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Chapter

Crystallography of Precipitates in Metals and Alloys: (1) Analysis of Crystallography

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Abstract

This chapter and the following chapters describe crystallography of second-phase precipitate particles in metals and alloys. The focus of this chapter is placed on technical aspects in the analysis of their crystal structure, composition, and crystal orientation relationship with the matrix. Characterization of fine precipitates embedded in solid matrix is technically rather difficult; the signal from the matrix always hinders the signal from the precipitates. Although even state-of-the-art characterization techniques are still incomplete, it is becoming possible to assess the validity of assumptions involved in classic theories related to the crystallography of precipitates. For instance, recent experimental studies demonstrated that evolution of their crystal structure during nucleation seems to contradict the so-called classical nucleation theory, in terms of fluctuations in size and composition. Recent studies also demonstrated that their crystal orientation relationship with the matrix is often different from the one predicted by energy considerations related to the interfacial lattice mismatch. Furthermore, crystal orientation relationship with the matrix was found to be a factor controlling the magnitude of precipitation hardening, contrary to the conventional Orowan’s hardening model based on continuum elasticity theory calculations without considering crystallography.

Keywords: precipitates, nucleation, crystal structure, strength, dislocations

1. Introduction

This chapter and the following chapters review recent progress of our knowledge about crystallography of precipitate particles in metals and alloys [1–3]. The main focus is placed on the following three subjects:

1. Evolution of crystal structure during nucleation
2. Crystal orientation relationship with the matrix
3. Effect of crystallography of precipitates on mechanical properties

These subjects are closely related to the following three basic theories, each of which has a long history greater than a half century:
From an engineering viewpoint, the knowledge provided here is primarily useful for developing stronger materials. Dispersing fine precipitate particles over the matrix at high density is a common engineering technique for improving the strength of metals and alloys. By introducing a minor amount of second-phase precipitate particles, such as 2% in volume fraction, the material strength is increased by several times greater. In the traditional theory of precipitation hardening (a.k.a. dispersion strengthening) established in the 1950s–1960s, the primary factor controlling the magnitude of strengthening effect is assumed to be the shear modulus, whether or not precipitates are harder than the matrix. This concept has been partly revised in the past few years. Recent experimental studies using state-of-the-art material characterization techniques demonstrated that crystallography of precipitate particles is another factor dominating their obstacle strength. When the slip plane of dislocations in precipitates is not parallel to that in the matrix, dislocations are unable to cut through the precipitates, resulting in large hardening, regardless of the shear modulus. This subject is extensively discussed in the next chapter.

This chapter may also be of interest for the audience outside of the research community of materials science and solid-state physics. Nucleation is one of the areas of basic science related to a wide variety of research subjects including chemical reactions in liquid and gas. In fact, the first theory was originally developed for the nucleation of droplets from gas. Nucleation of crystals in solid is more complicated than the situation assumed in liquid and gas, in a sense that the formation of a new crystal is highly constrained by the surrounding matrix, in terms of the strain energy associated with the precipitate/matrix interface and the diffusivity of atoms for their agglomeration. A long-standing open question is the critical condition for nucleation regarding size and composition of nucleus. Precipitates are in many cases compounds consisting of multiple elements such as carbides and oxides. Unlike in gas and in liquid, the diffusivity of each element is not the same in solids. For instance, the diffusivity of light elements like carbon and oxygen is several orders of magnitude greater than that of metallic elements. Although the classical nucleation theory assumes that the crystal structure and composition of precipitates are the same as those of the final product from the beginning of embryo growth, the diffusivity difference indicates a possibility that the composition of precipitates fluctuates during the nucleation process. The classical nucleation theory also assumes that nucleation occurs when the embryos have grown up to a critical size. In many cases the critical size of precipitates for nucleation is 2–3 nm. Assessing the composition of such small precipitates has been technically impossible until recently. The highlights of recent studies are discoveries that, in the early stage of precipitation, the crystal structure and composition of precipitates are different from those of the final product and that the precipitates structurally transform into the final product at a critical size with a critical composition. Precipitates are clusters of solute elements when they start spontaneous growth, which is defined as the state of “nucleation” in the classical nucleation theory. An implication of this finding is that the obstacle strength of precipitates in precipitation hardening may change during precipitation. They are weak obstacles in the early stage of precipitation regardless of the crystal structure of the final product. They can become strong obstacles due to a change in the shear modulus or...
the crystal structure. In some cases, precipitates become brittle by the structural change, while they are ductile in the state of solute clusters. Brittle precipitates are considered to serve as the nucleation site of cracks via particle cracking. Hence, from the viewpoint of fracture mechanics, the ductile-brittle transition of precipitates during precipitation considered a factor controlling the engineering lifetime of materials.

As a result of the constraints from the surrounding matrix, precipitation of the second phase often occurs with a specific crystal orientation relationship with the matrix. Precipitates and matrix share a specific atomic plane in such a way to minimize the mismatch between them. The orientation relationship is dependent on their crystal structure. For instance, in the Burgers orientation relationship, bcc precipitates in hcp matrix share atomic planes as follows (Figure 2) [13]:

\[
\text{(0001)}_{\text{hcp}} \cap (\text{110})_{\text{bcc}} \cap (2\text{T0})_{\text{hcp}} = (\text{1T1})_{\text{bcc}}.
\]

Since the lattice parameter is specific to materials, a preferable orientation relationship changes depending on the degree of mismatch of lattice parameter between precipitates and matrix. The Burgers orientation relationship is the optimum configuration for the combination of bcc pure Zr and hcp pure Zr, but another orientation relationship is preferred for the bcc Nb precipitates containing a few amount of Zr. The Zr-Nb binary system is a complete solid solution in a bcc structure at high temperatures [14]. The difference of lattice parameter between the bcc Zr and the bcc Nb is \(~10\%\) [15]; the lattice parameter of bcc precipitates changes in accordance with Vegard’s law [2]. Apart from a remarkable progress in theoretical works on the orientation relationships, experimental studies have recently demonstrated that precipitates and matrix do not always follow such a theoretically predictable, ideal orientation relationships in reality. Recent analysis using electron backscatter diffraction (EBSD) (Figure 3)
typically 40 years), precipitation of Ni, Mn, and occasionally Si becomes dominant over Cu [44]. The Ni—Mn—Si precipitates have been called the late-blooming phase [45–47] since their structural and compositional features were unclear at that time. It was very recently that the late-blooming phase is in many cases found to be characterized as the G-phase [48, 49]. The composition of the late-blooming phase detected by APT is not always the same [31, 32]. The composition range of Ni—Si—Mn clusters to become brittle G-phase is a subject to be investigated further.

4. Crystal orientation relationship with the matrix

Crystal orientation relationship between precipitates and matrix is a potential factor controlling the mechanical properties of metals and alloys. Dislocations can glide on specific atomic planes, the choice of which is specific to crystal structure and material. For instance, the slip plane is the {111} plane for fcc metals, the {0001} plane for hcp magnesium, and the {10-10} plane for hcp titanium and hcp zirconium [9]. When the slip plane of precipitates is not parallel to that of the matrix, dislocations are in theory unable to cut through the precipitates. Although the orientation relationship has been extensively studied in the past [50], only a few studies have been reported on the effect of the crystal mismatch on the plasticity [1, 2]. The absence of such studies is partly due to a technical difficulty in determination of crystal orientation of fine precipitate particles as mentioned in the Section 2. Recently, Matsukawa et al. performed a systematic analysis on the parallelism of atomic planes between precipitates and matrix in a Zr—2.5Nb alloy: the precipitates are bcc Nb containing Zr—10% and the matrix is hcp Zr. Based on the analysis results obtained from 100 precipitate particles (~50 nm in diameter) by means of TKD, they demonstrated that the orientation is practically random. Only 1 out of 100 precipitates had a slip plane parallel to that of the matrix. Their experimental result is inconsistent with a preceding theoretical prediction by Zhang and Kelly [51, 52]. Judging from the mismatch of inter-planar spacings, the most favorable crystal orientation relationship for the Nb-rich bcc precipitates in the hcp Zr matrix is \( (1011)_{\text{hcp}} \equiv (11\overline{2}3)_{\text{bcc}} \equiv (113)_{\text{bcc}} \) (Figure 2). Matsukawa et al. further demonstrated that the absence of such a specific crystal orientation relationship is attributable to the recrystallization of the matrix. In the Zr—2.5Nb alloy, precipitation occurs in parallel with recrystallization as follows. The Nb atoms are fully dissolved in the matrix at high temperatures with a bcc structure (Figure 10). Quenching from this temperature range results in nucleation of bcc Nb nano-precipitates and hcp Zr fine martensites. Ostwald ripening of Nb precipitates occurs during annealing at medium temperatures (773—853 K) together with the recrystallization of the martensite Zr matrix. The initial orientation relationship between the precipitates and the matrix is overwritten by the recrystallization.

In the study of the Zr—2.5Nb alloy, the parallelism of slip planes between precipitates and matrix was analyzed as follows. This analysis is achieved by using the Euler angles obtained from EBSD/TKD measurements, though so far not automated. The analysis procedure is slightly different depending on the analysis software due to the different definition of the Euler angles. In the case of the TSL-OIM software based on Bunge’s description [53], the Euler angles \( (\alpha_1, \beta_1, \gamma_1) \) are given by three rotations along \( z_1-x-z_2 \) axes in accordance with passive rotation (intrinsic rotation), where the axes are rotated instead of the vectors of object, while the object is fixed in space (Figure 11). In this case, the rotation matrix \( (R) \) relative to the space coordinates is given as follows [54]:

\[ R = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} \]
typically 40 years), precipitation of Ni, Mn, and occasionally Si becomes dominant over Cu [44]. The Ni–Mn(Si) precipitates have been called the late-blooming phase [45–47] since their structural and compositional features were unclear at that time. It was very recently that the late-blooming phase is in many cases found to be characterized as the G-phase [48, 49]. The composition of the late-blooming phase detected by APT is not always the same [31, 32]. The composition range of Ni–Si–Mn clusters to become brittle G-phase is a subject to be investigated further.

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\[
\begin{pmatrix}
R_{11} & R_{12} & R_{13} \\
R_{21} & R_{22} & R_{23} \\
R_{31} & R_{32} & R_{33}
\end{pmatrix}
\]
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尼亚-锰-硅)沉淀物被称为晚生成相[45–47]，因为它们的结构和组成特征在当时并不清楚。直到最近，晚生成相在许多情况下被发现是G相[48, 49]。通过APT检测的晚生成相的组成并不总是相同的[31, 32]。Ni–Si–Mn簇变成脆性G相的组成范围是一个需要进一步研究的课题。

4. 晶格取向与基体的关系

晶格取向关系是决定金属和合金机械性能的潜在因素。位错可以在特定的原子平面上滑移，这取决于晶体结构和材料。例如，fcc金属的滑移面是{111}平面，hcp镁的滑移面是{0001}平面，hcp钛和hcp锆的滑移面是{10-10}平面[9]。当沉淀物的滑移面不平行于基体时，理论上位错将无法切过沉淀物。尽管晶格取向关系在过去的文献中被广泛研究[50]，但关于晶格错配对塑性影响的研究很少。缺乏此类研究的部分原因是由于技术难度，特别是对于细小沉淀物颗粒的晶格取向测定的挑战[2]。最近，Matsukawa等人对Zr–2.5Nb合金中的沉淀物和基体的平行界面进行了系统分析：沉淀物是含Zr<sub>10%</sub>的bcc Nb，基体是hcp Zr。基于对100个粒子（直径约50 nm）采用TKD方法获得的结果，他们证明了晶格取向是随机的。只有100个中的一个粒子的滑移面与基体平行。他们的实验结果与Zhang和Kelly先前的理论预测[51, 52]不一致。根据界面间距的匹配，Nb-rich bcc沉淀物在hcp Zr基体中的最有利晶格取向关系为

\[
\begin{align*}
\text{bcc} & \quad \langle 1011 \rangle,
\text{hcp} & \quad \langle 0001 \rangle,
\text{bcc} & \quad \langle 1123 \rangle,
\text{hcp} & \quad \langle 11\bar{3} \rangle
\end{align*}
\]

（图2）。Matsukawa等人进一步证明了这种特殊晶格取向关系的缺乏归因于基体的再结晶。在Zr–2.5Nb合金中，沉淀物的形成与基体的再结晶密切相关。Nb原子在高温度下完全溶解在基体中，并形成bcc Nb纳米沉淀物和hcp Zr细态马氏体。在773–853 K的温度范围内，通过位错扩散，Nb沉淀物会发生再结晶。基体中最初的晶格取向关系会因再结晶而被覆盖。在Zr–2.5Nb合金的分析中，沉淀物和基体的滑移面平行关系分析如下。该分析是通过使用EBSD/TKD测量获得的Euler角度实现的，尽管目前尚未实现自动化。分析程序取决于分析软件，因为不同的Euler角度定义。对于基于Bunge描述的TSL-OIM软件[53]，Euler角度（\(\alpha, \beta, \gamma\)）由沿z₁-x₂-z₂轴的三个旋转组成，这是在被动旋转（内部旋转）中完成的，其中轴旋转，而对象保持在空间中（图11）。在这种情况下，相对于空间坐标系的旋转矩阵（R）为

\[
R = \begin{bmatrix}
R_{11} & R_{12} & R_{13} \\
R_{21} & R_{22} & R_{23} \\
R_{31} & R_{32} & R_{33}
\end{bmatrix}
\]

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In the reference crystal, the z- and the x-axes of space coordinates are parallel to the [001] and to the [100] directions of cubic crystals. Here, we consider the orientation relationship between two cubic crystals, A and B, whose rotation matrices relative to the reference crystal are $R_A$ and $R_B$. The rotation matrix between these two crystals ($R_C$) is given as follows:

$$
R = R_{z_1}(\varphi_2)R_x(\Phi)R_{z_1}(\varphi_1) = \begin{pmatrix}
\cos \varphi_1 & \sin \varphi_1 & 0 \\
-\sin \varphi_1 & \cos \varphi_1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \Phi & \sin \Phi \\
0 & -\sin \Phi & \cos \Phi
\end{pmatrix}
\begin{pmatrix}
\cos \varphi_2 & \sin \varphi_2 & 0 \\
-\sin \varphi_2 & \cos \varphi_2 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos \varphi_1 & \sin \varphi_1 & 0 \\
-\sin \varphi_1 & \cos \varphi_1 & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

(1)

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$$
\begin{pmatrix}
H_1 \\
K_1 \\
L_1
\end{pmatrix}
= R_A
\begin{pmatrix}
0 \\
0 \\
1
\end{pmatrix}
\rightarrow
R_A^{-1}
\begin{pmatrix}
H_1 \\
K_1 \\
L_1
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
1
\end{pmatrix}
$$

(2)

$$
\begin{pmatrix}
H_2 \\
K_2 \\
L_2
\end{pmatrix}
= R_B
\begin{pmatrix}
0 \\
0 \\
1
\end{pmatrix}
\rightarrow
R_B^{-1}
\begin{pmatrix}
H_2 \\
K_2 \\
L_2
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
1
\end{pmatrix}
$$

(3)
Figure 11
Passive rotations of a cubic crystal with Euler angles (the Bunge Euler angles).

\[
\begin{pmatrix}
0 \\
1
\end{pmatrix} = R_B^{-1} \begin{pmatrix}
H_2 \\
K_2 \\
L_2
\end{pmatrix} = R_A^{-1} \begin{pmatrix}
H_1 \\
K_1 \\
L_1
\end{pmatrix} \rightarrow \begin{pmatrix}
H_2 \\
K_2 \\
L_2
\end{pmatrix} = R_B \ R_A^{-1} \begin{pmatrix}
H_1 \\
K_1 \\
L_1
\end{pmatrix}
\] (4)

\[
\begin{pmatrix}
H_2 \\
K_2 \\
L_2
\end{pmatrix} = R_C \begin{pmatrix}
H_1 \\
K_1 \\
L_1
\end{pmatrix} \rightarrow R_C = R_B \ R_A^{-1}
\] (5)
Crystallography

An atomic plane of crystal B, \((H_2' K_2' L_2')\), parallel to \((H_1' K_1' L_1')\) of the crystal A is expressed by using the Euler rotation matrix, \(R_D\), which rotates the sample coordinates in such a way as to match \([H_1' K_1' L_1']\) to \([001]\) in the space coordinates:

\[
\begin{pmatrix}
H_1' \\
K_1' \\
L_1'
\end{pmatrix} = R_D \begin{pmatrix} H_2' \\ K_2' \\ L_2' \end{pmatrix} = R_B R_A^{-1} \begin{pmatrix} H_1' \\ K_1' \\ L_1' \end{pmatrix} = R_B R_A^{-1} R_D \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}
\]

(6)

\(R_A\) and \(R_B\) are directly determined by EBSD measurements of crystals A and B. The Euler angles of the \(R_D\) are determined by using a simulation equipped on the TSL-OIM data collection software. This simulation module is capable of (1) calculating how the index of a crystal (in the ND and the RD directions) changes in accordance with rotations along the three axes and (2) visualizing where the index (of the ND direction) is located on the Kikuchi map (the inverse pole figure). By using these functions, the index \(H_{\text{ND}}\) (of the ND direction) is located on the Kikuchi map (the inverse pole figure). By plotting the data points, the practical accuracy of this analysis method is determined by EBSD data. In order to estimate the practical accuracy of this analysis method, they first analyzed a standard sample in which the atomic-plane parallelism between grains is already known. Their standard sample was a type-316 austenitic stainless steel containing annealing twins (Figure 12). The twin boundary of fcc metals is one of the four crystallographically equivalent \(\{111\}\) planes. The Euler angles of these \(\{111\}\) planes for the \(R_D\) rotation are, e.g., \((\varphi_1, \Phi, \varphi_2) = (0^\circ, 55^\circ, 45^\circ), (0^\circ, 55^\circ, 135^\circ), (0^\circ, 55^\circ, 225^\circ)\), and \((0^\circ, 55^\circ, 315^\circ)\). They performed this analysis on 50 twin couples and found that the largest offset from the exact \(\{111\}\) was 3.3°. This is the magnitude of practical error of this analysis method.

To date, several orientation relationships have been reported on bcc precipitates in hcp matrix (Figure 13). The parallelism of slip planes in those orientation relationships is as follows: (1) the Burgers orientation relationship \([13]\): \((0001)_{\text{hcp}}/\langle 110\rangle_{\text{bcc}} \cap (2\overline{1}00)_{\text{hcp}}/\langle 1\overline{1}0\rangle_{\text{bcc}}\), \(\{10\overline{1}0\}\), is not exactly parallel to the slip plane of bcc Nb precipitates, \(\{110\}\) or \(\{112\}\); however, the rotational offset between the \((1\overline{1}0)_{\text{hcp}}\) and the \((1\overline{1}0)_{\text{hcp}}\) is only 5.3°. (2) The Pitsch-Schrader orientation relationship \([55]\): \((0\overline{0}01)_{\text{hcp}}/\langle 1\overline{1}0\rangle_{\text{bcc}} \cap (1\overline{0}00)_{\text{hcp}}/\langle 1\overline{1}0\rangle_{\text{hcp}}\). The slip planes are exactly parallel to each other. (3) The Potter orientation relationship \([56]\): \((2\overline{1}\overline{1}0)_{\text{hcp}}/\langle 1\overline{1}1\rangle_{\text{hcp}} \cap (1\overline{0}10)_{\text{hcp}}/\langle 1\overline{1}1\rangle_{\text{hcp}}\). One of the \(\{112\}_{\text{bcc}}\) is not exactly but nearly parallel to one of the \(\{1\overline{0}00\}_{\text{hcp}}\). This orientation relationship is close to the Burgers, from which the rotational offset is only \(~1.5^\circ\). (4) The Rong-Dunlop orientation relationship \([57]\): \((0\overline{0}01)_{\text{hcp}}/\langle 1\overline{2}0\rangle_{\text{hcp}} \cap (1\overline{0}1\overline{2})_{\text{hcp}}/\langle 001\rangle_{\text{hcp}} \cap (1\overline{1}00)_{\text{hcp}}/\langle 2\overline{1}0\rangle_{\text{hcp}}\). The slip plane of hcp and bcc crystals is not parallel to each other. (5) The Zhang and Kelly orientation relationships \([51, 52]\): \((0\overline{0}01)_{\text{hcp}}/\langle 1\overline{1}0\rangle_{\text{hcp}} \cap (10\overline{1}0)_{\text{hcp}}/\langle 1\overline{1}3\rangle_{\text{hcp}}\). They proposed several orientation relationships. This one is the most favorable orientation relationship for the bcc Nb precipitates, in terms of the mismatch of the lattice parameter. Their analysis also
suggested that the Pitsch-Schrader and the Rong-Dunlop orientation relationships are favorable over the Burgers orientation relationship for Nb-rich precipitates. This orientation relationship is close to the Burgers, and the slip plane of matrix is not exactly parallel to that of precipitates.

The magnitude of error of the abovementioned analysis of atomic-plane parallelism is greater than the orientation difference between the Potter and the Burgers orientation relationships, 1.5°. It follows that these two orientation relationships are practically indistinguishable from each other in this analysis. On the other hand, the orientation difference between the Pitsch-Schrader and the Burgers orientation relationships is 5.3°; in theory, they are distinguishable. In both the Burgers and the Pitsch-Schrader orientation relationships, the basal plane of the hcp crystal is parallel to a {110} plane of the bcc crystal. In other words, when any one of {110} planes of a precipitate is not parallel to the (0001) plane of the matrix, it follows that the precipitate is in neither one of these two orientation relationships. The criterion for the judgment of whether the Burgers or the Pitsch-Schrader is given by

Figure 12
Evaluation of the magnitude of error of the EBSD analysis method on the atomic plane parallelism described in this chapter, using annealing twins in a type-316 stainless steel [2]. The largest offset from the exact {111} was ~3.3°. This is considered as the magnitude of practical error of this analysis method.
Figure 13
Examples of crystal orientation relationships between bcc and hcp crystals [2]: (a) the Burgers, (b) the Pitsch-Schrader, (c) the Potter, (d) the Rong-Dunlop, and (e) the Zhang-Kelly No. 5.
another atomic-plane parallelism, which is whether \( \{11\bar{2}0\}_{\text{hcp}}/\{111\}_{\text{bcc}} \) or \( \{1\bar{1}00\}_{\text{hcp}}/\{110\}_{\text{bcc}} \). As for the parallelism of slip planes, hcp crystals have three crystallographically equivalent \( \{10\bar{1}0\} \) planes, whereas bcc crystals have 12 equivalent \( \{110\} \) planes and another 12 equivalent \( \{112\} \) planes.

In the study of the Zr–2.5Nb alloy, Matsukawa et al. fixed the plane of hcp matrix and plotted its corresponding atomic planes of bcc precipitates on an inverse pole figure (Figure 4). In the TSL-OIM software, the Euler angles of hcp crystals are given in the orthogonal coordinate system. In the reference crystal, the z- and the x-axes of space coordinates are parallel to the \( [0001] \) hcp and \( [2\bar{1}00] \) hcp, respectively. The Euler angles for the RD rotation of the \( \{11\bar{2}0\} \) and the \( \{10\bar{1}0\} \) planes are shown in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Index</th>
<th>Euler angle ((\varphi_1, \Phi, \varphi_2) [^\circ])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal</td>
<td>0001</td>
</tr>
<tr>
<td>Prismatic (type 1)</td>
<td>01(\bar{1})0</td>
</tr>
<tr>
<td></td>
<td>10(\bar{1})0</td>
</tr>
<tr>
<td></td>
<td>(\bar{1})00</td>
</tr>
<tr>
<td>Prismatic (type 2)</td>
<td>21(\bar{1})0</td>
</tr>
<tr>
<td></td>
<td>(\bar{1})10</td>
</tr>
<tr>
<td></td>
<td>(\bar{7})10</td>
</tr>
</tbody>
</table>

5. Conclusion

Recent progresses in our understanding of the crystallography of precipitates in metals and alloys have been briefly reviewed. The major highlights are the following three: (1) crystal structure of precipitates changes during nucleation. This concept in itself has been known since the 1930s. Recent new findings concern the critical conditions for the structural change in terms of fluctuations in size and composition, discovered by means of combining transmission electron microscopy crystallographic analysis with atom probe tomography compositional analysis. It appears that the structural change occurs at a critical size with a critical composition. There is a long incubation period (in some cases a year long) before the structural change after the growth to be the critical size. During the incubation period, enrichment of solute elements occurs inside the precipitates without further size growth. It still remains unclear if these features are universal for any types of precipitates. This research field is expected to advance drastically in the years ahead. (2) In the past years, it has also become technically possible to examine the crystal orientation relationship of fine precipitate particles such as \( \sim 50 \) nm in diameter with the matrix, on numbers of samples numerically sufficient for statistical arguments. Transmission Kikuchi diffraction, which is an advanced technique of electron backscatter diffraction equipped with a scanning electron microscope, revealed that the crystal orientation of precipitates can be random even when they are in theory favorable to have a specific orientation relationship with the matrix from the viewpoint of lattice mismatch. It appears that such a situation is realized when the
matrix exhibits recrystallization after precipitation. (3) Crystal orientation relationship between precipitates and matrix was found to be a factor controlling the magnitude of precipitation hardening. This is a new concept beyond the scope of the traditional theory of precipitation hardening, which assumes that the hardening is controlled solely by the shear modulus, whether or not the precipitates are harder than the matrix. In cases where the slip plane of precipitates is not parallel to the slip plane of the matrix, dislocations gliding in the matrix are unable to cut through them, resulting in strong obstacles regardless of the shear modulus. Further information on this issue is provided in the next chapter.

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Conflict of interest

The author declares no conflicts of interest directly relevant to the content of this chapter.
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