Turk J Phy
24 (2000) , 737 – 745.
© TÜBİTAK

Crystallographic Analysis of Martensitic Transformation in CuSn Alloy

Ekrem ARTUNÇ, Seyfettin ÇAKMAK
Suleyman Demirel University, Physics Department,
32260 Isparta-TURKEY
Seval ÇAKMAK
Suleyman Demirel University, Institute of Science,
32260 Isparta-TURKEY

Received 09.04.1999

Abstract

In this study, the Kajiwara model has been applied to Cu-14.8at.%Sn alloy with good agreement with experimental results. For this alloy, the austenite phase has a body centered cubic (bcc) lattice and the martensite phase has a monoclinic 9R superlattice.

Using the lattice parameters of both phases, the calculated habit plane indices, magnitude of the lattice invariant shear and orientation relationships, have been compared with the observed results for this alloy.

1. Introduction

Crystallographic phenomenological theory of martensitic transformations has been presented by Wechsler, Lieberman and Read (WLR) [1] , and Bowles and Mackenzie (BM) [2]. WLR and BM applied their crystallographic phenomenological theory to many alloy systems and obtained a good agreement between theoretical and experimental values. However, measurements in many other alloy systems have also revealed discrepancies between experiment and theoretical predictions [3]. In order to overcome this difficulty, Acton and Bevis [4], and Ross and Crocker [5] generalized the theory by introducing multiple lattice invariant shears. The original formulations of these theories consist of rather lengthy and complicated matrix algebra. On the other hand, Suzuki [6] developed a much simpler method for calculating crystallographic parameters of martensitic transformation.

For the martensitic transformation of the *bcc* into orthorhombic *9R* in Cu-based alloys, a model was proposed by De Vos et al. [7]. The model is based on the WLR theory.

However, a more generalized model which is based on the Suzuki model, was proposed by Kajiwara [8]. In this model, the austenite lattice has the *bcc* (DO_3) and the martensite lattice has the monoclinic *9R* close-packed structure.

Crystallographic phenomenological theory of martensitic transformations is based on the assumptions that there should be no average distortion at the matrix-martensite interface (i.e., at the habit plane) and, furthermore, this interface should remain unrotated during the transformation. Only by using this basic condition and lattice parameters of austenite and martensite phases, and by assuming lattice invariant strain system (or twinning shear system), the theory can predict the habit plane indices, orientation relationships between the austenite and martensite lattices, and magnitude of the lattice invariant shear associated with the martensitic transformation.

In this work, the Kajiwara model is applied to the transformation of *bcc* to *monoclinic 9R* close-packed structure in the Cu-14.8 (% at.) Sn alloy, and analytical equations for the habit plane indices and orientation relationships and magnitude of the lattice invariant shear are derived. The martensitic crystallographic parameters were calculated with a program written in FORTRAN77. The theoretical calculations for the *bcc* to *9R* transformation in this alloy are compared with experimentally observed crystallographic features.

2. Experimental Observations

The study of martensite in Cu-Sn alloys has a long history, but their crystallography was not clear until electron microscopic observations were made. In order to obtain data about the mechanism of martensitic transformation in the Cu-14.8(%at.)Sn alloy, experiments were made by Nishiyama et al. [9,10]. They observed two kinds of martensite: banded (β') and wedgeshaped (β''). The β' martensite was produced by quenching from 700 °C into water at 0 °C. The electron diffraction pattern of this alloy suggests that the martensite lattice is orthorhombic or monoclinic. Therefore, the β' martensite structure of this alloy can assume as disordered or *monoclinic 9R* structure. Furthermore, Nishiyama et al. reported that the c-axis is rotated by almost 6° relative to the basal plane. In the present case, the martensite transformation is considered to be formed along the shear (110) plane in the $[1\,\bar{1}\,0]$ direction of the parent β_1 lattice (*bcc* or DO_3 type superlattice). The habit plane which as obtained by Greninger and Mooradian [11], is different from the $\{133\}_{\beta_1}$, but instead is rather near to the $\{223\}_{\beta_1}$ plane [12].

The β'' martensite was produced by quenching into water and then dipping in liquid nitrogen. In this martensite transformation, the shearing plane is (110) and shearing direction is $[1\,\bar{1}\,0]$, as observed in the β' martensite of the same alloy. The experiment was made by electron microscopy to clarify of the β'' martensite, with the conclusion that it had a Fe_3Al type superlattice β_1 (or DO_3) in the retained state [10]. From the diffraction patterns, it is found that the β'' martensite has a superlattice structure.

3. Analytical Equations for Calculations

3.1. Magnitude of the Lattice Invariant Shear and the Habit Plane Indices

For calculations, the martensite lattice was assumed to be a monoclinic *9R (M9R)* structure. The austenite lattice is in the *bcc* (or DO_3) type superlattice. The lattice deformation of *bcc* to *M9R* martensite was proposed by Kajiwara [8]. Using a similar lattice deformation (or twinning shear), the vector , $a_{bcc}[\bar{1}0\bar{1}]$, $a_{bcc}[0\bar{1}0]$ and $a_{bcc}[\bar{5}04]$ in the *bcc* phase are transformed into $a[100]$, $b[010]$, and $c[001]$ in *9R* phase, respectively, where a_{bcc} is a lattice constant of the *bcc* phase. For this transformation, the correspondence matrix can be expressed as

$$C = \begin{pmatrix} -1 & 0 & -5 \\ 0 & -1 & 0 \\ -1 & 0 & 4 \end{pmatrix}. \tag{1}$$

The matrix C transforms any vector $[uvw]_{bcc}$ to a vector $[uvw]_{9R}$. For brevity, put

$$\begin{bmatrix} u \\ v \\ w \end{bmatrix}_{bcc} = X_A, \begin{bmatrix} u \\ v \\ w \end{bmatrix}_{9R} = X_M \tag{2}$$

then we can write

$$X_A = CX_M \text{ or } X_M = C^{-1}X_A \tag{3}$$

where C^{-1} is the inverse of the matrix C. The corresponding relation between the planes $(hkl)_{bcc}$ and $(hkl)_{9R}$ is expressed by using the row matrices $n_A = (hkl)_{bcc}$ and $n_M = (hkl)_{9R}$:

$$n_M = n_A.C \text{ or } n_A = n_M.C^{-1}. \tag{4}$$

For the *bcc* to *M9R* transformation, the twinning shear is $(\bar{1}01)[\bar{1}0\bar{1}]_{bcc}$ or equivalently $(001)[100]_{9R}$ [13]. Thus, the lattice invariant deformation matrix G is

$$G = \begin{pmatrix} 1 & 0 & g \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{5}$$

where $g' = ga/(c\sin\beta_0)$ and g' is the magnitude of the lattice invariant shear. By this shear, the lattice vector X_M and the plane n_M are transformed into X'_M and n'_M, respectively. Then, we can write as follows:

$$X'_M = GX_M = TX_A \tag{6}$$

$$n'_M = n_M G^{-1} = n_A T^{-1}, \tag{7}$$

where the matrix T is equal to the matrix GC^{-1} and G^{-1} is the inverse of the matrix G. Using Eq. (1) and (5), the matrix T is calculated as follows:

$$T = -\frac{1}{9}\begin{pmatrix} 4+g & 0 & 5-g \\ 0 & 9 & 0 \\ 1 & 0 & -1 \end{pmatrix}. \tag{8}$$

It is therefore concluded that the matrix T transforms the vector $[uvw]_{bcc}$ and the plane $(hkl)_{bcc}$ into the vector $[u'v'w']_{9R}$ and the plane $(h'k'l')_{9R}$, respectively. But, an arbitrary vector $[1yz]$ lying in the habit plane $(1YZ)$ is invariant, since of there should be no average distortion at this habit plane. Then, the following equation holds:

$$1 + yY + zZ = 0. \tag{9}$$

The vector $[1yz]_{bcc}$ is transformed into the vector $[-\frac{1}{9}\{4+g(1-z)+5z\}, -y, \frac{1}{9}(z-1)]_{9R}$ by Eq. (6). The latter vector must also lie in the habit plane. Therefore, the lengths of the above two vectors must be the same. From this condition and using Eq. (9), we obtain the equation with respect to z as follows:

$$A(Y,Z,g)z^2 + B(Y,Z,g)z + C(Y,g) = 0. \tag{10}$$

This equation should hold for any value of z, hence each coefficient of z must be zero. As a result of this condition, g $(or\ g')$, Y and Z are obtained as follows:

$$Y = \pm 9\sqrt{\frac{a_{bcc}^2 - b^2}{a^2(4+g)^2 + 2ac(4+g)\cos\beta_0 + c^2 - 81a_{bcc}^2}} \tag{11}$$

$$Z = \sqrt{\frac{a^2(5-g)^2 - 2ac(5-g)\cos\beta_0 + c^2 - 81a_{bcc}^2}{a^2(4+g)^2 + 2ac(4+g)\cos\beta_0 + c^2 - 81a_{bcc}^2}}. \tag{12}$$

$$g' = \frac{a}{c\sin\beta_0} - ctg\beta_0 \pm \frac{9a_{bcc}}{\sqrt{2}c\sin\beta_0}\sqrt{(\frac{a^2}{2a_{bcc}^2} - 1)(\frac{2c^2\sin^2\beta_0}{81a_{bcc}^2} - 1)} \tag{13}$$

As seen in the above equations, g', Y and Z are dependent only on the lattice constants of both phases.

3.2. Orientation Relationships

The derivation of the orientation relationships was performed on a martensite variant of which the habit plane indices have positive sign. It is seen by Eq. (7) with g that the habit plane $(1YZ)_{bcc}$ is transformed into $(HKL)_{9R}$. Since the habit plane is invariant during the transformation, $(1YZ)_{bcc}$ must be parallel to $(HKL)_{9R}$. Any given vector lying on the habit plane must also be invariant during the transformation. For example, the intersection of $(100)_{bcc}$ plane with the habit plane $(1YZ)_{bcc}$ is $[u_1\, u_2\, u_3]_{bcc}$ and this direction is transformed into $[u_1'\, u_2'\, u_3']_{9R}$ by Eq. (6). Since the direction $[u_1\, u_2\, u_3]_{bcc}$ lies on the habit plane, it must be invariant and hence parallel to the direction $[u_1^{'}\, u_2^{'}\, u_3^{'}]_{9R}$. Therefore the following orientation relationship is obtained:

$$(1YZ)_{bcc}//(HKL)_{9R}$$

$$[u_1\, u_2\, u_3]_{bcc}//[u_1^{'}\, u_2^{'}\, u_3^{'}]_{9R}.$$

The orientation relationships between some prominent planes and directions are derived from the above relation by the following procedures. First, set up a new orthogonal coordinate system with its origin on the habit plane, of which x_0 - and y_0 - axes are taken to be parallel to $[u_1\, u_2\, u_3]_{bcc}$ and the habit plane normal $[1YZ]_{bcc}$, respectively. The unit length in the *bcc* lattice coordinate system is taken as the unit length in this new orthogonal coordinate system. That is, the unit vector along x_0 -axis in the above orthogonal coordinate system is taken equal to the normalized direction of $[u_1\, u_2\, u_3]_{bcc}$, and the unit vector y_0 -axis equal to the normalized direction of $[1YZ]_{bcc}$. A direction perpendicular to the above two directions is parallel to z_0 -axis and its unnormalized direction is $[w_1\, w_2\, w_3]_{bcc}$. Therefore the following relation holds between the direction $[u\, v\, w]_{bcc}$ in *bcc* coordinate system and the direction $[u\, v\, w]_0$ in the $x_0 y_0 z_0$ -coordinate system:

$$\begin{bmatrix} u \\ v \\ w \end{bmatrix}_{bcc} = \begin{pmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{pmatrix} \begin{bmatrix} u \\ v \\ w \end{bmatrix}_0 . \tag{14}$$

The next step is to obtain a similar relation between the direction $[uvw]_{9R}$ in monoclinic coordinate system of *9R* martensite and direction $[uvw]_0$. The vectors $[u_1\, u_2\, u_3]_{bcc}$ and $[w_1\, w_2\, w_3]_{bcc}$, which are the vectors along x_0- and z_0-axes, are transformed by Eq. (6) into $[u_1\, u_2\, u_3]_{9R}$ and $[w_1\, w_2\, w_3]_{9R}$, respectively. Since x_0- and z_0-axes lie on the habit plane, the above two vectors are invariant during the transformation. Therefore, the transformed vectors,$[u_1'\, u_2'\, u_3']_{9R}$ and $[w_1'\, w_2'\, w_3']_{9R}$, in monoclinic coordinate system of the *9R* martensite, correspond to the vectors along x_0- and z_0-axes in the $x_0 y_0 z_0$-coordinate system. A vector corresponding to the vector along y_0-axis is calculated to be $[v_1'\, v_2'\, v_3']_{9R}$ from these two vectors. Thus the following relationship is obtained:

$$\begin{bmatrix} u \\ v \\ w \end{bmatrix}_{9R} = \begin{pmatrix} u_1' & v_1' & w_1' \\ u_2' & v_2' & w_2' \\ u_3' & v_3' & w_3' \end{pmatrix} \begin{bmatrix} u \\ v \\ w \end{bmatrix}_0 . \tag{15}$$

Now a relation between $[u\, v\, w]_{bcc}$ and $[u\, v\, w]_{9R}$ is obtained from Eqs. (14) and (15).

$$\begin{bmatrix} u \\ v \\ w \end{bmatrix}_{bcc} = \begin{pmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{pmatrix} \begin{pmatrix} u_1' & v_1' & w_1' \\ u_2' & v_2' & w_2' \\ u_3' & v_3' & w_3' \end{pmatrix}^{-1} \begin{bmatrix} u \\ v \\ w \end{bmatrix}_{9R} . \tag{16}$$

A relation between the planes $(hkl)_{bcc}$ and $(hkl)_{9R}$ is obtained from the above equation by calculating the inverse of the multiplication of these two matrices:

$$(h\,k\,l)_{bcc} = (h\,k\,l)_{9R} \left(\begin{pmatrix} u_1 & v_1 & w_1 \\ u_2 & v_2 & w_2 \\ u_3 & v_3 & w_3 \end{pmatrix} \begin{pmatrix} u_1' & v_1' & w_1' \\ u_2' & v_2' & w_2' \\ u_3' & v_3' & w_3' \end{pmatrix}^{-1} \right)^{-1} . \tag{17}$$

From Eqs. (16) and (17) the orientation relationships between some prominent planes and directions are obtained.

4. Numerical Calculations for the Cu-14.8 at.%Sn Alloy

In this section, the predictions of the *bcc* to *9R* martensitic transformation theory are compared with the experimental results for this alloy. The lattice parameters of *bcc* austenite and orthorhombic martensite phases were measured by x-ray diffraction method to be $a_\beta = 2.981$ Å, $a_0 = 2.685$ Å, $b_0 = 4.554$ Å and c_0=4.342 Å, respectively [14]. For the calculations, the lattice parameters of the martensite phase were transformed to the lattice parameters of monoclinic *9R* structure: $a = a_0, b = b_0$ and $c = 9c_0/2$. The angle β_0 is between the basal plane and c-axis. But, the angle β_0 was assumed to be a parameter which is varying between 90° and 95°, as before reported in section 2.

The magnitude of the lattice invariant shear and indices of the habit plane were calculated using Eqs. (11)-(13) with the above lattice constants. As seen in Eq. (13), two values of the lattice invariant shears g' are obtained, but the larger one is discarded because it is physically unfavorable.

The calculated values of the normalized indices of the habit plane and the orientations of this habit plane according to the some planes, are given in Table 1. The deviations between the calculated and experimentally observed habit planes are also summarized in Table 2. As seen in the Table 1, the orientation of the habit plane in the Cu-14.8at.%Sn alloy lies near $(3\ 10\ 11)_{bcc}$ for $\beta_0 = 95°$. In the same alloy, it is reported [9,10] that the habit plane is within 2° from the $(1\ 3\ 3)_{bcc}$ plane. When the angle β_0 increases, this habit plane is nearer the $(1\ 3\ 3)_{bcc}$ plane (i.e. 3.7°). But, according to the comparison given in Table 2, the calculated habit plane is very close to the $(3\ 10\ 11)_{bcc}$ plane, and it agrees with the precise measurements in Kennon-Bowles work [14], for $\beta_0 = 95°$. The difference between the calculated ($\beta_0 = 95°$) and experimental values is within 1°. However, this discrepancy may be explained in the viewpoint of the accuracy of the lattice constants. Furthermore, the experimentally observed habit planes by Kennon [15] and Kennon-Bowles [14] for the Cu-14.8at.%Sn alloy, were located several degrees away from their calculations, for $\beta_0 = 90°$ or the transformation from *bcc* to orthorhombic.

Table 1. The angles between the calculated habit planes and some important planes.

β_0	h	k	l	*(1 3 3)*	*(2 6 7)*	*(2 10 11)*	*(3 10 11)*
90°	0.1540	0.6652	0.7306	5.2°	3.8°	1.2°	2.6°
91°	0.1548	0.6655	0.7302	5.1°	3.7°	1.2°	2.5°
92°	0.1573	0.6664	0.7288	5.0°	3.7°	1.4°	2.4°
93°	0.1616	0.6678	0.7266	4.7°	3.5°	1.7°	2.1°
94°	0.1677	0.6699	0.7233	4.2°	3.3°	2.0°	1.8°
95°	0.1757	0.6726	0.7188	3.7°	3.3°	2.6°	1.6°

Table 2. The deviations between calculated and experimentally observed habit planes.

Experimental values In ref.[14] and [15]	Calculated values			
	In ref.[15]	In ref.[14]	In present	
	$\beta_0 = 90°$	$\beta_0 = 90°$	$\beta_0 = 90°$	$\beta_0 = 95°$
Plate 1	3.6°	–	7.6°	6.4°
Plate 2	5.7°	–	2.4°	1.4°
Plate A	–	6.3°	1.9°	1.0°
Plate B	–	7.2°	2.0°	0.9°
Plate C	–	6.9°	1.3°	0.6°
Plate D	–	8.1°	1.0°	1.3°
Observed mean	–	6.5°	1.3°	0.4°

The calculated and measured values for the lattice invariant shear (g') are summarized in Table 3. As seen in this table, for $\beta_0 = 90°$, the calculated value of lattice invariant shear is very small than the experimentally observed ones. But, the calculated value for $\beta_0 = 95°$, is in good agreement with the experimental ones. When the angle β_0 increases, the magnitude of the lattice invariant shear are also nearer the experimentally observed values. In this case, we can assume that the unit cell of the martensite phase is monoclinic rather than orthorhombic.

Table 3. The calculated and measured values for the lattice invariant shear g'.

<table>
<tr><td colspan="2">The calculated values in the present work
For bcc → M9R
transformation</td><td>The calculated and measured values for g′ in
ref.[14] and [15]. For bcc → orthorhombic
transformation</td></tr>
<tr><td>β₀</td><td>g′</td><td rowspan="3">Calculated value: 0.118
Measured values : 0.125 and 0.122,
for plate 1 and 2. (In ref. [15])</td></tr>
<tr><td>90°</td><td>0.019</td></tr>
<tr><td>91°</td><td>0.037</td></tr>
<tr><td>92°</td><td>0.055</td><td rowspan="4">Calculated value: 0.119
Measured values : 0.108, 0.112, 0.110 and 0.104,
for plate A, B, C and D. (In ref. [14])</td></tr>
<tr><td>93°</td><td>0.073</td></tr>
<tr><td>94°</td><td>0.093</td></tr>
<tr><td>95°</td><td>0.112</td></tr>
</table>

The orientation relationship for some prominent directions and planes were obtained from Eqs. (16) and (17), respectively. The results of the calculations are summarized in Table 4, together with the available experimental observations. From the table, it can be seen that the orientations of the directions are not affected from the change in the angle β_0, and there is fair agreement between the theory and experiment. But, as seen in this table, the deviation between the calculated and observed values for $(1\ 1\ 0)_{bcc}$ plane is less than 2°, while that for $(0\ 1\ 1)_{bcc}$ plane is more than 2°, for $\beta_0 = 95°$. This difference is probably due to experimental error and precision of the calculation.

Table 4. The calculated and experimental values for the orientation relationships.

The directions and planes		Calculated values		Experimental values (for $\beta_0 = 90°$)		
bcc	*M9R*	$\beta_0 = 90°$	$\beta_0 = 95°$	In ref. [15]	In ref. [14]	In ref. [9,10]
$[\bar{1}0\bar{1}]$	[100]	6.4°	6.4°	6.3°	5.8°	–
$[0\bar{1}0]$	[010]	6.7°	6.7°	6.5°	4.6°	–
$[\bar{5}04]$	[001]	5.0°	4.8°	4.5°	4.0°	–
$[\bar{1}1\bar{1}]$	$[1\bar{1}0]$	0.8°	0.7°	–	–	$\sim 0.0°$
(110)	$(\bar{1}\,\bar{1}5)$	4.0°	1.9°	–	–	$\sim 0.0°$
(011)	$(\bar{1}\,\bar{1}4)$	0.5°	2.8°	–	–	$\sim 0.0°$

5. Conclusions

The crystallography of the martensitic transformation in the Cu-14.8at.%Sn alloy was analyzed using a computer program based upon the Kajiwara formulation. In the present case, the transformation is assumed from cubic (*bcc*) to monoclinic *9R*. In the calculations, the angle β_0 is also assumed to be a parameter which is varying between 90° and 95°.

The habit plane predicted from the theory is $(0.1757\ 0.6726\ 0.7188)_{bcc}$ plane for $\beta_0 = 95°$, and deviation from the observed mean $(0.1786\ 0.6657\ 0.7246)_{bcc}$ plane [14] is only 0.4°. This habit plane is very close to the $(3\ 10\ 11)_{bcc}$ plane (i.e. 1.6°).

The measured lattice invariant shear being in the range 0.104 to 0.122 is in good agreement with the calculated value 0.122 (for $\beta_0 = 95°$). The calculated orientation relationships for the direction and planes agreed within 0.3° and $\sim 2°$ with the measured ones, respectively.

As seen in the above discussion, the comparison between the theory and experiments shows clearly that the calculations agree well with the experiments. As a result, we can assume that the unit cell of the martensite phase in the above alloy is monoclinic rather than orthorhombic.

References

[1] M.S. Wechsler, D.S. Liberman and T.A. Read, Trans. AIME, 197(1953), 1502.

[2] J.S. Bowles and J.K. Mackenzie, *Acta Met.*, **2**(1954), 129, 138, 224.

[3] C.M. Wayman, "Introduction to the Crystallography of Martensitic Transformation", Macmillan Series in Materials Science. The Macmillan Company, New York(1964), Chap. 12.

[4] A.F. Acton and M. Bevis, *Mater. Sci.Eng.,* **5**(1969), 19.

[5] N.D.H. Ross and A.G. Crocker, *Acta Met.*, **18**(1970), 405.

[6] H. Suzuki, *Sci. Rep. Res. Inst. Tohoku Univ.*, **A6**(1954), 30.

[7] J. De Vos, E. Aernoudt and L. Delaey, Z. Metallkde, 69(1978), 438.

[8] S. Kajiwara, *Trans. Japan Inst. Metals*, **17**(1976), 435.

[9] Z. Nishiyama, K. Shimizu and H. Morikawa, *Trans. JIM*, **9**(1968), 307.

[10] H. Morikawa, K. Shimizu and Z. Nishiyama, *Trans. JIM*, **9**(1968), 317.

[11] A.B. Greninger and V.G. Mooradian, *Trans. AIME*, **128**(1938), 337.

[12] Z. Nishiyama, "Martensitic Transformation",*Academic Press, New York (1978)*, **p.91**.

[13] K. Marukawa and S. Kajiwara, *Phil. Mag. A*, Vol. **55** (1987), 85.

[14] N.F. Kennon and J.S. Bowles, *Acta Metall.*, Vol.**17** (1969), 373.

[15] N.F. Kennon, *Acta Metall.*, Vol.**20** (1972), 5.