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Phase Transition and Functional Characteristics of Shape Memory Alloys

O. Adiguzel

Firat University, Department of Physics, 23169 Elazig, Turkey

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Shape-memory alloys are a new class of functional materials with a peculiar property known as shape memory effect. These alloys have an ability to recover a particular shape. The origin of this phenomenon lies in the fact that the material changes its internal crystalline structure with changing temperature. Copper based ternary alloys exhibit shape memory effect in metastable β- phase field. These alloys undergo two ordered transitions on cooling, and bcc structures turn into B2(CsCl) or $DO_3(Fe_3Al)$ -type ordered structures. The ordered structures martensitically undergo the non-conventional layered structures on further cooling. These structures are called as 3R, 9R or 18R martensites depending on the stacking sequences on the close-packed planes of the matrix.

Keywords: Shape memory effect, Martensite, Atom sizes, Layered structures, Hexagonal distortion.

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1. INTRODUCTION

Shape memory alloys take place in a class of functional materials by exhibiting a peculiar property called shape memory effect. This property is characterized by the recoverability of a certain shape of material at different conditions. Shape memory effect is associated with martensitic transformation which is a solid state phase transformation and occurs with the cooperative movements of atoms in the alloy on cooling from high temperature austenite phase region. Shape memory effect refers to the shape recovery of materials resulting from reverse transformation, from martensite to parent austenite, when heated over reverse transformation temperature after deforming in the martensitic phase. These alloys also cycle between two certain shapes with changing temperature.

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.

Copper based alloys exhibit this property in metastable β-phase field. High temperature β-phase bcc-structures martensitically undergo the non-conventional structures following two ordered reactions on cooling, and structural changes in nanoscale level govern this transition cooling [1-3]. Atomic movements are also confined to interatomic lengths in sub-μm or angstrom scale. Martensitic transformations occur in a few steps with the cooperative movement of atoms less than interatomic distances by means of lattice invariant shears on a {110} - type plane of austenite matrix which is basal plane of martensite. These shears give rise the formation of unusual complex structures called long period layered structures such as 3R, 9R or 18R depending on the stacking sequences on the close-packed planes of the ordered lattice. The complicated long-period stacking ordered structures mentioned above can be described by different unit cells. In case the parent phase has a B2-type superlattice, the stacking sequence is ABCBCACAB (9R) [2, 4]. The stacking of $(110)_\beta$ -planes in DO_3-type structure and formation of layered structures are shown in Fig.1. Martensitic transformation is characterized by a change in the crystal structure of the material at the nano-level rather than micro- level, and the transformed region consists of parallel bands containing alternately two different variants.

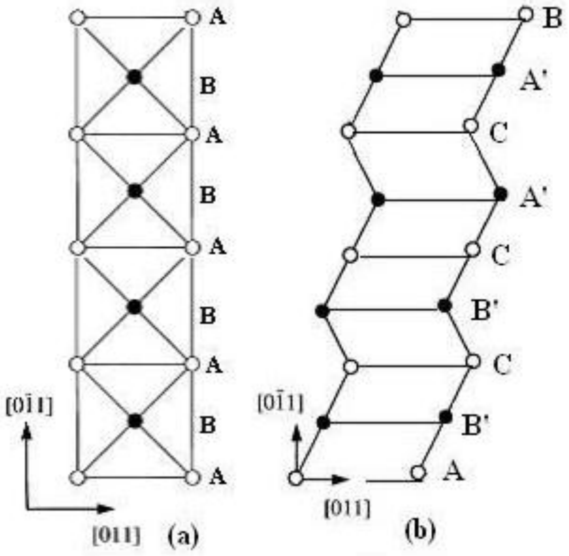

Fig. 1 – a) Stacking of $(110)_\beta$ planes viewed from $[001]_\beta$ direction in DO_3-type structures, b) Inhomogeneous shear and formation of layered structures

2. EXPERIMENTAL

In the present contribution, x-ray diffraction and transmission electron microscopy studies were carried out on two copper based alloys which have the chemical compositions in weight; Cu-26.1%Zn 4%Al and Cu-11%Al-6%Mn. Powder specimens for X-ray examination were prepared by filling the alloys. Specimens for TEM examination were prepared from 3 mm diameter discs and thinned down mechanically to 0.3 mm thickness.

These specimens were heated in evacuated quartz tubes in the β-phase field (15 minutes at 830°C for CuZnAl and 20 minutes at 700°C for CuAlMn) for homogenization, and quenched in iced-brine. These specimens were also given different post-quench heat treatments and aged at room temperature. TEM and X-ray diffraction studies carried out on these specimens.

TEM specimens were examined in a JEOL 200CX electron microscope, and X-ray diffraction profiles were taken from the quenched specimens using Cu-Kα radiation with wavelength 1.5418 Å

3. RESULTS AND DISCUSSION

An x-ray powder diffractogram taken from the quenched CuAlMn alloy samples is shown in Fig. 2. Two electron diffraction patterns taken from CuZnAl and CuAlMn alloy samples are also shown in Fig. 3a and b, respectively. X-ray powder diffractogram and electron diffraction patterns reveal that these alloys exhibit superlattice reflections. X-ray powder diffractograms and electron diffraction patterns taken from the specimens in a large time interval were compared with each other.

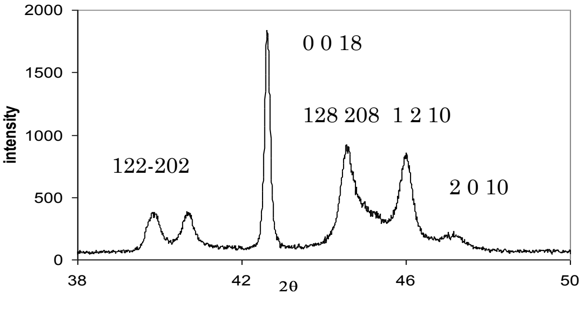

Fig.2 – An x-ray powder diffractogram taken from Cu-11%Al-6%Mn alloy sample

Fig. 3 – Two electron diffraction patterns taken from the CuZnAl and CuAlMn alloy samples

A series of 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. X-ray powder diffractograms and electron diffraction patterns taken from the specimens in a large time interval were compared with each other. It has been observed that electron diffraction patterns exhibit similar characteristics, but some changes have been occurred in the locations and intensities of diffraction peaks on the x-ray diffractograms with aging duration.

It has been observed that some peak pairs come close each other with ageing duration [5]. These changes imply new transitions which have diffusive character. It means that some neighbor atoms change their locations.

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 [1, 5]. These plane pairs can be listed as follow; (122)-(202), (128)-(208), (1 2 10) – (2 0 10), (040)- (320). This observation can be attributed to a relation between interplane distances of these plane pairs. In the disordered case, atom sizes can be taken nearly equal, and martensite basal plane becomes an ideal hexagon. Therefore, if the interplane distances are calculated, it can be seen that these values will be equal each other for the pairs and diffraction peaks overlap each other. In the ordered case, neighbour atom sizes are different, interplane distances of these plane pairs become different and each peak appears separately [5]. On the other hand, the alloys have the layered complex structure in martensitic state. The monoclinic distortion of 18R-type structure contributes to the martensite stabilization which proceeds by a diffusion-controlled process [6]. Metastable phases of copper-based shape memory alloys are very sensitive to the ageing effects, and heat treatments can change the relative stability and the configurational order of crystal planes. The parent phase has highly symmetric structure and the product phase has internally twinned and complex structures. Several types of microscopic deformation involving changes can occur in the stacking sequence of close-packed planes of material with martensite formation [2,7]. This change gives rise the increase in the complexity of crystal structure.

When the martensite is transformed from the parent phase with differently ordered states such as B2 or DO_3, 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. 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

Structural ordering is one of the important factors for the formation of martensite, and atom sizes have an important effect on formation of ordered structures [8-10].

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 [6]. In the disordered case, sublattices are occupied randomly by atoms, and the basal plane becomes ideal hexagon taking the atomic sizes approximately equal. In the ordered case, sublattices 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 [10].

Metastable β-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. The martensitic transformation obtained on cooling is called thermally induced phase transformation. The obtained martensite consists of up to 24 variants, which are regions of the same structure but with different crystallographic orientations [5, 6, 11]. CuZnAl alloys and other copper-based shape memory alloys exhibit a tendency to martensitic thermal stabilization. During the stabilization process, the pinning of martensitic variants can take place only in thermally induced martensite, while the atom rearrangement can take place in both thermal and stress-induced martensite [11]. For the stress-induced martensite, the stabilization manifests as a decrease of the stresses at which the reverse transformation takes place [5, 6, 10]. Martensite stabilization is closely related to the disordering in martensitic state, and atom locations in the lattice sites in the crystal unit cell are very important for the analysis and process of transformation.

Shape memory alloys have the important ability to remember their original shape on heating after deformation in low temperature martenstic state, and they are used as shape memory elements in devices due to this property. These alloys cycle between two particular shapes with changing temperature. In the cycling processes; the martensite normally returns to a self-accommodated structure after cooling from austenite in the one way shape memory case, whereas two way shape memory effect causes the martensite to adopt a detwinned -single variant configuration [9, 11, 12, 13].

4. CONCLUSION

It has been observed that electron diffraction patterns exhibit similar characteristics, but some changes have been occurred in the locations and intensities of diffraction peaks on the x-ray diffractograms with aging duration. In particular, some peak pairs satisfying a specific relation between miller indices come close each other with ageing [5]. These changes imply new transitions which have diffusive character.

It can be concluded from the above results that the copper-based shape memory alloys are very sensitive to the ageing treatments, and heat treatments can change the relative stability and the configurational order of atoms in the material. This result attributes to rearrangement of atoms in diffusive manner. Although martensitic transformations are diffusionless, the disordering reaction occurring with the ageing treatment has a diffusive character, and this also gives rise to a change in the configurational order.

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