

C. $\Lambda = 400$ nm sample

Figure 8 shows x-ray spectra taken on samples with $\Lambda = 400$ nm in the as-fabricated condition and after the samples had been annealed to 335 and 375 °C. After the 335 °C anneal both the Al_3Ni and the η phase are present. After the 375 °C anneal, the Al_3Ni is still present but the η phase is no longer observed. Because $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, it is expected that additional solid-state reactions will occur upon further annealing which will produce either the Al_3Ni_2 or AlNi phase. The small area under the DSC curve for the $\Lambda = 400$ nm sample is consistent with this expectation.

The phase identifications made using the x-ray data after the different thermal treatments are summarized in Table I. The listed temperatures are the heat treatment temperatures and not the onset reaction temperatures as determined by the DSC.

V. EXPERIMENTAL RESULTS, $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$

Motivated by the difference between our results on Al/Ni multilayers with $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$ and those of Ma and co-workers⁸ with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, we decided to investigate multilayers with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$. The objective was to determine whether the difference in phase formation was due to the average composition or some other cause.

A. $\Lambda = 11.4$ nm sample

Figure 9 shows the heat released per mg of a 2.110 mg sample with $\Lambda = 11.4$ nm during a DSC scan. There is a broad feature at 150 °C and a sharp feature at 250 °C. X-ray examination of a sample heated to 200 °C shows no evidence of any compound formation, and therefore it is likely that the

FIG. 9. Heat released during DSC temperature scans for samples with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda = 11.4$ and 100 nm. The samples weights were 2.110 and 1.050 mg for the $\Lambda = 11.4$ and 100 nm samples, respectively.

broad feature is due to diffusion. The x-ray spectrum, shown in Fig. 10 of a sample heated to 285 °C provides clear evidence for the formation of Al_3Ni . There is no evidence for any other phase although some unreacted Ni should be present.

B. $\Lambda = 100$ nm sample

Figure 9 also shows the heat released per mg of a 1.050 mg sample with $\Lambda = 100$ nm during a DSC scan. There are now three features. The x-ray spectrum, shown in Fig. 10, of a sample that had been heated to 260 °C shows that the sharp peak at 240 °C in Fig. 9 is due to the exothermic formation of the η phase. The x-ray spectrum of this sample that had been heated in the DSC scan to 450 °C also indicates the presence of the η phase and provides no evidence for another phase although some unreacted Ni should be present.

FIG. 10. X-ray spectra of samples with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda = 11.4$ and 100 nm.

VI. DISCUSSION

For the shortest Λ sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, Al_3Ni is the only phase observed in the present work and that of Ma and co-workers.⁸ The present results, however, differ from those of Ma and co-workers,⁸ because of the appearance of other phases at other values of Λ and $\langle c \rangle$. Specifically, the $\Lambda = 100$ nm sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$ showed the formation of the η phase and not Al_3Ni as Ma and co-workers found. Thus, the difference between our results for equal thickness layers and their results is not simply due to the difference in $\langle c \rangle$. The most obvious remaining difference is that their samples were prepared using e -beam evaporation whereas our samples were prepared using ion-beam sputtering.²⁹ There are at least three major differences between the two deposition techniques. First, in e -beam evaporation the deposition rate is usually faster than in ion-beam sputtering. In e -beam evaporation one easily achieves rates of several nanometers per second whereas the deposition rate was of order 0.1 nm/s for our ion-beam sputtering. The effect of impurities is unclear. Impurities can reside at the interfaces and within the layers. The lower deposition rates in sputtered films allows more time for the possible incorporation of impurity atoms into the layers, e.g., Ar. Interface impurity effects should be most pronounced at small Λ ; however, the expected phases formed at small Λ . Second, atoms evaporated from an e -beam source arrive with low energies corresponding to thermal energies kT where T is typically less than 1200 °C. In ion-beam sputtering, the atoms can arrive at the substrate with much greater energy (several eV). Besides having a direct effect, the differences in deposition rates and arrival energies can also change the substrate temperature. Third, e -beam deposition is usually performed at low chamber pressures and, hence, is a line-of-sight process. Sputtering is performed at higher chamber pressures and collisions occur in route to the substrate. Because of these major differences it is likely that these two deposition techniques produce films with different microstructures.

Different microstructures may influence the number and nature of the nucleation sites. For example, Shutthanandan, Saleh, and Smith reported³⁰ that the initial Al/Ni phase formed when Ni was deposited on Al depended on the crystallographic orientation of their Al single crystal. Elastic stress can effect the growth kinetics and the sequence of phase formation in thin-film systems.³¹ According to Ma and co-workers, the formation rate of the first intermediate phase also depends on the crystalline size.

Regions with suitable compositions for forming new phases are established by diffusion. Initially, the Al and Ni atoms only diffuse through Al- and Ni-rich solid solutions. Although the equilibrium solubility is small, metastable solid solutions containing approximately 20% Ni have been reported.¹⁶ Since Ni and Al are isostructural, even greater supersaturation is possible and, indeed, appears to occur in the initial regions containing steep concentration gradients. The known activation energies for the diffusion of Al in Ni and in Al are listed in Table II. The activation energy for the diffusion of Ni in Al is very similar to that for self-diffusion of Al in Al. On the other hand, the activation energy for diffusion of Al in Ni is almost twice the value for Ni in Al.

TABLE II. Selected activation energies Q for diffusion in the Al-Ni system.

Diffusing species	Matrix	Q (kcal/mol ⁻¹)	Temperature range (°C)	Ref.
Al	Al	34.0	450–650	1
Al	Ni	64.6 ^a	1000–1390 ^a	42
Ni	Al	34.82	470–650	42
Ni	Ni	67.2	870–1404	42
Al	AlNi			
	(50% Ni)	58 ^a	1000–1350 ^a	43
Ni	AlNi	73.4	1000–1350	44
	(50% Ni)	41	428–610	45

^aIn tracer diffusion.

Therefore, Ni should diffuse faster in Al than Al will diffuse in Ni. Thus, the Ni concentration should fall off more slowly than the Al concentration in the region of interdiffusion. The concentration profiles reported by Ma and co-workers,⁸ exhibit such an asymmetry. Although other factors such as residual stresses can affect the diffusion rate, the diffusion of Ni in Al should determine the initial phase formation.

Due to the importance of the initial phase formation, a number of rules and analysis approaches has been proposed for predicting the initial phase formed under a given set of conditions.^{1,32–35} The rules are often based upon thermodynamic terms, as represented in a phase diagram or in the heat of formation. Most of the rules have limited applicability, but the effective heat of formation $\Delta H'$ model is known to be generally successful.³⁵ Unless there are favorable interface energies, when the thermodynamic driving free energy for phase formation is large, $\Delta H'$ will also be large. The phase nucleation will tend to reflect this relative driving force. For the Al–Ni system and the compositions examined in this work, the effective heat of formation model^{34,35} yields $\Delta H'$ values for Al_3Ni and Al_9Ni_2 that are similar. Thus, minor kinetic preferences could determine the initial phase formed; however, even when the phase formation rules do account for the observed initial phase, they do not provide insight into the kinetics of phase formation.

To better understand the initial phase selection and subsequent phase sequencing, it is useful to consider the relative thermodynamic phase stability and the free-energy changes for various reactions. It should be appreciated that phase nucleation in multilayer diffusion couples is fundamentally different from the case where a precipitating phase develops from an initially compositionally uniform, supersaturated solid solution. For multilayer samples, extensive supersaturation can develop, but a concentration gradient with a high initial value is also present.

The initial interdiffusion forms a solid solution. As a first level of analysis, consider the intermediate phases that result from polymorphic reactions. The polymorphic reaction pathway and the free-energy changes between fcc solid solution and the various intermediate phases were evaluated using the detailed thermodynamic model analysis and phase equilibria assessment of Ansara, Sundman, and Willemin.³⁶ For the analysis, the thermodynamic functions that have been established for the stable phase equilibria from a sublattice solution model and experimental measurements were extended

TABLE III. Free-energy changes ΔG_v for polymorphic transformations (fcc Al_xNi_y) (in kJ/cm^3).

Temperature (°C)	Al_9Ni_2	Al_3Ni	Al_3Ni_2	AlNi
175	1.28	2.12	3.02	2.58
250	1.01	1.85	2.71	2.40
310	0.88	1.64	2.63	2.32
335	0.81	1.57	2.56	2.28
375	0.67	1.43	2.48	2.23

into metastable regions and separate measurements for the η phase were incorporated to complete the calculations.³⁷ The results are listed in Table III and provide a lower bound on the level of driving free energy available for phase formation from an initial supersaturated fcc solid solution at different annealing temperatures. A calculation based on a polymorphic reaction path will underestimate the driving free energy for a reaction involving phases with different compositions. Based upon the equilibrium phase diagram, the stable state for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$ is a mixture of AlNi and Al_3Ni_5 but, due to limited data, the Al_3Ni_5 phase was not included in the analysis. Moreover, for $\Lambda \geq 80$ nm some Ni-rich regions remain after the formation of Al-rich intermediate phases. For these reactions, the evaluation of the free-energy changes requires a more complete description of the composition changes and layer microstructures.

Following an initial interdiffusion and the establishment of supersaturation conditions in a multilayer sample, the intermediate phases usually form by a heterogeneous nucleation process. In previous work⁸ on Al/Ni multilayers in which $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, the nucleation of Al_3Ni was observed to be associated with grain-boundary triple-junction sites. The increase in phase nucleation onset temperature with increasing Λ was related to the decrease in triple-junction site density with increasing Λ . In the present results both the phase nucleation onset temperature and phase selection are dependent on Λ . Thus, other factors appear to contribute to the kinetic control. In traditional nucleation analysis, the critical size or thickness L^* of a nucleus of a new phase in the form of a slab can be estimated from $-2\gamma/\Delta G_v$, where γ is the interfacial energy. A more complete analysis of nucleus shape has been made by Hoyt.³⁸ The listing in Table III for ΔG_v of polymorphic reactions can be used to obtain a lower bound on ΔG_v for phase nucleation. The interfacial energies between the intermediate phases and the supersaturated solution are not known, but a typical value for an incoherent interface is $0.5 \text{ J}/\text{m}^2$. The effect of a heterogeneous nucleation site is to lower the effective value of γ . Within the limiting estimates for ΔG_v and γ , L^* should not be larger than about 1–1.5 nm and is most likely smaller.

In multilayer samples it is necessary to consider whether the large concentration gradients affect phase formation. It is likely that Λ and the concentration gradient play an important and, perhaps, decisive role in determining phase nucleation. Consider how heating a short Λ multilayer and a long Λ multilayer sample to the same temperature affects the average concentration and concentration gradient ∇c . One ex-

pects that the Ni concentration is higher and ∇c is lower in the Al layer at short Λ , because Ni atoms diffuse into the Al layer from both sides. As is discussed below, both the higher Ni concentration and smaller ∇c facilitate phase formation.

Although diffusion decreases ∇c , ∇c can still be large when phase nucleation occurs. For example, at 252 °C, Ma and co-workers⁸ observed a gradient of $4 \times 10^5 \text{ cm}^{-1}$ extending across a 25 nm zone. This is approximately the temperature at which they observed the formation of Al_3Ni . The thermodynamic analysis of Desré and Yavari³⁹ incorporates the idea that such a large value for ∇c tends to suppress the thermodynamic driving force for the nucleation of a new phase from an amorphous phase. Amorphous layers form and persist to a critical thickness before intermediate crystalline phases heterogeneously nucleate. The critical thickness increases with increasing ∇c . For ∇c greater than a critical value the new phase cannot nucleate. It is important to note that their analysis can be generalized to include systems such as Al-Ni where a solid solution, instead of an amorphous region, forms prior to intermediate phase nucleation. The major effect of a concentration gradient is to provide an additional barrier to phase nucleation. This suppression, which typically extends over a distance of $(\nabla c)^{-1}$, will be larger for a line compound such as Al_3Ni . Based upon the analysis presented by Desré and Yavari, the critical thickness at which intermetallic compound formation is possible decreases as one approaches closer to the pure components. Thus, the most Al-rich phase, Al_9Ni_2 , would be favored. It is noteworthy that in the Al-Co system, which is analogous to the Al-Ni system, the first phase to develop during annealing of bilayers is Al_9Co_2 , which is the most Al-rich equilibrium phase. Our x-ray results are consistent with the η phase being Al_9Ni_2 and having the same structure as Al_9Co_2 , namely, monoclinic. Further, the dynamics of the system must also play a role. As noted by Highmore *et al.*⁴⁰ transient effects during phase evolution can significantly suppress the development of new crystalline intermediate phases during interdiffusion in multilayer samples and act to alter phase selection.

A. Early diffusion and initial phase formation

We now discuss the phase evolution as a function of Λ and consider why the initial phase nucleated depends upon Λ and $\langle c \rangle$.

1. Small Λ

As discussed earlier, a broad feature at 150 °C in the DSC spectrum for a sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda = 11.4$ nm, is probably due to diffusion. Based upon this result, it is likely that diffusion also broadens the peak in the DSC spectrum shown in Fig. 2 for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 10$ nm.

After annealing the interdiffusion region in short-wavelength samples is comparable to Λ . Annealing short Λ samples with average concentrations corresponding to equilibrium phases will probably directly produce those equilibrium phases without forming intermediate phases. This statement is supported by the fact that Al_3Ni was formed both in our sample with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda = 11.4$ nm, and in Ma and co-workers samples with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$ at small Λ . It

also is supported by the fact that AlNi was formed in our sample with $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 10$ nm. After annealing samples with $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, ∇c becomes small at positions where the composition c is equal to $\text{Al}_{0.75}\text{Ni}_{0.25}$. Thus, the volume having the composition c equal to $\text{Al}_{0.75}\text{Ni}_{0.25}$ was large. This facilitated forming Al_3Ni . Because our samples with $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$ contained a higher average concentration of Ni, it was likely that when the composition was correct for forming Al_3Ni at some position the gradient was large.

2. Intermediate Λ

At intermediate modulation wavelengths, such as 80 nm, complete multilayer mixing is not achieved when the onset reaction temperature for phase formation is reached. A concentration gradient exists within the interdiffusion zone which acts to suppress crystallization. The asymmetry in the interdiffusion leads to relatively larger regions with small composition gradients on the Al-rich side of the interdiffusion zone than on the Ni-rich side. This favors the development of the most Al-rich phase, which is the η phase. This is consistent with the strong influence of ∇c on phase formation indicated by the Desré and Yavari analysis. It is also possible that the η phase is favored because the interface energy between the η phase and Al may be small. Bendersky⁴¹ found that there is an orientation relationship between precipitated $\text{Al}_3(\text{Fe},\text{Ni})_2$ and the α -Al matrix which permits the formation of interfaces that have a small mismatch between the two phases. A more complete analysis requires detailed microstructural analysis and kinetic measurements which are in progress.

3. Long Λ

At the still longer modulation wavelength of 400 nm, the first phase formation occurs at a higher temperature than it did in the 80 nm sample. The higher temperature increases the diffusion rate and decreases ∇c . A smaller ∇c can facilitate the formation of a line compound such as Al_3Ni which was observed for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 400$ nm after the first heat treatment. The microstructure also might be different at longer Λ .

B. Later diffusion and subsequent phase formation

After a new phase has formed, diffusion through the intermetallic must be included and is likely to be the rate-controlling step for further reactions. Experiments show⁸ that Al diffuses more readily than Ni in the intermetallics. The SAXS data determined the thickness of the interface region and permits an estimate of how far the atoms must diffuse through the interface layer. After the initial phase formation, the thickness of the interface layer was approximately the same, namely 2.0 and 2.1 nm for the $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 10$ and 80 nm samples, respectively. This implies that large concentration gradients confined to relatively narrow interface zones still remain at 175 and 310 °C for the $\Lambda = 10$ and 80 nm samples, respectively.

If diffusion through the η phase is the rate-controlling step, and if Al is the faster diffusing species, then one reaction that can occur is further growth of the η phase. Under

these conditions thickening will occur faster at the Ni/ η phase interface. In any case, it should be noted that the Al phase is consumed before the Ni phase in the $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$ samples. This is to be expected since the η phase contains more Al than Ni. In the $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 80$ nm sample, after the 370 °C anneal, Al_3Ni_2 appears. This phase is closer in composition and structure to the equilibrium phase, AlNi, than either Al_3Ni or the η phase.

VII. SUMMARY

Multilayer samples provide enhanced sensitivity for detecting phase nucleation reactions at interfaces. An indication of this sensitivity is that the initial phases of short modulation samples were observed to form at lower temperatures than the 250–300 °C observed in bilayer studies.⁴ This enhanced sensitivity facilitated the phase identification as a function of Λ , composition, and heat treatment. For our Al/Ni multilayer samples, the initial phase formed and the subsequent phase sequencing is a function of Λ . This result is in contrast to bilayer studies and Ma and co-workers multilayer study⁸ in which the initial phase was always Al_3Ni . We have found that for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, $\Lambda = 10$ nm, only AlNi forms. At longer Λ , for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, the metastable η phase forms but decomposes on further heat treatment to Al_3Ni_2 . The η phase was also formed in our $\langle c \rangle = \text{Al}_{0.75}\text{Ni}_{0.25}$, $\Lambda = 100$ nm, sample. Other investigations have observed the η phase only in rapidly quenched bulk samples and not in multilayer samples. In contrast to the earlier work on Al/Ni multilayers and bilayers, we found that, for $\langle c \rangle = \text{Al}_{0.40}\text{Ni}_{0.60}$, Al_3Ni only enters the phase sequencing at larger Λ , i.e., $\Lambda = 400$ nm. The asymmetry of the component diffusivities and the concentration gradient in multilayers appear to play important roles in controlling initial phase formation.

ACKNOWLEDGMENTS

Conversations with H. I. Aaronson, C. Vold, L. J. Martinez-Miranda, J. Hoyt, D. R. Allen, and M. H. Da Silva Bassani and the support of this research by the Office of Naval Research at NRL and at the University of Wisconsin (Grant No. N00014-92-J-1554) are gratefully acknowledged.

¹ *Proceedings of an International Conference on Solid-Solid Phase Transformations* (TMS-AIME, Warrendale, PA, 1982).

² *In Situ Composites: Science and Technology* (TMS-AIME, Warrendale, PA, 1993).

³ *Proceedings of the International Symposium on the Reactivity of Solids* (Plenum, New York, 1977).

⁴ E. G. Colgan, *Mater. Sci. Rep.* **5**, 1 (1990).

⁵ R. B. Schwarz and W. L. Johnson, *Phys. Rev. Lett.* **51**, 415 (1983).

⁶ D. G. Stearns, M. B. Stearns, Y. Cheng, J. H. Stith, and N. M. Ceglio, *J. Appl. Phys.* **67**, 2415 (1990).

⁷ E. J. Cotts, W. J. Meng, and W. L. Johnson, *Phys. Rev. Lett.* **57**, 2295 (1986).

⁸ E. Ma, C. V. Thompson, and L. A. Clevenger, *J. Appl. Phys.* **69**, 2211 (1991).

⁹ A. Tonejc, D. Rocak, and A. Bonefacic, *Acta Metall.* **19**, 311 (1971).

¹⁰ K. Chattopadhyay, P. Ramachandrarao, S. Lele, and T. R. Anantharaman, in *Proceedings of the 2nd International Conference on Rapidly Quenched Metals*, edited by N. J. Grant and B. C. Giessen (MIT Press, Cambridge, MA, 1976), p. 157.

- ¹¹A. Bonefacic, K. Kranjc, and D. Kunstelj, in *Proceedings of the Fourth International Conference on Rapidly Quenched Metals*, edited by T. Masumoto and K. Suzuki (The Japan Institute of Metals, Sendai, Japan, 1982), Vol. 2, p. 1569.
- ¹²D. B. Miracle, *Acta Metall. Mater.* **41**, 649 (1993).
- ¹³Y. Gao and K. L. Merkle, *J. Mater. Res.* **5**, 1995 (1990).
- ¹⁴P. Nash, M. F. Singleton, and J. L. Murray, *Phase Diagrams of Binary Nickel Alloys* (ASM International, Metals Park, OH, 1991), Vol. 1.
- ¹⁵T. B. Massalski, *Binary Alloy Phase Diagrams* (ASM International, Metals Park, OH, 1986).
- ¹⁶B. Cantor and R. W. Cahn, in *Proceedings of the 2nd International Conference on Rapidly Quenched Metals*, edited by N. J. Grant and B. C. Giessen (MIT Press, Cambridge, MA, 1976), p. 59.
- ¹⁷J. E. E. Baglin and F. M. d'Heurle, in *Ion Beam Surface Layer Analysis*, edited by O. Meyer, G. Linker, and F. Käppeler (Plenum, New York, 1976), p. 385.
- ¹⁸M. Nastasi, L. S. Hung, and J. W. Mayer, *Appl. Phys. Lett.* **43**, 831 (1983).
- ¹⁹J. H. Perepezko and D. U. Furrer, in *Dispersion Strengthened Aluminum Alloys*, edited by Y.-W. Kim and W. M. Griffith (TMS-AIME, Warrendale, PA, 1988), p. 77.
- ²⁰J. C. Liu, J. W. Mayer, and J. C. Barbour, *J. Appl. Phys.* **64**, 651 (1988).
- ²¹X.-A. Zhao, H.-Y. Yang, E. Ma, and M.-A. Nicolet, *J. Appl. Phys.* **62**, 1821 (1987).
- ²²C. Kim, S. B. Qadri, M. Twigg, and A. S. Edelstein, *J. Vac. Sci. Technol. A* **126**, 3466 (1990).
- ²³C. Kim, S. B. Qadri, P. Lubitz, T. E. Schlesinger, R. C. Cammarata, and A. S. Edelstein, *Mater. Sci. Eng. A* **126**, 25 (1990).
- ²⁴B. K. Argarwal, *X-Ray Spectroscopy*, 2nd ed. (Springer, New York, 1991), p. 1.
- ²⁵D. G. Stearns, *J. Appl. Phys.* **65**, 491 (1989).
- ²⁶G. Richardson, J. L. Makous, H. Y. Yu, and A. S. Edelstein, *Phys. Rev. B* **45**, 12 114 (1992).
- ²⁷E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruynseraede, *Phys. Rev. B* **45**, 9292 (1992).
- ²⁸A. S. Edelstein (unpublished).
- ²⁹E-gun deposition is discussed in *Deposition Technologies in Films and Coatings*, edited by R. F. Bunshah (Noyes, Park Ridge, NJ, 1982) and ion-beam sputtering is discussed in *Handbook of Thin-Film Deposition Processes and Techniques*, edited by K. K. Schuegraf (Noyes, Park Ridge, NJ, 1988).
- ³⁰V. Shutthanandan, A. A. Saleh, and R. J. Smith, *Bull. Am. Phys. Soc.* **39**, 865 (1994).
- ³¹W. C. Johnson and G. Martin, *J. Appl. Phys.* **68**, 1252 (1990).
- ³²R. M. Wasler and R. W. Bené, *Appl. Phys. Lett.* **28**, 624 (1976).
- ³³M. Ronay, *Appl. Phys. Lett.* **42**, 577 (1983).
- ³⁴R. Pretorius, R. D. Reus, A. M. Vredenberg, and F. W. Saris, *Mater. Lett.* **9**, 494 (1990).
- ³⁵R. Pretorius, T. K. Marais, and C. C. Theron, *Mater. Sci. Eng. Rep.* **10**, 1 (1993).
- ³⁶I. Ansara, B. Sundman, and P. Willemin, *Acta Metall.* **36**, 977 (1988).
- ³⁷D. U. Furrer, M.S. thesis, University of Wisconsin, Madison, 1988.
- ³⁸J. J. Hoyt, *Mater. Res. Soc. Symp. Proc.* **321**, 257 (1994).
- ³⁹P. J. Desré and A. R. Yavari, *Phys. Rev. Lett.* **64**, 1533 (1990).
- ⁴⁰H. J. Highmore, A. L. Greer, J. A. Leake, and J. E. Evetts, *Mater. Lett.* **6**, 401 (1988).
- ⁴¹L. Bendersky, *Met. Trans. A* **16**, 683 (1985).
- ⁴²*Smithells Metals Reference Book*, 6th ed. (Butterworths, London, 1983).
- ⁴³A. Lutze-Birk and H. Jacobi, *Scr. Metall.* **9**, 761 (1975).
- ⁴⁴G. F. Hancock and B. R. McDonnell, *Phys. Status Solidi A* **4**, 143 (1971).
- ⁴⁵M. M. P. Janssen and G. D. Rieck, *Trans. TMS-AIME* **239**, 1372 (1967).