# Characterization of strain in annealed Cu–Ni multilayers using X-ray diffraction

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The strain profile of annealed Cu–Ni multilayers was analysed using an X-ray diffraction (XRD) theory. The annealing times of the multilayers ranged from 0 to 20 h. The strain in each layer was found by fitting the theoretical peak intensities with the experimental ones by iteration and using a kinematical/dynamical theory of XRD. It was found that for increasing annealing times, there was a decrease in the strain profile due to increased interdiffusion between the Cu and Ni layers. The increase in diffusion changed the composition modulation of the multilayers progressively from a trapezoidal wave for the 0 h annealed sample to a sinusoidal wave for the 20 h annealed sample.

## 1. Introduction

Metallic multilayers could be considered a one-dimensional composition modulation [1]. The strain state as well as the mechanical properties, such as the tensile strength and hardness, are known to change with the profile of the multilayers [2]. In this paper an XRD theory is used to characterize the strain profile in annealed Cu–Ni multilayers. At first the composition modulation of the multilayers was obtained using the information from the high-angle satellites around the [0 0 0] reflection. Then the strain profile was obtained from the diffraction data at the [1 1 1] reflection and its adjoining satellites, and the composition modulation.

## 2. Experimental procedure

### 2.1. Multilayer synthesis

Cu–Ni multilayers were deposited using the planar magnetron sputtering technique [3]. This technique allows for semicontinuous coating/deposition by means of translating the substrate table past a facing parallel target source. The substrate table and the target source were both located in a vacuum chamber that was pumped to a base pressure of $6.5 \times 10^{-6}$ Pa. The target sources were placed 9 cm away from the stainless steel substrate table. Argon gas was used as the sputtering gas and it had a pressure of 0.67 Pa during the sputtering process. The Cu and Ni targets were found to have a purity of 99.94% or greater and were deposited onto the substrate with a mass flow rate of 20.4 $cm^3 min^{-1}$. The magnetron sources were operated in the direct current (d.c.) mode with the Cu source discharged at 190–210 V, while the Ni source was discharged at 250–400 V. Microbalances of 6 MHz were used to calibrate the instantaneous deposition rates to the power of the applied target. The deposition rate was found to be 1.0 and 1.6 nm $s^{-1}$ for Cu and Ni, respectively. The substrate was made of cleaved mica and had the dimensions of $38 \times 78$ mm with a thickness ranging between 50 and 70 μm. During the deposition process, the substrate was held to a temperature between 293 and 323 K. The multilayers had a total number of five atomic layers of each component within each layer pair or repeat period. The thickness of the repeat period was 2.06 nm and the total thickness of the thin film was 1.28 μm. The average concentrations of the Cu and Ni elements were assumed to be 50% each.

### 2.2. Heat treatment

The specimens were then subjected to isothermal heat treatment for the purpose of annealing them. The multilayers were placed in a quartz tube that was then evacuated using a turbomolecular pump to a base pressure of $1.2 \times 10^{-6}$ Pa and not exceeding $2.7 \times 10^{-5}$ Pa during the heat treatment process. The specimens were heated in a Lindberg furnace from room temperature to 673 K for a period of 2, 6, 14 and 20 h, respectively. One specimen was not heat treated to serve as a base specimen for comparison purposes.

### 2.3. X-ray diffraction

The specimens were characterized by XRD using $CuK_\alpha$ radiation and a graphite monochromator placed before the detector. A θ–2θ scan was made up to $2\theta = 110^\circ$.

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## 3. Discussion

The satellite peaks around the [0 0 0] superlattice, as well as the satellite peaks for the [1 1 1] and [2 2 2] superlattices, were obtained in the XRD pattern. The presence of satellite peaks in the [0 0 0] reflection (Fig. 1) denotes that the grown multilayers were of good quality.

The presence of only [1 1 1] and [2 2 2] type reflections and the absence of any other reflections indicate that the multilayers are highly textured along the [1 1 1] growth direction. The average layer pair spacing, i.e. 2.06 nm, was obtained from the angular separation between the satellite reflection and the [0 0 0] incident beam and agree quite well with the value determined from the sputter deposition procedure. The total amount of fluctuation in the layer pair spacing over the entire film was found to be only 0.03 nm or 1.6% from another study [4]. From the XRD pattern, a strong [1 1 1] superlattice reflection of the Cu–Ni multilayers was found to occur between the [1 1 1] Bragg peaks of Cu and Ni, which indicates the presence of a single phase structure [5]. The composition and strain profile for the multilayers could be obtained fromt the diffraction pattern.

### 3.1. Composition modulation

In order to obtain the strain profile in these multilayers, information on composition modulation is necessary. From the satellites peaks around the [0 0 0] superlattice, the composition profile of the multilayers could be obtained.

Jankowski *et al.* [3] found that for these samples, the integrated intensity of the normalized $I(t)/I(0)$ of the high-angle satellite around the [1 1 1] superlattice to have a linear decay when plotted against time in the

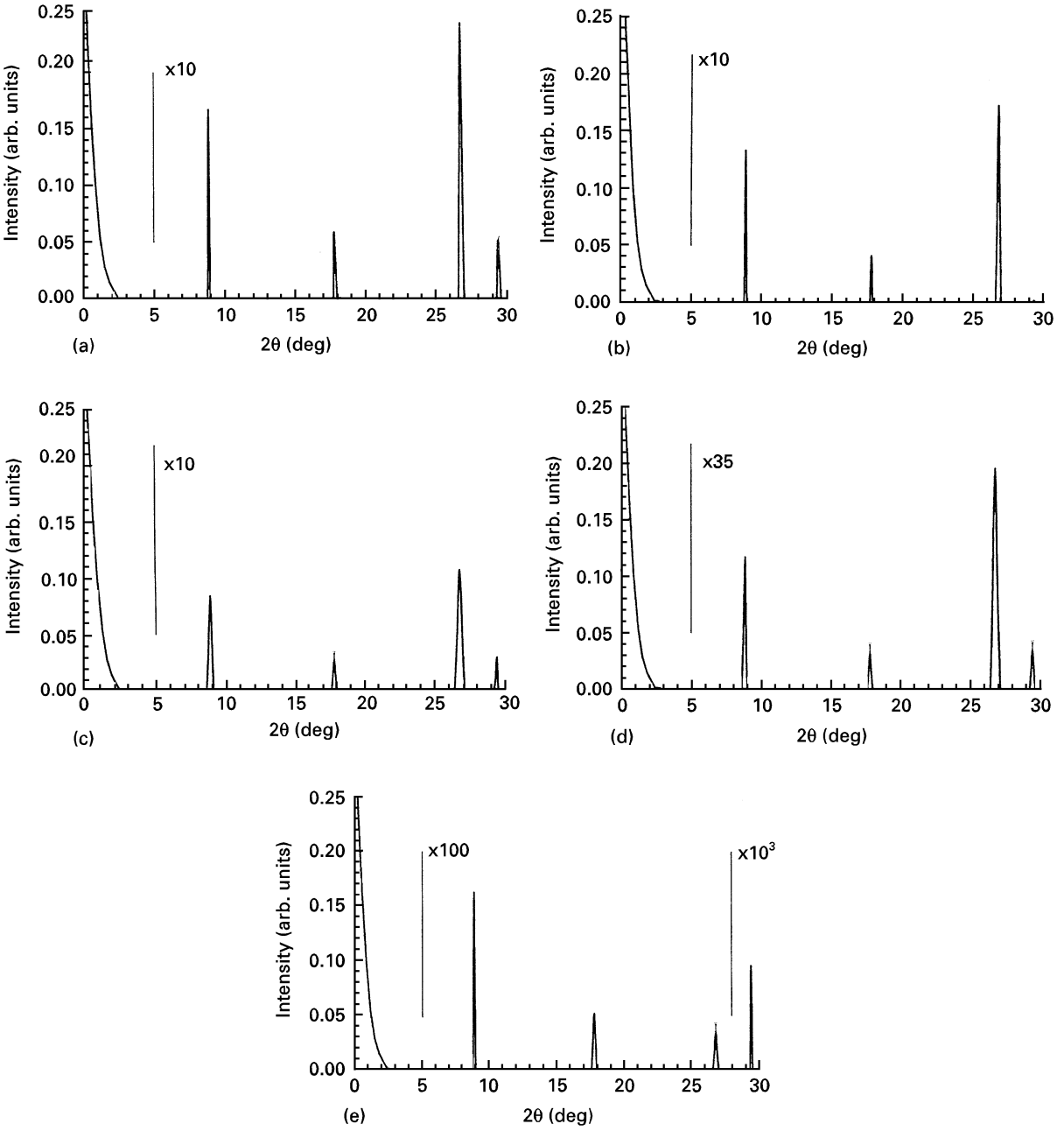


*Figure 1* Experimental intensities for high-angle satellites (second; fourth; sixth-and seventh-order peaks from left to right, respectively) around the [0 0 0] superlattice for annealing times of (a) 0 h, (b) 2 h, (c) 6 h, (d) 14 h and (e) 20 h.

logarithmic scale, which shows the decrease in the satellite intensities and disappearing upon complete diffusion of the two different material species. This is graphically shown in Fig. 2, which indicates that the diffusion of the multilayers follows that of the linearized diffusion equation. The interdiffusivity, $D_B$, for these samples was calculated to be $1.76 \times 10^{-20}$ $cm^2 s^{-1}$, which is in good agreement with the $2–3 \times 10^{-20}$ $cm^2 s^{-1}$ value obtained by Tsakalakos for a 2.0 nm repeat period Cu–Ni multilayer that was prepared by thermal evaporation and annealed at 400 °C [6].

The occurrence of a composition modulation waveform could result in periodic modulation of the atomic scattering factor of the $j$th plane and also the interplanar spacing of the superlattice structure. The equations to simulate the composition modulation can be described as a Fourier sum in direct space [5, 7–9].

$$C(z) = C_{Cu}\left[1 + \sum_m Q_m \cos(mkz)\right] \quad (1)$$

where $C(z)$ is the concentration of copper, $C_{Cu}$ is the average concentration of copper, $Q_m$ is the amplitude of the $m$th harmonic of the modulation waveform and $k = 2\pi/\lambda_{mod}$. The modulation wavelength, $\lambda_{mod}$, is described as the repeat period of the Cu–Ni multilayer, which is the total thickness of one Cu layer and one Ni layer. $Q_m$ is obtained from the following equation

$$Q_m = 2\left(\frac{F_{m-}q_+ - F_{m+}q_-}{q_+\eta_- + q_-\eta_+}\right) \quad (2)$$

where $F_{m\pm}$ is the relative intensity or amplitude of the $\pm m$th order satellite, $q$ is then obtained by

$$q^{\pm} = \frac{1}{d} \pm mk \quad (3)$$

where $d$ is the plane spacing of the [1 1 1] superlattice. The dispersion corrections for the atomic scattering factors are given by

$$f_m = |f_{0m} + \Delta f_{1m} + \Delta f_{2m}| \quad (4)$$

where $f_{0m}$ is the atomic scattering factor for Cu and Ni, $\Delta f_{1m}$ and $\Delta f_{2m}$ the real and imaginary dispersion terms for Cu and Ni, respectively [10]. The differences in the atomic factor $\Delta f = (f_{Cu} - f_{Ni})$ and the average scattering factor, $F_{hkl} = (f_{Ni} + f_{Cu})/2$ were used to obtain the term $\eta$

$$\eta = \frac{\Delta f_{\pm}}{F_{hkl}} \quad (5)$$

A variety of waveforms, i.e. square, trapezoidal and sine waves, were tried to obtain a fit to the composition modulation and it was found that a trapezoidal wave gave the best fit to the experimental results. This model is shown in Fig. 3. The resulting one-dimensional composition modulations of all the specimens are shown in the Fig. 4 and the calculated $Q_m$ values are shown in Table I. The trapezoidal model composition modulation indicates intermixing of the two elements Cu and Ni at the interface. Thus the composition modulation deviates from the ideal step

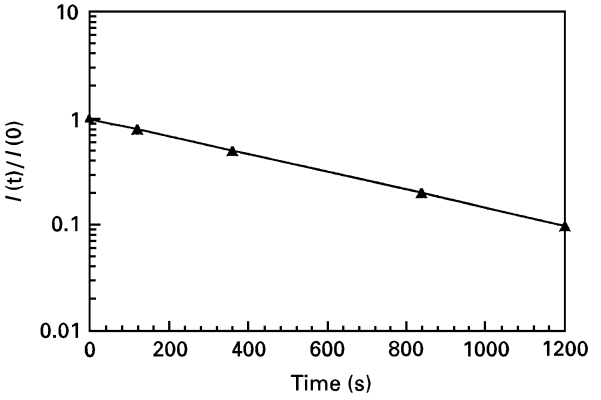


*Figure 2* A linear decay with time is found for a semilogarithmic plot of the integrated intensity $I(t)/I(0)$ (normalized to the Bragg reflection) of the low-angle satellite (at $2\theta = 39.3°$ from [3] $n = 5$ Cu–Ni [1 1 1] at 400 °C).

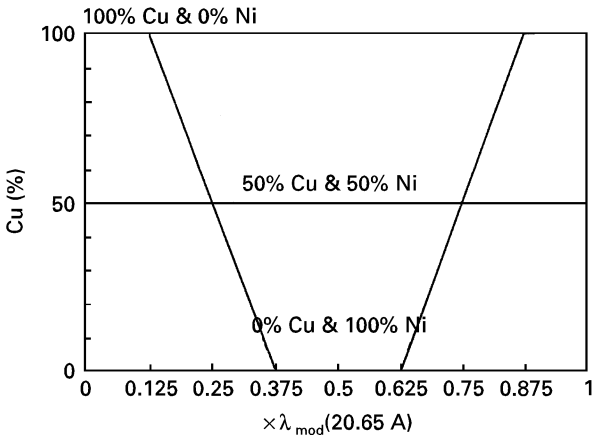


*Figure 3* Trapezoidal wave model used to obtain the composition profile.

model, which has a sharp interface. Also, the modulation profiles clearly show that the Cu layers diffuse more rapidly into the Ni layers as the modulation intersects at a concentration of approximately 52% Cu. The modulation waveforms were found to have occurred with a regularity that extended over the several modulation periods. This is an indication of structural coherence in the system as reported by Yahalom *et al.* [11].

For the 0 h anneal specimen, the composition modulation shows that there was very little mixing at the interface between the Cu and Ni layers. This is illustrated by a slightly slanted line at the interface or a compositionally near-abrupt interface that is an indication of good chemical order within the multilayer system [12]. The chemical order decreased as more mixing occurred between the Cu and the Ni layers, which is illustrated in the composition modulation waveform where at the interface the slope of the composition waveline decreased as the annealing time increased. In addition to the reduction in the slope, the maximum amount of Cu at the interface also decreased as the annealing time increased; an indication of increasing mixing between the Cu and Ni layers.

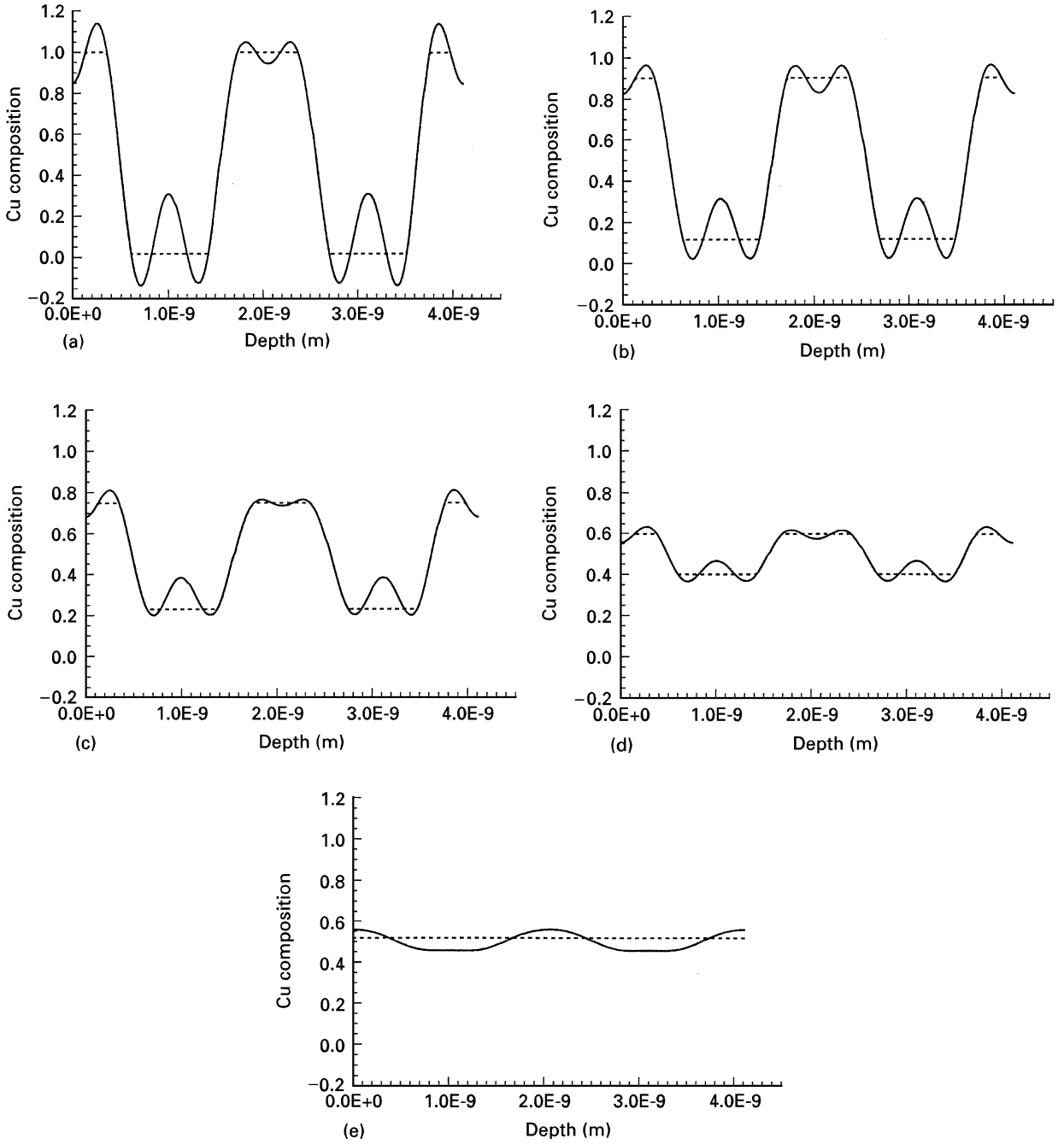


*Figure 4* Composition profile of the Cu–Ni multilayers indicating the variation of the Cu composition for annealing times of (a) 0 h, (b) 2 h, (c) 6 h, (d) 14 h and (e) 20 h.

TABLE I $Q_m$ values for the Cu–Ni multilayer specimens

| Annealing time (h) | $Q_2$ | $Q_4$ | $Q_6$ | $Q_7$ |
|---|---|---|---|---|
| 0 | 0.218 37 | 0.037 98 | 0.104 44 | 0.018 99 |
| 2 | 0.174 70 | 0.026 93 | 0.076 31 | 0.009 619 |
| 6 | 0.109 18 | 0.016 74 | 0.046 10 | 0.010 40 |
| 14 | 0.043 67 | 0.005 75 | 0.024 52 | 0.003 61 |
| 20 | 0.021 18 | 0.003 31 | 0.001 40 | 3.537 58E-5 |

## 3.2. Strain profile

The satellite peaks around the [1 1 1] superlattice reflection were found to be symmetrically spaced, with the intensity of the $\pm 2$ satellites higher than the $\pm 1$ satellites. From the experimental XRD data, the coherence of the composition wave could be estimated from the variations in the strain in the multilayer [13]. Because the thickness of the sample is small, the strain profile could be approximated using a kinematical/dynamical theory for thin crystals with zero absorption as set forth by Zachariasen [14].

To approximate the strain profile, two quantities $A$ and $y$ are introduced as

$$A = \pi k_0 K |\psi_H| \frac{t_0}{(|\gamma_0 \gamma_H|)^{1/2}} \tag{6}$$

where

$$k_0 = \frac{\sin\theta_0}{\lambda} \tag{7}$$

where $\theta_B$ is the Bragg angle, $\theta_0$ is the angle of incidence, $e^2/mc^2$ is the classic electron radius

$$K = \frac{1 + \cos 2\theta_B}{2} \tag{8}$$

$$\psi_H = -\frac{e^2}{mc^2}\frac{\lambda^2}{\pi}\frac{F_H}{V} \tag{9}$$

($2.818 \times 10^{-15}$ m), $\lambda$ is the the wavelength of the $CuK_\alpha$ radiation ($1.5418 \times 10^{-10}$ m), $F_H$ is the structure factor of the crystal, $t_0$ is the thickness of the individual layers, and $V$ is the unit cell volume of the crystal.

$$y = \frac{(1 - b/2)}{(|b|)^{1/2}}\frac{\psi_0 + (b/2)^\alpha}{K|\psi_H|} \tag{10}$$

where

$$b = \frac{\gamma_0}{\gamma_H} \tag{11}$$

$$\alpha = \theta - \theta_B + (\varepsilon \tan \theta_B) \tag{12}$$

where $F_0$ is the structure factor at 0° of Cu and Ni; $\theta$ is the angle of incidence with respect to the diffracting planes; $\gamma_0$ and $\gamma_H$ are the direction cosines of the incident and diffracted beam with respect to the inward surface normal, respectively; and $\varepsilon$ is the strain in the individual layer. The ensuing theoretical intensity of the satellite peaks as well as the superlattice reflection, $I_H$, using an assumed strain profile can be obtained by the following equation

$$I_H = \frac{\sin^2 Ay}{y^2} \tag{13}$$

For the calculation, the following assumptions were made:

1. The interplanar spacing within the Cu layers was assumed to be $d_{Cu}$, while that within Ni layers was assumed to be $d_{Ni}$.
2. Similarly, the unit cell volume and structure factors of Cu and Ni crystals were assumed within the Cu and Ni layers, respectively.
3. Because there was some mixing of Cu and Ni at the interface, weighted average of interplanar spacing, unit cell volume and structure factors were assumed at those layers. The weighted average value was

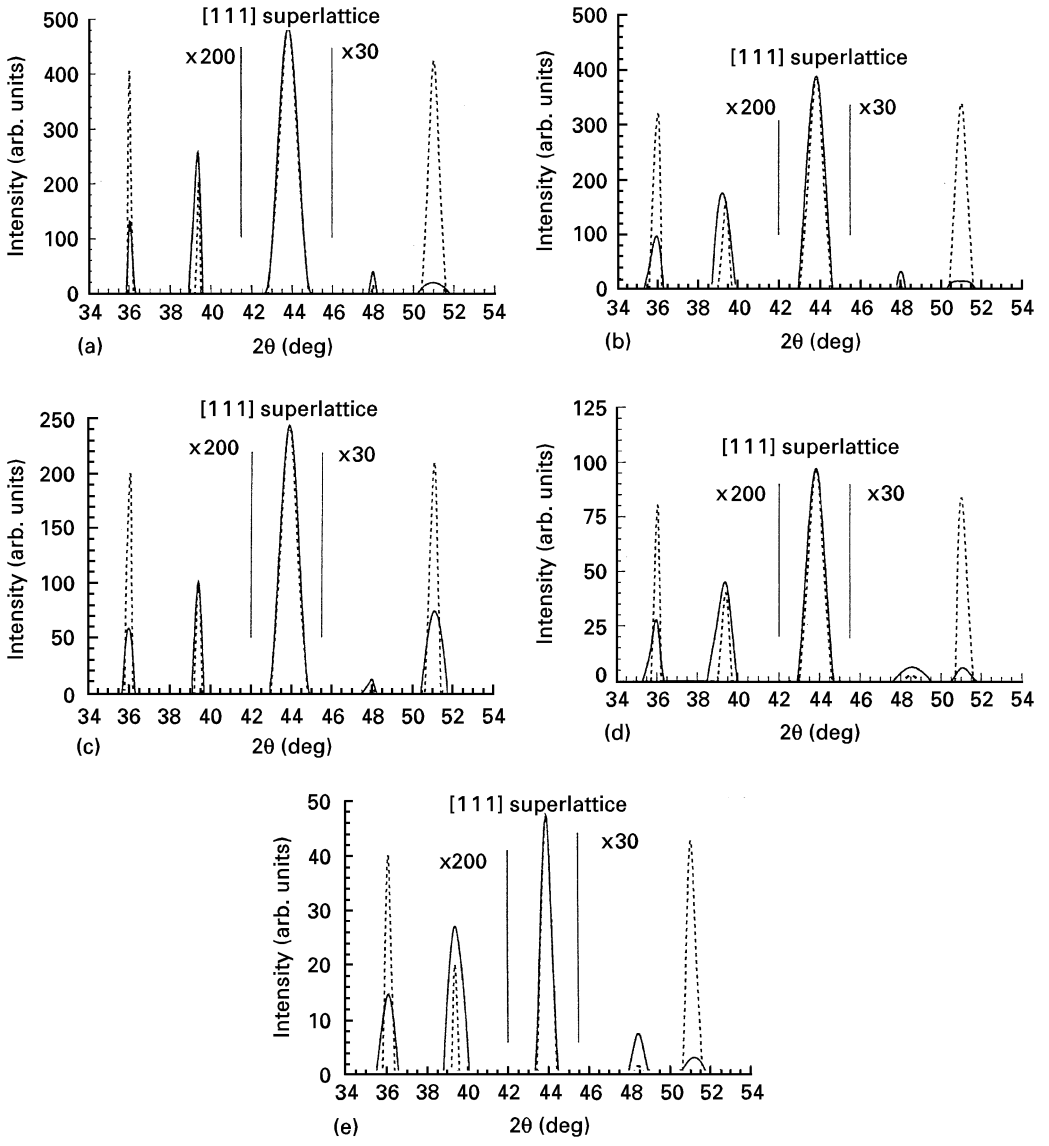


*Figure 5* Theoretical (——) and experimental (– – – – –) intensities of [1 1 1] superlattice and adjoining satellites obtained from strain profile calculations for annealing times of (a) 0 h, (b) 2 h, (c) 6 h, (d) 14 h, and (e) 20 h.

considered from the composition profile of the annealed samples.

Each layer pair was divided into ten layers of approximately atomic layer thickness and an average strain was assumed within each layer [15]. The XRD intensity obtained was then the accumulated intensity from the entire sample. Starting with an initial assumption of a particular strain profile and the experimental 2θ positions of the intensity peaks, the first theoretical intensity peaks were obtained. From this, a series of iterations were made with a minor variation each time to the strain values as well as the angular positions of the intensity peaks to obtain the best fit to the experimental XRD data. This variation in the strain profile in addition to the defect densities in the multilayers could lead to variations in the interdiffusion mechanism as well as physical properties [16].

The theoretical as well as the experimental diffraction patterns for all the specimens are shown in Fig. 5. The calculated or theoretical intensity peaks reproduce very well the experimental data for the angular position. For all the specimens, the theoretical intensities for the [1 1 1] superlattice and $\pm 1$ satellites reproduced the experimental intensities very well. However, the theoretical intensities for the $\pm 2$ satellites were consistently lower than the experimental intensities. The difference between the theoretical and experimental data could be attributed to a variety of sources. The strain profile of any system could only be approximated and a certain amount of error has to be taken into account [17]. The lattice spacings as well as the thickness of each of the layers that were assumed for the calculations could also vary from the assumed values Cu and Ni had been found to interdiffuse during growth, which could have led to the aforementioned variations [18].

Because the XRD data for the [1 1 1] reflection were used to analyse the strain profile, the strain values obtained in this research were along the modulation direction. It was found that the amount of strain assumed in each layer played a significant role in dictating the angular positions as well as the inten-

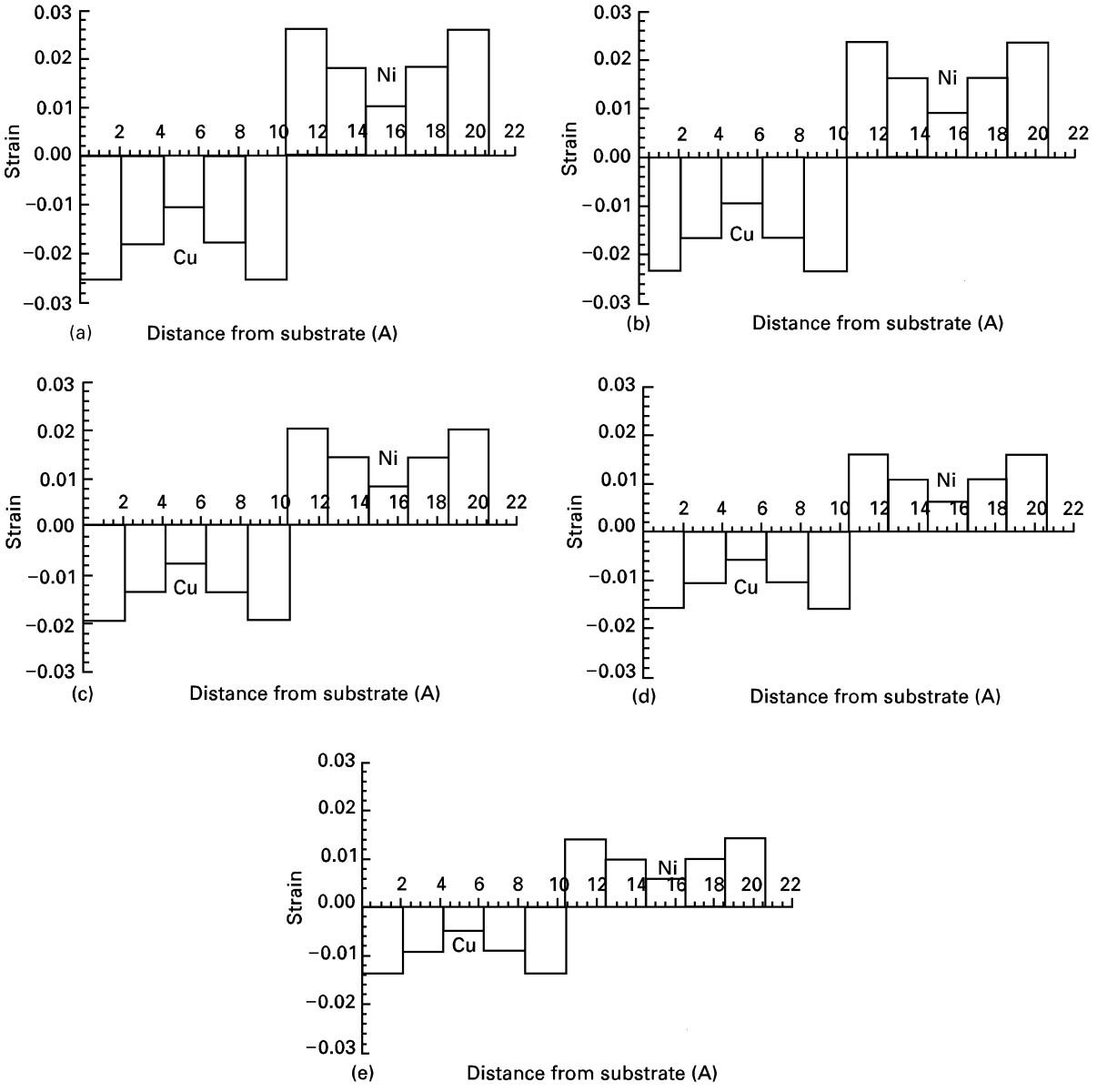


*Figure 6* Depth profile of perpendicular strain within one repeat period for the Cu–Ni multilayers for annealing times of (a) 0 h, (b) 2 h, (c) 6 h, (d) 14 h, and (e) 20 h.

sities of the theoretical peaks [15, 19]. The strain occurring from the lattice mismatch arose due to the differences in the lattice parameters of the Cu and Ni species. The presence of satellite peaks in both the experimental and theoretical data coupled with the composition profile indicate that the strain in the system was close to coherent strain for 0 h annealing. However, because the differences in the lattice parameters of Cu and Ni were relatively small, the ensuing strain from lattice mismatch was also small. For the 0 h annealed specimen, the strain at the interface of the Cu layer was found to be 2.4015% compression and the Ni layer interface strain was found to be 2.3946% tension. The strain in the Cu layers was in compression because the lattice parameter of Cu was larger than that of Ni, therefore it had to contract to form a coherent interface. These results are consistent with the trends found in other multilayer systems [15]. The strain values that were obtained by using this kinematical theory were slightly lower than the lattice mismatch strain (2.5151% for Cu and 2.51% for Ni). This proves that there had already been some diffusion between the Cu and Ni layers during growth and that Cu diffused into Ni at a faster rate.

As the layers progressed away from the interface, the strain values were found to decrease and reached a minimum at the middle of the Cu and Ni layers, as illustrated in Fig. 6 [1, 15]. The strain values were also found to decrease as the annealing time increased. This was caused by subsequent interdiffusion between the two species caused by annealing. This decrease translated to a decrease in the intensities of the adjoining satellites. This was also true for the experimental data.

## 4. Conclusions

X-ray diffraction was found to be a useful and powerful tool in extracting information about the strain profile of the Cu–Ni multilayers. The composition modulations in the multilayers were predicted to be in the form of trapezoidal waves and altered to resemble sinusoidal waves as the annealing time progressed. This was attributed to increased diffusion between Cu and Ni species at the interface. A simple kinematical model was used to extract the strain profile in this multilayer system. The strain at the interface was found to be tensile for Ni and compressive for Cu. As the layers progressed away from the interface, the strain values were found to decrease. The overall strain values also decreased as the annealing time increased resulting in an overall decrease in the theoretical intensities of the satellites. This decrease in strain value was attributed to continuous mixing and diffusion between the Cu and Ni layers.


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