CLUSTERING EFFECTS IN Cu-Ni

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While concentrated Cu-Ni alloys show local correlations characteristic of clustering, it is re-emphasized, in light of the recent claim of Kidron, that normal solution heat treatment of them (which includes nearly any cooling procedure) yields a small deviation from randomness of the atomic arrangements and no Guinier-zone formation or phase separation.

We question here the conclusions of Kidron who in his recent article[1] refutes via x-ray arguments the assertion of Seib and Spicer[2] (SS) that their optical studies were performed on essentially random samples. It is important not only because of Kidron's claim that the rigid-band model may be valid in Cu-Ni alloys if SS are very wrong about the clustering in their specimens, but also because he raises the issue of cluster formation in Cu-Ni and presents evidence purporting to demonstrate the presence of large distinct clusters of Ni atoms. These clusters, should they exist, would be extremely important in the interpretation of electrical and magnetic effects as well as optical properties. But SS estimated their clustering from the neutron results of Mozer, Keating, and Moss[3] and we shall briefly show that Kidron's analysis is probably unrelated to the conclusions of that work (and of the more recent study by Hicks et al.[4]).

Kidron claims that the analysis of the neutron scattering tells us nothing about the actual atomic configurations in the alloy, and he uses a Rudman-Averbach result on Al-Ag[5] as an example. He suggests that the first-neighbor correlation parameter ($\alpha_1 = 0.15$) in an Al-10at.% Ag alloy does not conflict with the low-angle x-ray data on preprecipitation in Al-Ag alloys.[6] But the latter data were collected on samples, quenched from a single-phase field, which had begun phase separation—Guinier-zone formation—into distinct Ag-rich clusters, and it is these clusters that are responsible for the small-angle x-ray scattering photographs that show halos. The halos are just the appearance of a low-angle maximum, not at $k = 0$ (θ_m of Kidron), and they cannot appear with a sample in single-phase equilibrium above a phase-separation temperature. They are due in dilute alloys either to interparticle interference effects or to a distinct composition profile across the interface of the preprecipitation phase. The Rudman-Averbach data were taken at 540°C, above the phase boundary, and have nothing to do with halos or zones.

In Cu-Ni, as has been discussed in detail,[3] the diffusion is so sluggish that almost any simple cooling procedure—after the usual high-temperature solution heat treatment—will trap in the atomic arrangements characteristic of around 500°C. The results of Ref. 3 did, however, enable us to calculate a critical temperature for phase separation—the spinodal maximum—and this is around 300°C; so $T_c/T \simeq 0.73$. It thus seems that Kidron has perhaps pinned down this critical temperature for Cu-Ni. By annealing his sample for 50 h at 300°C he has apparently achieved the beginnings of spinodal decomposition. We might, however, quarrel with his interpretation of his Fig. 1 in terms of Guinier-zone formation because in concentrated alloys it is difficult to conceive of a distinct precipitate and matrix phase. We prefer the spinodal interpretation not just because it is aesthetically more satisfying, but also because it is the thermodynamically correct one.[7] It is difficult to assess the extent of the decomposition, but from the position of θ_m in Kidron's Fig. 1 it might be supposed that the predominant wavelength $\lambda_m = 2\pi/S_m$ in the fluctuating composition profile—Au-rich, Ni-rich, Au-rich, etc.—was about 30 Å. In order to estimate the amplitude of composition excursion from the mean that accompanies the above fluctuation, one needs a bit better data.

The analysis so far seems reasonable enough—namely that SS were perfectly justified in assigning only a small deviation from randomness to their samples. If their conclusions about the rigid-band model depended upon this assignment, then they were certainly all right on that score. It would also appear as if Kidron has measured the scattering from a sample held long enough below T_c to have diffused sufficiently to form 30-Å composition fluctuations. We mentioned earlier, however, that diffusion is very sluggish in Cu-Ni. In fact, using the relation $L(\mathrm{cm}) \cong (Dt)^{1/2}$, where t is in sec and D is the usual diffusion co-

efficient quoted in Ref. 3, at 600°C for $L = 10^{-7}$ cm (10 Å), $t = 1$-2 sec, while at 300°C in order to diffuse 10 Å we require a time of between 10^4 and 10^6 h, or substantially longer than the 50-h anneal of Kidron. It is likely, therefore, that Kidron's samples were rapidly quenched and contained a high enough supersaturation of vacancies to enhance sufficiently the diffusion at 300°C. It would be very interesting to perform x-ray or neutron experiments on samples heat treated and quenched in various ways to elucidate this point or to detect possibly anomalous diffusion behavior near T_c. A similar effect was also noted by Woodilla and Averbach in their electron diffraction study of phase separation in Au-Ni.[8] Rapidly quenched and annealed foils showed sidebands within the spinodal, but when these same foils were then annealed above the spinodal and the modulated structure was dissolved, subsequent annealings below T_c would never bring it out again. The excess quenched-in vacancies were needed to assist the phase separation and once they had been used up, normal diffusion times were too long—a phenomenon that is apparently quite general in aging and reversion cycles.

We should also note that, while the measured clustering in $Cu_{0.52}Ni_{0.48}$ appears mainly confined to nearest neighbors, even in a random alloy of that composition an average of 9-10 atom regions of pure Ni will exist by definition.[9] In addition, the results of a computer analysis of the short-range order parameters of Ref. 3 by Cohen and co-workers[9] indicate that larger planarlike regions of pure Ni may exist and that, in any case, more detailed information on the atomic arrangements is possible than a mere glance at the measured correlations would indicate.[10] Those results, interesting in themselves, are not, however, related to Kidron's work. They are an interpretation of the correlation functions derived from scattering curves from an alloy well above its T_c, where no low-angle maximum was observed save at $k = 0$.

The Kidron conclusion still would seem insupportable both because any normally cooled sample will show a nuclear scattering profile (or x-ray pattern) characteristic of $T_c/T \simeq 0.75$ and because it is difficult to imagine a simple heat treatment of Cu-Ni that would yield his intensity profile. Thus, if Cu-Ni alloy data (electronic specific heat, magnetization, susceptibility and magnetic scattering, resistivity, optical properties, etc.) are to be understood in terms of a small-cluster theory of the disordered state, the Kidron data probably ought not to be invoked. In samples specially treated to enhance the clustering tendency (rapid quenching or irradiation followed by a long anneal below T_c) there will be property changes directly attributable to the clusters. Otherwise, we would here merely suggest caution in the interpretation of extraordinary behavior, such as the low-angle magnetic-scattering curves of Hicks et al. (and their composition dependence), in terms of the local atomci configurations and distinct cluster formation.

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[4]T. J. Hicks, B. Rainford, J. S. Kouvel, G. G. Low, and J. B. Comly, Phys. Rev. Letters 22, 531 (1969).

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[7]See, especially, K. B. Rundman and J. E. Hilliard, Acta Met. 15, 1025 (1967) in which a small-angle x-ray scattering study in the Al-Zn system verified all of the predictions of J. W. Cahn's spinodal theory.

[8]J. E. Woodilla, Jr., and B. L. Averbach, Acta Met. 16, 255 (1968).

[9]J. B. Cohen, "A Brief Review of the Properties of Ordered Alloys" (to be published). See also his article in "Phase Transformations" (American Society for Metals, Cleveland, Ohio, to be published).

[10]This tendency of Cu-Ni to form two-dimensional clusters, even above T_c, has been confirmed in independent calculations by P. C. Clapp (private communication).