STRUCTURE OF ORDERED ALLOYS *

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ABSTRACT

Our recent progress in studying ordered alloys by lattice fringe imaging is reviewed. Firstly the optimum experimental conditions for producing images suitable for interpretation are outlined. Secondly lattice and conventional imaging are compared and the advantages of the former for obtaining atomic level detail and compositional estimates are described. Finally some important results from this program are discussed, particularly the evidence for a micro-domain model of short-range order and the fine structure of various ordered lattice defects.

I. INTRODUCTION

At the time of a previous review on the structure of short-range order (SRO) in alloys (1), the stage had been reached where conventional transmission electron microscopy (TEM) experiments had been utilized to their limit. These particularly involved analysis of diffuse scattering phenomena in electron diffraction patterns, and dark field images taken from diffuse superlattice reflections. Unfortunately, as was pointed out in ref. 1, the interpretation of these data is not always unambiguous. Thus diffuse scattering may arise from the presence of ordered microdomains (2,3) or from Fermi surface effects (4). Small ($\sim 10 \text{ \AA}$) bright spots in dark field micrographs may be due to statistical fluctuations (5) rather than microdomains. It appeared that little further progress would be made by these techniques. Consequently the advent of TEM's with the capability of $2 \text{ \AA}$ line resolution led the present authors to undertake an investigation into the application of high resolution methods in the study of ordering. This article reviews our work in this area utilizing lattice imaging.

II. EXPERIMENTAL APPROACH

The interpretation of lattice images is not straightforward. Similarly the conditions under which the images are best obtained are critically dependent on a number of experimental variables. Our approach to these problems was therefore guided by computer simulated images, using the dynamical theory of electron diffraction (6), to predict the optimum conditions for imaging and the metallurgical information (e.g. degree of order) which can be obtained. Both specimen and microscope parameters are important, particularly specimen thickness and orientation, the beams used to form the image and the value of the objective lens defocus.

For example, to image the (001) B19 superlattice in Mg_3Cd , foils should be $\sim 140\text{--}260 \text{ \AA}$ thick, using (000), (001) and (002) reflections in image formation, with $s_{002} = 0$, tilted illumination and an objective lens under-focus of $280 \text{ \AA}$ (7).

Whenever feasible, superlattice and fundamental reflections are employed simultaneously in image formation. This gives the greatest sensitivity to the variation of fringe visibility with degree of order and also ensures that ordered and disordered regions both appear in the image. However, in this situation (e.g. fig. 1) the superlattice fringe profile shows a cyclical behavior with defocus (Δf). At some objective lens settings (e.g. $\Delta f = -140 \text{ \AA}$ in fig. 1) the predominant electron wave interactions occur between transmitted and fundamental beams whereas at other values (e.g. $\Delta f = -280 \text{ \AA}$ in fig. 1) the predominant interactions are between transmitted and superlattice beams. Thus a fundamental fringe profile may be obtained from an ordered lattice at certain defocus, whilst at others the optimum conditions are met for observing the superlattice. This indicates the importance both of taking a complete through-focal series of micrographs and of a thorough understanding of the image formation process before appropriate use may be made of the images.

The superlattice fringe profile is a function of degree of order (S) but is not a monotonically varying one. In Cu_3Au superlattice fringe visibility is low up to $S \sim 0.25$, increases rapidly up to $S \sim 0.5$ but shows little variation thereafter (6). This means that the fringe imaging method can primarily detect the difference between disordered and well-ordered regions, can give a fairly accurate value of S below $S \sim 0.5$ but does not show a sufficiently sensitive variation to describe degree of order over

the complete order-disorder range. It must also be borne in mind that since specimen thickness and lens defocus are difficult to quantify to great precision, accurate absolute values for S do not appear possible. Thus to obtain detailed information directly about atomic arrangements in alloys, atomic resolution TEM must be awaited, which requires further advances in instrumentation.

For a complete description of the structure of ordered alloys further desirable information concerns localized variations in composition (particularly the effects of non-stoichiometry) and the nature of lattice defects. The former can be analysed from the fringe spacing (8). This allows determination of local composition at non-conservative antiphase boundaries (8,9) and fine-scale segregation which may result from competing transformation processes such as spinodal decomposition (as occurs in Cu-Mn-Al alloys (10)). Lattice defects and their importance to the ordering reaction can be studied at the atomic plane level from their effect on the lattice fringes.

Finally our analysis is completed by taking optical diffraction patterns from the lattice image (11). These serve several purposes. Firstly, if the image is a faithful representation of the specimen lattice then the optical pattern will be geometrically identical to the original electron diffraction pattern of the specimen. Such patterns are used to assess how the image can be employed to give information about the specimen. Secondly the optical method is a microdiffraction tool since the selecting aperture size, when converted back to the specimen plane by the micrograph magnification, becomes extremely small (11). Patterns from $10 \text{ \AA}$ dia. areas are possible and these can be used to build up the component parts of a microdiffraction pattern (which, as indicated earlier, may be ambiguous).

Thirdly the method can provide average information in localized regions of the image and this has proved particularly useful in analysing fringe spacing variations in spinodal alloys (12,13).

III. COMPARISON WITH CONVENTIONAL TEM

3.1 Applicability of Dark Field Imaging

Although Cowley has pointed out that bright spots in dark field images of diffuse scattering need careful interpretation (5) the compatibility of dark field and lattice images has not undergone investigation. Figure 2 shows such a comparison. It can be seen that the areas exhibiting superlattice spacing ($5.4 \text{ \AA}$) correspond exactly to the light contrast areas in the conventional superlattice dark field micrograph, even when very small features are involved. Thus the same regions are indicated to be ordered by both techniques, an observation made in several systems (e.g. 7.9). It can be concluded that in many circumstances dark field imaging can in fact be used with confidence to reveal ordered regions, although the information it contains is somewhat limited (see below). On the other hand, the lattice fringe visibility of small ordered domains depends on their position in the foil, and thus an exact correspondence as above may not always be achieved (6).

3.2 Information from Lattice Images

Conventional electron microscopy methods, including even the critical voltage effect in high voltage TEM (14), have their limitations when applied to ordered systems. It has been found that lattice imaging provides several important improvements for obtaining atomic level information, which are summarized below.

- 1) Local variations in degree of order can be detected by variations in fringe profile. Conventional superlattice dark field images reveal

ordered regions as bright, disordered as dark, and it is impossible to assess whether the structure is intermediate between these extremes. Thus the order-disorder interface in Mg_3Cd was found to possess a degree of order profile over at least $25 \text{ \AA}$ (7).

ii) The presence or absence of ordered microdomains in SkO alloys may not always be demonstrated by dark field microscopy alone. In lattice images regions with the superlattice structure can only arise if a high degree of order is present, thus providing unequivocal evidence of ordered microdomains (e.g. 9,15).

iii) The images of lattice defects in conventional bright and dark field micrographs are considerably wider than their true width. For example translational antiphase boundaries (APB's) in Ni_4Mo and Cu_3Au appear to be $20 \text{ \AA}$ and $50 \text{ \AA}$ wide respectively in dark field (8,16,17) whereas lattice imaging shows them as having atomic dimensions only (8,15,16). This advantage is emphasized in section IV.

iv) Compositional information can be derived from the fringe spacings, the resolution being determined by the degree of segregation and the variation of interplanar spacing with composition (8). In favorable circumstances such as at non-conservative APB's, individual plane resolution may be achieved. Of course conventional images and diffraction patterns yield no data on localized composition.

v) The direct measurement of lattice strain is possible from lattice images so long as appropriate experimental conditions are met (e.g. $s = 0$, in a parallel faced flat foil region). Again this is impossible by conventional TEM. Strain often has an important effect on ordering reactions and subsequent microstructure (18). In partially ordered

alloys any variation in S (with its commensurate variation in d -spacing) may complicate the analysis (8).

Direct lattice resolution is clearly a powerful technique in examining the structure of ordered alloys, affording many advantages over conventional TEM. More recently the latter itself has become more versatile, through the use of scanning TEM modes. It is now possible to obtain electron microdiffraction patterns at about $30 \text{ \AA}$ resolution on a conventional TEM with scanning capability (19) and to perform chemical analyses with about several hundred $\text{\AA}$ resolution (20). (These compare with lattice image microdiffraction of $10 \text{ \AA}$ (11) and indirect chemical analysis over tens of $\text{\AA}$ (8)). Further electron optical developments through dedicated STEM instruments will continue to improve these capabilities and expand the ability to examine structure at high resolution.

IV. SUMMARY OF RESULTS

A wide range of alloys has been investigated in this program (6-16), including Cu_3Au , CuAu , Ni_4Mo , Au_4Cr , Au_3Cr , NiTi and Mg_3Cd . A complete review would be impossible here and so only a few significant results are described.

IV. 1 Short-Range Order

The main conclusion from previous TEM work (1-3) is that the best description of SRO is in terms of a microdomain model, subject to the reservations discussed above. Lattice imaging has confirmed this interpretation in the particular case of two important binary alloys, Cu_3Au (15) and Au_4Cr (7). This model has advantages in theoretical descriptions of ordering (21).

In Cu_3Au , SRO is manifested by diffuse scattering at the superlattice positions in diffraction patterns. A series of at-temperature 650 kV electron diffraction patterns obtained in this study reproduced the behavior described previously (22,23). A notable feature is the exact intensity distribution, with elongation of $\{h00\}$ scattering (h odd) in $\langle 0h0 \rangle$ reciprocal lattice directions and an Maltese cross shape for $\{hk0\}$ scattering. Cu_3Au foils

quenched from above the critical ordering temperature (T_c) show the same features, except that the scattering is stronger than that at the temperature from which the specimen was quenched. For instance the pattern of a foil quenched from 400°C above T_c corresponds to an at-temperature pattern of about 40°C above T_c . Thus the SRO state is maintained but is characteristic of a temperature nearer T_c , which probably arises from atomic rearrangements during the quench. This is an important point as high resolution microscopy is, at present, limited to room temperature, and hence on quenched samples.

A lattice image of this material shows the presence of roughly equiaxed ordered regions 3-8 unit cells dia., possessing the superlattice periodicity (e.g. fig. 3). The size and distribution of these ordered domains is identical to those predicted from x-ray diffuse scattering analyses (23,24). However, in a previous analysis (15) it was not clear how the diffuse spot shape arose. A similar behavior in partially ordered Cu_3Au can be clearly correlated with a distribution of domain groups, with successive domains in antiphase (11,15). No such groups were found in the SRO state (15). More recently it has been appreciated that a single APB can create superlattice spot splitting (25). The degree to which this occurs varies inversely with the diffracting aperture size for an APB in a fully ordered structure, or as the domain size in an alloy possessing small isolated domains. The proportion of the ordered domains seen in the lattice image to possess APB's (15) is sufficient to produce the observed elongation of the diffuse scattering. This is further confirmed by the shape of superlattice scattering in the optical diffraction pattern from the lattice image (fig. 3).

Au_4Cr , like Ni_4Mo , shows $\{1\frac{1}{2}0\}$ type diffuse scattering. This is not a position of the superlattice reflections, the interpretation of which has resulted in some controversy (1-3, 26). Ordered domains

appear in the lattice images, 10-15 Å dia., with a faint $\{1\frac{1}{2}\}$ superlattice fringe profile (9). It is concluded that microdomains, similar to those predicted by Okamoto and Thomas (2); do indeed exist in this system and, since many other alloys show a similar behavior (1), that they probably occur elsewhere also. Such domains now have a theoretical basis, through a spinodal-ordering model (21). However, the determination of the exact composition profile in the domains (2,21) requires resolution of the (420) fcc lattice planes (0.8 Å spacing) which is extremely difficult to achieve with current instrumentation.

IV.2 Fine Structure of Lattice Defects

As indicated in section III, considerably more structural detail can be perceived about defects in ordered alloys from the lattice imaging method. Some quite fundamental information has thus been obtained.

Figure 4 compares translations APB's in Cu_3Au and Mg_3Cd . The conventional TEM images indicate that both are flat and appear on particular crystallographic planes. However, their fine structure is quite different. In Mg_3Cd the APB is virtually flat at an atomic level but contains small discrete interface steps (7). In Cu_3Au there is considerable roughness on a scale of 5-10 Å, which is not resolved conventionally (6). APB's in Ni_4Mo and Au_4Cr appear to be smooth and curved (8,9). In all cases the lattice fringe visibility is constant right up to the defect, indicating there is little variation in degree of order in their vicinity.

Similar structural details can be obtained for rotational domain boundaries. In CuAu it had long been predicted (27) that the rotational domain variants would form the lowest strain energy configuration by producing boundaries on {101} planes. Although this idea has been confirmed by conventional TEM (27), lattice imaging reveals that the interface is not

so simple and in fact resembles a "staircase" arrangement. Thus instead of a perfectly flat $\{101\}$ type interface, the boundary is composed of small $\{100\}$ steps, often one, two and occasionally three (001) spacings in height (fig. 5). On the other hand the rotational domain boundaries in Mg_3Cd are predominantly flat at an atomic level (7). Individual unit cell high steps occur in these boundaries (e.g. fig. 6) rather than the regular arrangement in CuAu . The order-disorder interface in Mg_3Cd is also found to contain steps and it is thought that these observations indicate a ledge mechanism for both ordering and domain growth in this system (7). Corresponding boundaries in Au_4Cr are smoothly curved (9) and so a different mechanism is responsible here.

The lattice image of dislocations must be interpreted with caution (28) but nevertheless some interesting observations have still been made. The APB, which separates the dislocations comprising a superdislocation in Cu_3Au , has been imaged and its width found to be consistent with that obtained by conventional TEM observations (6). Dislocations in an order-disorder interface, necessary to accommodate the lattice contraction on ordering, have also been detected and shown to possess a Burger's vector equal to a fundamental lattice vector (7).

V. SUMMARY

Our recent work on lattice imaging of ordered alloys has been reviewed, with examples chosen from a range of systems. For studying fine-scale structure, this technique has been shown to be considerably superior to the conventional TEM approach, particularly in the areas of short range order and the detailed structure of ordered lattice defects. The lattice image has its own limitations, not least because the information is obtained

about one set of lattice planes only. It is expected that when atomic resolution TEM's become available, further diversification of high resolution methods will occur. Thus the study of ordering should benefit considerably both from these and the new scanning TEM methods. An area needing considerable improvement is high resolution ($20 \text{ \AA}$ spatial) spectroscopy in order to obtain composition directly. In the meantime estimates of composition for suitable solutes can be obtained by combining lattice imaging with optical microdiffraction (8,13) so as to obtain localized "d" spacings ($10\text{-}20 \text{ \AA}$ areas).

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REFERENCES

1. DAS, S.K., and THOMAS, G., "Order-Disorder Transformations in Alloys", edited by H. Warlimont, Springer (Berlin) p.332 (1974).
2. OKAMOTO, P.R., and THOMAS, G., Acta Met., 19 (1971) 825.
3. DAS, S.K., OKAMOTO, P.R., FISHER, P.M.J., and THOMAS, G., Acta Met., 21, (1973), 913.
4. MOSS, S.C., Phys. Rev. Lett., 22, (1969) 1108.
5. COWLEY, J.M., Acta Cryst. A29, (1973) 527.
6. SINCLAIR, R., SCHNEIDER, K., and THOMAS, G., Acta Met., 23 (1975) 873.
7. SINCLAIR, R., and DUTKIEWICZ, J., Acta Met., 25, (1977) 235.
8. SINCLAIR, R., and THOMAS, G., Met. Trans. submitted for publication.
9. DUTKIEWICZ, J., and THOMAS, G., Met. Trans., 6A (1975) 1919.
10. GRONSKY, R., OKADA, M., SINCLAIR, R., and THOMAS, G., Proc. 33rd Ann. Conf. EMSA, edited by G. W. Bailey, Claitor's, Baton Rouge, p 22 (1975).

11. SINCLAIR, R., GRONSKY, R., and THOMAS, G., Acta Met., 24 (1976) 789.
12. THOMAS, G., SINCLAIR, R., and GRONSKY, R., Proc. 6th Europ Congr. on Electron Microscopy, Jerusalem, 1, (1976) 114.
13. WU, C.K., SINCLAIR, R., and THOMAS, G., Met. Trans. submitted for publication.
14. SINCLAIR, R., CORINGE, M.J., and THOMAS, G., Phil. Mag., 32 (1975) 501.
15. SINCLAIR, R., and THOMAS, G., J. Appl. Cryst., 8 (1975) 206.
16. SINCLAIR, R., and DUTKIEWICZ, J., Proc. 33rd Ann. Conf. EMSA, edited by G. W. Bailey, Claitor's, Baton Rouge, p. 10 (1975).
17. MORRIS, D. G., BESAG, F.M.C. and SMALLMAN, R. E., Phil. Mag., 29 (1974) 43.
18. TANNER, L.E. and LEAMY, H.J., "Order-Disorder Transformations in Alloys", edited by H. Warlimont, Springer (Berlin) p. 180 (1974).
19. GEISS, R. H., Appl. Phys. Lett. 27 (1975) 174.
20. MAHER, D.M., and JOY, D.C., J. Metals, 29 (2), (1977) 26.
21. DE FONTAINE, D., Acta Met., 23 (1975), 553.
22. HASHIMOTO, S., and OGAWA, S., J. Phys. Soc. Japan, 29 (1970), 710.
23. HADHAM, P. and COHEN, J.B., Acta Cryst. A32 (1976) 597.
24. GEHLEN, P.C., and COHEN, J.B., Phys. Rev., A139 (1965) 844.
25. SINCLAIR, R., Trans. Amer. Cryst. Ass'n. 13, in press (1977).
26. CLAPP, P.C., and MOSS, S.C., Phys. Rev. 142 (1966) 418.
27. SATO, H., and TOTH, R.S., "Alloying Behavior in Concentrated Solid Solutions", edited by T. B. Massalski, Gordon and Breach, New York (1965) 295.
28. COCHAYNE, D.J.H., PARSONS, J.R., and HOELKE, C.W., Phil. Mag., 24 (1971) 139.

FIGURE CAPTIONS

Figure 1. The variation of $\{010\}$ lattice images with objective lens defocus in Mg_3Cd . The microdensitometer traces (b) from the areas marked on the image, and the computed fringe profiles (c) can be seen to be in excellent agreement.

Figure 2. A comparison of the lattice image (a) and superlattice dark field image (b) of partially ordered Mg_3Cd . Bright areas in the latter are ordered, and appear with superlattice periodicity in the former.

Figure 3. (a) A lattice image of short-range ordered Cu_3Au showing the presence of ordered microdomains. The electron diffraction pattern from the specimen (b) and optical diffraction pattern from the image (c) are similar.

Figure 4. Lattice images of translational antiphase boundaries in (a) Cu_3Au , (b) Mg_3Cd .

Figure 5. Lattice image of a rotational domain boundary in CuAu showing the fine staircase-type structure.

Figure 6. Lattice image of a rotational domain boundary in Mg_3Cd showing the presence of interface ledges.

Mg_3Cd (0, g, 2g)

XBB 752-1170

FIG. 1

FIG. 2a

XBB 777-7292

XBB 777-7295

FIG. 2b

XBB 777-7296

FIG. 3

XBB 777-7293

FIG. 4a

XBB 777-7290

FIG. 4b

XBB 777-7291

FIG. 5

XBB 777-7294

FIG. 6