Lawrence Berkeley National Laboratory
Recent Work

Title

DISCUSSION OF ""AN ELECTRON DIFFRACTION STUDY OF SHORT-RANGE ORDER IN QUENCHED Ni.Mo ALLOY""

Permalink

https://escholarship.org/uc/item/379335xc

Author

Thomas, G.

Publication Date

1977

eScholarship.org Powered by the California Digital Library
University of California

0 0 0 0 4 5 0 4 0 5 8

Submitted to Acta Metallurgica

LBL-4983
Preprint c.1

DISCUSSION OF "AN ELECTRON DIFFRACTION STUDY OF SHORT-RANGE ORDER IN QUENCHED Ni_4Mo ALLOY"

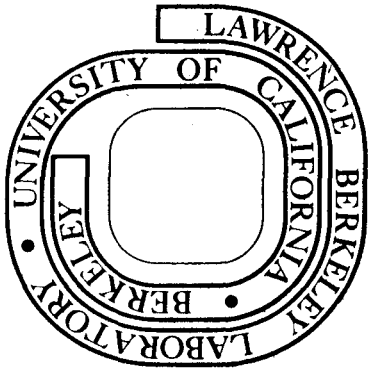
G. Thomas and R. Sinclair

January 1977

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

For Reference

Not to be taken from this room



LBL-4983
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 4 5 0 4 0 5 9

LBL-4983

DISCUSSION OF "AN ELECTRON DIFFRACTION STUDY OF SHORT-RANGE ORDER IN QUENCHED Ni_4Mo ALLOY"

G. Thomas and R. Sinclair

Department of Materials Science and Engineering and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720, USA

ABSTRACT

A close analysis of the quenched Ni_4Mo diffraction patterns of Chevalier and Stobbs (C-S) (1) shows not only that their conclusions, critical of our previous work, are unsubstantiated but that their data in fact support the multi-microdomain model previously proposed by our group (2-4). Weak diffraction effects, previously observed in particular diffraction patterns (2-4), were undetected by C-S (1) and this is attributed to the unnecessary use of thicker foils by the latter. We also emphasise that real space lattice imaging studies are more likely to resolve the physical nature of short-range order than conventional electron diffraction studies as performed by C-S.

1. INTRODUCTION

A recent publication (1) by Chevalier and Stobbs (C-S) describes the results of a conventional electron diffraction study on short-range order in quenched Ni_4Mo and criticises previous experiments and interpretations by our group (2-4) on this alloy. The purpose of this article is to reply to the points raised by C-S showing both that their conclusions are unfounded and that their data in fact support our previous suggestions.

Short-range order (SRO) in solid solutions is a highly localised phenomenon which generally involves the intercorrelation of atomic species over a few unit cells or less. It is therefore an extremely difficult state to study and characterise unambiguously. Progress has been made in establishing the most probable atomic arrangements from detailed diffuse x-ray scattering data (5-8) and alternatively in our group by application of electron microscopy methods (2-4, 9-14). From a concerted effort at identifying SRO in a variety of alloy systems (e.g. Ni_4Mo (2,3,12), Fe_3Al (9), Ni_3Mo (3), Au_4Cr and Au_3Cr (3,10), Au_4V and Au_3Mn (3) and Cu_3Au (11-14)) we have concluded that the best structural description of SRO is a microdomain model. In this, small, but highly ordered, regions exist in a predominantly disordered matrix. These microdomains explain the presence of weak superlattice reflections in diffraction patterns, the diffuseness of which is attributed to the small domain size and probable imperfect order in the microdomain. Our interpretation is generally in agreement with that from diffuse x-ray scattering analyses (5-8).

0 0 0 0 4 5 0 4 0 6 0

However, diffraction data can also be explained by an alternative model, which is couched in terms of the statistical distribution of atomic species homogeneously dispersed in the material (15,16) rather than heterogeneously as in the microdomain model. Interpretation of reciprocal space information has therefore not been unambiguous and has been responsible for much controversy. Accordingly, we have a basic criticism of the C-S approach of using electron diffraction alone for studying SRO. Their belief that real space images "are more open to misinterpretation than diffraction patterns" (1) (although, in fact, no real space analyses were performed) is contrary to our own experience, including Ni_4Mo. We contend that real space images, via direct lattice imaging, is far more likely to resolve the nature of SRO.

2. SHORT-RANGE ORDER IN Ni_4Mo AND THE PRESENT CONTROVERSY

In all electron and x-ray diffraction studies of quenched Ni_4Mo, the principal feature is the presence of diffuse intensity at $\{1\frac{1}{2}0\}$ fcc positions in reciprocal space. As these do not coincide with the equilibrium long-range ordered, $D1_a$ reflections of the alloy, Okamoto and Thomas (2,17) suggested that microdomains, observed by field-ion microscopy, possessed an imperfect DO_{22} structure with a short wavelength, sinusoidal composition variation. It was shown that DO_{22} can be generated from the $D1_a$ structure by periodic non-conservative antiphase boundaries so that the two structures can be appreciated as being quite closely related. The existence of such regions has recently been given a theoretical basis in terms of spinodal-ordering models (18,19) but has not been conclusively demonstrated experimentally.

The main point of contention between C-S and our group does not concern this major aspect of SRO in Ni_4Mo, but rather the suggestion (2-4,17) that microdomains with other related structures are also present,

principally those based on the equilibrium D1a structure (2) and on the Ni_2Mo structure (3). These were inferred from the detection of extremely weak reflections in addition to the stronger {1½0} intensities. C-S claim that these weak reflections are due to {1½0} scattering into the plane of the patterns from nearby reciprocal lattice sections. Whilst we have already recognised that this as a possibility for some reciprocal sections (e.g. the description of fig. 4 by Das et al. (3)), the evidence presented by C-S does not rule out our suggestion but in fact tends to support it (as the analysis in the next section shows).

D1a and Ni_2Mo scattering is indicated by two important diffraction patterns. Firstly the [112] patterns of Okamoto and Thomas (2) (O-T) showed scattering at D1a positions, clearly revealed by microdensitometer traces (fig. 5 of O-T). The presence of Ni_2Mo type order is indicated by the shape of the $\{1\frac{1}{2}0\}$ intensities in [001] patterns of Das et al (3) (DOFT), plotted in detail by iso-intensity contours from the photographic plate. This observation was confirmed in other reciprocal space sections, notably [110] and [130], with the effect of off-section scattering being described for the latter.

The above features are not detected in the corresponding C-S diffraction patterns. We believe this arises from the use of thick foils in their study for recording diffraction information. Unfortunately the diffuse background intensity increases markedly with foil thickness and so when one is examining for very weak effects, it is essential to use areas as thin as possible. The interested reader may compare the following figures from the two studies to appreciate the considerably

0 0 0 0 4 5 0 4 0 6 1

inferior quality of the C-S diffraction patterns: fig. 4(b) (O-T) with fig. 1(c) C-S); fig. 4(a) (O-T) with fig. 4(a) (C-S); fig. 4(c) (O-T) or fig. 4 (DOFT) with fig. 5(a) (C-S); fig. 5(a) (DOFT) with fig. 8(a) (C-S).

A worse aspect of the majority of the C-S diffraction patterns is the presence of strong Kikuchi scattering, which itself introduces highly non-uniform diffuse background intensity. As well as affecting the visibility of weak diffraction phenomena, apparently extra "reflections" may be introduced at the excess line intersections and also the positions of existing diffuse spots may be altered. The following C-S patterns suffer from this fault: figs. 1a, 1d, 1e, 3a, 5a (text description), 7a and 9a.

C-S give the reason for using thick areas as the necessity "to ensure an accurate knowledge of specimen orientation" (1), presumably directly from the Kikuchi patterns. This is quite unnecessary for such diffraction studies. Two alternative methods are possible which have been used with success by the present authors. Firstly, the appropriate pole can be found in bright field by use of the bend contour maps, tilting the thin area into the appropriate orientation and subsequently positioning the intermediate aperture. Secondly, highly accurate zone axis orientations can be achieved by tilting the specimen so as to make the intensity of high angle reflections symmetrical in intensity about the transmitted beam. It may be noted that this latter approach is also used by Iijima to accurately tilt mineralogical specimens for structure imaging, for which the orientation must be exact to within a fraction of a degree (20).

The discrepancy concerning the detection of weak diffraction effects in certain orientations is thus attributed to the unnecessary use of thicker foils by C-S.

3. ANALYSIS OF C-S DIFFRACTION PATTERNS

While bearing the above reservations in mind, a careful analysis of the C-S patterns is now described from which it emerges that their data do not preclude the presence of Dla and Ni_3Mo scattering but in fact support it. Measurements were made on prints provided by C-S by ten independent, unbiassed investigators unfamiliar with the Ni_4Mo system and the present controversy.

Firstly, the width of the $\{1\frac{1}{2}0\}$ spots was established by the C-S tilting experiments to be 0.15a* (1). Although this is sufficient to introduce off-section $\{1\frac{1}{2}0\}$ scattering in non-rational orientations, it is not diffuse enough to produce scattering on several important rational sections. Figure 1 shows a schematic representation of the [001] diffraction pattern of SRO Ni_4Mo with the radius of $\{1\frac{1}{2}0\}$ spots drawn as 0.15a*. It can be seen that, along the [220] and [420] reciprocal lattice rows, the $\{1\frac{1}{2}0\}$ spots do not reach the following sections even allowing for curvature of the Ewald sphere: $[3\bar{3}4]$, $[1\bar{1}0]$, $[1\bar{1}1]$, $[1\bar{2}1]$, $[1\bar{2}0]$, corresponding to figs. 3, 8, 9, 1, 7 respectively of C-S. The scattering near $\frac{1}{3}\underline{g}_{220}$ in the first three and $\frac{2}{5}\underline{g}_{420}$ in the latter two cannot therefore be ascribed to $\{1\frac{1}{2}0\}$ scattering on the basis of the C-S $\{1\frac{1}{2}0\}$ spot width. Considerable tilt away from these sections is necessary for the $\{1\frac{1}{2}0\}$ spots to appear, as the 6^o tilts of C-S fig. 1 demonstrate. Inspection of the diffraction patterns previously published by our group shows, from the relative spot intensities, that they are indeed very close to exact zone axes, which is further confirmed by comparison with the corresponding C-S patterns. This precaution has already been emphasised (2,3). The weak scattering detected by our group is thus unlikely to be due to off-section $\{1\frac{1}{2}0\}$

intensity.

Table 1 compares the figures for the predicted position of Dla or Ni_2Mo spots and the projected $\{1\frac{1}{2}0\}$ spots with those obtained from the measurements on the C-S prints. It should be noted that an accurate determination of the projected $\{1\frac{1}{2}0\}$ positions on $[1\bar{1}0]$, $[1\bar{1}1]$ and $[3\bar{3}4]$ is $0.375\underline{g}_{220}$ and not $0.35\underline{g}_{220}$, as given by C-S (1). A distinction from the position of the Ni_2Mo spot at $0.333\underline{g}_{220}$ should therefore be possible.

Table 1

	Measurements	Ni_2MO (DOFT)	$\{1\frac{1}{2}0\}$ (C-S)
$[3\bar{3}4]$[1]	0.34 ± .02	0.333	0.375
$[1\bar{1}0]$[2]			
(a)	0.32 ± .03	0.333	0.375
(b)	0.65 ± .02	0.667	0.625
a-b	0.33 ± .04	0.33	0.25
$[1\bar{1}1]$[3]			
(a)	0.33 ± .01	0.333	0.375
(b)	0.64 ± .03	0.667	0.625
a-b	0.31 ± .03	0.33	0.25

Figures are fractions of $\underline{g}_{220}$

	Measurements	Ni_2Mo (DOFT)	Dla (O-T)	$\{1\frac{1}{2}0\}$ (C-S)
$[1\bar{2}0]$[4]	0.37 ± .01	0.33	0.40	0.40

Figures are fractions of $\underline{g}_{420}$

1. Fig. 3 C-S
2. Fig. 8 C-S
3. Fig. 9 C-S
4. Fig. 7 C-S

The following points can be made:

(i) Measurements on figs. 3, 8 and 9 of C-S all show that the diffuse intensity is centred at Ni_2Mo positions rather than $\{1\frac{1}{2}0\}$ projected positions. C-S noted that the inner weak spot in fig. 8a "is, if anything nearer to the central beam than would be expected" (1). This is confirmed by our measurements, which show that it should not be confused with the $\{1\frac{1}{2}0\}$ projection at $0.375g_{\bar{2}20}$.

(ii) The difference of position between weak spots along <220> reciprocal lattice rows is a sensitive distinction of the two models. The data again are consistent with the presence of Ni_2Mo spots rather than $\{1\frac{1}{2}0\}$ projections.

(iii) The positions of Dla and projected $\{1\frac{1}{2}0\}$ spots along <420> reciprocal lattice rows are identical and no distinction can be made between them. Thus C-S cannot disprove the multi-microdomain model on this basis.

(iv) Measurements on fig. 7 indicate that the weak diffuse intensity occurs at smaller angles than that due to Dla or $\{1\frac{1}{2}0\}$ projected positions. While we hesitate to draw conclusions from this, it may be noted that this is midway between the Ni_2Mo and Dla positions and is consistent with overlap of these two spots according to the multi-microdomain model of DOFT (3).

Our measurements indicate that the diffuse intensities observed on rational zone sections by C-S are not centred, as they claim, on $\{1\frac{1}{2}0\}$ projected positions but are extremely close to Ni_2Mo spot positions. Their data in fact supports the multi-microdomain model (3,4) rather than disproves it and their conclusions 3,4 and 5 are thus totally unfounded.

0 0 0 0 4 5 0 4 0 6 3

4. SUMMARY

The experiments of Chevalier and Stobbs (1) essentially repeat and support the previous electron diffraction work performed in our group (2-4). Our analysis of their data shows that their observations are in agreement with ours, not otherwise. In addition, the absence of weak Ni_2Mo and Dla reflections from some of their patterns is explained by the higher diffuse background due to their use of unnecessarily thick foils. Their conclusions in contradiction with ours are therefore incorrect.

Two further propositions by C-S are unnecessary. Firstly, the emphasis (conclusion 1 of C-S), that analysis of the three-dimensional distribution of diffuse intensity is essential for complete data on SRO, has already been made in our original (2,3) and all subsequent research. This is attested to, for instance, by the differentiation between the shape of SRO scattering in Au_4Cr (see fig. 12 of DOFT) from that in Ni_4Mo. Specific reciprocal sections were chosen for publication purposes, as principally done by C-S. Secondly, although C-S conclude that their data "might be compatible with a SRO clustering model related to the DO_{22} structure (see deFontaine)," de Fontaine's model is in fact identical to the one first proposed by Okamoto and Thomas (2,17), as clearly stated by de Fontaine (18).

Finally the C-S article does not contribute further to our understanding of SRO in Ni_4Mo. No conclusive demonstration has been made concerning the presence or otherwise of microdomains with the proposed structures. This is a disadvantage of using electron diffraction alone. A recent lattice image study (10) of ordering in Au_4Cr (which like Ni_4Mo also gives {1½0} diffraction peaks) supports the Okamoto-Thomas microdomain model in this system. From this and other recent experimental work (11,13,14) we believe that lattice imaging (i.e. real space imaging) is

the best currently available method for characterising the early stages of phase transitions and short-range order.

5. CONCLUSIONS

1. The positions of extra diffuse reflections on specific C-S reciprocal lattice sections have been measured by us and found to be extremely close to Ni_2Mo positions and sufficiently far from the projection of $\{1\frac{1}{2}0\}$ spots to rule out the latter. The conclusions of C-S (1) concerning the multi-microdomain model (2-4) are therefore quite unsubstantiated.

2. Weak diffraction phenomena previously reported by our group (2,3) are not detected in the C-S electron diffraction experiments (1). This may be attributed to their use of thick foils whereby low intensity peaks are lost in the high, diffuse background scattering.

3. Lattice imaging is more likely to solve the short-range order problem than conventional electron diffraction experiments as described by Chevalier and Stobbs.

ACKNOWLEDGEMENTS

Financial support for this work has been provided by the National Science Foundation and the U.S. Energy Research and Development Administration through the Lawrence Berkeley Laboratory. We are grateful to past and present members of our group (especially Dr. S. K. Das) for helpful discussions, and to several of the latter for making independent experimental measurements. We would also like to thank J-P.A.A. Chevalier and W. M. Stobbs for sending their manuscript prior to publication.

0 0 0 0 4 5 0 4 0 6 4

REFERENCES

1. J-P.A.A. Chevalier and W. M. Stobbs, Acta Met., in press.
2. P. R. Okamoto and G. Thomas, Acta Met., 19, 825 (1971).
3. S. K. Das, P. R. Okamoto, P. M. J. Fisher and G. Thomas, Acta Met., 21, 913 (1973).
4. S. K. Das and G. Thomas, Order-Disorder Transformations in Alloys, edited by H. Warlimont, p. 332, Springer, Berlin (1974).
5. P. C. Gehlen and J. B. Cohen, Phys. Rev., A139, 844 (1965).
6. L. H. Schwartz and J. B. Cohen, Jnl. Appl. Phys., 36, 598 (1965).
7. E. Metcalfe and J. A. Leake, Acta Met., 23, 1135 (1975).
8. P. Bardhan and J. B. Cohen, Acta Cryst., submitted for publication.
9. H. Warlimont and G. Thomas, Met. Sci. Jnl., 4, 47 (1970).
10. J. Dutkiewicz and G. Thomas, Met. Trans., 6A, 1919 (1975).
11. R. Sinclair and G. Thomas, Jnl. Appl. Cryst., 8, 206 (1975).
12. R. Sinclair, M. J. Goringe and G. Thomas, Phil. Mag., 32, 501 (1975).
13. R. Sinclair, K. Schneider and G. Thomas, Acta Met., 23, 873 (1975).
14. R. Sinclair, R. Gronsky and G. Thomas, Acta Met., in press.
15. S. C. Moss and P. C. Clapp, Phys. Rev., 171, 764 (1968).
16. S. C. Moss, Phys. Rev. Lett., 22, 1108 (1969).
17. P. R. Okamoto, Ph.D. Thesis, University of California, Berkeley, U.C.R.L. Report No. 19175 (1969).
18. D. de Fontaine, Acta Met., 23, 553 (1975).
19. H. E. Cook, Jnl. Appl. Cryst., 8, 132 (1975).
20. J. M. Cowley and S. Iijima, Z. Naturforsch. 27a, 445 (1972).

FIGURE CAPTIONS

Fig. 1. A schematic diagram of the [001] diffraction pattern of quenched Ni_4Mo. The width of the {1½0} type SRO spots is insufficient for them to appear on <420> and <220> reciprocal lattice rows. The positions of Ni_2Mo spots along <220> directions (marked A) can be seen to be clearly separate from the projection of {1½0} spots, whereas the Dla positions marked B along <420> directions are identical to the projected nearby {1½0} positions.

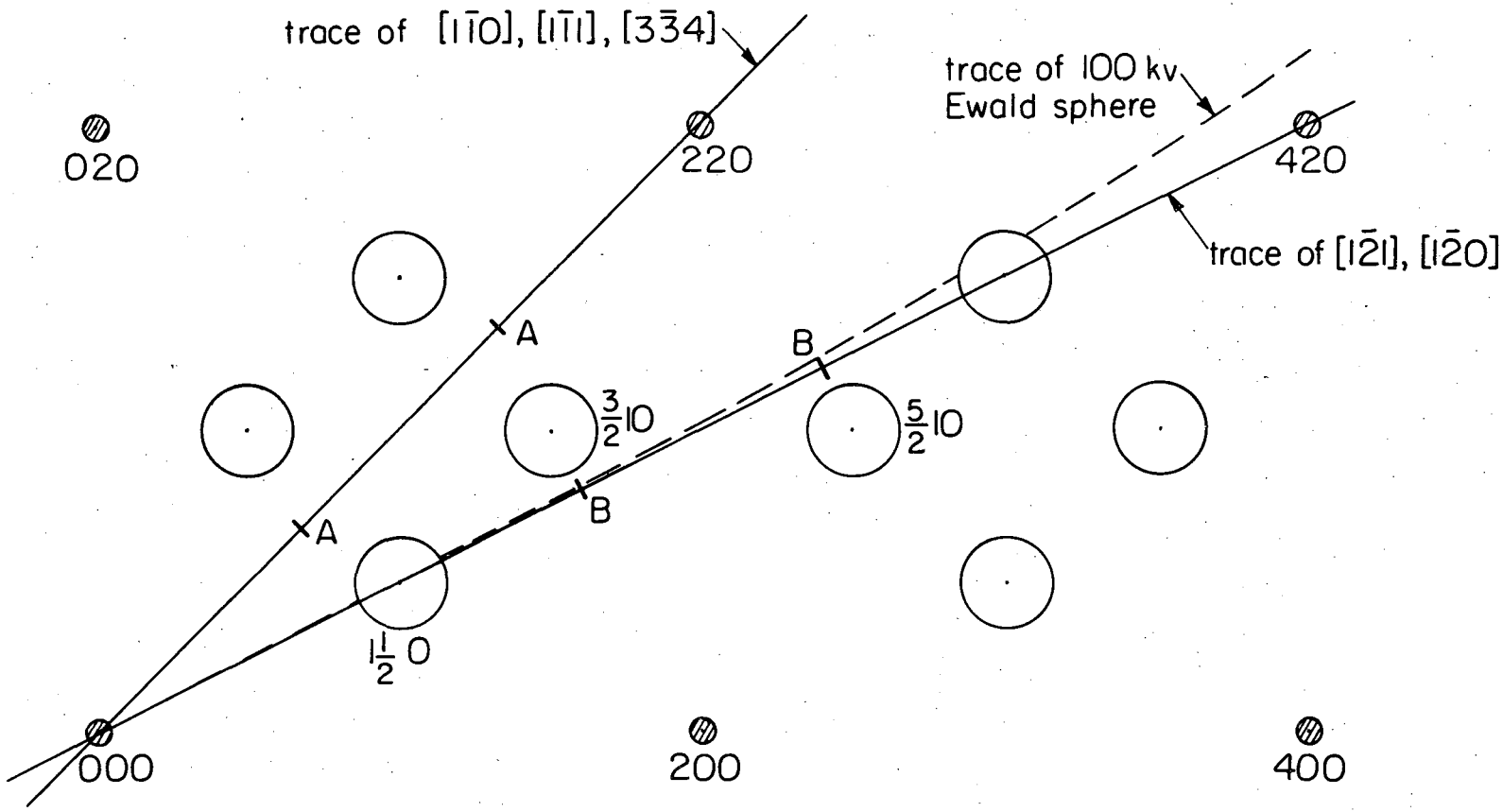


Fig. 1

0 0 0 4 5 0 4 0 5 1

0 3 0 3 4 5 0 4 0 6 6

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720