Commun. Fac. Sci. Univ. Ank. Series A_2, A_3
V. 36, pp 47-55 (1987)

MARTENSITE STRUCTURE DETERMINATION IN SHAPE MEMORY CuAlMn ALLOY

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(Received 6 June 1987)

ABSTRACT

Shape memory alloys are characterized by a thermoelastic martensitic transformation and the presence of ordering in the parent phase and martensite. Crystal structure studies of parent and martensite phases in a CuAlMn alloy show that a thermoelastic transformation from an ornered parent phase of DO_3 type to an M18R martensite takes place. This orthorombic structure of M18R form consists of an array of close-packed planes. The eighteen layer martensite structure (AB′CB′CA′CA′BA′BC′BC′AC′AB′) can form as a result of periodic shifts on the martensite basal plane in the c-direction.

INTRODUCTION

The shape memory effect which has been intensively stiudied in the noble metal alloys is now a well known metallurgical phenomenon and involves the deformation of specimen in the martensitic condition following which the initial undeformed shape is regained by heating throguh the A_s to A_f reversal temperature range. The origin of memory effect lies in the mobile property of the boundaries between martensite and matrix, and between twins, and in the coherent nature of these boundaries (1). This phenomenon is found in a large number of alloys which exhibit a thermoelastic martensitic transformation (2-5).

In the last two decades, many alloys have been reported to show the shape memory effects (SME), a phenomenon apparently dependent on the crystallographic reversibility of a thermoelastic martensite. In particular, noble metal copper based alloys have recently attracted considerably attention because of their peculiar memory effect (5-8). Since the crystallography of the martensite transformation in these alloys is well established (8-10), the nature of the memory effect can be found more clearly.

In certain copper based SME alloys, the reverse transformation temperatures, A_s and A_f, progressively increase with prolonged holding time at temperatures below As (2, 3, 8). If the stabilised martensite phase is heated to temperatures above the increased A_S and A_f, the samples are restored to their original state. Although many studies have been reported on the binary CuZn and ternary CuZnAl alloys (6-10), any work has not been reported on the shape memory CuAlMn alloys. But recently, a study has been done on the martensite ageing effect in a shape memory CuAlMn alloy (11).

In the present study, product martensite forming in Cu-11 wt % Al-6 wt % Mn alloy has been investigated and compared with that of CuZnAl alloy. Both electron microscope and X-ray examinations confirm that SME CuAlMn alloy investigated has the same character as observed in SME CuZnAl alloys. For this alloy, the M_S temperature determined with Differential Scanning Calorimetry (DSC) measurement is 133°C, M_f temperature is also 98°C and the alloy is fully martensitic at room temperature.

EXPERIMENTAL DETAILS

A CuAlMn alloy containing nominally 11 wt % Al and 6 wt % Mn which has an M_S temperature of 133°C was supplied by Delta Research Ltd., England, in the form of a spring about 1.5 cm diameter and 3 cm length. A coil was taken by cutting from this alloy of spring form and homogenised by heating in the β-phase field at 700°C for 30 minutes and subsequently quenched into water to retain β-phase and produce martensite.

1. TEM Observation

A part of as-quenched alloy was sectioned by a low-speed diamond saw and punched into 3 mm discs and mechanically thinned up to 0.3 mm and polished. These discs were then electropolished using a Struers

Tenupol-2 jet machine in a solution of 20 % nitric acid in methanol at around -20°C. Transmission electron microscope studies were carried out using JEOL JEM 100B and 200CX electron microscopes operated at 100 kV and 160 kV, respectively.

2. X-Ray Diffraction Studies

In addition to the TEM observations, X-ray powder diffraction studies were also carried out in the powder samples of the same CuAlMn alloy. For the X-ray measurements, a part of as-quenched alloy was made powder by filing with steel file.

This powder sample was then reheated in the evacuated quartz capsules and homogenised at 700°C for 15 minutes and immediately quenched into water, in order to remove the strain effect which has produced during filing. As-quenched powder sample was divided into four parts and given different post quench heat treatments. These β-phase post quench treatments have been explained in elsewhere (11).

X-ray diffractograms were taken immediately after quenching from the as-quenched sample and at intervals from the aged samples. The powver X-ray diffractograms were taken with copper K_α radiation and a nickel filter used to eliminate the K_β radiation. The scanning speed of the Geiger counter was fixed at 2°, 2θ a minute for all the diffactograms

RESULTS AND DISCUSSION

The β-phase with the DO_3 type of ordered structure is transformed into 18R type martensite by cooling the alloy below the M_S temperature Figure 1 shows the transmission electron micrographs of martensites taken from the as-quenched CuAlMn alloy. As seen in these micrographs, CuAlMn martensites have also typical plate configuration which has the same character as CuZnAl martensites. Figure 2 also shows a group of selected area diffraction patterns of martensites taken from the same as-quenched sample. These diffraction patterns have been taken at room temperature at which the alloy is fully martensitic. As seen in Fig. 2, diffraction patterns consist of strong and weak spots and this confirms that the alloy has a superlattice structure in the martensitic condition. On the patterns, the strong spots represent fundamental reflections and

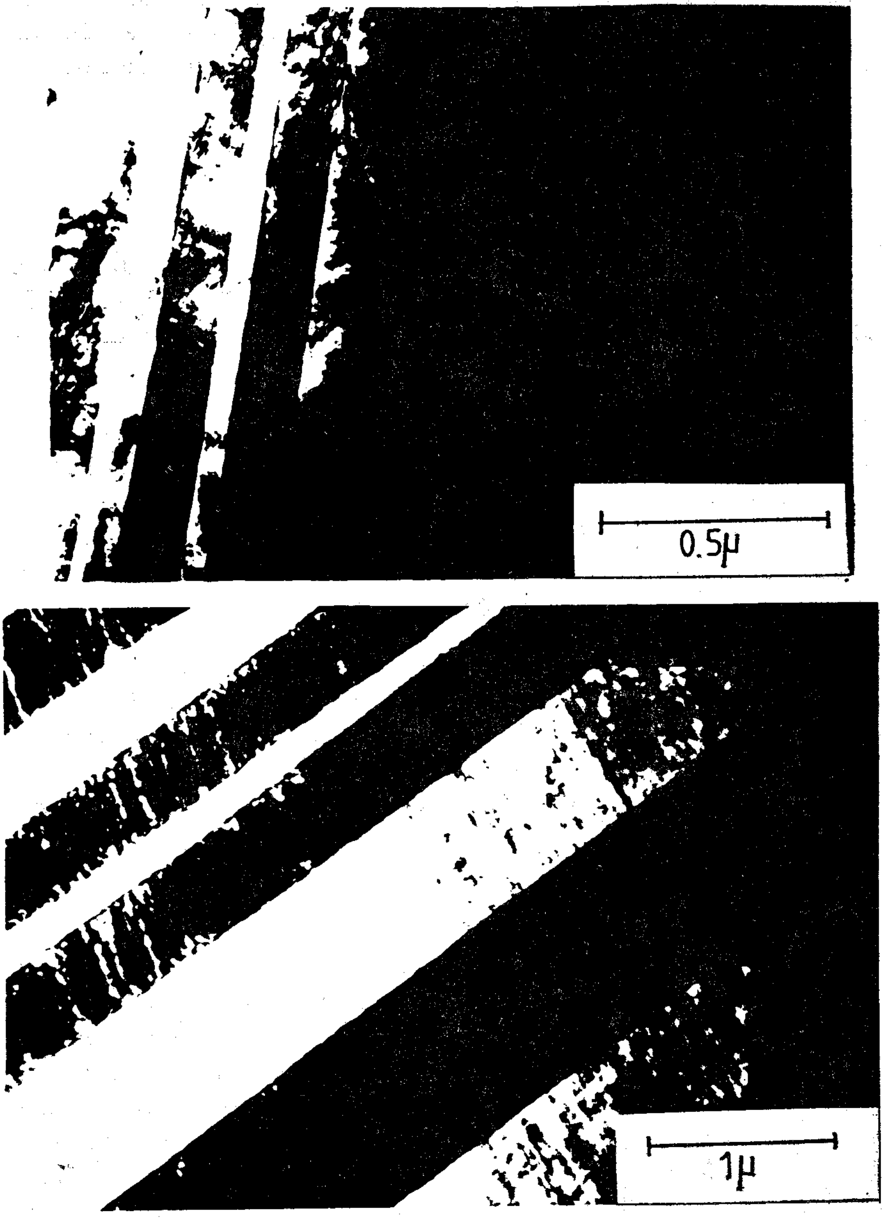

Figure 1 Electron micrographs of CuAlMn martensites taken from the as-quenched sample.

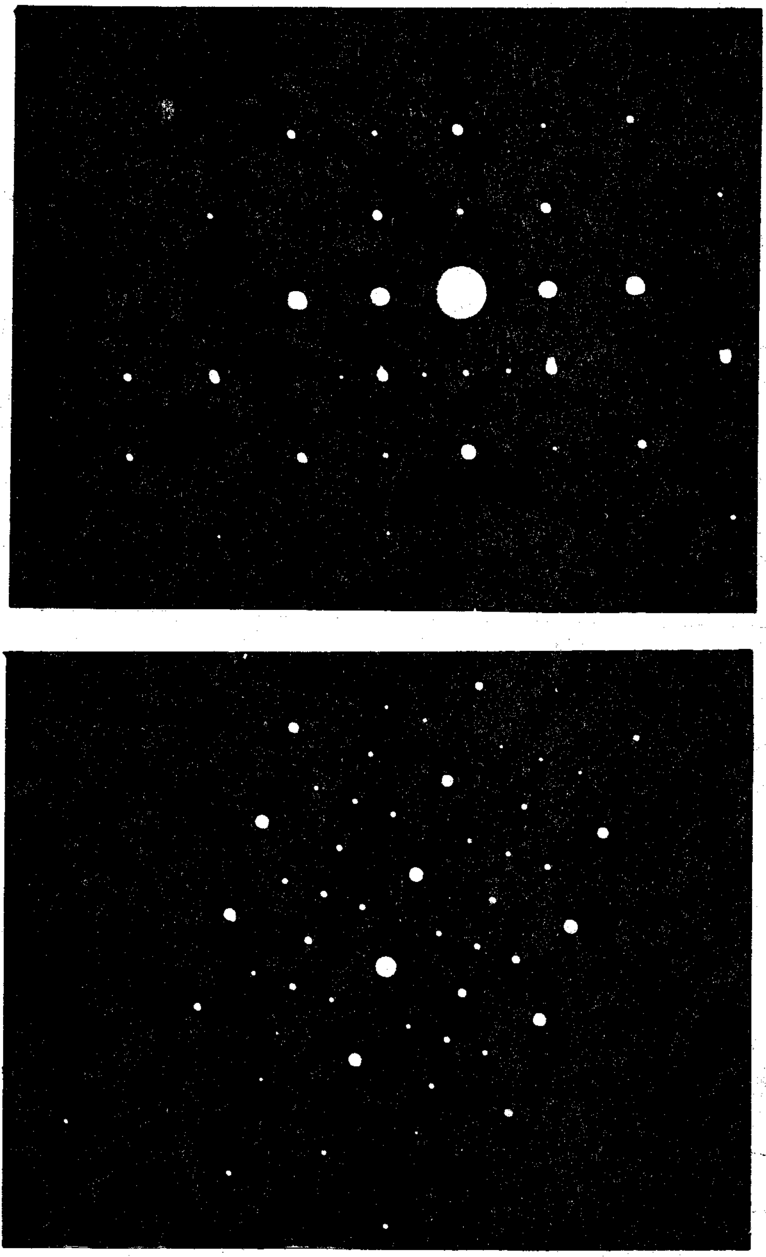

Figure 2 Electron diffraction patterns of CuAlMn martensites.

weak spots superlattice reflections. Electron diffraction patterns taken from the as-quenched samples and others of CuAlMn alloy are quite compatible with the M18R structure. These patterns indicate that the martensite phase of this alloy has an ordered structure in the M18R form produced from the parent phase of the ordered bcc structure in DO$_3$ form.

The powder X-ray diffractogram taken from the as-quenched sample is shown in Fig. 3 on which diffraction peaks have been indexed. As determined by the electron diffraction patterns, indexed diffraction peaks on the X-ray diffractogram indicate that the alloy in the martensitic condition has an orthorombic M18R structure, and diffraction patterns have been indexed on the basis of orthorombic unit cell. As mentioned in the TEM results, Cu-11 wt % Al- 6 wt % Mn martensites have the orthorombic structure of M18R form and this is supported by the X-ray diffraction results.

The structure of martensite is closely related to the structure of austenite matrix (12). If the matrix phase is ordered, product martensite

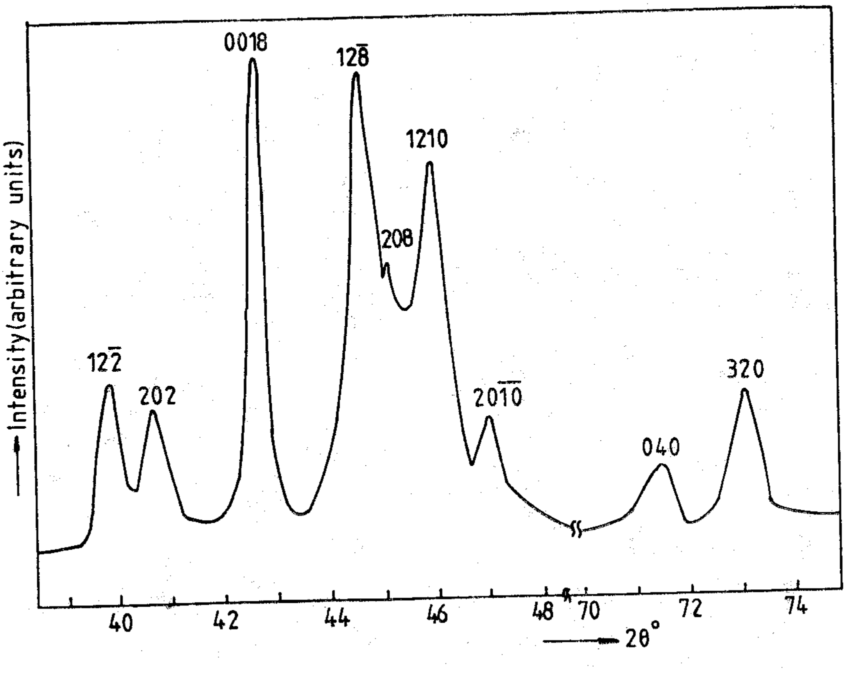

Figure 3 Typical X-ray diffractogram taken from the powder sample of CuAlMn allloy in martensitic condition.

phase has an ordered structure, and the ordered state of martensitic phase is the same as in the parent phase. This is due to the diffusionless nature of the transformation. Effects of ordering are responsible for orthorombic and monoclinic distortion of martensitic structure. Due to the different ordered structures of the parent phase in different alloy systems, a further differentiation is required for decribing the superlattice structure of martensite.

Formally, the 9R structure can be considered to form from the B2 matrix and 18R structure from DO_3 matrix. Actually 9R and 18R structures are quite similar except for a doubling of the unit cell in the [001] direction in the 18R case because of a change in order from the B2 to the DO_3 type. Electron microscopy and X-ray studies (12, 13) have shown that such structures can exist in the normal (N9R, N18R) or modified (M9R, M18R) condition, depending on the relative positions of the close-packed layers. The normal structure is orthorombic, whereas the modified version is monoclinic. In the monoclinic case $\beta = 87.5°$ (4) and this can be also regarded as orthorombic.

The common feature of these structures is that both have a close packed layer structure in the martensitic condition and since this property these structures are generally called internally faulted structures. These structures are schematically illustrated in Figures 4 and 5. These internally faulted martensites have close packed layers in the [001] direction. These structures are also characterized by a long period stacking order (LPSO) depending on the number of close packed layers that stack up to form the unit cell. The number of these layers in the c-direction is 18 for 18R structure and 9 for 9R structure. This stacking sequence is AB′CB′CA′CA′BA′BC′BC′AC′AB′ for M18R structure and ABCBCACAB for M9R structure (9, 14, 15).

In conclusion, internally faulted martensites exhibit thermoelactic behaviour and are usually derived from an ordered parent phase and thus martensite interface must be capable of both forward and backward movements when the temperature is decreased or increased, respectively. The crystal structure of produtc martensite in SME alloys is closely related to the structure of austenite matrix before transfromation and if the matrix phase is ordered the atom distribution in the martensite is also ordered.

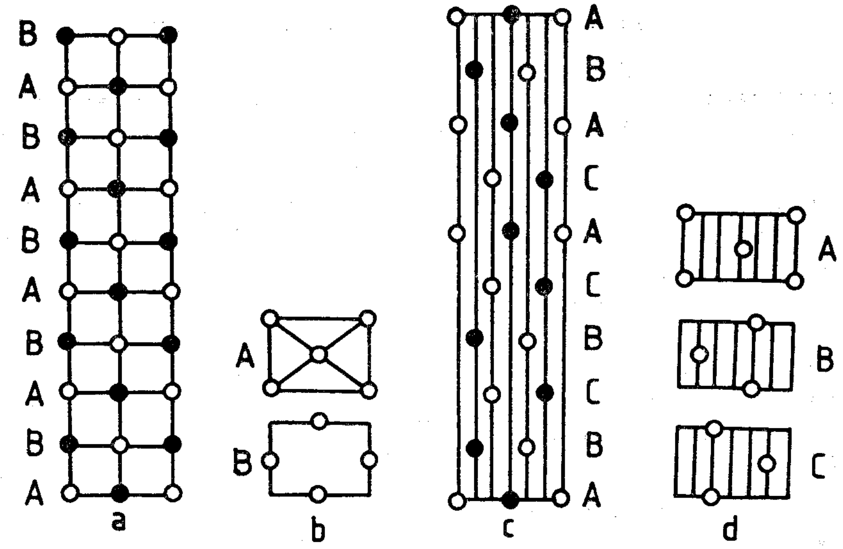

Figure 4 Atomic positions of the β-bcc phase in B2 form and β-type martensite in 9R form; a: The stacking perpendicular to the $(110)_\beta$ plane and projected onto (100)β, b: the atomic posotions in the $(110)_\beta$ plane, c: Stacking sequence of 9R martensite perpendicular to the basal plane and projected into the a-c plane, d: the atomic positionsin the close packed A,B,C planes (15).

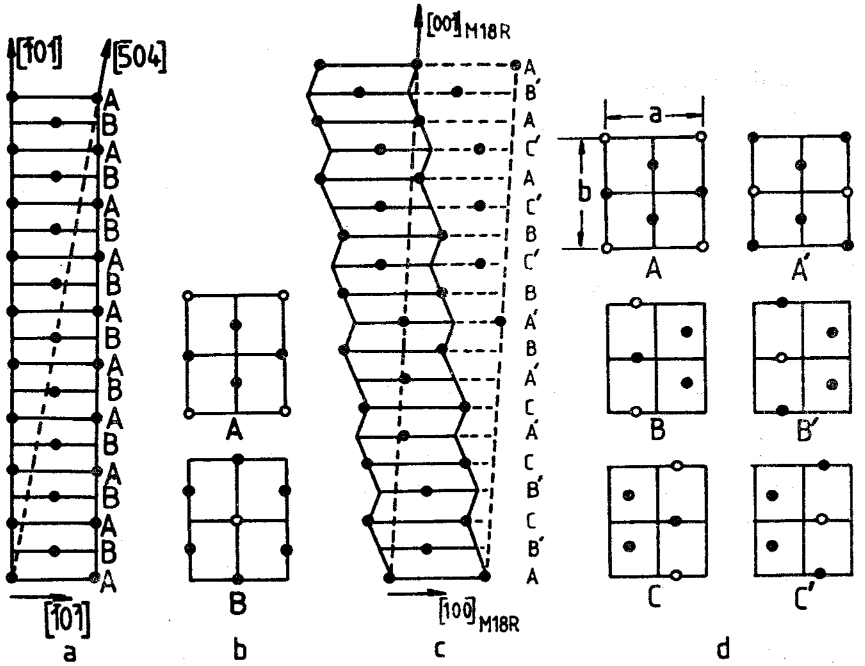

Figure 5 Stacking order of DO$_3$ parent phase and 18R martensite planes; a: Stacking of $(\bar{1}01)_\beta$ planes in DO$_3$ matrix, b: atomic psoitions in $(\bar{1}01)_\beta$ planes, c: Stacking sequence of 18R martensites on the basal plane, d: atomic positions in the close packed A,B,C,A′, B′, C′ planes (9, 14).

ACKNOWLEDGEMENTS

Expetimental part of this work was carried out at the Micro-Structural Studies Unit (MSSU) of Surrey University, England. The author wishes to thank Professor A.P. Miodownik, Head of Department of Materials Science and Engineering, Surrey University, for useful discussion and the provision of laboratory facilities.

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