

Martensitic Transition and the Role of Ordering in Copper Based Shape Memory Alloys

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Shape memory effect is a peculiar property exhibited by certain alloy system, and shape memory behavior is evaluated by the structural changes in microscopic scale. Shape-memory effect is based on martensitic transformation, which occurs on cooling from high-temperature parent phase region with the cooperative movements of atoms on $\{110\}$ -type close-packed planes of parent austenite phase by means of shear-like mechanism. The material changes its internal crystalline structure with martensitic transition, and the ordered structure or super lattice structure is essential for the shape memory quality of the material. Copper based alloys exhibit this property in metastable β -phase field which has bcc-based high symmetric structure at high temperature parent state. These structures turn into non-conventional stacking ordered structure with low symmetry following two ordered reactions on cooling from high temperatures.

Keywords: Martensitic transition, Shape memory effect, Ordered structures, Layered structures.

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1. INTRODUCTION

A series of alloy systems exhibit a peculiar property which involves which repeated recovery of macroscopic shape of material at different temperatures. The origin of this phenomenon lies in the fact that the material changes its internal crystalline structure with changing temperature. The basis of this phenomenon is the stimulus-induced phase transformations, martensitic transitions, which govern the remarkable changes in internal crystalline structure of the materials [1-5].

In the shape memory alloys, the austenite lattice has a higher order of symmetry than that of martensite. Martensite variants have identical crystal lattice, but are oriented in different directions [2]. Shape memory alloys are easily deformed at low temperature martensitic phase, and recover the original shape on heating over the reverse transformation temperature.

On the other hand, martensitic transformations have diffusionless character, and product martensite inherits the order of the parent phase [3, 4].

The martensitic transformation is a shear-dominant solid-state phase transformation, and, shape memory materials transform from the parent phase to one or more of the different variants of the martensitic phase in thermal induced manner [6, 7]. The variants of the martensite usually arrange themselves in a self-accommodating manner through twinning [6, 7]. The shape memory effect is based on martensitic transformation, and shape memory properties are intimately related to the microstructures of the material, especially orientation relationship between the various martensite variants [6, 7].

Twinning and detwinning processes can be considered as elementary processes activated during the transformation. These processes are responsible for shape memory effect, as well as martensitic transformation. In particular, the detwinning is essential as well as martensitic transformation in reversible shape memory effect [6, 7]. By applying external stress, the

martensitic variants are forced to reorient into a single variant leading inelastic strains.

Deformation of shape memory alloys in martensitic state proceeds through a martensite variant reorientation or detwinning of twins. The basic mechanism of shape memory effect is schematically illustrated in Fig. 1 [6]. As seen from this figure; the ordered parent phase turns into twinned martensite in thermal manner on cooling from high temperature, and the twinned martensites turn into the detwinned martensites or oriented martensites in stress-induced manner by applying external forces.

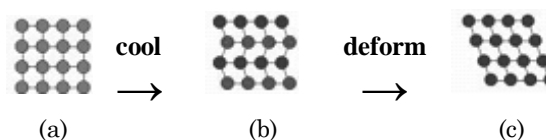


Fig. 1 – Schematic illustration of the mechanism of the shape-memory effect: (a) atomic configuration on $\{110\}$ -type planes of parent austenite phase, (b) twinned martensite phase occurring thermally on cooling, (c) detwinned martensite occurring with deformation [6]

Copper-based alloys exhibit shape memory effect in metastable beta-phase region. Beta phases of copper-based alloys have the A2-type disordered structures at high temperatures and undergo the ordered structure with B2 or DO3 - type superlattice with disorder-order transition on cooling, and these ordered structures also transform into martensite with further cooling. The basic ordered β -phase structures are schematically illustrated in Fig. 2. Martensitic transformations occur in a few steps in Copper-based alloys. The first one is Bain distortion and the second one is lattice invariant shear. Bain distortion consists of an expansion of 26 % parallel to the $[001]_{\beta}$ axis and a compression of 11 % parallel to the $[110]_{\beta}$ and $[\bar{1}10]_{\beta}$ directions. Lattice invariant shear occurs on a $\{110\}$ -type plane of austenite matrix, which is basal plane of martensite. With these distortions, 9R (or 18R)-type layered structures occur in the material.

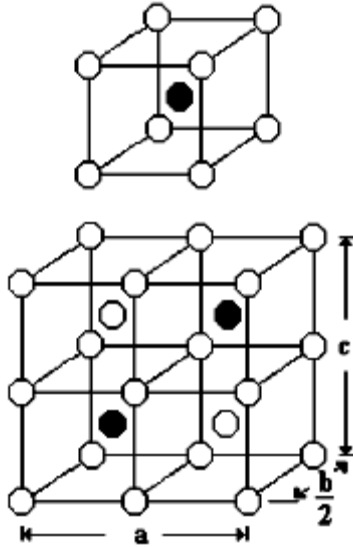


Fig. 2 – Basic ordered beta-phase structures; CsCl-type unit cell (B2) and Cu_3Al - (DO_3)- type unit cell

The β -type martensites have the layered structures which consist of an array of close-packed planes. Formation of the layered structures and sequence of β to 8R martensite transformation is shown in Fig. 3. The layered structures are characterized by the stacking sequences depending on the order in parent phase.

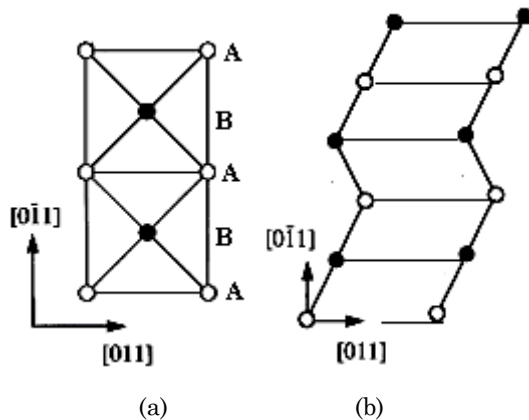


Fig. 3 – a) Stacking of $[110]_{\beta}$ planes viewed from $[001]_{\beta}$ direction, b) inhomogeneous shear and formation of layered structures

Internally faulted martensites in Cu-Zn-Al alloys are characterized by a long period stacking order such as the 9R or 18R type structures, depending on the number of close-packed layers in the unit cell.

Copper based ternary alloys have the DO_3 (or B2)-type superlattice prior to the transformation, and stacking sequence is $\text{AB}'\text{CB}'\text{CA}'\text{CA}'\text{BA}'\text{BC}'\text{BC}'\text{AC}'\text{AB}'$ (18R) in martensitic case. Monoclinic distortion takes place in some cases and 18R structure is modified as M18R [4, 8]. It has been reported that the basal plane of 18R martensites originates from one of the $[110]_{\beta}$ planes of the matrix and the inhomogeneous shear occurs on the basal plane in two opposite directions ($a < \bar{1}10 > \beta$ -type direction and its opposite) [8-10].

2. EXPERIMENTAL

Two copper based ternary shape memory alloys were selected for investigation; Cu-26.1 %Zn 4 %Al and Cu-11 %Al-6 %Mn (in weight). The martensitic transformation temperature of these alloys is over the room temperature and both alloys are entirely martensitic at room temperature. Specimens obtained from these alloys were solution treated for homogenisation in the β -phase field (15 minutes at 830 °C for the Alloy 1 and 20 minutes at 700 °C for the Alloy 2), then quenched in iced-brine to retain the β -phase and aged at room temperature after quenching (both alloys).

Powder specimens for X-ray examination were prepared by filling the alloys. These specimens were then heated in evacuated quartz tubes at 830 °C for 15 minutes and immediately quenched into iced-brine for homogenisation. X-ray diffraction profiles were taken from the quenched specimens using $\text{Cu-K}\alpha$ radiation with wavelength 1.5418 Å. The scanning speed of the Geiger counter was chosen as 2° , $2\theta/\text{min}$ for the diffractograms.

Specimens for TEM examination were prepared from 3 mm diameter discs and thinned down mechanically to 0.3 mm thickness. These specimens were heat-treated for homogenization at 830 °C for 15 minutes and quenched into iced-brine to obtain β -type martensite. The quenched disc-shaped specimens were electropolished in a Struers Tenupol-2 instrument at -20°C in a solution of 20 % nitric acid in methanol, and examined in a JEOL 200CX electron microscope operated at 160 kV.

3. RESULTS AND DISCUSSION

When the copper based beta-phase alloys are cooled below a critical temperature called martensite start temperature, M_s , the martensitic transformation occurs and martensite forms as plates in groups of variants. It enables the shape memory alloys to deform under low stresses by variant coalescence because the total shape change on transformation becomes nearly zero for the group [6]. Product martensite phase including 24 variants undergoes the single crystal of martensite by means of reorientation mechanism on stressing in martensitic condition, and deformed single crystal of martensite undergoes the single crystal of parent phase as a reverse transformation on heating over the austenite finish temperature. This single crystal retransform to the 24 martensite variants on cooling below M_s . The mechanism of this formation has been given elsewhere [9, 10]. On the other hand, a single variant cannot have a coherent interface with the austenite. However a region consisting of fine twins of two martensitic variants can form a coherent interface with the parent austenite [11].

It has been reported that some copper based ternary alloys (cubic \rightarrow monoclinic transformation) exhibit an undeformed interface between austenite and a single variant of martensite [12].

A typical X-ray powder diffraction profile taken from CuZnAl alloy specimen in as-quenched case is shown in Fig. 4. This diffractograms which exhibits superlattice reflection has been indexed on the mono-

clinic M18R basis. Two electron diffraction patterns taken from the quenched samples of Alloy 1 and 2 are also shown in Fig. 5 (a and b). Both X-ray diffractogram and electron diffraction patterns reveal that both alloys exhibit superlattice reflections.

Many X-ray diffractograms have been taken from both of the alloy samples in a long time interval, and some changes in peak characteristics on the diffractogram with aging duration have been observed. Although all of the diffractograms exhibit similar properties, it was observed that peak locations of some diffraction planes have changed. In particular, some of the neighbour peak pairs have moved toward each other.

It is interesting that miller indices of these plane pairs provide a special relation: $(h_1^2 - h_2^2)/3 = (k_2^2 - k_1^2)/n$ where $n = 4$ for 18R martensite [4]. These plane pairs can be listed as follow; (122)-(202), (128)-(208), (12 10)-(20 10), (040)-(320). This observation can be attributed to a relation between inter-plane distances of these plane pairs.

When the martensite is transformed from the parent phase with differently ordered states such as B2 or DO₃, the close-packed plane may consist of atomic sites with different sizes due to the ordering arrangement. The different sizes of atomic sites lead to a distortion of the close-packed plane from an exact hexagon and thus a more close-packed layered structure may be expected.

The martensitic phase in copper-based β -phase alloys is based on one of the $\{110\}_\beta$ planes of parent phase called basal plane for martensite. The lattice invariant shears occurs, in two opposite directions, $\langle 110 \rangle$ -type directions on the $\{110\}$ -type planes of austenite matrix. $\{110\}$ -plane group has the following planes; (110), (1 $\bar{1}$ 0), (101), (10 $\bar{1}$), (011) and (0 $\bar{1}$ 1). With the lattice invariant shears in two opposite directions on both sides of these planes, 24 martensite variants occur.

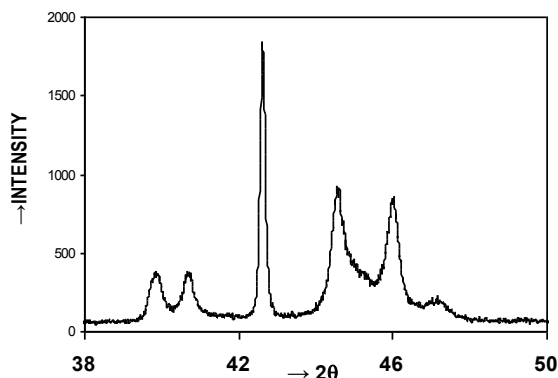


Fig. 4 – A X-ray powder diffractogram of CuZnAl alloy

On the other hand, (110)-type planes of the parent phase are rectangular in original case, and it transforms to a hexagon with hexagonal distortion. The detailed explanation and illustration related to these distortions has been given elsewhere [4].

Structural ordering is one of the important factors

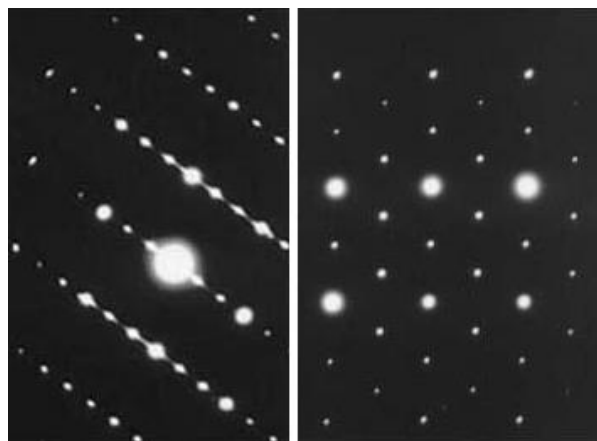


Fig. 5 – Electron diffraction patterns taken from CuZnAl and CuAlMn alloy samples

for the formation of martensite, and atom sizes have an important effect on formation of ordered structures [9, 10]. The martensite basal plane $(110)_\beta$ has an ideal hexagonal form in case atom sizes of alloying elements are equal, and it undergoes a hexagonal distortion in case atom sizes are different.

In the disordered case, lattice sites are occupied randomly by different atoms, and the basal plane becomes ideal hexagon taking the atomic sizes approximately equal. In the ordered case, sub-lattices are occupied regularly by certain atoms which have different atomic sizes, and basal plane undergoes a hexagonal distortion owing to the differences in atom sizes.

Metastable phases of copper-based shape memory alloys are very sensitive to the ageing effects, and any heat treatment can change the relative stability of both martensite and parent phases. Martensite stabilization is closely related to the disordering in martensitic state. Although martensitic transformations are diffusionless, the transitions occurring during the ageing in the martensitic condition have a diffusive character because this transition requires a structural change and this also gives rise to a change in the configurational order.

4. CONCLUSIONS

On the basis of austenite-martensite relation, the basal plane of 9R (or 18R) martensite originates from one of the $\{110\}_\beta$ planes of the parent phase, which have six different planes, and inhomogeneous shears occur in two opposite directions. The basal plane of martensite is subjected to the hexagonal distortion by means of Bain distortion with martensite formation on which atom sizes have important effect. In case the atoms occupying the lattice sites have the same size, the basal plane of martensite becomes regular hexagon. Otherwise the deviations occur from the hexagon arrangement of the atoms in case atom sizes are different. In the light of this knowledge, the atom sizes can be taken approximately equal, in the disordered lattice case, and basal plane becomes nearly ideal hexagon. In the superlattice case, the sizes of atoms occupying the hexagonal lattice sites are different, and the hexagon deviates from regular one.

In conclusion, the changes in the location of the

above mentioned plane pairs reveal the rearrangements of the atom in displacive manner; and this result

provides us information on the degree of ordering in the martensitic state of the material.

REFERENCES

1. R.D. James, K.F. Hane, *Acta Mater.* **48**, 197 (2000).
2. J.J. Zhu, K.M. Liew, *Acta Mater.* **51**, 2443 (2003).
3. J. Pons, et al., *Acta Mater.* **48**, 3027 (2000).
4. O. Adiguzel, *J. Mater. Proc. Tech.* **185**, 120 (2007).
5. Y. Sutou, et al., *Acta Mater.* **53**, 4121 (2005).
6. J. Ma, I. Karaman, R.D. Noebe, *Int. Mater. Rev.* **55**, 257 (2010).
7. Y. Liu, *Proc. SPIE* **4234**, 82 (2001).
8. T. Uhera, T. Tamai, *Mech. Adv. Mater. Struc.* **13**, 197 (2006).
9. Y.F. Guo, et al., *Acta Mater.* **55**, 6634 (2007).
10. A. Aydogdu, Y. Aydogdu, O. Adiguzel, *J. Mater. Proc. Tech.* **153-154**, 164 (2004).
11. C. LExcellent, P. Blanc, *Acta Mater.* **52**, 2317 (2004).
12. K.F. Hane, *J Mech. Phys. Solids* **47**, 1917 (1999).