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INTERDIFFUSION IN COMPOSITION MODULATED COPPER-NICKEL THIN FILMS

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Résumé. — Les coefficients d'interdiffusion ont été mesurés dans les couches minces de Cu-Ni déposées sous vide à partir de la phase vapeur, chaque couche contenant une modulation de composition dans la direction [111] de longueur d'onde comprise entre 0,8 et 5 nm. Les coefficients d'interdiffusion dans le domaine 375-450 °C, mesurés par rayons X à partir de la diminution d'intensité des pies satellites, sont en bon accord avec une extrapolation des données existantes à haute température obtenues sur des échantillons conventionnels. Le coefficient de diffusion effec tif \( D_b \) à 400 °C présente un minimum en fonction de la relation de dispersion \( B^2(h) \), contrastant ainsi avec le comportement de plusieurs autres systèmes étudiés jusqu'à présent. Une nouvelle formulation de \( D_b \) décomposé en puissances de \( B^2 \), a été développée et six potentiels interatomiques ont été calculés à partir des paramètres d'ordre à courte distance : ce calcul fournit un minimum de \( D_b \) à environ 1,6 nm qui est la valeur observée expérimentalement. Des singularités d'écragement sont révélées sur la courbe \( D_b - B^2 \) par l'apparition d'un pic abrupt à la longueur d'onde 2,5 nm.

Abstract. — Interdiffusivities were measured in vapor-deposited Cu-Ni foils containing [111] composition modulations with wavelengths between 0.8 and 5 nm. The interdiffusivities in the range of 375-450 °C, measured from the decay rate of X-ray diffraction satellite intensities, were in good agreement with an extrapolation of existing high temperature data obtained with conventional diffusion specimens. The effective diffusion coefficient \( D_b \) at 400 °C as a function of the dispersion relation \( B^2(h) \) showed a minimum, in contrast with the behavior of several other systems investigated so far. A new formulation of \( D_b \) in powers of \( B^2 \) was developed and six interatomic potentials were calculated from short range order parameters which yielded a minimum in \( D_b \) at approximately 1.6 nm as was observed experimentally. Screening singularities showed up in the \( D_b - B^2 \) by the appearance of a sharp peak at a wavelength 2.5 nm.

Introduction. — According to the linearized treatment of diffusion the amplitude, \( A(t) \), of a composition modulation defined by the wavevector :

\[
k = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3,
\]

will vary with time, \( t \), according to :

\[
A(t) = A(0) \exp[-\alpha(h) t],
\]

(1)

where \( \alpha(h) \) is an amplification factor defined by :

\[
\alpha(h) = B^2(h) \bar{D}_b,
\]

(2)

in which \( B^2(h) \) is the dispersion relationship :

\[
B^2(h) = \frac{1}{a^2} \sum_{\mathbf{r}} \left[ 1 - \cos \mathbf{k}(h).\mathbf{x}(\mathbf{r}) \right],
\]

(3)

in which \( a \) is the lattice parameter and the summation is over the nearest neighbor sites to the origin. The quantity \( \bar{D}_b \) is an interdiffusion coefficient which, in a derivation to be published elsewhere, can be related to the diffusion coefficient, \( D \), measured in a macroscopic couple by :

\[
\bar{D}_b = \bar{D} \left[ 1 + \omega + (2f^\prime) \sum_{m=1}^\infty K_m B^{2m}(h) \right],
\]

(4)

where \( f^\prime \) is the second derivative with respect to composition of the Helmholtz free energy per unit volume, \( \omega \) is a coherency strain term [1] which depends on the elastic constants and the variation of lattice parameter with composition and the \( K \)'s are gradient-energy coefficients. Eq. (4) is a generalization of an expression [2] which included only the first term in the summation and this, in turn, was a generalization of a continuum model developed by Cahn [1] that is valid for the limit \( B^2(h) \rightarrow 0 \). Expressions for the \( K \)'s in terms of the interatomic potentials have been derived for the [111] and [100] directions in a f.c.c. lattice.

Experimental procedure and results. — Composition modulated Cu-Ni foils were prepared by co-evaporating the two components through a rotating
pinwheel shutter onto a mica substrate; details of the technique have been given elsewhere [3]. The foils had a strong [111] texture and the modulations were coherent. The wavelength (0.8-5 nm) and amplitude of the modulations were determined from the location and intensity \( I \) of the satellites about the 111 Bragg peak. The diffusivity \( D_B \) was estimated from the terminal slope of a plot of \( \ln \left( \frac{I(t)}{I(0)} \right) \) versus isothermal annealing time.

The variation of \( D_B \) with \( B^2(h) \) is shown in figure 1. It will be noted that the dependence is strongly non-linear indicating that the higher-order terms in Eq. (4) are significant. We believe that the strong peak at a wavelength of \( \sim 2.5 \) nm is not due to the gradient-energy coefficients but instead is a result of a large increase in the elastic modulus that we have observed (and will be reporting elsewhere) in composition modulated Cu-Ni foils having wavelengths \( \lessapprox 2.5 \) nm. The increase in the modulus increases the coherency-strain term \( \omega \) in Eq. (4) and hence the value of \( D_B \). An increase in elastic modulus has also been observed [4] in Au-Ni and Cu-Pd composition modulated foils and we believe that the effect is due to change in the band structure resulting from the introduction of a new Brillouin zone.

As previously noted, the \( K \)'s can be related to the interatomic potentials. The first six of these were calculated from short-range order parameters determined by Vrijen, van Dijk and Radelaar [5]. The values derived for \( K_1, K_2 \) and \( K_3 \) agreed with the observed ones in respect to sign but were smaller by approximately an order of magnitude. There was a corresponding discrepancy in the values of \( D_B \) calculated from Eq. (4) but they did exhibit a minimum at about the same wavelength as the experimental values plotted in figure 1. The differences between the observed and calculated quantities are probably due to the omission of higher-order interatomic potentials since these are heavily weighted in the expressions for the \( K \)'s.

The results described here for the Cu-Ni system differ from those so far observed in other systems in two respects, both of which are related to the long-range interactions in Cu-Ni. First, in all systems so far studied \( K_1 \) has the same sign as the heat of mixing whereas in Cu-Ni it is of opposite sign. Secondly, in measurements of \( D_B \) in Au-Ag [3] and Cu-Pd [6] composition modulated foils the data could be adequately fitted using only the first term of the summation in Eq. (4).

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Fig. 1. — Diffusivities \( D_B \) versus \( B^2 \) for 50 at. pct. Cu-Ni foils at 400 °C.

References