

An X-ray Diffraction Method for the Determination of Composition Distribution in Inhomogeneous Binary Solid Solutions

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The pure diffraction line profile from an inhomogeneous binary solid solution is analyzed to give the composition distribution $N(x)$ defined as the number of unit cells of composition x . The minimization of instrumental broadening is performed by Stokes's Fourier-series method and by $K\alpha_2$ elimination from high-angle reflections. The analysis is applied to Cu-Ni powders (36 at.% Cu) interdiffused at 780 °C. Curves of x versus $\int_0^x N(x)dx$ and $\int_0^1 N(x)dx$ which are shown to be analogous to interdiffusion concentration-penetration curves, are presented for various interdiffusion times. The average composition was determined by the X-ray analysis to $\pm 1.5\%$. The results of the Stokes's analysis and the $K\alpha_2$ elimination method are compared with the conclusion that in the case considered the $K\alpha_2$ elimination method is more reliable and about ten times more rapid.

Introduction

When composition variations occur over distances of 1μ or more, distributions may sometimes be obtained by microscopic examination or by X-ray (or electron) micro-beam scanning. Here we shall consider the case where the variations occur over a scale much finer than the dimensions of the X-ray beam. In this case diffraction lines will be broadened due to the continuous lattice-parameter distribution. Although this phenomenon has no doubt been observed many times, quantitative analysis has apparently not previously been made.

Jones (1938) has shown that the observed diffraction line profile, $h(\theta)$, is related to the pure diffraction line profile, $f(\theta)$, and to the instrumental-broadening function, $g(\theta)$, by the integral equation

$$h(\theta) = \int_{-\infty}^{\infty} f(\varphi)g(\theta - \varphi)d\varphi.$$

The function $g(\theta)$ includes both geometric instrumental effects and X-ray spectrum effects. (i.e. natural line shape including the $\alpha_1 - \alpha_2$ doublet for $K\alpha$ radiation). It is experimentally determinable as the diffraction line from 'perfect' diffracting material (i.e. particle size $> 3000 \text{ \AA}$, strain free, homogeneous). The inhomogeneity determination is thus resolvable into two independent problems—the extraction of the pure diffraction profile, $f(\theta)$, from the observed profile, $h(\theta)$; and the calculation of the composition-distribution function, $N(x)$ (the number of unit cells of composition x) from $f(\theta)$.

Extraction of the pure diffraction line profile

Stokes (1948) has shown that the integral equation may be approximately solved for $f(\theta)$ by employing

Fourier-series representations for h , f , and g . Assuming that these operations are performed by the Lipson-Beevers method (Beevers, 1952), the calculations are described by the following equations (not including irrelevant constants):

$$f(n) = \sum_m \left\{ \frac{H_r G_r + H_i G_i}{G_r^2 + G_i^2} \cos(2\pi mn/120) + \frac{H_i G_r - H_r G_i}{G_r^2 + G_i^2} \sin(2\pi mn/120) \right\},$$

where:

$$G_r(m) = \sum_n [g(n) + g(-n)] \cos(2\pi mn/120)$$

$$G_i(m) = \sum_n [g(n) - g(-n)] \sin(2\pi mn/120)$$

$$H_r(m) = \sum_n [h(n) + h(-n)] \cos(2\pi mn/120)$$

$$H_i(m) = \sum_n [h(n) - h(-n)] \sin(2\pi mn/120).$$

That is, the line profiles are divided into discrete intervals ($-60 \leq n \leq 60$), the ordinate being the average over the interval. The Fourier method is obviously rather tedious and this partially vitiates its usefulness.

The problem of instrumental broadening may be neglected if the function $f(\theta)$ is much broader than the function $g(\theta)$. If, owing to inhomogeneity, a range of lattice parameters d to $d + \delta d$ is included, the pure diffraction line will extend from θ to $\theta - \delta\theta_x$, where

$$\delta\theta_x = (\delta d/d) \tan \theta.$$

The instrumental broadening function's breadth can be approximated by the expression (Eckstein & Siegal, 1949)

$$\delta\theta_I = \Delta + (\delta\lambda/\lambda) \tan \theta,$$

where:

Δ = geometric instrumental effects,
 $\delta\lambda$ = spectral breadth,
 λ = wave length.

Optimum experimental conditions minimize $\delta\theta_I/\delta\theta_x$ which according to the above expressions means using high-angle reflections. As $\theta \rightarrow 90^\circ$, $\tan \theta \rightarrow \infty$; thus the limiting possible resolution is

$$\delta\theta_I/\delta\theta_x = \frac{\delta\lambda/\lambda}{\delta d/d}.$$

In Fig. 1 is plotted $10 \delta\theta_I/\tan \theta$ where $\delta\theta_I$ was experimentally obtained on a Philips wide-range diffractometer using Cu K radiation and a silicon powder specimen. For the curve $\alpha_1 + \alpha_2$ the entire $K\alpha$ doublet is included, while the curve α_1 is for the α_1 component only.

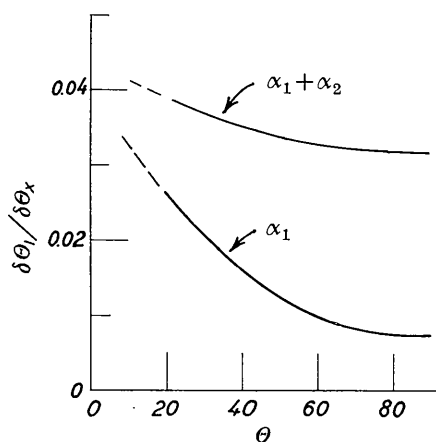


Fig. 1. Ratio of instrumental broadening to inhomogeneity broadening for the case that the lattice parameter varies over a range of 10%.

The great advantage in resolution that accrues when the α_2 component is eliminated is notable. It is also seen that for $\theta > 40^\circ$, the angular dependence is weak so that a wide angular range is available with comparable resolution.

The composition distribution can be determined as averages over intervals δx such that

$$\delta\theta_I = (1/d)(\partial d/\partial x)\delta x \tan \theta.$$

If the lattice parameter is linearly dependent on concentration, the breadth of the diffraction line is similarly given as

$$\delta\theta_x = (1/d)(\partial d/\partial x)\Delta x \tan \theta,$$

where Δx is the range of composition. The 'resolution' is thus $\delta x/\Delta x = \delta\theta_I/\delta\theta_x$. Thus from Fig. 1, for a reflection occurring at $\theta = 60^\circ$, from a solution where a composition range Δx gives rise to a 10% lattice-parameter variation the composition distribution can be determined as averages over intervals of $\delta x = \Delta x/100$ if the α_2 component can be eliminated.

Keating (1959) has described a method for the mathematical elimination of $K\alpha_2$ by assuming identical line shapes for both the α_1 and α_2 components and an intensity ratio of one half. The method used here is a simplification of this method adequate for the case considered. By dividing the observed line into unit intervals of the $\alpha_1 - \alpha_2$ angular separation, the α_1 component alone is obtained as

$$h(i) = \sum_{n=0}^i (-\frac{1}{2})^{i-n} H(n),$$

where:

$h(i)$ = resolved α_1 component,

$H(n)$ = observed intensity above background.

Two methods of minimizing instrumental broadening are thus available: Stokes's Fourier method and mathematical α_1 component resolution for high-angle reflections.

Composition distribution from the pure diffraction line profile

Taking into account only those factors in the X-ray intensity expression that can vary significantly over the breadth of the pure diffraction line we obtain for the diffracted intensity from the composition interval x to $x + \delta x$

$$I(x)\delta x = K[xf_A + (1-x)f_B]^2 A(\theta, \mu) LP(\theta) N(x)\delta x,$$

where:

$x, (1-x)$ — atomic fractions of A and B respectively,
 f_A, f_B — scattering factors of A and B respectively,
 $N(x)$ — number of unit cells of composition x in the irradiated volume,
 $A(\theta, \mu)$ — absorption factor,
 $LP(\theta)$ — Lorentz-polarization factor,

where for powder lines,

$$LP = (1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta).$$

The intensity per unit composition interval is related to the pure diffraction profile by the relation $I(x)\delta x = f(\theta)\delta\theta$.

Differentiating Bragg's law we obtain that

$$\delta\theta = d'(x)/d(x) \tan \theta \delta x,$$

where:

$$d'(x) = \partial d(x)/\partial x,$$

so that

$$I(x) = f(\theta) d'(x)/d(x) \tan \theta.$$

Combining this result with the previously given expression for $I(x)$, we obtain the composition distribution in terms of the experimentally obtainable pure diffraction profile

$$N(x) = \frac{d'(x)/d(x)}{KA(\theta, \mu)[xf_A + (1-x)f_A]^2} \times \frac{\sin^3 \theta}{1 + \cos^2 2\theta} f(\theta) = Q \cdot f(\theta).$$

In problems of interdiffusion the composition variations are described by so-called concentration-penetration curves. For interdiffusion in a diffusion couple as illustrated in Fig. 2(a), the concentration-penetration

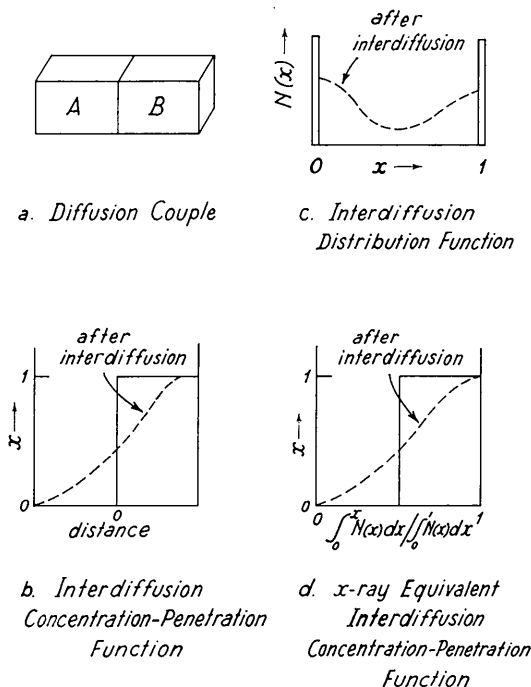


Fig. 2. Comparison of descriptions of interdiffusion.

curves before and after interdiffusion would appear as in Fig. 2(b). A plot of $N(x)$ versus x in these two cases would appear as in Fig. 2(c) and a plot of x versus

$$\int_0^x N(x) dx / \int_0^1 N(x) dx$$

would appear as in Fig. 2(d). Thus the variable

$$\int_0^x N(x) dx / \int_0^1 N(x) dx$$

has much the same character as the penetration. In this simple geometry they are simply related as:

$$\text{Penetration} \propto \int_0^x a(x)N(x) dx \simeq \bar{a} \int_0^x N(x) dx,$$

where: $a(x)$ = lattice parameter.

The X-ray equivalence to the concentration-penetration curve can only be equated to the usual concentration-penetration curve by the addition of further information about the geometry and size of the inter-

diffusing systems. The X-ray determined interdiffusion curve also possesses the convenient property that the area under the curve is proportional to the average composition. This is easily obtained by the definition

$$\bar{x} = \int_0^1 xN(x) dx / \int_0^1 N(x) dx$$

and integrating by parts we obtain

$$\begin{aligned} \bar{x} &= 1 - \int_0^1 \left[\int_0^x N(x) dx \right] dx / \int_0^1 N(x) dx \\ &= \text{area under } x \text{ versus } \int_0^x N(x) dx / \int_0^1 N(x) dx. \end{aligned}$$

Application to interdiffusion in Cu-Ni powders

Cu and Ni powders of about 5μ diameter were mixed and cold pressed under 2500 kg.cm^2 into briquets $2 \text{ cm.} \times 1 \text{ cm.} \times 0.3 \text{ cm.}$ After heating for various times at $780 \pm 10^\circ \text{C.}$ in a H_2 atmosphere, the Cu $K\alpha$ 311 reflection was recorded with a Philips wide-range diffractometer. Under these experimental conditions the absorption factor, $A(\theta, \mu) = \mu^{-1} \simeq \text{const.}$ The absorption factor can be so simply disposed of only if all the diffracting regions have nearly the same linear absorption coefficient or if the regions are small compared to the depth of penetration of the X-ray beam. If these conditions are not satisfied the absorption is complicated by the micro-absorption effect (Wilchinsky, 1951).

The correction factor, Q , for converting the pure diffraction profile, $f(\theta)$, into the distribution function, $N(x)$, for the Cu $K\alpha$ 311 reflection decreases almost linearly by a factor of about $\frac{2}{3}$ from the pure Ni to pure Cu reflection positions. For this calculation the lattice-parameter data was taken from Pearson (1958). The scattering factors do not vary significantly over the breadth of the line and average values of $f_{\text{Cu}} = 11.3$ and $f_{\text{Ni}} = 9.6$ (including Hönl correction (James, 1950)) were used. The composition is very nearly a linear function of diffraction angle so that Q is a linear function of θ and x simultaneously.

Diffractometer traces of interdiffused 0.36 Cu-0.54 Ni (atomic fraction) powders are presented in Fig. 3. Also plotted in Fig. 3 are the profiles after α_2 elimination by the method previously described.

Concentration-penetration curves obtained by the α_2 elimination method, averaging over composition intervals of $\delta x = 0.1$, are given in Figs. 4 and 5. The composition intervals $\delta x = 0.1$ correspond to the 'resolution' of the experimental conditions, $\delta\theta_1/\delta\theta_x = 0.1$. Fig. 5 compares the curve obtained by the α_2 elimination method with that obtained by the Fourier method. There is a significant difference between the two results only near the end points. This is apparently due to the effect of errors on the Fourier transformation (Stokes, 1948) which have resulted in spurious tails. The tails were of a slowly damped oscillatory

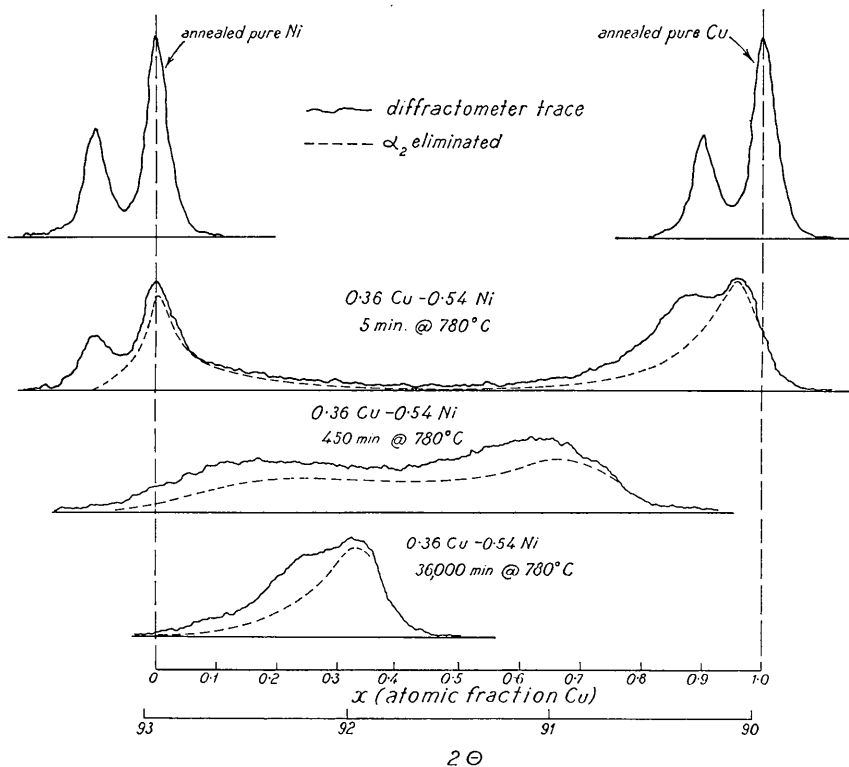


Fig. 3. Diffractometer traces of Cu $K\alpha$ 311 reflection from interdiffused Cu-Ni powders.

nature extending beyond the physically meaningful limits of the positions of the unalloyed components thus making for a certain arbitrariness in assigning the background level and the limits for the integrations for

$$\int N(x) dx .$$

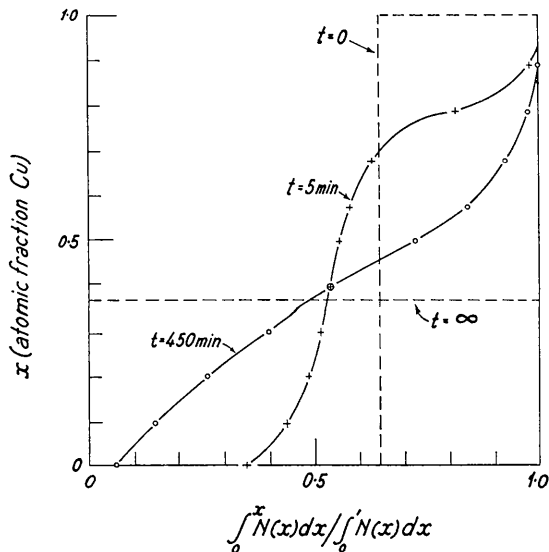


Fig. 4. X-ray equivalent concentration-penetration curves from 0.36 Cu-0.54 Ni powders interdiffused at 780 °C. Determined by the α_2 elimination method.

The integration sufficiently smooths out the oscillations for them not to be discernible on the scale of Fig. 5.

The compositions obtained from the area under the concentration-penetration curves are all 0.36 ± 0.005 .

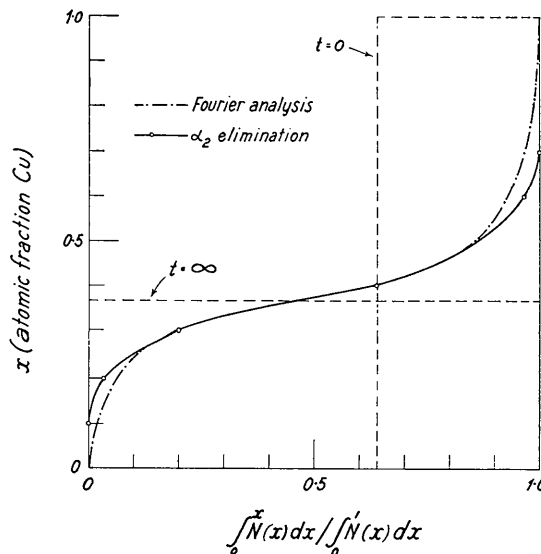


Fig. 5. Comparison of the Fourier with the α_2 elimination method of obtaining concentration-penetration curves; for 0.36 Cu-0.54 Ni powder interdiffused at 780 °C. for 36,000 min.

Although it is not the purpose here to consider the analysis of the interdiffusion process by this X-ray technique (this will be published elsewhere) it is of interest to note briefly some of the more striking conclusions from the results presented. First it is seen from Figs. 4 and 5 that although significant interdiffusion has already occurred in 5 min., after 36,000 min. the homogenization is far from complete. Secondly, Ni diffuses into Cu much more rapidly than Cu into Ni; after 5 min. no pure Cu remains although there is considerable pure Ni.

Summary

The broadening of a diffraction line from an inhomogeneous binary solid solution has been quantitatively analyzed to yield the composition distribution, $N(x)$, defined as the number of unit cells of composition x . The analysis hinges on the minimization of diffraction-line instrumental broadening. Stokes's Fourier method of instrumental-effect minimization has been reviewed. An alternative method has also been described; it is shown that by choosing a high angle reflection and mathematically eliminating the $K\alpha_2$ component the instrumental effect can be made negligible in cases of moderate dependence of lattice parameter on composition.

The analysis has been applied to mixed Cu-Ni powders (36 at.% Cu) interdiffused at 780 °C. The results have been presented in the form of diagrams of x versus

$$\int_0^x N(x) dx / \int_0^1 N(x) dx$$

which have been shown to be analogous to the description of interdiffusion by the usual concentration-penetration curve. The average compositions of the resulting inhomogeneous solid solutions have been determined by the X-ray analysis to $\pm 1.5\%$.

The method of analysis by $K\alpha_2$ elimination has been compared with Stokes's Fourier method with the conclusion that the former, in the example considered, was more reliable and about ten times more rapid.

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The Crystal Structure of PuNi₄*

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The structure of PuNi₄ has been determined by single crystal X-ray methods. The unit cell is monoclinic, space group $C2/m$ with

$$a = 4.87, b = 8.46, c = 10.27 \text{ \AA}, \beta = 100^\circ.$$

There are six formula units per unit cell. Two of the six Pu atoms have a coordination essentially identical to that of the Pu in PuNi₅. The other Pu atoms have a coordination somewhat similar to the Pu in PuNi₅. The PuNi₄ structure can be obtained by removing the Ni atoms at $z = \frac{1}{2}$ from every third unit cell of PuNi₅ and by slightly shifting the remaining atoms.

Introduction

There are six binary compounds in the Pu-Ni system (Wensch & Whyte, 1951). The structures of PuNi₂, PuNi₅ and Pu₂Ni₁₇ have been reported by Coffinberry & Ellinger (1956). The structure of PuNi has been reported by Cromer & Roof (1959) and that of PuNi₃

by Cromer & Olsen (1959). The structure of PuNi₄, the remaining compound of the series, is the subject of the present report.

Experimental

An alloy containing 78.5 at.% Ni was prepared by melting the components in vacuum and then annealing the resulting ingot at 1240 °C. for 10 hr.

* Work done under the auspices of the U.S. Atomic Energy Commission.