Nanoscale characterization of martensite structures in copper based shape memory alloys

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Abstract. Martensitic transformations are first order displacive transitions and occur in the materials on cooling from high temperature. Shape memory effect is an unusual property exhibited by certain alloy systems, and leads to martensitic transition. Copper-based alloys exhibit this property in beta phase field which possess simple bcc- structures, austenite structure at high-temperatures. As temperature is lowered the austenite undergoes martensitic transition following two ordering reactions, and structural changes in nanoscale govern this transition. Atomic movements are also confined to interatomic lengths in sub-μm or angstrom scale in martensitic transformation. The formation of the layered structures in copper based alloys consists of shears and shear mechanism. 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 or stacking plane of martensite. The lattice invariant shears occurs in two opposite directions, <110> -type directions on the {110}-type plane. These shears gives rise to the formation of layered structure.

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 occurring 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 martensite to austenite transformation when heated above reverse transformation temperature after deforming in the martensitic phase. These alloys also cycle between two certain shapes with changing temperature. Copper based shape memory 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.

In the shape memory alloys, the austenite lattice has a higher order of symmetry than that of martensite. More than one martensite variant can be induced from one austenite. Martensite variants have identical crystal lattice, but are oriented in different directions [2].

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The relationship of microstructures in shape memory alloys is essential for a better understanding of the mechanism using the basic characteristic of shape memory alloys. The basic characteristic of shape memory alloys is the occurrence of different variants in the low temperature martensitic phase. The martensitic transformation is a shear-dominant diffusionless solid-state phase transformation, and when a shape memory alloy undergoes a martensitic phase transformation, it transforms from the parent phase to one or more of the different variants of the martensitic phase [4, 5].

In the absence of applied stresses or mechanical loading, the variants of the martensitic phase usually arrange themselves in a self-accommodating manner through twinning, resulting in no observable macroscopic shape change [5]. By applying mechanical loading the martensitic variants are forced to reorient (detwin) into a single variant leading to large macroscopic inelastic strains. The multiple martensite variants begin to convert to single variant, the preferred variant determined by alignment of the habit planes with the axis of loading [4-8].

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.

All of these martensite phases are long-period stacking ordered structures that is the underlying lattice is formed by stacks of close-packed planes. In case the parent phase has a B2-type superlattice, the stacking sequence is ABCBCACAB(9R) [2, 9]. The stacking of (110)$_{\beta}$ -planes in DO$_3$-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 nano-level rather than micro-level, and the transformed region consists of parallel bands containing alternately two different variants.

**Figure 1.** a) Stacking of (110)$_{\beta}$ planes viewed from [001]$_{\beta}$ direction in DO$_3$-type structures, b) atomic configuration on first and second layers of (110) $\beta$ - plane in DO$_3$-type structures, c) inhomogeneous shear and formation of layered structures.
All of these martensite phases have the long-period stacking ordered structures, and microstructural evaluation provides a mechanism by which the transformation from the high temperature austenite phase to the low temperature martensite phase takes place.

The fundamental structures of the beta-type martensites are orthorhombic close-packed structures, and monoclinic distortion takes place in some cases by means of microstructural evaluation depending on the atomic distribution in nanoscale or angstrom level, and 18R structure is modified as M18R.

2. 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.

3. Results and Discussion

An x-ray powder diffractogram taken from the quenched CuZnAl alloy samples is shown in Figure 2. An electron micrograph and two electron diffraction patterns taken from CuZnAl and CuAlMn alloy samples are also shown in Figure 3a, b and c, respectively. X-ray powder diffractograms and electron diffraction patterns reveal that this alloys exhibit superlattice reflections. As seen from the electron micrograph, the main characteristics martensite in copper-based β-phase alloys are the prevalence of groups of essentially parallel-sided plates [10].

X-ray powder diffractograms and electron diffraction patterns taken from the specimens in a large time interval were compared with each other.

![Figure 2. An x-ray powder diffractogram taken from CuZnAl alloy sample aged at room temperature for more than ten years.](image-url)
Figure 3. a) An electron micrograph showing the fine martensite structure in CuZnAl alloy (x 90k), (b) electron diffraction patterns taken from CuZnAl alloy, (c) electron diffraction patterns taken from CuAlMn alloy sample.

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 move and come close each other with ageing [10]. These changes imply new transitions which have diffusive character. It means that some neighbour atoms change their locations. The monoclinic distortion of 18R-type structure contributes to the martensite stabilization which proceeds by a diffusion-controlled process [11].

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. Also, several types of microscopic deformation involving changes can occur in the stacking sequence of close-packed planes of material with martensite formation [2, 12]. This change gives rise to the increase in the complexity of crystal structure. Atom locations in the lattice sites in the crystal unit cell are very important for the analysis and process of transformation.

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.

Key Words: Martensitic transition, shape memory effect, layered structures, stacking sequence.

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