The $\beta' \rightarrow \zeta$ Transformation in Equiatomic AgZn Alloy

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An analysis was made of the X-ray diffraction intensity distribution in a series of single crystal patterns of an equiatomic AgZn alloy recorded at the initial stage of the phase transformation from β' (B2-type ordered structure) to ζ (trigonal structure). It was shown that the displacements of atoms and the partial disordering, the two atomistic mechanisms involved in the transformation, proceed simultaneously. The ζ phase nuclei grow gradually in the β' phase matrix with a definite orientation relationship. Two types of the nuclei form; one with a structure similar to the structure proposed for the ζ phase by Edmunds and Qurashi (ζ phase-type structure) and the other with a structure obtained by reversing the direction of the displacements of some of the atoms in the ζ phase-type structure (anti- ζ phase-type structure).

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I. Introduction

In the silver-zinc binary alloy system a β phase with the body-centered cubic structure forms at the equiatomic composition, which is however stable only at temperatures higher than 530 K and undergoes transition with decreasing temperature into the ζ phase having a trigonal symmetry (space group $P\bar{3}$). When the β phase alloy is quenched into iced water, the transition is completely suppressed and a metastable β' phase having the B2-type ordered structure (hereafter abbreviated as B2 structure) forms. This remains unchanged as long as the alloy is kept at ambient temperature, but upon heating to 330 K or higher a transition into the stable ζ phase takes place. Investigations were made on the stability of the metastable phase and the transformation into the stable phase. It was shown by Kitchingman⁽¹⁾, Matsuo, Takahashi and Nagasawa⁽²⁾ and Matsuo and Torii⁽³⁾ that the trigonal ζ phase structure can be obtained by displacing some of the atoms in the B2 structure in the $[1\bar{1}0]$ (and equivalent) directions and in the $[111]$ directions. Later, Yamada and Noda⁽⁴⁾ showed that the displacements of atoms can be described by the superposition of two sets of transverse lattice waves, one with the wavevectors of the $(1/3)\langle 110 \rangle$ type and the other with the wavevectors of the $(1/3)\langle 211 \rangle$ type. Since there exists mixed occupation by Ag and Zn atoms of two thirds of the sites in the ζ phase structure, as shown by Edmunds and Qurashi⁽⁵⁾, partial disordering of atoms (interchange of atoms) must be involved in the transformation.

Two atomistic mechanisms are thus involved in the $\beta' \rightarrow \zeta$ transformation: the displacements of atoms and the partial disordering. It is of interest to see whether they occur simultaneously or one of them proceeds first and the other follows. X-ray diffraction measurements using sin-

gle crystal samples with particular attention to the initial stage of the transformation will be the most appropriate to investigate the atomistic mechanism, but no study has hitherto been made. In 1990 we made an attempt to employ a highly sensitive X-ray detector, Imaging Plate, for the time-resolved two-dimensional observation of the structure changes on a synchrotron radiation source⁽⁶⁾. Single crystal of the AgZn alloy was chosen as a sample and it was shown that the intensity distribution in a wide area of the plane section of the reciprocal lattice could be recorded within a reasonable time. In a number of patterns taken those have been included which show the change in the intensity distribution at the initial stage of the $\beta' \rightarrow \zeta$ transformation.

The aim of the present work is to analyse the diffraction intensity data obtained in that study to elucidate the atomistic mechanism involved.

II. Analysis of the Diffraction Intensity Distribution

1. Change in the intensity distribution at the initial stage of the $\beta' \rightarrow \zeta$ transformation

Figure 1(a) shows an X-ray diffraction pattern taken on the synchrotron radiation source (Photon Factory) of the AgZn alloy which was quenched from 720 K to obtain the β' phase⁽⁶⁾. It represents the intensity distribution in the (111) plane section of the reciprocal lattice of the B2 structure. Three intensity maxima seen on the right, upper left and lower left are respectively the 220, $2\bar{3}\bar{1}$ and $3\bar{2}\bar{1}$ reflections, which are the so-called fundamental reflections. Strong but diffuse streaks emanating from the three maxima are thermal diffuse scattering arising from the transverse acoustic phonons of the (110) $[1\bar{1}0]$ type, which are excited strongly in the B2 structure owing

Fig. 1 Synchrotron X-ray diffraction patterns showing the change in the intensity distribution on the (111) section of the reciprocal lattice of AgZn as the $\beta' \rightarrow \zeta$ transformation proceeds. (a) After quenching from above 530 K. The alloy is in the β' phase state. (b) After 1200 s holding at 330 K. (c) After 21.6×10^3 s holding at 330 K. The patterns shown here were obtained by photographing the image reproduced on the screen of the display system.

to its remarkable elastic anisotropy⁽⁷⁾.

After the alloy sample was kept at 330 K for 1200 s, a slight change in the intensity distribution has taken place, as seen in Fig. 1(b). Weak diffraction spots appear in the center of the triangle formed by the three maxima and on the upper right and the lower right of the 220 reflection. Additional weaker spots can also be seen in the pattern. Any notable change is not seen in the intensity of the diffuse scattering, suggesting that phonon mode softening is not involved in the transformation.

The intensity of newly appearing spots increases gradually with the elapse of time. Figure 1(c) shows the pat-

Fig. 2 Indexing of the newly appearing spots, indicated by open circles, in the pattern shown in Figs. 1(b) and (c) in terms of the hexagonal lattice with $a=0.764$ nm and $c=0.564$ nm. For the fundamental reflections, indicated by full circles, indices are assigned in terms of the cubic and hexagonal lattices.

tern taken after 21.6×10^3 s holding of the sample at 330 K. The positions of the spots can more clearly be recognized and it is possible to index them including the three maxima in terms of the hexagonal lattice with the a -axis ($a=0.764$ nm) in the $[2\bar{1}\bar{1}]$ and $[\bar{1}2\bar{1}]$ directions of the B2 structure and the c -axis ($c=0.564$ nm) in the $[111]$ direction. The results of indexing are shown in Fig. 2. This lattice just corresponds to that of the ζ phase structure, suggesting that the newly appearing spots are the reflections from the nuclei of the ζ phase forming in the β' phase matrix with a definite orientation relationship. The relationship is such that $(00.1)_{\zeta} \parallel (111)_{\beta'}$ and $[2\bar{1}.0]_{\zeta} \parallel [2\bar{1}\bar{1}]_{\beta'}$. It is to be noted that polycrystallization of a single crystal grain of the β' phase, often observed when the transformation sets in, does not occur in the sample used in the present study. This may be due to the relatively low annealing temperature and the particular sample shape, a plate with the surface parallel to the (110) plane of the B2 structure.

2. Structure analysis of the ζ phase nuclei

Figure 3(a) depicts the B2 structure projected along the $[111]$ direction, top, and along the $[11\bar{2}]$ direction, below. It is convenient to express the B2 structure in terms of the hexagonal lattice defined above.

The most notable reflections of the ζ phase nuclei are 30.2, 03.2 and 33.2, as seen in Fig. 1(b), and therefore the structure model of the nuclei should be sought in those which give stronger intensities to these reflections. It was found that introducing any type of partial disorder in the B2 structure without displacing atomic positions does not give the intensity of the reflections compatible with the observation. This suggests that partial disordering, or interchange of atoms, does not proceed first at the initial stage of the $\beta' \rightarrow \zeta$ transformation, in contrary to the suggestion by Kitchingman⁽¹⁾.

Next, displacements of atoms have been introduced into the B2 structure without changing atomic order. The

Fig. 3 (a) Atomic arrangements of the B2 structure of AgZn projected along the $[111]$ direction, top, and the $[112]$ direction, bottom. The arrows shown at the bottom indicate the direction referred to the hexagonal lattice. (b) Atomic arrangements of the B2 structure with the ω phase-formation-like displacements.

displacements which give stronger intensity to the three reflections are those in the $[00.1]$ direction with the magnitude of $c/4$ for the atoms on the A-layer and $c/12$ for the atoms on the B- and C-layers (Figs. 3(a) and (b)). These displacements result in the uneven spacing of the layers: from $c/3, c/3, c/3, c/3, c/3, c/3 \dots$ in the B2 structure[†] to $c/4, c/2, c/4, c/4, c/2, c/4 \dots$. The change in the spacing reminds us of the $\beta \rightarrow \omega$ transformation in the transition metal-based alloys⁽⁸⁾, in which the (111) planes of the body-centered cubic structure are displaced (collapsed) to form a new periodicity in the $[111]$ direction.

Introduction of the displacements in the $[00.1]$ direction is, however, not sufficient to explain the intensity of the other weaker reflections and additional displacements in the direction lying in the (00.1) plane are to be introduced for the atoms on the B- and C-layers. The dis-

placements give rise to an asymmetry in the calculated intensity between the pairs of reflections such as 21.2 and 12.2, 31.2 and 13.2, 42.2 and 24.2, etc., whereas no asymmetry has been observed, as seen in Fig. 1(c). The difficulty can be removed if it is assumed that what is observed in the diffraction pattern is a superposition of the two intensity distributions, one from the displaced structure and the other from the structure in which the direction of some of the displacements is reversed. The latter structure gives the intensity with the asymmetry opposite in sense for those pairs of reflections.

It was further found that more satisfactory results can be obtained for the calculated intensity if the partial disordering is introduced in addition to the atom displacements: one third of the sites are occupied exclusively by zinc atoms and the rest by the "mixed atom" $(3/4)\text{Ag} + (1/4)\text{Zn}$. This is nothing else the partial disorder in the ζ phase structure⁽⁵⁾. The atomic coordinates of the structure with the displacements and the partial disorder are listed in the first four columns in Table 1. In the other four columns are listed the atomic coordinates of the structure with the direction of the displacements reversed, in which the sign of δ_x , δ_y and δ_{z1} is changed while that of δ_{z2} is kept unchanged. Table 2 shows the intensity calculated for the two structures with $\delta_x=0.021$ and $\delta_y=0.042$ with $\delta_{z1}=1/4$ and $\delta_{z2}=1/12$ in the third and fourth columns and the intensity averaged for them in the fifth column. The intensity of the reflections estimated on the diffraction pattern in Fig. 1(c) is shown in the second column. It is seen that, though its accuracy is not necessarily high due to the weakness, the averaged calculated intensity is comparable with the observed one. The magnitudes of δ_x and δ_y are larger than those determined by Edmunds and Qurashi⁽⁵⁾ for the ζ phase structure, 0.017 and 0.032. These values were obtained from the intensity measurements on powder samples and less accurate than our values. The structure of the ζ phase nuclei with the atom displacements shown in the first four columns in Table 1 is here called ζ phase-type structure and the structure with the direction of the displacements reversed is called anti- ζ phase-type structure.

The atomic arrangements of the two types of structures are depicted in Figs. 4(a) and (b). There is no differ-

Table 1 Atomic coordinates of the ζ phase-type and anti- ζ phase-type structures in AgZn referred to the hexagonal lattice. $a=0.764$ nm and $c=0.564$ nm. "AZ" represents a mixed atom $(3/4)\text{Ag} + (1/4)\text{Zn}$. $\delta_x=0.021$, $\delta_y=0.042$, $\delta_{z1}=1/4$ and $\delta_{z2}=1/12$.

ζ phase-type structure				Anti- ζ phase-type structure			
Atom	x	y	z	Atom	x	y	z
Zn	0	0	0	Zn	0	0	0
Zn	$1/3$	$-1/3$	$-\delta_{z1}$	Zn	$1/3$	$-1/3$	δ_{z1}
Zn	$-1/3$	$1/3$	δ_{z1}	Zn	$-1/3$	$1/3$	$-\delta_{z1}$
"AZ"	$1/3 + \delta_x$	δ_y	$2/3 + \delta_{z2}$	"AZ"	$1/3 - \delta_x$	$-\delta_y$	$2/3 + \delta_{z2}$
"AZ"	$-\delta_y$	$1/3 + \delta_x - \delta_y$	$2/3 + \delta_{z2}$	"AZ"	δ_y	$1/3 - \delta_x + \delta_y$	$2/3 + \delta_{z2}$
"AZ"	$-1/3 - \delta_x + \delta_y$	$-1/3 - \delta_x$	$2/3 + \delta_{z2}$	"AZ"	$-1/3 + \delta_x - \delta_y$	$-1/3 + \delta_x$	$2/3 + \delta_{z2}$
"AZ"	$-1/3 - \delta_x$	$-\delta_y$	$-2/3 - \delta_{z2}$	"AZ"	$-1/3 + \delta_x$	δ_y	$-2/3 - \delta_{z2}$
"AZ"	δ_y	$-1/3 - \delta_x + \delta_y$	$-2/3 - \delta_{z2}$	"AZ"	$-\delta_y$	$-1/3 + \delta_x - \delta_y$	$-2/3 - \delta_{z2}$
"AZ"	$1/3 + \delta_x - \delta_y$	$1/3 + \delta_x$	$-2/3 - \delta_{z2}$	"AZ"	$1/3 - \delta_x + \delta_y$	$1/3 - \delta_x$	$-2/3 - \delta_{z2}$

Table 2 Intensity of the reflections appearing at the initial stage of the $\beta' \rightarrow \zeta$ transformation. $I_{\text{cal}} = |F(hk.l)|^2 / 100$. I_{obs} is normalized so that I_{obs} is equal to I_{cal} for the 33.2 reflection.

$hk.l$	I_{obs}	I_{cal}	I_{cal}	I_{cal}
		ζ phase-type structure	anti- ζ phase-type structure	ζ phase-type + anti- ζ phase-type
21.2	20	4	55	30
12.2	20	55	4	30
30.2	90	193	193	193
03.2	85	193	193	193
22.2	#	16	16	16
(220)				
31.2	25	1	55	28
13.2	25	55	1	28
32.2	10	55	<1	27
23.2	10	<1	55	27
41.2	7	12	5	9
14.2	7	5	12	9
33.2	74	74	74	74
42.2	30	46	40	43
24.2	30	40	46	43
51.2	20	31	48	39
15.2	—	48	31	39
43.2	10	53	3	28
34.2	10	3	53	28
52.2	#	<1	5	3
(23 $\bar{1}$)				
25.2	#	5	<1	3
(32 $\bar{1}$)				

Overlapped by the fundamental reflection (the indices in bracket) of the B2 structure.

ence in the nearest interatomic distances between them and the structural stability seems to be the same. It is to be noted that they can not be distinguished in a powder diffraction pattern.

From the observed change in the diffraction intensity distribution, it can be concluded that the displacements of atoms and the partial disordering proceed simultaneously at the initial stage of the $\beta' \rightarrow \zeta$ transformation, thereby the ζ phase-type and anti- ζ phase-type structures forming with the same volume ratio in the β' phase matrix. With further holding of the alloy sample at 360 K, the reflections of the ζ phase nuclei grow in intensity, as observed by Iwasaki *et al.*⁽⁶⁾, until the reflections of the β' phase vanish completely.

III. Discussion

Results of the analysis of the intensity distribution have shown that the most notable structure change occurring in AgZn is the ω phase-formation-like displacements of atoms in the $[00.1]$ direction ($[111]$ direction in the B2 structure). This was pointed out previously by Matsuo *et al.*⁽²⁾ and attempts were made to find a precursor phenomenon by measuring elastic constants⁽²⁾ and neutron inelastic scattering⁽⁹⁾, but no clear evidence supporting its existence was found.

Although the $\beta' \rightarrow \zeta$ transformation is not of the phonon-assisted type, the lattice dynamical interpretation by Yamada & Noda⁽⁴⁾ is helpful to have an insight into the

Fig. 4 Atomic arrangements of the ζ phase-type structure, (a), and of the anti- ζ phase-type structure, (b). Note that the direction of the displacements of some of the atoms is opposite for the two structures.

significance of the atom displacements. According to their analysis, the ω phase-formation-like displacements are described not by a single acoustic lattice wave but by the combination of the two transverse lattice waves, one with the $(1/3)\langle 110 \rangle$ type wavevector and the other with the $(1/3)\langle 211 \rangle$ type wavevector. The latter produces the displacements in the $[00.1]$ direction of the atoms on the B- and C-layers, Fig. 3(a), and the amplitude $Q_2 = 0.028$ assigned yields the value $\delta_{z2} = 1/12$, in agreement with that determined by the present analysis, while the former produces the displacements of the atoms on the A-layer, but the amplitude $Q_1 = 0.083$ assigned is too small to yield $\delta_{z1} = 1/4$. In order to get the ω phase-formation-like displacements, Q_1 must be 0.102. This lattice wave produces the in-plane displacements also and the revised Q_1 value yields the values of δ_x and δ_y which are in accord with those determined by the present analysis. Difference between the ζ phase-type and anti- ζ phase-type structures lies in the direction of the atom displacements and, in terms of the lattice waves, the wave with the $(1/3)\langle 110 \rangle$ type wavevector (amplitude Q_1) in one structure is out of phase to the wave in the other, whereas the wave with the $(1/3)\langle 211 \rangle$ type wavevector (amplitude Q_2) has the same phase in the two structures. There is no preference as to which lattice wave, that with the amplitude Q_1 or that with the amplitude $-Q_1$, is excited in the transformation and hence the two structures form with the same volume ratio. In the real process from β' to ζ , the displacements of atoms are accompanied by the interchange of atoms and the mechanism is complicated.

Since there are four equivalent $\{111\}$ planes in the B2 structure and the ζ phase nuclei can be formed with their (00.1) plane parallel either to one of them. The ζ phase-type structure and the anti- ζ phase-type structure can be regarded as a kind of structure variants and, when they

form parallel to only one of the $\{111\}$ planes, no polycrystallization occurs, as observed in the present study, while, when they form simultaneously parallel to all of the $\{111\}$ planes, a single crystal breaks up.

In the $\beta \rightarrow \zeta$ transformation the interchange of atoms involved is not toward partial disordering but toward partial ordering, but the displacements of atoms involved are of the same type and hence the transformation process may be similar to that of $\beta' \rightarrow \zeta$.

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