Interpretation of High Resolution Transmission Electron Microscope Images of Short Range Ordered Ni₄Mo

Satoshi Hata*, Daisuke Shindo**, Noriyuki Kuwano*,
Syo Matsumura*** and Kensuke Oki*

*Department of Materials Science and Technology, Kyushu University, Kasuga 816-8580, Japan

**Institute for Advanced Materials Processing, Tohoku University, Sendai 980-8577, Japan

***Department of Nuclear Engineering, Kyushu University, Fukuoka 812-8581, Japan

High resolution transmission electron microscope (HRTEM) image contrast of short-range order (SRO) in Ni₄Mo alloys has been investigated by means of multi-slice simulations. The HRTEM image contrast of SRO in Ni₄Mo coincides with a projection contrast of an SRO structure which involves D1_a, D0₂₂ and Pt₂Mo-type subunit cells in a disordered matrix. Multi-slice simulations revealed that the SRO structure exhibit a projection contrast in the HRTEM image when the fundamental fcc lattice reflections contribute sufficiently to HRTEM imaging. The results indicate that the image of SRO in Ni₄Mo can be interpreted in terms of projected potential of atomic columns under an appropriate imaging condition.

(Received February 5, 1998; In Final Form April 27, 1998)

Keywords: high resolution transmission electron microscopy (HRTEM), short range order (SRO) in Ni₄Mo, multi-slice simulations, image contrast, projection contrast, dynamical diffraction effects of electrons

I. Introduction

A high resolution transmission electron microscope (HRTEM) is a powerful tool to analyze local arrangements of atoms in real space. However, it becomes often difficult to interpret a structure of short-range order (SRO) in alloys from HRTEM images, since many small segments of ordered structures with different orientations superimpose to one another along the direction of the electron beam. It is known that HRTEM images do not straightforwardly correspond to projected potential of atoms owing to multiple scattering of electrons in a foil-specimen, the dynamical diffraction effects of electrons. To overcome the problems in the image interpretation of SRO, the dynamical diffraction effects on HRTEM imaging of SRO have been discussed in various papers⁽¹⁾⁻⁽⁵⁾, but there is much to be clearly understood. This may be due to the difficulties in modeling appropriate atomic arrangements of SRO for image simulation and in observing the dynamical effects experimentally.

Recently, the present authors made a breakthrough in investigating the SRO structure of fcc-based Ni₄Mo alloys by HRTEM and Monte Carlo studies⁽⁶⁾⁽⁷⁾. The locations of diffuse scattering intensity maxima, $1\ 1/2\ 0$, and the equivalent positions, for the SRO state do not coincide with those of the superlattice reflections, $4/5\ 2/5\ 0$, for the long-range order (LRO) state of D1_a structure⁽⁸⁾⁽⁹⁾. Therefore, the SRO structure in Ni₄Mo has long been enigmatic. Our Monte Carlo simulations of the ordering process in a three-dimensional Ising lattice system explained successfully the relationship between the diffuse intensity distribution and the atomic arrangements of SRO⁽⁶⁾. Some remarkable features of SRO in Ni₄Mo were

found as shown in **Fig. 1**, which demonstrates the atomic arrangement in an SRO structure obtained by the Monte Carlo method. Figure 1(a) shows a cross-sectional view consisting of two adjoining (001)_{fcc} planes, with the open and closed circles denoting Ni and Mo atoms, respectively. As indicated by the solid lines, the SRO structure contains subunit cells of stable D1_a (slanting squares) and of metastable D0₂₂ (fat rhombi) and Pt₂Mo (slanting rhombi) structures formed in the matrix. Figures 1(b) and (c) show [001] projections of the SRO structure. One can see that the SRO structure exhibits different projection patterns, depending on its gray level for output. When atomic columns with Mo concentration more than 25 at% are represented as solid circles in (b), dot-patterns of subunit cell clusters of D1_a, D0₂₂ and Pt₂Mo structures appear in the projection. The dot-patterns resemble the arrangement of atoms in the cross-sectional view (a). If the threshold value between open and solid circles is set at 20 at%Mo (the matrix composition) in (c), double-dot patterns appear as seen in encircled areas. The double-dot patterns correspond to the projection of N₂M₂ structure⁽¹⁰⁾ which is one of the candidates for the SRO structure in Ni₄Mo. The appearance of the N₂M₂-pattern is quite interesting since no atomic configuration of N₂M₂ structure is found in the cross-sectional view of the simulated SRO structure in (a). It is interpreted that the N₂M₂-pattern is a statistically averaged view of mixture of D1_a, D0₂₂ and Pt₂Mo-type subunit cells.

Figure 2 shows an HRTEM image of the SRO state in Ni₄Mo taken by a 300 kV conventional TEM. Bright dot-patterns corresponding to the N₂M₂-pattern are actually observed in the encircled areas. We also carried out semi-quantitative analysis of the HRTEM images of Ni₄Mo using the Imaging Plate (IP) system⁽⁷⁾. The IP possesses

Fig. 1 Atomic arrangement of the SRO state with the system of $20(x) \times 20(y) \times 60(z)$ fcc unit cells obtained by Monte Carlo simulation. (a): (001) cross-sectional view; the open and closed circles denoting Ni and Mo atoms, respectively. (b) and (c): [001] projections with the different gray levels. Closed circles denote atomic columns with Mo concentrations more than 25 at% in (b) and 20 at% in (c).

Fig. 2 [001] HRTEM image of Ni-19.5 at%Mo quenched from 1373 K taken by JEM-3010. Double-dot-patterns corresponding to the projection of N_2M_2 structure are observed in the enclosed areas.

high sensitivity, wide dynamic range and good linearity between the intensity of image signals and the number of incident electrons⁽¹¹⁾. It was clearly observed that the N_2M_2 -patterns turn into dot-patterns of mixture of $D1_a$, $D0_{22}$ and Pt_2Mo subunit cells with changing the gray scale

for output, as demonstrated in Fig. 1. The good correspondence between the results of experiment and simulation suggests that the simulated SRO structure in Ni₄Mo is a quite real one.

In the present study, multi-slice simulations have been

carried out to examine the relationship between images and projections of the simulated SRO structure. The HRTEM image formation of SRO in Ni_4Mo is discussed taking dynamical diffraction effects into account. The validity of the SRO structure simulated by Monte Carlo method is examined with the results of multi-slice simulations.

Table 1 Parameters used for the multi-slice simulations.

Crystal thickness for one slice	0.36 nm
Number of beams	256×256
Accelerating voltage	300 kV
Spherical aberration coefficient	1.1 mm
Defocus due to chromatic aberration	12 nm
Objective aperture radius	6 nm^{-1}

Fig. 3 Simulated HRTEM images as a function of foil-thickness (a). The dot-contrast of N_2M_2 -type appears at 18 nm thickness, and it corresponds to Mo concentration in atomic columns shown in (b). Both intensity maxima at 200 and $1\ 1/2\ 0$ positions are clearly recognized in the Fourier power spectrum of the image at 18 nm, as shown in (c).

II. Simulation Procedures

The SRO atomic arrangement in $10(x) \times 10(y) \times 100(z)$ fcc unit cells for image simulations was obtained using the Monte Carlo algorithm and considering appropriate pairwise interaction parameters of atoms up to the fifth coordinate shells⁽⁶⁾. **Table 1** shows the values of parameters used for the present multi-slice simulations. The thickness of each slice is 0.36 nm corresponding to one fcc unit cell, and $256(x^*) \times 256(y^*)$ diffracted beams were taken into account to calculate the scattering intensity of electrons. The transfer of electrons through the microscope was simulated for a 300-kV instrument which was used for the HRTEM observation shown in Fig. 2. The defocus value was set at -56 nm for the Scherzer defocus condition.

III. Results and Discussion

Figure 3(a) demonstrates the simulated HRTEM images as a function of foil thickness. Bright dot-patterns of N₂M₂-type clearly appear at 18 nm thickness, as actually observed in the HRTEM image in Fig. 2. **Figure 3(b)** shows projections of atomic columns, which should be compared with the images (a). Brightness of the circles represents the Mo concentration in the atomic columns. It should be noted that the image contrast at 18 nm thickness corresponds to the projection contrast. The Fourier power spectrum from the image at 18 nm exhibits fcc spots and distinct intensity maxima at $1\ 1/2\ 0$, as shown in Fig. 3(c). On the other hand, the poor coincidence between the images and the projections is obtained when both fcc spots and $1\ 1/2\ 0$ maxima do not contribute to imaging, as seen at 9, 27 and 36 nm thicknesses. At 9 and

36 nm, for example, the double-dots in N₂M₂-patterns can be hardly resolved owing to an insufficient contribution of the 200 fcc lattice reflections. The present results reveal that the fundamental fcc lattice reflections also have an important role in the image formation of SRO in Ni₄Mo.

Figures 4(a) and **(b)** show spectra of the scattering intensity at 18 nm thickness obtained by the kinematical calculation and the exact dynamical calculation, respectively. The spectra look similar to each other. If they are compared carefully, however, it is to be recognized that the diffuse intensity distribution near the $1\ 1/2\ 0$ maxima is different among the spectra. On the kinematical condition which assumes the projected potential of atoms (a), the scattering intensity at hkl , $I(hkl)$, is equal to $I(\bar{h}\bar{k}\bar{l})$ according to Friedel's law. On the dynamical calculation which takes multiple scattering of electrons into account (b), the breakdown of Friedel's law occurs in the diffuse intensity distribution. This suggests that the coincidence between the image contrast and the projection contrast for 18 nm thickness in Fig. 3 is not necessarily complete. Therefore, the estimation of column composition or projected potential from the image contrast should be done very carefully, as previously discussed⁽²⁾⁽⁵⁾.

Figure 5 shows several displays of the simulated image at 18 nm thickness with different gray levels in the same way as Figs. 1(b) and (c). The image (a) is output in 256 gray levels from 0 (black) to 255 (white). Images (b), (c) and (d) are the output in 2 gray levels with the threshold values of 70, 100 and 120, respectively. Transitions of the dot-patterns from the N₂M₂-type to a mixture of D1_a, D0₂₂ and Pt₂Mo subunit cells are clearly visible with increasing threshold value from (b) to (d). The changes in the dot-pattern are in good agreement with those demonstrated in Fig. 1. Thus the characteristic features in

Fig. 4 Spectra of scattering intensity for an 18 nm thickness specimen obtained by the kinematical calculation (a) and by the exact dynamical calculation (b). The breakdown of Friedel's law is recognized in the diffuse intensity distribution of the specimen (b).

Fig. 5 Several displays of the simulated HRTEM image at 18 nm thickness with different gray levels. 256 gray levels from 0 (black) to 255 (white) (a), 2 gray levels with threshold values of 70 (b), 100 (c) and 120 (d), respectively. Dot-patterns of N_2M_2 -type are recognized in (a) and (b). However, the N_2M_2 -pattern turn into mixture of $D1_a$, $D0_{22}$ and Pt_2Mo subunit cells when the threshold value is increased, as seen in (c) and (d).

projection contrast of the SRO structure are maintained for 18 nm thickness after HRTEM imaging with dynamical effects of electron diffraction.

Figure 6 shows the calculated scattering amplitude of the transmitted wave, $hkl=000$, and two diffracted waves, $hkl=200$ and $1\ 1/2\ 0$, as a function of the number of slices. One slice corresponds to 0.36 nm in foil-thickness (one fcc unit cell). The amplitudes of 000 and 200 waves oscillate with a periodicity of the extinction distance of about 12 nm. On the other hand, the amplitude of the $1\ 1/2\ 0$ wave is much smaller than that of the 200 wave and increases gradually with the number of slices without oscillation. It must be noted that the amplitude of 200 diffracted wave shows considerably different values at the foil thicknesses for the image calculations shown in Fig. 3. At 18 nm the amplitude is quite large, but at 9, 27 and 36 nm it becomes less than the half maximum. Such a low amplitude of the 200 wave gives rise to the insufficient contrast-coincidence between HRTEM images and projections of the SRO structure, as shown in

Fig. 6 Calculated scattering amplitude of $hkl=000$, 200 and $1\ 1/2\ 0$ waves as a function of the number of slices. One slice corresponds to 0.36 nm in foil-thickness (one fcc unit cell). The foil-thicknesses for the image calculations in Fig. 3 are depicted by arrows. At 18 nm the amplitude of 200 diffracted wave is quite large, but at 9, 27 and 36 nm it becomes less than the half maximum.

Fig. 3.

IV. Conclusion

The HRTEM image contrast of SRO in Ni₄Mo alloys was investigated by means of multi-slice simulations. The structural model of SRO⁽⁶⁾, which involves mixture of D1_a, D0₂₂ and Pt₂Mo-type subunit cells in the disordered matrix, rationalize the HRTEM image contrast of Ni₄Mo. It is shown that a sufficient contribution of the fundamental fcc lattice reflections to HRTEM imaging is required to get a projection contrast of the SRO structure. The present results suggest that projected structures of SRO can be clarified from HRTEM image intensity.

Acknowledgments

This study was partly supported by Grants-in-Aid for Scientific Research (B) (2) (#08455293) as well as for Scientific Research (1) (#09242102, #09242106) on the Priority Area 'Investigation of Microscopic Mechanisms

of Phase Transformations for the Structure Control of Materials' from the Ministry of Education, Science, Sport and Culture, Japan.

REFERENCES

- (1) G. Van Tendeloo, S. Amelinckx and D. De Fontaine: *Acta Cryst.*, **B41** (1985), 281.
- (2) N. Tanaka and J. M. Cowley: *Acta Cryst.*, **A43** (1987), 337.
- (3) D. Shindo and M. Hirabayashi: *Acta Cryst.*, **A44** (1988), 954.
- (4) M. J. Hytch and J.-P. Chevalier: *Ultramicroscopy*, **52** (1993), 415.
- (5) P. De Meulenaere, D. Van Dyck, G. Van Tendeloo and J. Van Landuyt: *Ultramicroscopy*, **60** (1995), 171.
- (6) S. Hata, S. Matsumura, N. Kuwano and K. Oki: *Acta Mater.*, **46** (1998), 881.
- (7) S. Hata, S. Matsumura, N. Kuwano and K. Oki: *J. Surface Analysis*, **3** (1997), 401.
- (8) J. E. Spruiell and E. E. Stansbury: *J. Phys. Chem. Solids*, **26** (1965), 811.
- (9) E. Ruedl, P. Delavignette and S. Amelinckx: *Phys. Status Solidi*, **28** (1968), 305.
- (10) U. D. Kulkarni and S. Banerjee: *Acta Metall.*, **36** (1988), 413.
- (11) A. Taniyama, D. Shindo and T. Oikawa: *J. Electron Microsc.*, **46** (1997), 303.