Ageing dependence and martensite stabilization in copper based shape memory alloys

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Abstract. Shape memory alloys exhibit a peculiar property called shape memory effect based on a first order solid state phase transformation, martensitic transformation which occurs in thermal manner on cooling the materials. Martensitic transformation is evaluated by the structural changes in microscopic scale. Copper-based ternary alloys exhibit shape memory effect in metastable beta phase region. These alloys have bcc-based ordered structures at high temperature, and transform martensitically to the long-period layered structures on cooling. The material atoms move cooperatively on \{110\}-type close packed planes of parent phase by means of a shear-like mechanism, and structural and fundamental properties of these alloys are altered by aging in the martensitic state. Therefore, the ageing gives rise to the structural changes in both long and short-range order in material. X-ray powder diffraction studies carried out in a long time interval on copper based shape memory alloys reveal that peak locations and intensities change with ageing duration in martensitic condition, and these changes lead to the martensite stabilization in the redistribution or disordering manner, and stabilization proceeds by a diffusion-controlled process.

1. Introduction
Martensitic transformations are first order lattice-distorting phase transformations and occur with the cooperative movement of atoms by means of lattice invariant shears in the materials on cooling from high temperature parent phase region. Shape memory effect is based on martensitic transformation, and microstructural mechanisms are responsible for shape memory behaviour. In particular, the detwinning is essential as well as martensitic transformation in reversible shape memory effect [1, 2]. Thermal induced martensite occurs by means of a shear-like mechanism as multivariant martensite in self-accommodating manner and consists of lattice twins. Also, this martensite is called twinned martensite or multivariant martensite.

Shape memory alloys can be deformed plastically in low temperature martensitic condition, and recover the original shape on heating over the austenite finish temperature. The material cycles between the deformed and original shapes on cooling and heating. By applying external stress, the martensitic variants are forced to reorient into a single variant leading inelastic strains, and deformation of shape memory alloys in martensitic state proceeds through a martensite variant reorientation or detwinning of twins. The twinning occurs with internal stresses, while detwinning occurs with the external stresses. The basic mechanism of shape memory effect is schematically illustrated in Figure 1 [1, 2]. The deformed material recovers the original shape on heating over the
Figure 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 [1].

austenite finish temperature, and returns to the multivariant martensite structures in irreversible shape memory effect on cooling below the martensite finish temperature; in contrast, the material returns to the detwinned martensite structure in reversible shape memory case.

Shortly one can say that the microstructural mechanisms responsible for the shape memory effect are the twinning and detwinning processes as well as martensitic transformation. Therefore, the detwinning process has great importance for the processing of reversible shape memory effect. Copper based alloys exhibit this property in metastable \(\beta\) phase region, which has B2 or DO\(_3\)-type ordered lattice at high temperature, and these structures martensitically turn into layered complex structures with lattice twinning process, on cooling from high temperature austenitic phase region.

Martensitic transformations occur in a few steps with the cooperative movement of atoms less than interatomic distances by means of lattice invariant shear on a \{110\} - type plane of austenite matrix which is basal plane of martensite. First one is Bain distortion, and second one is lattice invariant shear. Bain distortion consists of an expansion of 26% parallel to the \(<001>\)-type axes, called Bain axes, and a compression of 11% parallel to the \(<110>\) and \(<1\bar{1}0>\)-type directions, perpendicular two Bain axes. The compressed directions are \{110\} and \{1\bar{1}0\} directions for \{001\} - Bain axes. For the illustration of Bain distortion, an fct cell is delineated in matrix, and this cell undergoes to the corresponding fcc cell with Bain distortion [3]. Lattice invariant shears occur with cooperative movement of atoms less than interatomic distances on \{110\}-type close packet plans of austenite matrix. The lattice invariant shears occurs, in two opposite directions, \(<110>\) -type directions on the \{110\}-type basal planes and this kind of shear can be called as \{110\} \(<110>\) - type mode and has 24 variants in self-accommodating manner [4-6]. These lattice invariant shears give rise to the formation of unusual complex layered 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.

Figure 2. (a) Stacking of \((1\bar{1}0)\)\(_{\beta}\) planes viewed from \([001]\)\(_{\beta}\) direction,(b) Atomic configuration on first and second layers of \((1\bar{1}0)\)\(_{\beta}\) plane in DO\(_3\) - type structures, (c) inhomogeneous shear and formation of layered structures, stacking sequences of half 18R or M18R unit cell in direction z.
The periodicity and therefore the unit cell are completed through 18 layers in direction z in 18R case. Formation of these layered structures is schematically illustrated in Figure 2.

2. Experimental

In the present contribution, 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 temperatures of these alloys are over the room temperature and both alloys are entirely martensitic at room temperature. Specimens obtained from these alloys were solution treated for homogenization in the \( \beta \)-phase field (15 minutes at 830\(^{\circ}\)C for CuZnAl alloy and 20 minutes at 700\(^{\circ}\)C for CuAlMn alloy), then quenched in iced-brine to retain the \( \beta \)-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 heated in evacuated quartz tubes in the \( \beta \)-phase field (15 minutes at 830\(^{\circ}\)C for CuZnAl and 20 minutes at 700\(^{\circ}\)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. X-ray diffraction studies carried out on these specimens, and X-ray diffraction profiles were taken from the quenched specimens using Cu-K\( _\alpha \) radiation with wavelength 1.5418 Å.

3. Results and Discussion

X-ray powder diffractograms were taken from CuZnAl and CuAlMn samples. An x-ray powder diffractogram taken from the long term aged CuAlMn alloy sample is shown in Figure 3. This diffractogram has been indexed on the monoclinic M18R basis. On the other hand, electron diffraction pattern were also taken from the samples these alloys, the details were given elsewhere [3, 6]. X-ray diffractograms and electron diffraction patterns reveal that both alloy have the ordered structure in martensitic condition, and exhibit superlattice reflections. A series of 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 [3, 6, 8]. 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 \( \beta \)-phase field for adequate duration.

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 this result 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 intensities.

The martensitic phase in copper-based \( \beta \)-phase alloys is based on one of the \{110\}_\beta planes of parent phase called basal plane for martensite. The (110) basal plane which has a rectangular shape in parent phase is subjected to hexagonal distortion and undergoes a hexagon. This process is schematically illustrated in Figure 4.

The powder specimens were aged at room temperature after quenching process, and many x-ray diffractograms have been taken from both of the alloy samples in a large time interval. Although all of the diffractograms exhibit similar characteristics, some changes have been observed in peak locations on the diffractograms with aging duration. These changes are attributed to new transitions which have diffusive character. It means that some neighbour atoms change locations.
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: 
\[
\frac{h_1^2 - h_2^2}{3} = \frac{k_2^2 - k_1^2}{n}
\]
where \(n=4\) for 18R martensite. These plane pairs can be listed as follow; (122)-(202), (128)-(208), (1210) – (2010), (040) – (320). This result can be attributed to a relation between interplane distances of these plane pairs and rearrangement of atoms on the basal plane. In these changes, atom sizes play important role. 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. In the disordered case, atom sizes can be taken nearly equal, and martensite basal plane becomes an ideal hexagon. Although martensitic transformations are displacive, the post-martensitic transitions have the diffusive character because this transition requires a structural change and this also gives rise to a change in the configurational order. The interplane distances of the diffracted plane pairs are calculated using the following relation in the monoclinic case.

\[
\frac{1}{d^2} = \frac{1}{a^2} \frac{h^2}{\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \frac{\cos^2\beta}{ac \sin^2\beta} - \frac{2hl}{ac \sin^2\beta}
\]

It can be seen with this calculation that dhkl values of the diffracted plane pairs become approximately equal each other in the disordered case, and diffraction peaks overlap each other, considering atom
sizes approximately equal each other. In the ordered case, neighbour atom sizes are different, interplane distances become different and each peak appears separately. 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 [8, 9]. Martensite stabilization is closely related to the disordering in martensitic state. Structural ordering is one of the important factors for the formation of martensite, while atom sizes have important effect on the formation of ordered structures [9, 10, 11].

4. Conclusions
It can be concluded from the above results that the copper-based shape memory alloys are very sensitive to the ageing treatments. The diffracted angles and intensities of x-ray diffraction peaks chance with ageing duration in martensitic condition. In particular, some successive peak pairs come close each other. These changes lead to the martensite stabilization in the redistribution or disordering manner, and stabilization proceeds by a diffusion-controlled process. The martensite stabilization is a diffusion controlled phenomena and leads to redistribution of atoms on the lattices sites, although martensitic transformation has displacive character. The basal plane of martensite turns into a hexagon 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. The above mentioned diffracted plane peaks come close each other in the disordered case, and occur separately in the ordered case. The changes in the diffraction angles of the selected plane pairs can be a measure of the ordering degree in martensite.

5. References
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