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# Isothermal transformation and decomposition of $\beta_1$ phase in a CuZnAl alloy

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In the present paper, the crystallography of isothermal transformation and decomposition of $\beta_1$ phase have been studied by means of transmission electron microscopy and diffraction in the CuZnAl shape memory alloy. It has been proved that the bainite formed in $\beta_1$ matrix when the samples were transformed isothermally at moderate temperature. The crystallography of the isothermal bainitic transformation is identical to that of martensite in the same system. When the specimens were aged at moderate temperatures for longer time, the bainite and matrix decomposed to equilibrium phases. The decomposition process can be summarized as follows:

$$\text{bainite (9R)} \rightarrow 9\text{R} + \alpha\ (\text{fcc}) \rightarrow \alpha + \beta\ (\text{bcc})$$

$$\text{matrix (B2)} \rightarrow 2\text{H} + \text{B2} \rightarrow \beta\ (\text{bcc})$$

There are definite orientation relationships among these phases during the decomposition process and they are shown below:

$$(1\,1\,1)_\alpha \parallel (0\,0\,1)_B,\ [0\,\bar{1}\,1]_\alpha \parallel [\bar{1}\,1\,0]_B$$

$$(1\,1\,1)_\alpha\ 5^\circ \text{ away from } (1\,1\,0)_\beta,\ [0\,\bar{1}\,1]_\alpha \parallel [1\,\bar{1}\,\bar{1}]_\beta$$

$$(1\,1\,0)_M \parallel (0\,0\,1)_{2H},\ [0\,0\,1]_M \parallel [0\,1\,0]_{2H}$$

Thus, the crystallography of isothermal transformation and decomposition of $\beta_1$ phase and the sequence of transitions have been revealed.

## 1. Introduction

The martensitic transformations in the $\beta_1$ phase have been studied extensively with the development of copper based shape memory alloys in the past years [1–3]. Recently the isothermal transformation and decomposition of these alloys have received more and more attention due to their important significance in the understanding of the nature of bainitic transformation and ageing behaviour of shape memory alloys, respectively [4–6]. The bainitic transformation was found in CuZn $\beta$ alloy by Garwood [7] and then by others [8, 9]. Recently this transformation has also been revealed in CuZnAl shape memory alloys combined with macroscopical shape change which is similar to the shape change during cooling in two-way shape memory effect [6, 10]. The mechanism of this transformation is still a controversial topic [11, 12].

The decomposition process will take place after the bainitic transformation happened when the bainite and $\beta_1$ matrix is further aged. The decomposition process of $\beta_1$ phase in some alloys such as CuSn [13] and CuAlNi [6] has been studied in detail, however few systematic investigations have been made about the decomposition of $\beta_1$ phase to equilibrium phase in CuZnAl alloys. As is well known, like most other kinds of copper based shape memory alloys, CuZnAl shape memory alloy shows considerable ageing effect [14] which has constrained potential applications. To overcome difficulties resulting from the ageing effects and to achieve a long lifetime of shape memory capacity it is important first to clarify details of the structure changes which occur in the alloy during ageing.

In the present work the isothermal transformation of a Cu–26Zn–4Al (wt %) shape memory alloy aged at about 533 K has been studied by transmission electron microscopy and diffraction. It has been proved that the bainitic transformation takes place first, then both bainite and $\beta_1$ matrix decompose to equilibrium phase and the transition sequence has been revealed.

## 2. Experimental details

The alloy studied has a composition of Cu–26Zn–4Al (wt %) melted under atmosphere. It was homogenized at 1073 K for 48 h then rolled to thin plate of 0.15 mm in thickness. The alloy has good shape memory effect and the $M_s$† temperature of it is about 313 K. After annealing at 923 K, specimens were held at 1073 K for 5 min and quenched into water at room temperature. The quenched structure is martensite. They were subsequently aged isothermally at the temperature range from 493 to 573 K in an oil bath.

The thin discs were punched out from the thin plate,

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†Start temperature of martensite transformation.

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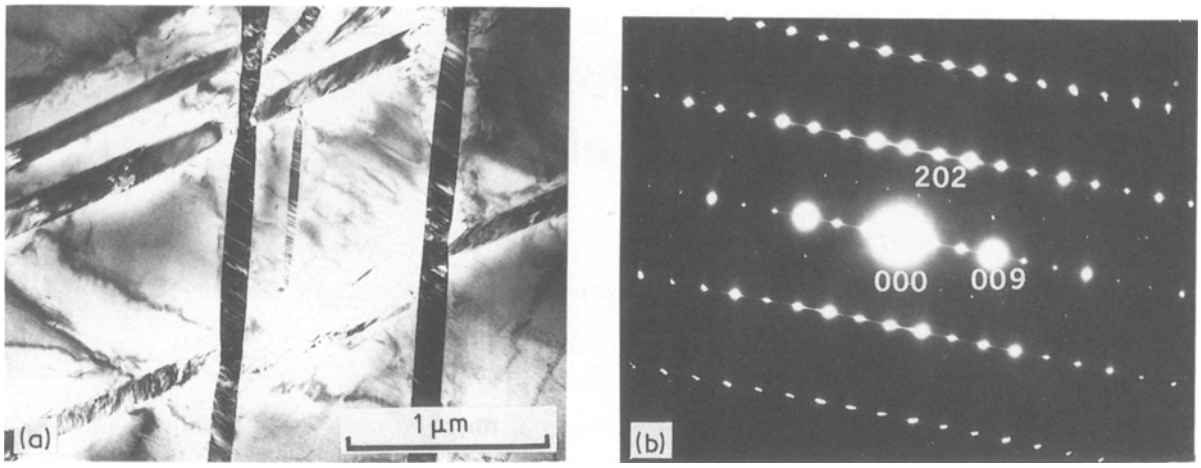


*Figure 1* (a) The morphology of bainite plate formed in CuZnAl $\beta_1$ matrix and (b) the [0 1 0] diffraction pattern of bainite.

aged for different times, then electrolytically thinned to a thin foil for transmission electron microscopy by jet polishing in a solution of 33% nitric acid and 67% methanol at 243 K. Mechanical thinning was avoided in order to prevent the formation of stress induced martensite. The TEM experiment was carried out in a JEM-100CX electron microscope operated at 100 kV equipped with a $\pm 60°$ and $\pm 45°$ double tilting stage.

Optical microscopes were taken to examine the morphology and structural change of the ageing process. Combined with a computer calculation the habit plane of the bainite has also been determined using the method proposed by Pak *et al.* [15].

## 3. Results and discussion

### 3.1. Crystallography of bainitic transformation

When the thermoelastic martensite obtained by quenching is heated at moderate temperature, it transforms back to the $\beta_1$ phase. Then isothermal transformation takes place and the kinetic curve of transformation has been found to be similar to that reported by Flewitt and Towner in CuZn alloy [16]. This kind of transformation has been regarded as a bainite transformation due to its similarity to the isothermal transformation of austenite. Figure 1a and b is the morphology of bainite and corresponding diffraction pattern. It can be seen that the bainite has a thin plate morphology which is different from that of thermoelastic martensite in the same alloy. By tilting specimens to different orientations a series of electron diffraction patterns have been obtained and the crystal structure of bainite is determined to be N9R by the indexing of them. The lattice parameters of it are $a = 0.469$ nm, $b = 0.264$ nm, $c = 1.972$ nm and $\alpha = \beta = \gamma = 90°$. This result is also different to that of M18R structure of thermoelastic martensite in the same alloy.

By using, the general geometric method of habit plane determination proposed by Pak *et al.* [15], the habit plane of bainite plate is found to be close to {1 2 3} type. It has been known that the {1 2 3} and {2 11 12} are all possible habit planes of bainite which is determined by the composition of alloys [17]. However the habit plane of martensite in CuZnAl $\beta_1$ phase has been reported to be {2 11 12} type [18, 19]. So, it can be concluded that the habit plane of martensite and bainite in CuZnAl $\beta_1$ phase can be different.

Despite the difference between martensite and bainite in the same alloy, it has been found that the crystallography of these two transformations is identical. Figure 2a is the composite diffraction pattern of bainite and $\beta_1$ matrix, and Fig. 2b is the morphology corresponding to Fig. 2a. The orientation relationship between bainite and matrix can be derived from

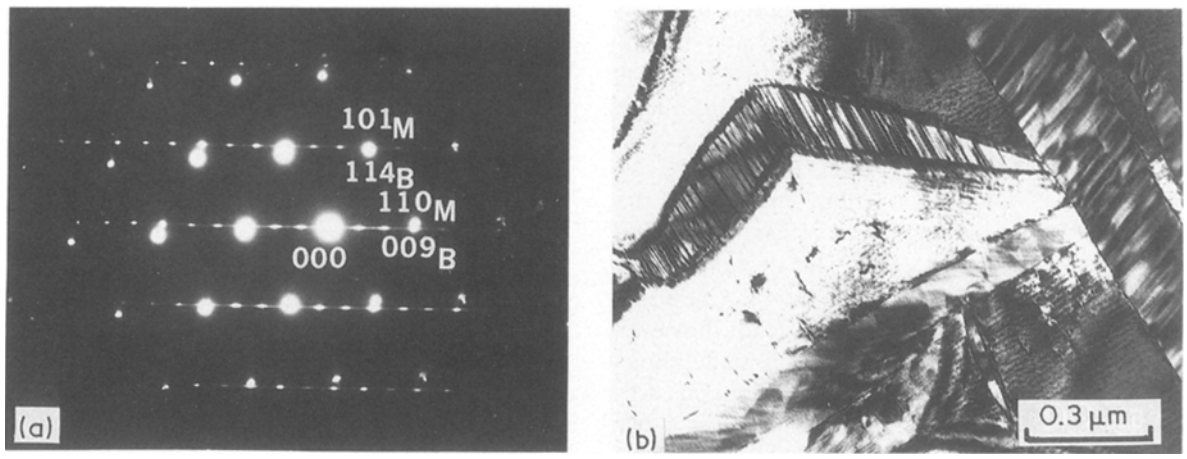


*Figure 2* (a) Composite diffraction pattern of bainite and matrix showing the orientation relationship between them and (b) corresponding morphology.

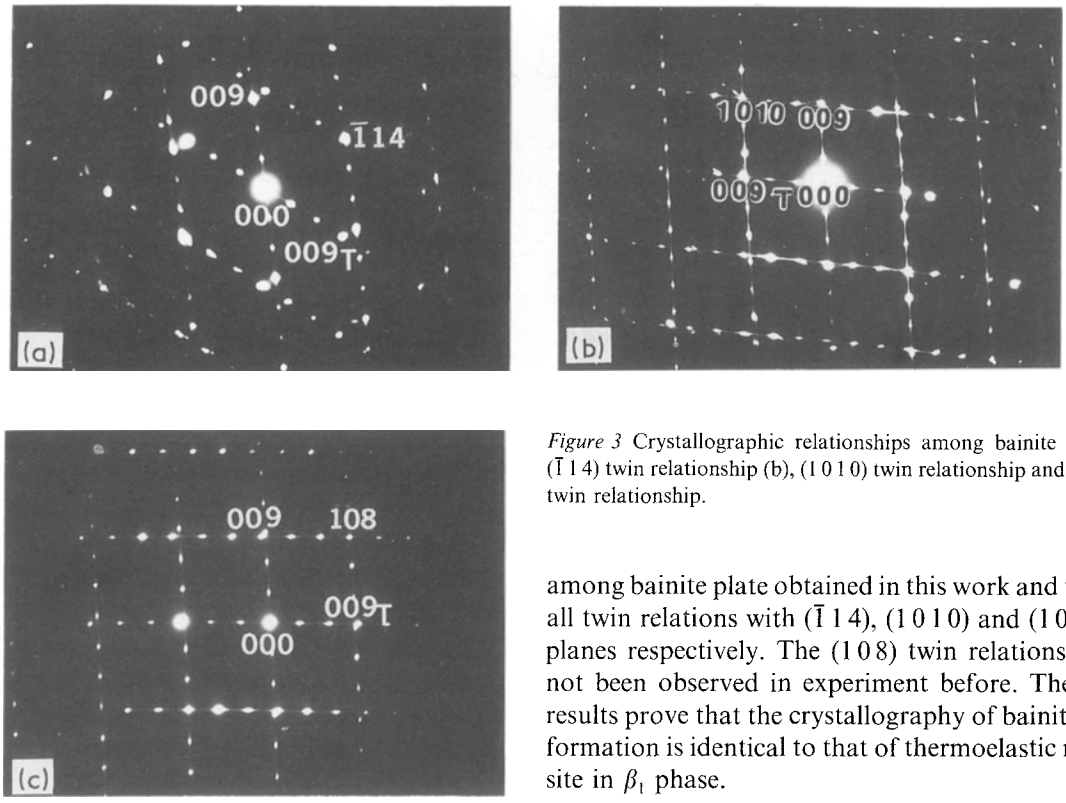


*Figure 3* Crystallographic relationships among bainite plate, (a) ($\bar{1}$ 1 4) twin relationship (b), (1 0 1 0) twin relationship and (c) (1 0 8) twin relationship.

Fig. 2a as follows:

$$[\bar{1}\,1\,0]_B \parallel [1\,\bar{1}\,\bar{1}]_M,\ (1\,1\,4)_B \parallel (1\,0\,1)_M,$$

$$(0\,0\,1)_B\ 5^\circ \text{ away from } (1\,1\,0)_M$$

where the B and M denote the bainite and B2 matrix respectively.

This orientation relationship is in agreement with that found in CuZn alloy [9], and it is also identical to that in martensitic transformations. This implies that the crystallography of this transformation is identical to that of martensite [10], although they are a little different in crystal structure. By applying the crystallographic theory of martensite in the same system [21] to the bainite transformation, all crystallographic relations among bainite plate identical to that in martensite can be deduced and these relations are all confirmed by electron diffraction in the present work. Figures 3a, b and c are orientation relationships among bainite plate obtained in this work and they are all twin relations with ($\bar{1}$ 1 4), (1 0 1 0) and (1 0 8) twin planes respectively. The (1 0 8) twin relationship has not been observed in experiment before. The above results prove that the crystallography of bainite transformation is identical to that of thermoelastic martensite in $\beta_1$ phase.

## 3.2. Decomposition of bainite plate during further isothermal transition

When the specimens were further heated at moderate temperature after the bainite has been formed, the bainite plate would be decomposed. Figure 4a is the electron micrograph showing that the microstructure of bainite has changed inside a part of bainite plate which was obtained in the specimen heated at 523 K for 10 h. The electron diffraction pattern shows that the structure of this part of plate had transformed from 9R to fcc, i.e. the $\alpha$ phase had precipitated from bainite plate and the lattice parameter of it is $a = 0.369$ nm. Figure 4b is the composite diffraction pattern of $\alpha$ phase and 9R obtained in the former bainite plate shown in Fig. 4a. By indexing it the orientation relationship between the $\alpha$ phase precipitated from bainite plate and retained 9R structure can be written as below:

$$[\bar{1}\,1\,0]_B \parallel [0\,\bar{1}\,1]_\alpha,\ (0\,0\,1)_B \parallel (1\,1\,1)_\alpha$$

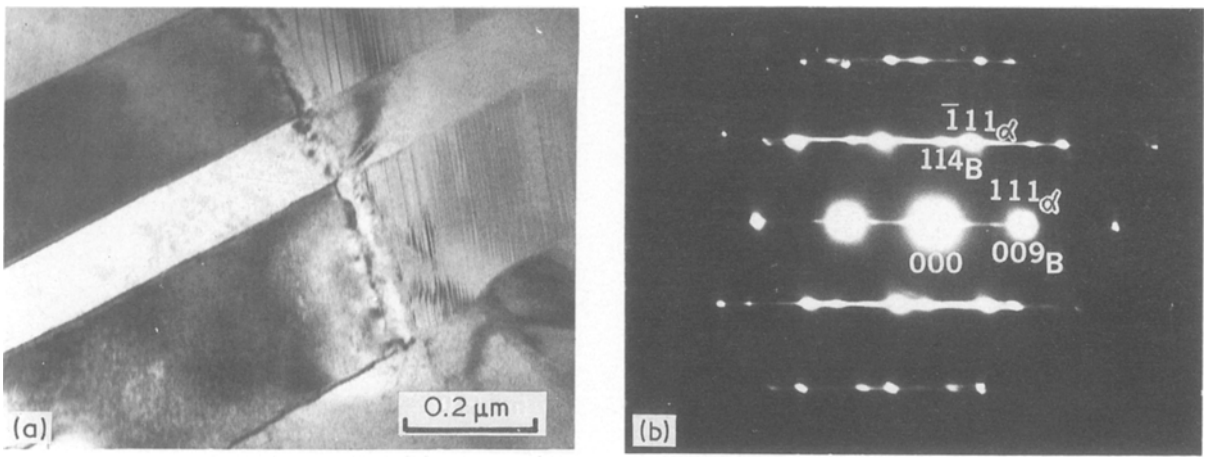


*Figure 4* The $\alpha$ phase precipitated inside bainite plate. (a) Morphology and (b) composite diffraction pattern of $\alpha$ phase and retained 9R showing the orientation relationship between them.

where B denotes the retained 9R structure in bainite.

Considering the structure similarities of 9R and fcc, the orientation relationship between α phase and 9R obtained when the α phase precipitated from bainite plate can be reasonably understood. As well known both fcc and 9R are close packed stacking structures and the $(0\,0\,1)_B$ and $(1\,1\,1)_\alpha$ are close packed planes. These two planes are identical and what is needed to change the 9R to fcc is to alter the stacking sequence of 9R while the close packed plane remained unchanged. So, when the α phase precipitated from 9R bainite plate, their close packed planes, i.e. $(1\,1\,1)_\alpha$ and $(0\,0\,1)_B$ should be parallel to each other. Furthermore, the $[\bar{1}\,1\,0]_B$ and $[0\,\bar{1}\,1]_\alpha$ are the two most identical in direction in those two close packed planes and it is reasonable to expect that they should be parallel to each other when the α phase precipitated from 9R bainite.

With increasing transition time, the amount of α phase increased and another product precipitated in the former bainite plate as shown in Fig. 5a. This product is disordered β phase as determined by electron diffraction and the lattice parameter of it is $a = 0.294$ nm. With the precipitation of β phase, the 9R structure retained in the former bainite plate disappeared and the structure obtained finally is α and β equilibrium phase as shown in Fig. 5a. By taking composite diffraction patterns of α and β, the orientation relationship between them can be obtained as shown in Fig. 5b which is summarized as follows:

$$[0\,\bar{1}\,1]_\alpha \parallel [1\,\bar{1}\,\bar{1}]_\beta,\ (1\,1\,1)_\alpha\ 5^\circ \text{ away from } (1\,1\,0)_\beta$$

This orientation relationship is a little different from the K–S orientation relationship. It has been known that the orientation relationship between α and β obtained when the α phase precipitated from β phase during annealing from high temperature [22]. Those mentioned above emphasized that the crystallography of α phase precipitated from β during annealing and β phase precipitated in bainite plate during ageing process are different. As has been observed, the β phase formed in the retained 9R region of former bainite plate. It suggests that the β phase is transformed from 9R but precipitated from α phase during isothermal transition. As mentioned in this work, the orientation relationship between $\beta_1$ and 9R is $[\bar{1}\,1\,0]_B \parallel [1\,\bar{1}\,\bar{1}]_M$, $(0\,0\,1)_B$ 5° away from $(1\,1\,0)_M$. Considering that the crystal structures of β and $\beta_1$ are identical, disregarding the ordering of atoms in them, it can be suggested that the transition process of 9R to β is the reverse of that of $\beta_1$ to 9R in crystallography. Thus the orientation relationship between 9R and β would be $[\bar{1}\,1\,0]_{9R} \parallel [1\,\bar{1}\,\bar{1}]_\beta$, $(0\,0\,1)_{9R}$ 5° away from $(1\,1\,0)_\beta$. According to the above consideration, the orientation relationship between α and β phase during isothermal transition inside former bainite plate can be derived as follows:

knowing that $[0\,\bar{1}\,1]_\alpha \parallel [\bar{1}\,1\,0]_B$, $(1\,1\,1)_\alpha \parallel (0\,0\,1)_B$

supposing that $[1\,\bar{1}\,\bar{1}]_\beta \parallel [\bar{1}\,1\,0]_B$,

$(1\,1\,0)_\beta$ 5° away from $(0\,0\,1)_B$

thus, have $[0\,\bar{1}\,1]_\alpha \parallel [1\,\bar{1}\,\bar{1}]_\beta$,

$(1\,1\,1)_\alpha$ 5° away from $(1\,1\,0)_\beta$

So, it can be concluded that the β phase is transformed from retained 9R region inside former bainite plate and the crystallography of it is the reverse one of $\beta_1$ to 9R transformation.

### 3.3. Isothermal transition of $\beta_1$ matrix during moderate temperature ageing

When the bainite formed in $\beta_1$ matrix as mentioned before, the matrix remained in its ordered B2 structure. When the samples were heated longer, however, a modulated microstructure appeared inside the $\beta_1$ matrix accompanied by the existence of 2H type electron diffraction. Figure 6a is a bright field image obtained in the specimen heated at 523 K for 30 min. As can be seen, the plate shaped products are bainite in which a lot of stacking faults exist; the matrix between the bainite plates has a modulated contrast. Figure 6b is the electron diffraction pattern taken in the modulated $\beta_1$ matrix in Fig. 6a. By indexing, it corresponds to the [0 1 0] zone diffraction pattern of the 2H structure. By tilting specimens to different orientations a series of diffraction patterns are obtained and the indexing of all of them confirms the existence of a 2H structure. Thus, it was concluded that the $\beta_1$ matrix presented the modulated contrast

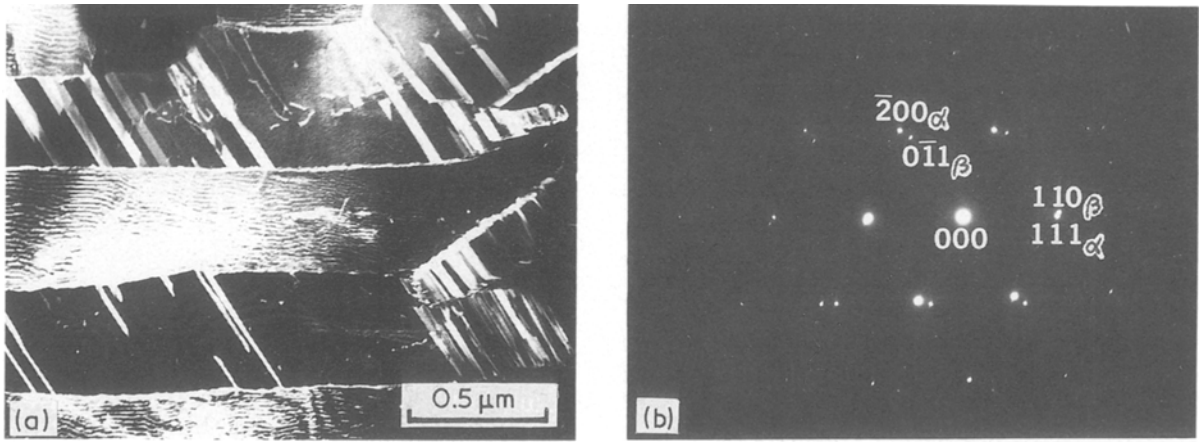


*Figure 5* The β phase formed inside the former bainite plate. (a) Dark field image formed by the reflection of β phase and (b) composite diffraction pattern of α and β phase showing the orientation relationship between them formed in the decomposition of bainite.

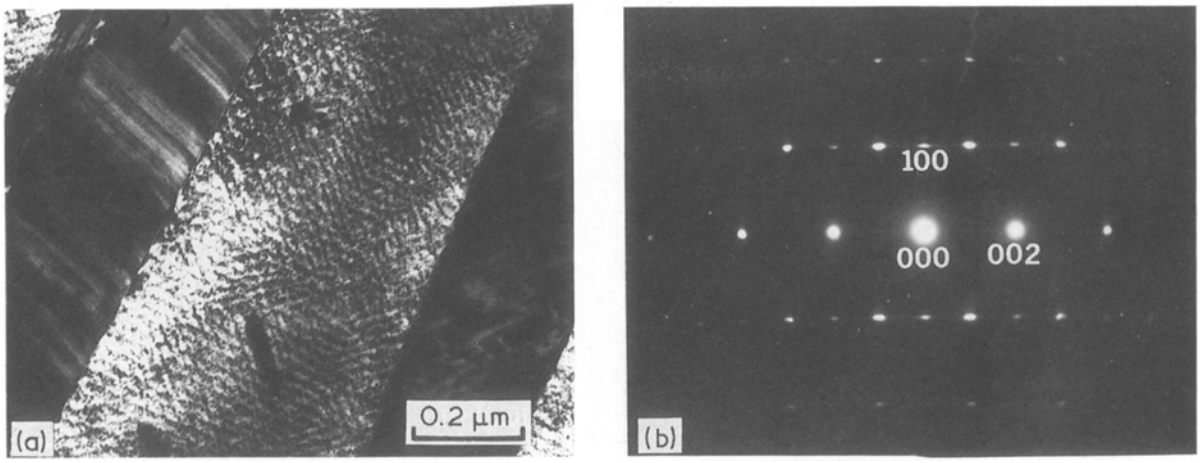


*Figure 6* (a) The modulated microstructure appeared in the $\beta_1$ matrix accompanied by the existence of 2H structure during ageing; morphology of modulated structure and (b) corresponding [0 1 0] diffraction pattern of 2H structure.

and a 2H structure appeared inside the $\beta_1$ matrix accompanied by the appearance of a modulated contrast after the bainitic transformation has taken place. The lattice parameters of the 2H structure calculated from the electron diffraction patterns are $a = 0.253$ nm and $c/a = 1.636$.

As the matrix exhibited a modulated contrast and a 2H structure, although it was often an uncertain thing to observe in the case of strong 2H reflections, the $\beta_1$ (CsCl) ordered structure still remained and coexisted with the 2H structure which was proved by the composite diffraction pattern of the 2H and the B2, as shown in Fig. 7b. Figure 7a is the bright field image corresponding to Fig. 7b. By indexing Fig. 7b, the orientation relationship between 2H and B2 can be summarized as follows:

$$[0\,1\,0]_{2H} \parallel [0\,0\,1]_M, (0\,0\,1)_{2H} \parallel (1\,1\,0)_M$$

where the H and M denote the 2H structure and B2 matrix respectively.

The 2H reflection observed has been found in the quenched CuSn $\beta$ phase [23] and proved to be metastable precipitates in the premartensitic transformation. In the present work, however, any attempt to identify the existence of 2H precipitates failed. In fact, the dark field image formed by the reflection of the 2H and the B2 structure shows a similar image resembling Figs 6a and 7a; no precipitates have been observed. It is more likely that a layer of the 2H structure has been formed on the surface of the specimens. Thus, the modulated contrast may be deduced to be the multiple diffraction effect, i.e. Moirè fringe. In fact, it has been found that the modulated microstructures are sensitive to the crystal orientation.

The experiment further showed that, with the increase of isothermal reaction time, the modulated contrast would slowly disappear and the 2H reflection vanish. The ordered $\beta_1$ matrix transformed to a disordered b c c equilibrium $\beta$ phase. Figure 8a shows the morphology of matrix obtained after the sample has been heated at 523 K for about 48 h and the diffraction shown in Fig. 8b, taken in the region of Fig. 8a, revealed that the crystal structure of it has been a b c c phase.

## 4. Summary

From the present investigation of the isothermal transformation and decomposition of $\beta_1$ phase of CuZnAl shape memory alloy by means of transmission electron microscopy the following conclusions can be made.

1. When the $\beta_1$ phase is heated at moderate

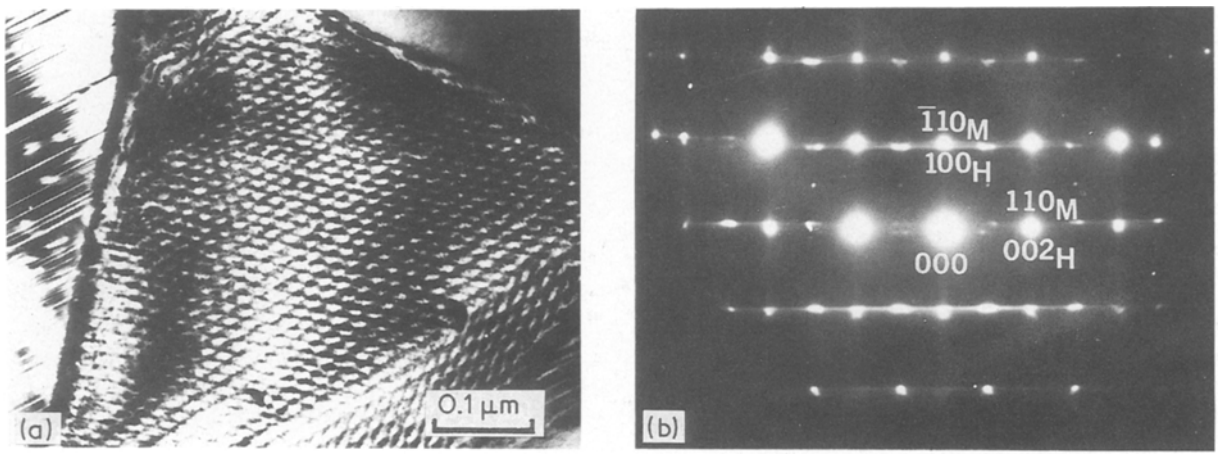


*Figure 7* The 2H structure is coexistant with the B2 phase. (a) Morphology of matrix and (b) composite diffraction pattern of 2H and B2 showing the orientation relationship between them.

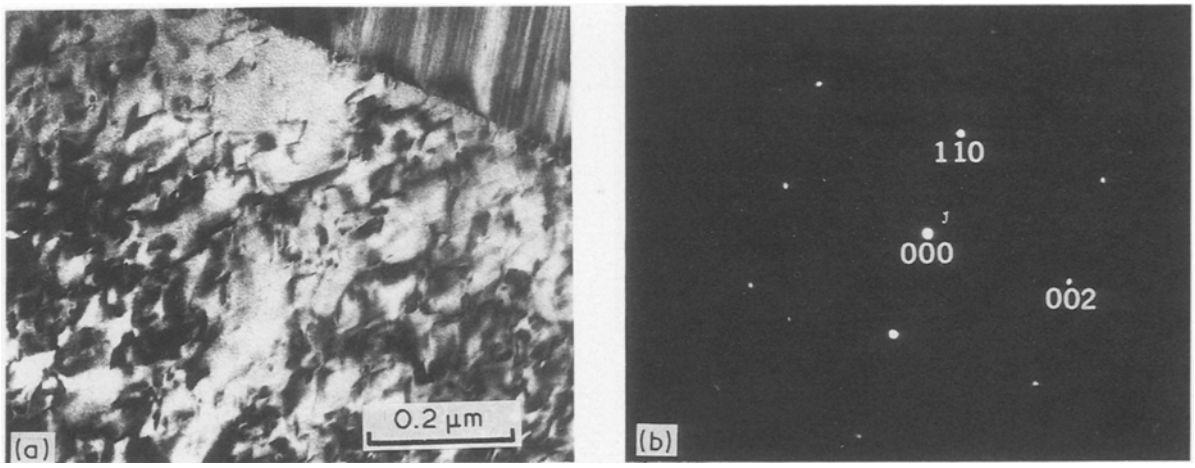


*Figure 8* The $\beta_1$ matrix transformed to $\beta$ phase finally. (a) Morphology and (b) the corresponding $[\bar{1}\,1\,0]$ diffraction pattern of $\beta$ phase.

temperature the bainitic transformation takes place first. The crystallography of bainite transition is identical to that of thermoelastic martensite in the same system.

2. When heated further, the $\alpha$ phase precipitates inside bainite plate and the former bainite becomes $\alpha$ and retained 9R. The orientation relationship between $\alpha$ phase and retained 9R is $(1\,1\,1)_\alpha \parallel (0\,0\,1)_B$, $[0\,\bar{1}\,1]_\alpha \parallel [\bar{1}\,1\,0]_B$.

3. The retained 9R region transforms to $\beta$ phase in the last step and the crystallography of this transition is the reverse of that of $\beta_1$ to 9R transition.

4. With the decomposition of bainite plate, the modulated contrast appears in the $\beta_1$ matrix and 2H type reflections exist. They transform to $\beta$ phase in the transition process gradually and the final product of isothermal transition is $\alpha$ and $\beta$ equilibrium phase.

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