Photoemission electron microscopy: application to an order/disorder reaction

It was in the mid-thirties that Brüche demonstrated the use of a photoemission electron microscope (PEEM) as a possible tool for scientific research. But only after considerable modifications had been incorporated by Wegmann and his co-workers [1] was the PEEM first used as a metallurgical microscope. Very briefly, the mode of operation of the instrument relies on the fact that electrons are emitted from a specimen surface when the latter is bathed in ultraviolet light, i.e. bombarded with photons. The electrons so generated are accelerated to about 40 kV and then imaged by conventional electron optics onto a fluorescent screen or a photographic plate. The resultant resolution is of the order of a 200 Å at room temperature with a slight deterioration at higher temperatures. The number of electrons emitted from the sample, which depends on the value of the work-function of the area under investigation, governs the degree of contrast in the image. Factors such as differences in orientation between neighbouring regions, composition fluctuations and topographic variations all affect the degree of electron emission and hence the contrast. The technique has been made even more attractive by incorporating a hot stage, which has enabled a number of studies of recrystallization phenomena and phase transformations to be undertaken. A Metioscope model KE3, manufactured by Balzers, was used in the investigation.

The present investigation is also to be included under the category of phase transformations, more specifically within the realm of order/disorder reactions. We believe this to be the first study of superlattice formation using PEEM. The alloy used was equiatomic CuAu which possesses a disordered fcc structure above 410°C. Below this temperature the two atom species arrange themselves on separate sublattices in a non-cubic superlattice. Between 410 and 383°C, a "long-period" orthorhombic ordered arrangement (CuAu II) exists, succeeded below 383°C (T_c) by an ordered tetragonal cell (CuAu I).

When held at 450°C, the sample's surface was quite featureless, except for the imaging of grain-boundaries. However, upon lowering the temperature to 425°C some slight surface rippling was observed (Fig. 1). This was attributed to the formation of short-range ordered configurations within the specimen. The temperature was then dropped further and held steady at 350°C (± 5°C). After 1 min at 350°C (and a total of about 3 min below T_c), the first signs of long-range order formation were visible. Regions of differing contrast, domains, were

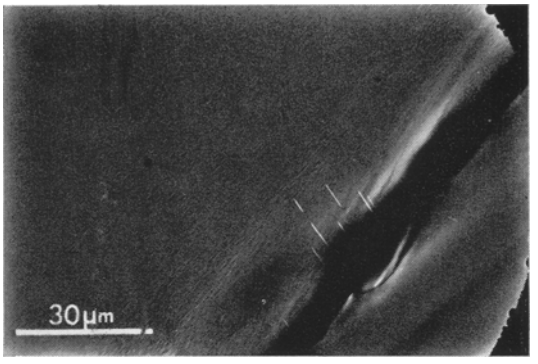

Figure 1 Short-range order at 425°C.

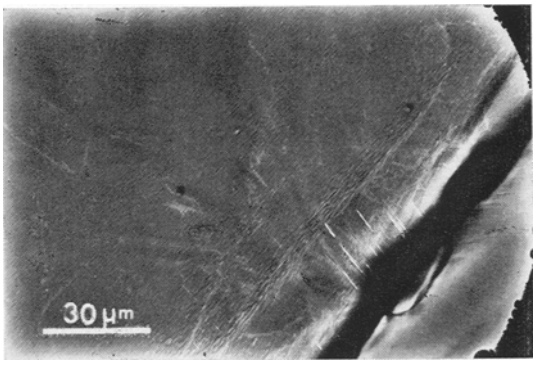

Figure 2 Long-range order, domain contrast after 1 min at 350°C.

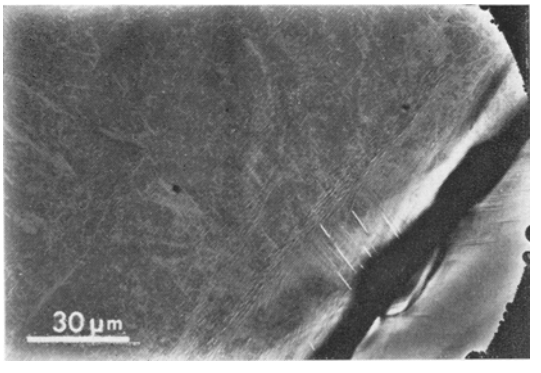

Figure 3 Commencement of microtwinning after 3 min at 350°C.

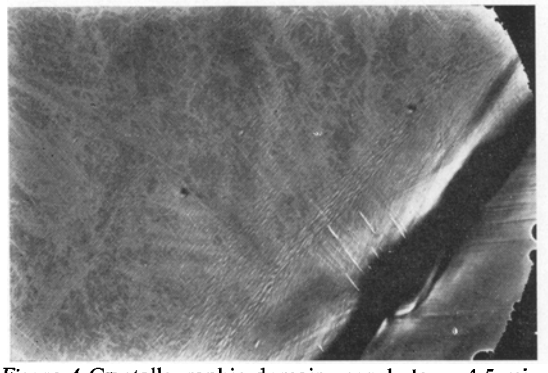

Figure 4 Crystallographic domain morphology, 4.5 min at 350°C.

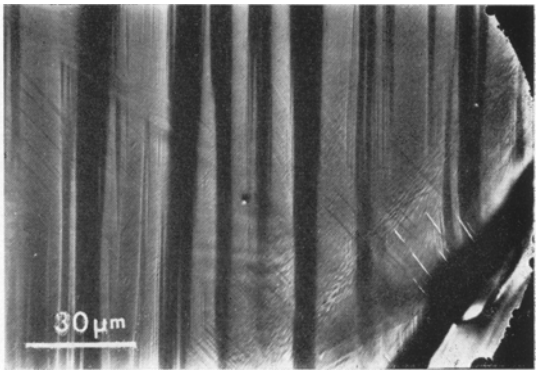

Figure 7 Coarsening of twins, 45 min at 350°C.

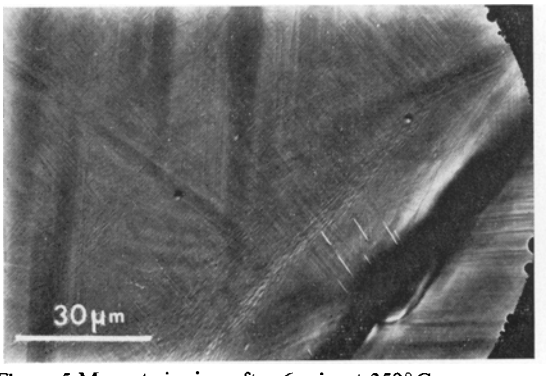

Figure 5 Macrotwinning after 6 min at 350°C.

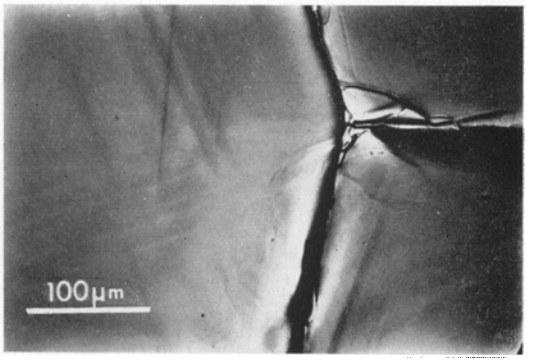

Figure 8 Temperature increased from 350 to 450°C (cf. Fig. 9).

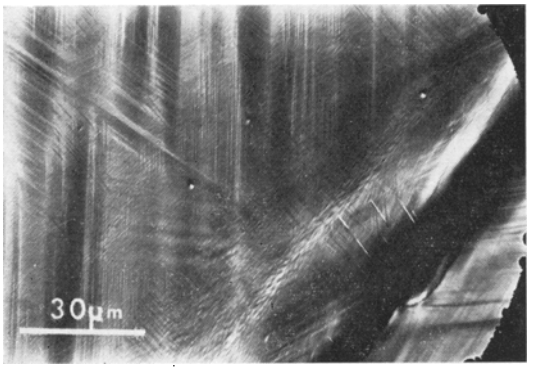

Figure 6 Formation of "order-twins", 12 min at 350°C.

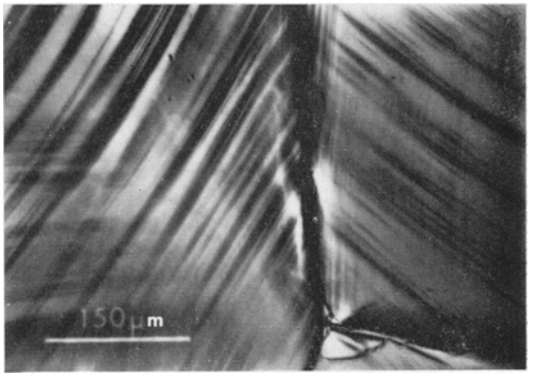

Figure 9 As in Fig. 7 but same area as Fig. 8.

imaged; they were randomly scattered throughout the sample but were predominant in the vicinity of grain-boundaries (Fig. 2). After a total of 3 min at 350°C, the volume fraction of the domains had increased and the domains began to show crystallographic features: in Fig. 3 the domain configuration is best described in terms of microtwinning. Such microtwinning has been documented in a previous electron microscopy study [2] and is necessary to reduce local stresses which are generated in the matrix, on account of the differences in lattice parameters between the ordered and disordered lattices. Furthermore, the discrete manner in which the domains were seen to form in a matrix of

apparently disordered alloy, provided evidence for a *Gibbsian Type I* reaction for the ordering in Cu Au. The significance of such a transformation in the field of disorder → order reactions has been fully documented elsewhere [3], and the present observations support this viewpoint; the growth of ordered domains in a predominantly disordered matrix is clearly visible. This implies a transient two-phase (ordered + disordered) structure during annealing, a fact already established by TEM in a number of superstructures [4, 5]. Domain shape anisotropy is emphasized after 4.5 min at 350° C (Fig. 4), while in Fig. 5 (6 min at 350° C) we can see the commencement of macrotwinning. The final stages of the isothermal reaction consist of coarsening the macrotwins already formed (Figs. 6 and 7), If the sample's temperature is raised to 450° C, i.e. well above the upper critical temperature, then most of the contrast instantaneously disappears as the temperature passes through 385° C. Although Fig. 8 shows some faint signs of contrast, this is due to irreversible surface relief, referred to above, and is not anything associated with residual order. Such a drastic (discontinuous) change in the sample's morphology as it traverses through T_c is a strong qualitative indicator of a first-order transformation. (A "first-order transformation" is a thermodynamic concept and is not to be confused with a "type I transformation" which refers to a particular kind of mechanism). For comparison, the appearance of the same area as in Fig. 8, before raising the sample's temperature from 350 to 450° C, is shown in Fig. 9.

Hence, the PEEM has proved to be a useful technique in providing qualitative morphological data in following the order/disorder transition in CuAu. The approach has provided us with strong evidence of a nucleation and growth (type I) mechanism as a superlattice forms in CuAu and also indicated that the disordering transformation at T_c is a first-order one. The unique feature of these observations is the fact that changes in morphology of a particular field could be followed as they were taking place. This cannot normally be achieved by either optical microscopy (insufficient resolution in the early stages) or TEM (too small a field of view). However, the PEEM is about 30 times more expensive than a high quality optical microscope, and so the improved performance is dearly bought.

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Correction for the effect of electron beam heating on Kossel pattern lattice spacing results

One of the chief uses of the Kossel diffraction technique has been the precise determination of lattice parameters. Since, however, the technique requires the specimen to be directly bombarded with electrons there is a heating effect which results in a systematic error in the calculated parameter. Heise [1] not taking this into account obtained an erroneous result for the lattice parameter of nickel, and other workers [2] underestimating the heating effect obtained a similar value. These results did not agree with those calculated from X-ray diffractometer measurements [3]. Mackay [4], using the pseudo-Kossel technique in which the X-ray