MULTIVARIANT NATURE OF DISPLACIVE TRANSITIONS IN COPPER BASED SHAPE MEMORY ALLOYS

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Shape memory effect is an unusual property exhibited by certain alloy systems, and based on a displacive transition, martensitic transition. Copper based alloys exhibit this property in metastable β-phase region and bcc-based high temperature parent phase structures martensitically turn into the layered complex structures on cooling from high temperature. Martensitic transformations occur with cooperative movement of atoms by means of lattice invariant shears on a [110] - type plane of austenite matrix which is basal plane of martensite. The lattice invariant shears occur, in two opposite directions, <110> -type directions on the [110]-type basal plane. This kind of shear can be called as [110]<110> - type mode, and possible 24 martensite variants occur. This lattice invariant shear gives rise to the formation of layered structure. Product martensitic phase has the unusual layered structures which consist of an array of close-packed planes with complicated stacking sequences called as 3R, 9R or 18R martensites depending on the stacking sequences on [110]- type planes of parent phase. The basal plane of martensite is subjected to the hexagonal distortion with martensite formation on which atom sizes have important effect. It is known that the local stress and composition conditions can play an important role in the final structures of the material.

Keywords: Martensitic transition, shape memory effect, martensite variants, Bain distortion.

INTRODUCTION

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 with changing temperature. These alloys involve the repeated recovery of macroscopic shape of material at certain temperature intervals. The origin of this phenomenon lies in the fact that the material changes its internal crystalline structure with changing temperature. The functional behavior of shape memory alloys, as thermoelastic and pseudoelastic effects, is related to the first-order martensitic transition. Copper based ternary alloys exhibit shape memory effect in metastable β-phase field. These alloys undergo the non-conventional structures on cooling from high temperatures, following two ordered reactions (Adiguzel, 2007; Zhu & Liew, 2003). Inhomogeneous shears, lattice invariant shears occur as martensite variants on a {110} - type planes of austenite matrix which is basal plane of martensite. The lattice invariant shears occur, in two opposite directions, <110> -type directions on the {110}-type planes, and this kind of shear can be called as {110} <110> - type mode and has 24 variants in self-accommodating manner (Adiguzel, 2007; Sutou et al., 2005). A pair of shears in the $\bar{1}10_\beta$ and $110_\beta$ - directions occur as two variants along the (110)$\beta$ plane. This lattice invariant shear causes to the formation of layered structure. These shears cause to the formation of layered structures. The {110} – type planes of parent phase turn into unusual layered structures which consist of an array of close-packed planes with complicated stacking sequences called as 3R, 9R or 18R martensites depending on the stacking sequences on the close-packed planes of the ordered lattice. The periodicity and therefore the unit cell are completed through 18 layers in direction z in 18R case (Zhu & Liew, 2003; Pelegrina & Romero, 2000). The martensitic transformations basically have the diffusionless character and exhibit the order of parent phase structure existing prior to the transformation. The complicated long-period
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Stacking ordered structures can be described by different unit cells. In case the parent phase has a B2-type superlattice, the stacking sequence is ABCBCACAB (9R) (Zhu & Liew, 2003; Pelegrina & Romero, 2000). The stacking of (110)_β planes in DO₃-type structure and formation of layered structures are shown in Figure 1. Martensitic transformation is characterized by a change in the crystal structure of the material at the atomic level, and martensite phases have the long-period stacking ordered structures that is the underlying lattice is formed by stacks of close-packed planes. More specifically, microstructural evaluation provides a mechanism by which the transformation from the high temperature austenite phase to the low temperature martensite phase takes place.

![Figure 1](image)

Figure 1. a) Stacking of (110)_β planes viewed from [001]_β direction, b) Atomic configuration on first and second layers of (110)_β plane in DO₃-type structures, c) inhomogeneous shear and formation of layered structures, stacking sequences of half 18R or M18R unit cell in direction z

EXPERIMENTAL

In the present contribution, two copper based ternary alloys were selected for investigation: a CuZnAl alloy with a nominal composition by weight of 26.1% zinc, 4% aluminium, the balance copper, while the other was a CuAlMn alloy with a nominal composition by weight of 11% aluminium, 6% manganese and the balance copper. Powder specimens for X-ray examination were prepared by filling the alloys. Specimens for TEM examination were also prepared from 3mm diameter discs and thinned down mechanically to 0.3mm 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.
RESULTS AND DISCUSSION

An x-ray powder diffractogram taken from the quenched and long term aged CuAlMn alloy sample is shown in Figure 2.

![Figure 2. An x-ray diffractogram taken from the long term aged CuAlMn alloy sample](image)

Two electron diffraction patterns taken from CuZnAl and CuAlMn alloy samples are also shown in Figure 3. X-ray powder diffractograms and electron diffraction patterns were taken from CuZnAl and CuAlMn samples. X-ray powder diffractograms and electron diffraction patterns reveal that this alloy has an ordered structure in martensitic condition, and exhibit superlattice reflections. X-ray powder diffractograms and electron diffraction patterns were taken from both CuZnAl and CuAlMn alloy samples in a large time interval and compared with each other. It has been observed that electron diffraction patterns exhibit similar characteristics, but some changes occur at the peak locations and intensities on the x-ray diffractograms with aging duration. These changes occur as rearrangement or redistribution of atoms in the material, and attribute to new transitions in diffusive manner (Adiguzel, 2007; Li et al., 2008). The ordered structure or super lattice structure is essential for the shape memory quality of the material. In the shape memory alloys, homogenization and releasing the external effect is obtained by ageing at β–phase field for adequate duration. Crystallization is essential for shape memory quality, and crystallization and formation of the ordered structure is also obtained by the quenching process in the suitable media. The quenching rate is also important for the formation of homogenous ordered structures and shape memory optimization. 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 (Li et al., 2008; Adiguzel, 2012; Paidar, 2008).
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Figure 3. Two x-ray diffractograms taken from the CuZnAl and CuAlMn alloy samples

On the other hand, post-quench ageing and service processes in devices affect the shape memory quality, and give rise shape memory losses. These kinds of results lead to the martensite stabilization in the reordering or disordering manner. In order to make the material satisfactorily ordered and to delay the martensite stabilization, copper-based shape memory alloys are usually treated by step-quenching after homogenization.

Although martensitic transformation has displacive character, martensite stabilization is a diffusion controlled phenomena, and leads to redistribution of atoms on the lattices sites. Stabilization is important factor and causes to memory losses, and changes in main characteristics of the material, such as transformation temperatures, and x-ray diffraction peak location and peak intensities.

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 crystal planes. This result attributes to a rearrangement of atoms.

REFERENCES


