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Publication Date

1975-07-01

Submitted to Acta Metallurgica

LBL-3970
Preprint c.1

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July 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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OPTICAL DIFFRACTION FROM LATTICE IMAGES OF ALLOYS

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ABSTRACT

Optical diffraction patterns have been obtained from optimum lattice images of partially ordered Cu_3Au and spinodally decomposed Au-Ni alloys. These diffraction results show excellent agreement with the corresponding portions of electron diffraction patterns, indicating that a direct correlation exists between the lattice images and the atomic lattices of the alloys studied. Compared to conventional 100kV selected area electron diffraction, the optical diffraction technique makes possible an outstanding improvement in field limitation, where the area contributing diffraction information may be reduced by over three orders of magnitude to $10\text{\AA}$ in diameter. A quantitative analysis of the spinodal and ordering transformations by combined lattice imaging and optical diffraction provides experimental detail on an extremely localized scale. The results are in agreement with conventional experimental results and modern theories of phase transformations and illustrate an exciting new approach to gaining information about localized atomic mechanisms of phase transformations in alloys.

1. INTRODUCTION

In establishing the atomic mechanism of phase transformations, it is essential to obtain reliable information at the highest resolution possible. The limitations of conventional bright and dark field transmission electron microscopy (TEM) in this respect are now well established, whereas the advantages of direct lattice imaging (1-3), under carefully controlled experimental conditions, have considerably broadened the application of TEM in this field.

Fringe images of lattice planes may be confidently interpreted when compared to profiles simulated using the standard theories of dynamical electron diffraction.^(2,4) It is also necessary to ascertain that the lattice image truly reflects the rearrangement of an atomic lattice during a phase transformation. The present paper describes an experimental method to accomplish this with regard to ordering and spinodal reactions. It involves the comparison of optical diffraction patterns obtained from lattice images, taken at optimum objective lens defocus, specimen thickness and orientation, with electron diffraction patterns derived directly from the specimen in the transmission electron microscope. Optical diffraction (from simulated atomic arrangements) has been used previously to aid interpretation of x-ray diffraction results⁽⁵⁾ and currently to complement high resolution electron micrographs, particularly of biological materials.⁽⁶⁾ However, this is the first attempt at deriving diffraction information from real space lattice images of metallurgical alloy systems.

A perfect crystal lattice image, formed by combining the transmitted and one diffracted electron beam, is a series of fringes parallel and of equal spacing to the relevant diffracting planes. Using

these periodic fringe images as an optical amplitude grating, a Fraunhofer optical diffraction pattern with uniformly spaced diffracted intensities⁽⁷⁾ is readily obtained. During a phase transformation (or near a lattice defect) distortions or imperfections in the crystal lattice may give rise to observable electron or x-ray diffraction effects. (A well-known example is the phenomenon of satellite spots around fundamental lattice reflections arising from the periodic redistribution of atomic species during spinodal decomposition). Thus, if lattice imaging is a reliable technique for studying fine-scale phenomena, the optical diffraction pattern from the image should also reproduce the essential features characteristic of the conventional electron diffraction pattern of the specimen, for those reflections used in the original image formation process. The application of this simple experiment is illustrated here for partially ordered Cu_3Au and a spinodally decomposed Au-Ni alloy.

A further advantage of this optical diffraction method is a drastic reduction in the area from which diffraction information can be selected. In the 100kV electron microscope, conventional selected area electron diffraction is limited by objective lens spherical aberration to a circular area having a minimum diameter of $\sim 2\mu\text{m}$.⁽⁸⁾ Optical diffraction from lattice images is not limited in this way. It will be shown how area selection down to $10\text{\AA}$ in diameter, or less, is possible, and the importance of this result will be discussed.

2. EXPERIMENTAL PROCEDURE

Lattice images and the corresponding electron diffraction patterns were taken using either a Philips EM 301 or a Siemens 102 transmission electron microscope. Specimen preparation techniques for Cu_3Au have

been described elsewhere (2). Homogenization of rolled Au-50wt%Ni (77 at %Ni) sheet was performed at 900°C followed by an iced brine quench in order to trap a high vacancy concentration and allow sufficient atomic diffusion at low temperatures. Aging at 150°C is known to give rise to satellite reflections in diffraction patterns⁽⁹⁾ and was consequently chosen for this study. Thin foils were prepared by jet-electropolishing in a heated cyanide electrolyte.

Optical diffraction patterns were obtained using a standard optical diffractometer (e.g. see Ref. 7) with a He-Ne laser illumination source. Electron micrograph negatives of the optimum lattice images, chosen from appropriate through-focal series, were directly mounted in the ray path at normal incidence, in the same manner as that for standard optical diffraction gratings. A variety of films (Polaroid PN55, Polaroid type 57 and Kodak EKTAPAN 4162) were used and compared in order to guarantee reliable photographic recording. Circular apertures with diameters in the range 5-15mm were employed to select regions of the lattice image negatives from which the diffraction patterns were taken. These correspond to a 100-300Å field limiting aperture at the specimen plane (micrograph magnification 500,000 times) where, by comparison, intermediate apertures in the electron microscope are typically 50μm (5×10^5 Å) in diameter. A 1mm aperture (20Å at 500,000 times magnification) was also employed to ascertain the minimum selected area possible by this technique.

A Joyce-Loebl MK III microdensitometer was used in the analysis of the Au-Ni spinodal alloy to establish satellite spacings and lattice fringe spacings. All scans were made directly on the appropriate

negatives. The accuracy of each individual fringe measurement was judged to be $\pm 0.1\text{\AA}$

As a standard for comparison, optical diffraction patterns were also taken from lattice images of evaporated Au films. The regularly spaced fringe profiles present on these negatives were used to evaluate any sources of experimental noise on the optical diffraction patterns and microdensitometer traces of the alloys studied.

3. RESULTS AND DISCUSSION

3.1 Pure Au

Figure 1 shows the (200) lattice fringes of an evaporated pure gold foil and its corresponding optical diffraction pattern. The diffraction spots are noticeably sharp with no subsidiary reflections. This and similar patterns taken from lattice images of other homogeneous materials establishes that no spurious optical diffraction effects were introduced by the experimental procedure.

3.2 Partially ordered Cu_3Au

A. Optical-electron diffraction comparison

During the early stages of the ordering reaction in Cu_3Au a characteristic splitting of the weak superlattice reflections occurs,⁽¹⁰⁾ the fundamental reflections remaining unaffected. The lattice imaging technique has recently confirmed directly that this effect arises from small ordered domains forming in groups with neighboring domains in antiphase.⁽¹¹⁾ Figure 2 shows a lattice image of this material in which disordered Cu_3Au has a regular fringe profile with spacing $1.9\text{\AA}$ (i.e. d_{200}) whereas in ordered domains alternate fringes are stronger and weaker corresponding to partitioning of Au atoms to alternate planes

($3.8\text{\AA}$ spacing) in the $L1_2$ structure.⁽²⁾ A group of several domains in antiphase can be resolved in Fig. 2. Details of the excellent correspondence between experimental and simulated fringe images in this situation have been described in full elsewhere (2).

Figure 3 compares the optical diffraction pattern from this image with the selected area electron diffraction pattern from the same part of the specimen. The two main features of the electron diffraction pattern are clearly illustrated in the optical pattern, viz., the presence of a weaker, more diffuse superlattice reflection and splitting of this reflection perpendicular to its reciprocal lattice vector. The degree of splitting varies inversely with the separation of the antiphase domains and in order to compare values from the two techniques a series of optical patterns was taken. Occasionally more than one pair of spots was found on the same pattern and this undoubtedly arises from the small number of domain groups in the statistical sample from which the data are derived. The analysis of the results is shown in Fig. 4 where it can be seen that the majority of split spots corresponds to domain separations in the range $20\text{--}30\text{\AA}$. From the average value of the splitting, the average domain separation was found to be $30 \pm 2\text{\AA}$, in exact agreement with the value of $29 \pm 3\text{\AA}$ obtained⁽¹¹⁾ from the electron diffraction pattern and of $26 \pm 3\text{\AA}$ determined directly from the lattice images.

B. High Resolution Optical Diffraction

The domain size in this alloy lends itself well to a test of the microdiffraction capability of the optical diffraction technique. Figure 5a shows the diffraction pattern obtained from a disordered region

possessing uniform $1.9\text{\AA}$ spacing fringes by suitably positioning the 1mm aperture (equivalent to $20\text{\AA}$ at the specimen plane). Only the fundamental (200) reflections are present. They are broader than those in Figure 3b owing to the finely restricted area from which diffraction is originating.

On moving the aperture onto a single ordered domain, superlattice (100) reflections appear (Figure 5b) in addition to the fundamental spots. No splitting is apparent as an individual domain is being examined. This result was easily reproduced elsewhere on the image, showing that routine $20\text{\AA}$ diffraction analysis is possible. Furthermore, this experiment demonstrates that the superlattice reflections in partially ordered Cu_3Au arise from the small ordered domains and not the disordered matrix, confirming that diffuse diffraction effects in short-range ordered alloys may be produced by microdomains. (12)

The series of rings about the central beam in Figs. 5a and 5b is the Fraunhofer diffraction pattern of the aperture itself and this introduces a practical limit on the minimum area from which it is possible to obtain diffraction information. It can be seen that the superlattice reflection in Fig. 5b (corresponding to $3.8\text{\AA}$ spacing fringes) overlaps with the outer aperture diffraction rings. Thus a reflection from $2\text{\AA}$ spacing fringes would be affected by the pattern from an aperture approximately half the size of the present one, setting the lower size limit to about $10\text{\AA}$ diameter for typical $2\text{\AA}$ alloy studies. Nevertheless, the gain over the conventional 100kV transmission electron diffraction minimum of $2\mu\text{m}$ is considerable (greater than three orders of magnitude) and is unsurpassed by any currently known x-ray, neutron or other non-

electron diffraction method. To the authors' knowledge the only technique reported to approach this limit is derived from a single-field condenser-objective lens rocking beam method in scanning transmission electron microscopy ($\leq 30\text{\AA}$)⁽¹³⁾. However, the advantage of the present technique is the ability to choose areas directly from the lattice image for which diffraction data is required.

The benefit of obtaining diffraction information from such very small areas should prove to be extremely useful. Many of the ambiguities and controversies concerning the interpretation of x-ray and electron diffraction patterns arise because an average is taken of many unit cells ($\sim 10^{18}$ for x-rays and $\sim 10^{12}$ for electrons). By the high resolution optical diffraction technique an individual feature of the image may be chosen and the diffraction effect associated with it can be identified. This is separate from the diffraction effects of other features in the image which may in their turn be examined. Thus the total diffraction pattern may be analysed in terms of its component parts. The example presented here has been for partially ordered Cu_3Au , but obviously the method is applicable to a wide range of transformation and defect phenomena. Thus direct lattice imaging and optical diffraction taken together is an extremely powerful and promising approach to studies of phase transformations in general.

3.3 Spinodally Decomposed Au-Ni.

The micrograph shown in Fig. 6 was taken from a specimen aged for 21 hours at 150°C . It displays both the fine lattice fringe periodicity of the (200) planes and the coarse variation in image contrast which is typical of a modulated microstructure imaged under two beam conditions.

Satellites are clearly visible about the (400) spot in the electron diffraction pattern (Fig. 7a) which records the tilted illumination imaging condition used to form this lattice image. The corresponding optical diffraction pattern (Fig. 7b) identically reproduces all essential diffraction effects, viz., the intense high angle and weak low angle satellites symmetrically positioned along $\langle 100 \rangle$ reciprocal lattice directions about (h00) fundamental lattice reflections. The different intensity of the two satellites is due to the asymmetrical (Ni-rich) alloy composition.

Direct measurements from micrographs similar to and including Fig. 6 yield an average composition wavelength (λ) of $31 \pm 5 \text{ \AA}$. Complementary analysis of satellite spacings reveals that the optical diffraction patterns are once again in excellent quantitative agreement. As determined from the electron diffraction patterns, $\lambda = 29 \pm 3 \text{ \AA}$, whilst from the optical diffraction patterns, $\lambda = 29 \pm 2 \text{ \AA}$.

A smoothed plot of fringe spacing, as measured from the microdensitometer analysis against distance normal to a reference fringe, is presented in Fig. 8; each point n ($n = 1, 2, 3, \dots$) represents the average of raw data points n to $(n + 4)$. This figure gives direct evidence that the origin of satellites in the optical diffraction patterns is due to a periodic variation in fringe spacing. It was further established that satellites were absent about (000) in the optical patterns by taking a series of photographs using short exposure times to determine the intensity profile near the intense transmitted beam. This indicates that any contribution from a variation in fringe intensity (e.g. see Fig. 6) is negligible, and that the satellites therefore arise from the

the lattice spacing modulation. The periodicity of the modulation from this analysis, averaged over 12 wavelengths, is $29 \pm 8\text{\AA}$, also in excellent agreement with the diffraction data.

This type of plot may be utilised to establish the local composition profiles produced during a phase transformation, once the relationship between the interplanar spacing and alloy composition is known. In the present case a continuous composition variation, characteristic of a spinodal reaction⁽¹⁴⁾, is clearly illustrated. In some regions, however, the modulation amplitude is greater than the maximum possible from the equilibrium phase compositions, the reasons for which are currently being further investigated.

4. SUMMARY AND CONCLUSIONS

1. Optical diffraction patterns from lattice images of partially ordered Cu_3Au and spinodally decomposed Au-Ni are identical both qualitatively and quantitatively to electron diffraction patterns taken in the electron microscope. This result indicates that the information present in the lattice images directly reflects the atomic lattice in the alloys and that lattice imaging is a viable investigative method for studying the early stages of phase transformation processes.

2. Using the optical diffraction technique, diffraction information may be routinely obtained from areas as small as $10\text{\AA}$ in diameter at the specimen plane. This is a remarkable reduction over conventional methods.

3. The combination of direct lattice imaging and high resolution optical diffraction is extremely valuable in studying phase transformations at the atomic level. The experimental results obtained in this way are also consistent with current theories⁽¹⁴⁻¹⁶⁾ of these transformation processes.

ACKNOWLEDGEMENTS

Financial support for this work from the National Science Foundation
U.S.
and the Energy Research and Development Administration is gratefully
acknowledged. The authors would also like to thank Professor R. M.
Glaeser for the use of the optical diffractometer and Mr. D. G. Howitt
and Dr. D. R. Clarke for helpful discussions.

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FIGURE CAPTIONS

- Fig. 1. Lattice image (a) and corresponding optical diffraction pattern (b) of pure gold. The diffraction spots in the latter can be seen to be sharp.
- Fig. 2. Lattice image (negative print of the original plate) of partially ordered Cu_3Au . A group of ordered domains in anti-phase is indicated.
- Fig. 3. Comparison of the electron diffraction pattern (a) from the partially ordered Cu_3Au specimen with the optical diffraction pattern (b) from the lattice image shown in Fig. 2. The (010), (0 $\bar{1}$ 0) reflections are absent from the optical pattern as they were not included in the objective aperture for formation of the lattice image.
- Fig. 4. Distribution of domain spacings determined from the splitting of superlattice spots in individual optical diffraction patterns.
- Fig. 5. Optical diffraction pattern, from the lattice image shown in Fig. 2, using an aperture size corresponding to $20\text{\AA}$ diameter at the specimen plane. The pattern from a disordered region is shown in (a) and that from an ordered region in (b).
- Fig. 6. Lattice image (positive print of the original plate) of spinodally decomposed Au-Ni.
- Fig. 7. Comparison of the electron diffraction pattern (a) from the decomposed Au-Ni specimen with the optical diffraction pattern (b) from the lattice image shown in Fig. 6. Satellites (s) about the fundamental (200) reflection (f) are arrowed.
- Fig. 8. Smoothed plot of fringe spacing with distance for Au-Ni as determined from a microdensitometer trace from the lattice image.

XBB 757-5131

Fig. 1

0 0 0 0 4 3 0 6 2 5 5

-15-

XBB 757-5129

Fig. 2

$\bar{2}00$ $\bar{1}00$ 000 100 200

XBB754-2715

Fig. 3

-17-

XBL 757-6647

Fig. 4

$\bar{2}00$ $\bar{1}00$ 000 100 200

XBB 757-5370

Fig. 5

XBB 757-5130

Fig. 6

XBB 757-5132A

Fig. 7

XBL757-6648

Fig. 8

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