Transmission Electron Microscopy Study of Strengthening Precipitates in 18% Ni Maraging Steel*

By Ken'ichi Shimizu** and Hisaki Okamoto**

Transmission electron microscopy and electron diffraction studies were carried out in order to make clear the crystallographic properties of strengthening precipitates in an 18% Ni maraging steel. The primary precipitates observed in specimens in the maximum hardness state were rod in shape, the size being about 25 Å in width and 500 Å in length. The length directions of the rod precipitates were parallel to the $\langle 111 \rangle$ direction of the matrix, and the crystal structure was identified as the orthorhombic Ni_3Mo intermetallic compound. The orientation relationship between the Ni_3Mo precipitate and matrix was proposed possibly to be

$$(010)_{\text{Ni}_3\text{Mo}} // (011)_{\alpha'}, \quad [100]_{\text{Ni}_3\text{Mo}} // [\bar{1}\bar{1}1]_{\alpha'},$$

that is, the closest packed plane and direction in precipitates were parallel to those in the matrix, as observed in many other precipitation phenomena. When the ordering of atoms in the Ni_3Mo crystal was disregarded, the crystal could be described in terms of the hcp lattice and the relationship was represented by the Burgers relationship which is well known in the bcc to hcp phase transformation. The length direction of Ni_3Mo precipitates, $\langle 111 \rangle_{\alpha'}$, was verified to be the $[\bar{1}\bar{1}1]_{\alpha'}$ direction involved in the above orientation relationship.

The interfacial coherency between the Ni_3Mo precipitate and the matrix was examined referring to the orientation relationship and the length direction. The hexagonal Ni_3Ti phase was also detected as the secondary precipitates.

(Received February 1, 1971)

I. Introduction

Since maraging steels were developed at the International Nickel Company in the 1950's, many improvements have been made in order to obtain steels having higher tensile strength and better ductility. The steels obtained are now used in many industrial fields. The two characters of high tensile strength and good ductility in maraging steels are explained generally in such a way that the ductile martensites are hardened by precipitates of intermetallic compounds of the matrix elements with supplemental elements Mo, Ti and Al. However, the crystallographies of the strengthening precipitates are not made clear; that is, the structure has been variously reported as Ni_3Mo ^{(1)~(7)}, Ni_3Ti ^{(2)~(3)~(5)~(8)~(11)}, Fe_2Mo ^{(4)~(9)~(11)}, Fe_2Ti ^{(1)~(2)}, $\sigma\text{-FeMo}$ ⁽⁷⁾, $\sigma\text{-FeTi}$ ⁽⁶⁾ and austenite^{(1)~(12)}, and the shape as sphere^{(1)~(5)~(8)~(10)}, disk⁽⁹⁾, ribbon^{(3)~(6)}, and needle^{(6)~(9)~(10)}. The major reasons for such difficulties in determining the crystallographies of strengthening precipitates are that the precipitates are very small at the maximum hardness stage and also that various precipitates which have very similar d-spacings can be anticipated from the compositional considerations. So, many identifications have been made for precipitates in over-aged specimens by means of the extraction technique, from which the structure of

precipitates at the maximum hardness stage have been speculated. In addition to the above difficulties, when thin specimen foils were observed directly by the transmission method, the diffraction patterns were complicated due to double reflections and a simultaneous appearance of many zonal patterns from the variant precipitates.

In this transmission electron microscopy, strengthening precipitates at the maximum hardness stage have been identified successfully by taking various zonal diffraction patterns of precipitates using a tilting stage, and the crystallographic relations between the precipitates and the matrix were obtained consistently. To report these results is the purpose of the present paper.

II. Experimental Methods

The composition of the specimen investigated was analysed chemically, the result being shown in Table 1. Ribbons of 0.2 mm in thickness and 30 mm in width were provided, from which specimens of 20 mm length were cut. These specimens were annealed in vacuum at 1000°C for 1 hr followed by quenching into water at room temperature, and subsequently aged at 480°C for 10 min or 3 hr.

Thin foils for transmission electron microscopy were prepared at first by chemical polishing in a mixed solution of 85% hydrogen peroxide, 5% hydrofluoric acid and 10% water, and subsequently by electro-polishing

* This paper was read before the Annual Meeting of the Japan Institute of Metals, October, 1970 and was published in J. Japan Inst. Metals, 35 (1971), 204.

** The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, Japan.

(1) B. G. Reisdorf : Trans. ASM, 56 (1963), 733.

(2) G. P. Speich : Trans. Met. Soc. AIME, 227 (1963), 1426.

(3) A. J. Baker and P. R. Swann : Trans. ASM, 57 (1964), 1008.

(4) H. Marcus, L. H. Schwartz and M. E. Fine : Trans. ASM, 59 (1966), 468.

(5) R. B. Banerjee, J. M. Capenos and J. J. Hauser : Advances in Electron Metallography, 6, ASTM STP 396, Am. Soc. Testing Metals, (1966), 115.

(6) J. M. Chilton and C. J. Barton : Trans. ASM, 60 (1967), 528.

(7) W. R. Bandi, J. L. Lutz and L. M. Melnick : J. Iron Steel Inst., 207 (1969), 348.

(8) R. K. Pitler and G. S. Ansell : Trans. ASM, 57 (1964), 220.

(9) G. P. Miller and W. I. Mitchell : J. Iron Steel Inst., 203 (1965), 899.

(10) R. D. Garwood and R. D. Jones : J. Iron Steel Inst., 204 (1966), 512.

(11) M. J. Fleetwood, G. M. Higginson and G. P. Miller : British J. Appl. Phys., 16 (1965), 645.

(12) J. R. Mihalisin : Trans. ASM, 59 (1966), 60.

Table 1 Chemical composition of steel investigated

Element	Ni	Co	Mo	Ti	Al	C	Si	Mn	P	S	Zr	B	Fe
wt%	18.97	9.91	4.46	0.44	0.05	0.034	0.086	0.04	0.002	0.012	0.003	0.003	Bal.

in a mixed solution of 135 mL of acetic acid, 25 g of chromium trioxide and 7 mL of water kept at 15°C. The window method was employed and the electric current density was about 0.15 A/cm². The electron microscope used in this work was of the Hitachi HU-11D type, operated at 100 kV.

III. Experimental Results

1. Microstructures of as-quenched martensites

Photo. 1 shows an example of electron micrographs of the as-quenched martensites, which is very similar to the structures of Fe-6~25% Ni martensites⁽¹³⁾. That is, the martensites are in the form of laths and have a high density of randomly arranged dislocations. Neither the micrographs nor diffraction patterns showed retained austenites and precipitates.

Photo. 1 Electron micrograph of maraging steel annealed at 1000°C for 1 hr followed by water quenching.

2. Microstructures at the early stage of aging and nucleation sites of precipitates

Photo. 2 shows an example of electron micrographs taken from the specimen aged at 480°C for 10 min. In the aged lath martensites, small precipitates are observed along dislocation lines and lath boundaries. It is difficult to know the shape of the precipitates due to their smallness. However, diffraction patterns taken from such areas showed very weak spots which can be explained as those from the Ni₃Mo intermetallic compound as described later. Thus, the small precipitates were considered to be the Ni₃Mo phase. As the aging time was increased, the vestiges of dislocation lines and lath boundaries became indistinct while the precipitates grew into a size which enables us to distinguish the shape. The reason why the precipitation occurs at dislocation

Photo. 2 Electron micrograph of steel aged at 480°C for 10 min, showing small precipitates at dislocation lines and a lath boundary.

lines and lath boundaries may be explained to be due to a small activation energy for the nucleation.

3. Determinations of the shape and preferred growth direction of precipitates

Photo. 3 is an example of electron micrographs taken from the specimen subjected to the normal maraging heat-treatment (1000°C, 1 hr → W.Q. → 480°C, 3 hr → W.Q.) which gives the maximum hardness⁽¹⁴⁾⁽¹⁵⁾. There are seen precipitates with such a size that the shape can be known. That is, rod-like ones and point-like ones (↑) are seen, the former being in three directions which make an angle of about 60° with each other. The point-like ones can be considered to be a cross section of the rod-like ones because the diameter of the former is nearly equal to the width of the latter. Therefore, the rod-like appearance of precipitates may be due to the rod-shape and not a projection of the plate nearly perpendicular to the specimen surface. Since the electron beams are parallel to the $\langle \bar{1}\bar{1}\bar{1} \rangle_{\alpha'}$ direction of the

Photo. 3 Electron micrograph of precipitates in steel aged at 480°C for 3 hr followed by W.Q., electron beams being parallel to $\langle \bar{1}\bar{1}\bar{1} \rangle_{\alpha'}$.

(13) G. R. Speich and P. R. Swann : J. Iron Steel Inst., 203(1965), 480.

(14) R. E. Decker, J. T. Eash and A. J. Goldman : Trans. ASM, 55 (1962), 58.

(15) S. Floreen and R. F. Decker : Trans. ASM, 55 (1962), 518.

matrix, the above consideration leads to a conclusion that the length direction of rod-shape precipitates is nearly parallel to the $\langle 111 \rangle$ of matrix. If so, when three $\langle 111 \rangle$ directions which are not parallel to the electron beams are projected to the specimen surface, the projections must appear as rods along three $\langle 211 \rangle$ directions which make an angle of 60° with each other. This appearance is consistent with the observation in Photo. 3. If the specimen surface is parallel to $\{100\}$, the projection of rod precipitates growing in four $\langle 111 \rangle$ directions into the specimen surface should appear as rods oriented along two $\langle 110 \rangle$ directions which make an angle of 90° with each other. Such a case will be found in Photo. 4. The same consideration was applied to other 6 cases of different orientation, and subsequently the shape and length direction of precipitates could be explained perfectly. Thus, it was concluded that the precipitates took the shape of a rod and its length direction was parallel to the $\langle 111 \rangle$ direction of the matrix.

It is difficult to estimate the exact size of precipitates because of the existence of strain contrasts around precipitates. However, the exact estimation is possible if the dark-field image is examined which is formed by using a reflection from precipitates. The examinations of the dark-field micrographs of Photos. 4 (c) and 6 (b) gave a result that the size was about $25 \text{ \AA}$ in width and $500 \text{ \AA}$ in length.

4. Identification of the precipitates

Photo. 4 (a) is an electron micrograph taken from the same specimen as in Photo. 3, in which rod-like precipitates along two $\langle 110 \rangle$ directions are visible as described in the previous section. (b) is the diffraction pattern corresponding to (a), and shows that the specimen surface is parallel to $(\bar{1}00)$ of the matrix as known from the key diagram (d). (c) is the dark-field micrograph formed with a precipitates reflection ($\odot$), in which one of the two oriented precipitates turns over the contrast. In (b), many diffraction spots are seen in addition to the matrix spots. Of these extra spots, one zonal pattern including the spot used to form the dark-field image (c) can be represented as shown with open circles in (d). This zonal reflections are indexed assuming that the precipitates are the Ni_3Mo intermetallic compound ($a=5.064$, $b=4.224$, $c=4.448 \text{ \AA}$, Cu_3Ti type, orthorhombic crystal)⁽¹⁶⁾ and the zone axis is parallel to $[\bar{1}02]$ of the Ni_3Mo crystal. Table 2 shows a comparison of electron diffraction data on the zonal pattern with those calculated from the Ni_3Mo . The observed d-values were obtained by referring to the d-spacings of matrix spots*. The comparison shows a good agreement and therefore indicates that the assumption of precipitates as the Ni_3Mo phase and the indexing for spots are reasonable. Forbidden reflections $\{010\}_{\text{Ni}_3\text{Mo}}$ visible in (b) might appear due to double reflections. Diffraction spots from the Ni_3Mo precipitates are asso-

Photo. 4 (a) Electron micrograph of steel aged at 480°C for 3 hr, showing precipitates along two $\langle 011 \rangle_{\alpha'}$ directions. A is a reference point for comparison with the dark-field micrograph in (c). (b) Electron diffraction pattern taken from the whole area of (a). (c) Dark-field image formed by the (211) reflection of Ni_3Mo precipitates. (d) Key diagram of (b), showing the Ni_3Mo $[\bar{1}02]$ zone as well as the matrix $[\bar{1}00]$ zone.

Table 2 Comparison of electron diffraction data of precipitate reflection in Photo. 4 (b) with their calculations of Ni_3Mo

	Planes	Obs. ($\text{\AA}$)	Calc. ($\text{\AA}$)
d-spacings	(020)	2.07	2.112
	(201)	2.18	2.200
	(211)	1.94	1.952
Ratios of d-spacing	(020)/(201)	0.95	0.960
	(020)/(211)	1.07	1.082
	(201)/(211)	1.12	1.127
Interplanar angles	(020) $\wedge$ (201)	$62^\circ 30'$	$62^\circ 29'$
	(020) $\wedge$ (211)	$90^\circ 00'$	$90^\circ 00'$
	(211) $\wedge$ (201)	$27^\circ 30'$	$27^\circ 31'$

ciated by streaks in the direction** perpendicular to the rod. The streaks can be explained to be intersections by the Ewald sphere of rel. planes at the reciprocal lattice points which are formed due to the narrow width of precipitates. Table 3 shows a comparison of experimentally determined d-spacings with those calculated from the Ni_3Mo , which was done using various zonal diffraction patterns. In the determination of d-spacings, the spots were indexed in such a way that the orientation relationship described below was satisfied consistently, double reflection spots were excluded, and

(16) S. Saito and P. A. Beck : Trans. Met. Soc. AIME, 215 (1959), 938.

* The lattice parameter of the matrix was determined as $a=2.869 \pm 0.001 \text{ \AA}$ by X-ray diffraction using the specimen subjected to the same heat-treatment.

** Corrections were made for the azimuthal rotation due to the change of intermediate lens current from microscopy to diffraction.

Table 3 Comparison of experimentally determined d-spacings with the calculations of Ni_3Mo

(h k l)	Obs. (Å)	Calc. (Å)
(002)	2.22	2.224
(201)	2.21	2.200
(020)	2.08	2.112
(012)	1.98	1.968
(211)	1.95	1.952
(022)	1.52	1.531
(221)	1.51	1.524
(203)	1.28	1.279
(400)	1.27	1.266
(032)	—	1.190
(231)	1.17	1.186
(004)	1.11	1.112
(402)	1.09	1.100
(223)	1.09	1.094
(420)	1.08	1.086
(014)	1.07	1.075
(412)	1.07	1.065
(040)	1.04	1.056

a distortion of the Debye-Scherrer ring was corrected for each pattern as well as the camera length. Table 3 shows again a good agreement in d-spacings. Thus, the precipitates may be concluded to be the Ni_3Mo phase.

5. Orientation relationship between the Ni_3Mo and the matrix

The diffraction pattern of Photo. 4 (b) was explained to consist mainly of the $[\bar{1}00]$ zone pattern of the matrix and the $[\bar{1}02]$ zone pattern of Ni_3Mo . However, the electron beam direction for the matrix is not exactly parallel to the $[100]$ zone axis but is inclined slightly about the $[011]$ axis because the intensity of the $(02\bar{2})$ matrix spot is weaker than that of the (011) spot. On the other hand, for Ni_3Mo precipitates, the beam direction is fairly parallel to the $[102]$ axis in view of the nearly uniform intensities of the zonal spots. Therefore, Photo. 4 (b) shows a parallelism of the (011) matrix plane with the (010) Ni_3Mo plane, but no definite information on parallelisms of directions in these planes is available. So, another zonal pattern is taken in which zone axes are the $[011]$ for matrix and the $[0\bar{1}0]$ for Ni_3Mo phase. Photo. 5(a) is the pattern, from which the parallelism between $[1\bar{1}1]_{\alpha'}$ and $[100]_{\text{Ni}_3\text{Mo}}$ can be deduced because the $(2\bar{2}2)$ matrix spot and (400) Ni_3Mo spot are seen on the same line, as explained in the key diagram (b). Thus, the orientation relationship between the Ni_3Mo and the matrix may be represented as follows :

$$(011)_{\alpha'} // (010)_{\text{Ni}_3\text{Mo}}, [\bar{1}\bar{1}1]_{\alpha'} // [\bar{1}00]_{\text{Ni}_3\text{Mo}} \quad (1)$$

This result is essentially identical with that reported by Chilton and Barton⁽⁶⁾, but this paper is the first to present the orientation relationship showing diffraction patterns.

However, the above representation is not the unique one because another representation is possible as follows. As known from Tables 2 and 3, in the Ni_3Mo crystal, differences in d-spacings between (201) and (002) planes and between (400) and (203) planes are only 0.2 and 1.0%, respectively, and interplanar angles between (201) and $(20\bar{1})$ planes and between (002) and (201) planes are $59^\circ 18'$ and $60^\circ 21'$, respectively. That is, the $[010]$

Photo. 5 (a) Electron diffraction pattern showing matrix $[011]$ and Ni_3Mo $[010]$ zones.

(b) Key diagram of (a).

(O) $(011)_{\alpha'} // (010)_{\text{Ni}_3\text{Mo}}$; $[\bar{1}\bar{1}1]_{\alpha'} // [\bar{1}00]_{\text{Ni}_3\text{Mo}}$

(Δ) $(011)_{\alpha'} // (010)_{\text{Ni}_3\text{Mo}}$; $[\bar{1}\bar{1}1]_{\alpha'} // [\bar{1}00]_{\text{Ni}_3\text{Mo}}$

(o) Double reflections

zone pattern of Ni_3Mo crystal is nearly of the six-fold symmetry. Moreover, each spot from the Ni_3Mo is elongated by the size effect. Therefore, the indexing of Ni_3Mo spots in Photo. 5 (b) is not unambiguous. Rotating the indexing by 60° , the (400) Ni_3Mo spot lying on the $(2\bar{2}2)_{\alpha'}$ reciprocal lattice vector can be indexed changing into the (203) Ni_3Mo . In such a case, the orientation relationship can be represented as follows :

$$(011)_{\alpha'} // (010)_{\text{Ni}_3\text{Mo}}, [\bar{1}\bar{1}1]_{\alpha'} 0^\circ 42' [\bar{1}02]_{\text{Ni}_3\text{Mo}} \quad (2)$$

It is difficult to distinguish between the relationships (1) and (2) in view of the accuracy in electron diffraction. In the present study, however, the relationship (1) is adopted since the misfit between the interatomic distances along $[\bar{1}\bar{1}1]_{\alpha'}$ and $[010]_{\text{Ni}_3\text{Mo}}$ is smaller than that between those along $[\bar{1}\bar{1}1]_{\alpha'}$ and $[\bar{1}02]_{\text{Ni}_3\text{Mo}}$. The detailed discussion will be given later. Thus, the following analysis will be done by using the orientation relationship (1).

In Photos. 4 (b) and 5 (a) are seen many spots in addition to the zonal patterns included in the above orientation relationship. These additional spots were explained by double reflections and by reflections from a few variants of precipitates (there are twelve variants of the orientation relationship) as will be described below.

Fig. 1 Key diagram of Photo. 4 (b) in regard with extra spots except for $\text{Ni}_3\text{Mo}[\bar{1}02]$ zonal spots.

Figure 1 is a key diagram for the additional spots in Photo. 4 (b) and there are five kinds of zonal patterns of the Ni_3Mo phase, their orientation relationships and zone axes being shown in the caption of Fig. 1. Spots represented with triangles in Photo. 5 (b) are explained in the same way as the above, and the orientation relationship and the zone axis are shown in its caption.

The length direction of rod precipitates was described to be parallel to the $\langle 111 \rangle$ directions of the matrix in the previous sections. The $\langle 111 \rangle$ directions were verified to be a $[\bar{1}\bar{1}1]$ direction included in the orientation relationship.

VI. Discussion

1. Identification of precipitates

Most of diffraction patterns taken have been explained to consist of reflections from the matrix and Ni_3Mo precipitates. Let us, now, examine a few diffraction patterns referring to other types of precipitates which have been reported so far. Photo. 6 (a) is a diffraction pattern, the beam direction of which is nearly parallel to $[\bar{1}\bar{1}1]$ of the matrix. Showing a similar pattern to this, Chilton and Barton⁽⁶⁾ reported that the σ -FeTi phase was formed in maraging steels. In the present experiment, however, the diffraction pattern was successfully explained to be the $[\bar{1}02]$ zonal pattern from Ni_3Mo as shown in the key diagram (c). Ni_3Mo , of course, is formed with the orientation relationship (1) or (2) described in the previous section. Photo. 6 (b) is a dark-field image formed by the $(\bar{2}01)$ Ni_3Mo reflection, and shows that the shape of precipitates is a rod as in Photo. 4 (c).

Some other workers have reported that strengthening

Photo. 6 (a) Electron diffraction pattern showing $\text{Ni}_3\text{Mo}[\bar{1}02]$ zone.

(b) Dark-field image formed by the $\text{Ni}_3\text{Mo}(\bar{2}01)$ reflection.

(c) Key diagram of (a).

precipitates might be Laves phases ($\text{Fe}_2\text{Mo}^{(4)(9)(11)}$, $\text{Fe}_2\text{Ti}^{(1)(2)}$). In the present experiment, however, their characteristic d-spacings of 2.37 and 1.33 Å of Fe_2Mo and 4.14, 1.83, 1.76 and 1.34 Å of Fe_2Ti were not detected as shown in Table 3. Moreover, the observed intensities of precipitate spots are different from those of the Laves phase. There are also some reports which concluded that precipitates were austenite⁽¹⁾⁽¹²⁾. But the observed d-values in Table 3 also ruled out the possibility of the austenite precipitates.

However, there are a few diffraction patterns such that the existence of Ni_3Ti phase must be taken into consideration. Photo. 7 is an example showing the situation, in which the spots indexed as (020), (201), (211), etc. can be explained as those of the $[\bar{1}02]$ Ni_3Mo

Photo. 7 Electron diffraction pattern and the key diagram of the $\text{Ni}_3\text{Ti}[\bar{1}210]$ zone in addition to the $\text{Ni}_3\text{Mo}[\bar{1}02]$ zone.

zonal pattern. In addition to these spots, there are seen very weak spots at the middle points ($\uparrow$) between (201) and (211) or (211) and (221), etc. These extra spots could not be explained if precipitates were only the Ni_3Mo phase. They can be interpreted by assuming that the η -phase (Ni_3Ti , $a = 5.101 \text{ \AA}$, $c = 8.307 \text{ \AA}$ hexagonal crystal) is formed and that the orientation relationship between the η -phase and the matrix is $(011)_{\alpha} // (0001)_{\eta}$, $[\bar{1}\bar{1}1]_{\alpha} // [\bar{1}\bar{1}\bar{2}0]_{\eta}$, as shown in the key diagram. Missing of the (1010), (1011) and other spots in Photo. 7 may be due to the small structure factors and little amounts of Ni_3Ti precipitates. It can, thus, be concluded that the majority of the strengthening precipitates in the maraging steel investigated is the Ni_3Mo phase, and the supplemental precipitates are the Ni_3Ti phase. In Photo. 5 (a), the diffraction pattern from precipitates was explained as the $[010]$ zonal one of Ni_3Mo phase. However, they can also be explained consistently as the $[0001]$ zonal pattern of the Ni_3Ti phase, in regard with their d-spacings, interplanar angles, structure factors and orientation relationship. In such a case, the (201) and (400) spots from the Ni_3Mo phase should be indexed as (0220) and (2240) of the Ni_3Ti phase, respectively, so far as the zonal pattern represented by circles is concerned. Nevertheless, since many other diffraction patterns were explained only with the Ni_3Mo phase, precipitate spots in Photo. 5 (a) are considered to be those from the Ni_3Mo precipitates mainly and from the Ni_3Ti precipitates supplementarily.

2. Atomic arrangements of both phases at the interface and the orientation relationship

As the experimental result, the following two possible orientation relationships were obtained :

$$(011)_{\alpha} // (010)_{\text{Ni}_3\text{Mo}}, [\bar{1}\bar{1}1]_{\alpha} // [\bar{1}00]_{\text{Ni}_3\text{Mo}} \quad (1)$$

$$(011)_{\alpha} // (010)_{\text{Ni}_3\text{Mo}}, [\bar{1}\bar{1}1]_{\alpha} // 42^{\circ}21' [\bar{1}02]_{\text{Ni}_3\text{Mo}} \quad (2)$$

To examine the validity of these relationships, let us now compare the atomic arrangements at the interface between the matrix and precipitate. The closest packed plane and direction in bcc crystals are well known to be $\{110\}$ and $\langle 111 \rangle$, respectively. On the other hand, those in the Ni_3Mo crystal are (010) and $[\bar{1}00]$, respectively, as shown in Fig. 2 (a). Therefore, the first relationship (1) is just such a relation that the closest packed plane and direction of both phases are parallel to each other. Figure 2 (b) shows the atomic arrangements in the closest packed planes which are overlapped according to the relationship (1). From the figure, it is known that the fitting between the two phases are fairly good. Therefore, the relationship (1) can be considered to be reasonable. The $[\bar{1}02]$ direction of the Ni_3Mo crystal included in the relationship (2) makes an angle of $60^{\circ}21'$ with the $[\bar{1}00]$ direction of Ni_3Mo , and the interatomic distances along their directions are different from each other by only 1.07%. Then, if the closest packed planes are overlapped according to the relationship (2), the overlapped atomic arrangements may become nearly the same situation as

Fig. 2 (a) Atomic arrangement in the Ni_3Mo (010) plane.
(b) Superimposed atomic arrangement in bcc (011) and Ni_3Mo (010) planes.
● Matrix, ○ Ni_3Mo

shown in Fig. 2 (b). This means that the relationship (2) is also reasonable. When the Ni_3Mo crystal was regarded as the hcp structure neglecting the ordered arrangement of Ni and Mo atoms, both the $[\bar{1}00]$ and $[\bar{1}02]$ directions are perfectly equivalent and can be represented as $\langle 11\bar{2}0 \rangle$ directions in the hcp lattice. In such a case, both the two relationships may be represented as follows :

$$(011)_{\alpha} // (0001)_{\text{Ni}_3\text{Mo}}, [\bar{1}\bar{1}1]_{\alpha} // [\bar{1}\bar{1}\bar{2}0]_{\text{Ni}_3\text{Mo}}$$

This relationship is identical with the Burgers relationship which is well known in the bcc to hcp phase transformations. Therefore, it may be natural that the two representation (1) and (2) expressed in orthorhombic axes are difficult to distinguish from each other. However, since the atomic misfit between the $[\bar{1}02]_{\text{Ni}_3\text{Mo}}$ and $[\bar{1}\bar{1}1]_{\alpha}$ directions was larger than that between the $[\bar{1}00]_{\text{Ni}_3\text{Mo}}$ and $[\bar{1}\bar{1}1]_{\alpha}$ directions, the relationship including $[\bar{1}00]_{\text{Ni}_3\text{Mo}} // [\bar{1}\bar{1}1]_{\alpha}$ was adopted.

Atomic misfits along the three crystal axes of Ni_3Mo lattice were 1.86, 3.93 and 5.35% as shown in Fig. 3 (a). The misfits are very small and hence the interface between Ni_3Mo and the matrix can be considered to be coherent. Figure 3 (b) shows schematically distortions of the matrix lattice around the Ni_3Mo precipitates, the projection plane being (011) of the matrix. In fact, strain contrasts were observed around the precipitates. These lattice strains were considered to play an important role in the hardening mechanism of maraging steels.

From the stereographic analysis, the length direction of Ni_3Mo rod precipitates, $\langle 111 \rangle$, was verified to be

* The crystal axes of hcp structure are shown in Fig. 2(a) as a , b and c (c -axis is taken perpendicular to a - and b -axes, and the unit cell was chosen to be two times those of the usual hcp structure in comparison with the Ni_3Ti phase). In such a case, the indices of planes and directions in the orthorhombic lattice (small letters) are transformed to those in the hexagonal lattice (capital letters : four-digit indices) as follows :

Transformation of the indices of planes

$$\begin{pmatrix} H \\ K \\ L \end{pmatrix}_h = \begin{pmatrix} \frac{1}{2} & 0 & 1 \\ \frac{1}{2} & 0 & -1 \\ 0 & 2 & 0 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}_0$$

Transformation of the indices of directions

$$\begin{pmatrix} U \\ V \\ W \end{pmatrix}_h = \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & 0 \\ -\frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & \frac{1}{2} \\ 1 & 0 & -\frac{1}{2} \\ 0 & \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}_0$$

Fig. 3 (a) Illustration of distortions of matrix lattice along the crystal axes of Ni_3Mo precipitates.
(b) Schematic diagram showing the distorted matrix around the Ni_3Mo precipitate.

the $[\bar{1}\bar{1}1]$ direction involved in the orientation relationship. That the length direction of Ni_3Mo is parallel to $[\bar{1}\bar{1}1]$ of the matrix may be due to the smallest value of misfit (1.86%) in this direction.

V. Conclusions

The conclusions drawn from the present experiments are as follows :

- (1) The microstructure of as-quenched martensites was in the form of laths with a high density of randomly arranged dislocations.
- (2) The nucleations of precipitates were observed along dislocation lines and lath boundaries in the martensites.
- (3) The precipitates observed in the maximum hardness state were rod in shape, the size being about 25 Å in width and 500 Å in length, and the length direction was parallel to $\langle 111 \rangle$ of the matrix.
- (4) The crystal structure of the primary precipitates

was identified as the orthorhombic Ni_3Mo intermetallic compound.

(5) The orientation relationship between the Ni_3Mo precipitate and the matrix was concluded to possibly be described as $(010)_{Ni_3Mo} // (011)_{\alpha'}$, $[100]_{Ni_3Mo} // [\bar{1}\bar{1}1]_{\alpha'}$, that is, the closest packed plane and the direction in the precipitates were parallel to those in the matrix, as observed in many other precipitation phenomena. When the ordering of atoms in the Ni_3Mo crystal was disregarded, the relationship was represented by the Burgers relationship which is well known in the *bcc* to *hcp* phase transformation.

(6) The misfits along the crystal axes $[100]$, $[010]$ and $[001]$ of Ni_3Mo precipitates were 1.86, 3.93 and 5.35%, respectively. These small values mean that the interface between the Ni_3Mo precipitate and the matrix is coherent in accordance with the appearance of strain contrasts around the precipitates.

(7) The length direction of Ni_3Mo precipitates, $\langle 111 \rangle_{\alpha'}$, was verified to be the $[\bar{1}\bar{1}1]$ direction involved in the above orientation relationship. That the length direction of Ni_3Mo is parallel to $[\bar{1}\bar{1}1]$ of the matrix is due to the smallest misfit (1.86%) in this direction.

(8) The hexagonal Ni_3Ti phase was also detected as the supplemental precipitate. The orientation relationship between the Ni_3Ti precipitate and matrix was represented by the Burgers relationship.

Acknowledgments

The authors wish to thank Mr. A. Kamata of the Central Research Laboratory of Kawasaki Seitetsu Co., Ltd. for supplying the material. A part of this research was supported by the Grant-in-Aid for Fundamental Scientific Research from the Ministry of Education.