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# X-RAY DIFFRACTION STUDY OF THE REVERSE MARTENSITIC TRANSFORMATION IN Cu-Al-Ni SHAPE MEMORY ALLOY

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## ABSTARCT

*The paper presents an X ray diffraction study for a cooper based shape memory alloy. The behavior of CuAl13Ni4 alloy, which exhibits a peculiar property, is evaluated by structural changes. On cooling, the martensitic transformation takes place from the ordered structures to the long period two layered structure. The crystalline phase transformations of those alloys are very sensitive to the heat treatments, deformation degrees and also to the undesired aging effects. In particular, the study has been made on the CuAl13Ni4 shape memory alloy samples after being hot extruded, quenched and aged in martensitic state.*

KEYWORDS: Shape memory alloy, Shape memory effect; Martensitic transformation, XRD

## 1. Introduction

The shape memory alloys (SMA) are in a so called class of smart materials whose properties have high performances especially their ability to recover the desired shape only by changing temperatures. SMAs are a typical smart material fully reversible. Martensitic transformation is a first-order diffusionless structural phase transformation between a high temperature austenite phase and low temperature martensite phase [1].

The shape memory effect is related essential by to a thermoelastic martensitic transformation [2]. A shape memory alloy plastic deformed at temperature below the martensite finish temperature, $M_f$, by heating over the austenite start temperature, $A_s$, recovers the undeformed original shape. The characteristic is called shape memory effect (SME). After thermomechanical treatments the change reoccurs during heating and cooling processes, the characteristic is called two way memory effect (TWSME). Due to the shape recoverable properties these alloys can be used as devices like sensors and actuators. Cooper based alloys exhibit shape memory within a certain range of composition. It is known that for the particular composition CuAl13Ni4 from the metastable beta phase whit $DO_3$ structures, after quenching, takes place a martensitic transformation with two long period layered structures (18R and 2H) [3-5].

## 2. Experiment

The CuAl13Ni4 shape memory alloy was obtained by a classic direct melting method using high purity for components and precised chemical composition. The cast ingots were turned in cylindrical shapes Φ35X35 mm. The samples were plastic deformed by extrusion in three steps until Φ4mm wires. After last extrusion the samples were cooled in air. The samples were 9 months hot extruded wires 4mm diameter and 145 mm length. The samples were machined for following tests. For X ray diffraction tests we studied the same sample: in extrusion state after nine months aged; a subsequent quenched; in quenched state after fourteen months aged. The experiments for quenched samples comprised heat treatment using a vertical furnace, air environment, holding at 850$^0$C during 30 minutes. After solubilization, the specimens were immediately quenched in ice water. Few samples were deliberately kept in martensitic state at room temperature.

Prior to experiments all samples were submitted to the chemical etching in order to remove the layer deformed by cutting operation as well as the oxide.

The XRD analysis was run in a RIGAKU (Cu sealed tube) at room temperature using 20mmX2mmX1mm dimension samples. The $2\Theta_{hkl}$ was between 10$^0$ and 90$^0$. The acquisition time was 1s per point.

The goniometer radius is 180 mm. The radiation used was Cu-$K_\alpha$. The widths of divergence, dispersion and transmission slots were $1^0$, $1^0$ and 0.15mm. The XRD analyses were made at 50kW/30mA. The (h k l) planes related to diffraction lines were identified using ICDD data base built in computer in EVA program 7.0 version.

## 3. Results and discussion

The CuAl13Ni4 shape memory alloy was studied in different stage of deformation respectively extruded and quenched samples.

The hot extruded sample had in structure: solid solution $\alpha$; a mechanical mixture $\alpha$ and $\gamma_2$ an intermetallic compound NiAl and premartensitic structure.

The subsequent quenched samples and after fourteen months aging were entirely martensitic structure at room temperature.

Two morphological types of martensite structure coexist in CuAl13Ni4. In table 1 are shown the crystalline parameter and the diffraction line specific to martensitic structures.

***Table 1***

| Martensite type | Parameters of crystal lattice | Angles of crystal lattice | Diffraction planes |
|---|---|---|---|
| Monoclinic $Al_7Cu_{23}Ni$ | a= 4.44<br>b = 5.31<br>c = 37.86 | a=$90^0$<br>b=$89.36^0$<br>g=$90^0$ | (-1 2 5)<br>(0 0 18)<br>(-1 1 15)<br>(3 2 4)<br>(-2 1 4) |
| Orthorhombic $AlCu_3$ | a= 4.494<br>b = 5.189<br>c = 46.61 | a=$90^0$<br>b=$90^0$<br>g=$90^0$ | (1 1 1 )<br>(0 1 11)<br>(0 2 1 )<br>(2 0 2 )<br>(2 0 12)<br>(3 2 13) |

The memory properties like SME and TWSME, transformation characteristic temperatures, thermal hysteresis, recovery deformation, generating mechanical work are influenced by heat treatments history and aging phenomena in initial state but also in martensitic state. The main objective of this work was to study the changes in fine internal structure for extruded and quenched samples the aging process accompanied by martensite stabilization. The XRD analyses taken three times, reveal important modification in crystallographic lattice. In figure 1 are shown the XRD diffractograms taken from alloy in extrusion state.

In figure 2 are shown the XRD diffractograms taken from alloy in quenched state.

In figure 3 are shown the XRD diffractograms taken from alloy in quenched state aged fourteen months at room temperature. The electron diffraction patterns of extruded alloy have a disordered structure. In this case it can be observed that the characteristic lines have large widths. The maximum line intensity is corresponding to the monoclinic martensite (-1 1 15) hkl plane. As seen from diffraction patterns from figure 2, CuAlNi martensite have the ordered structure and exhibit superlattice reflection. After the heat treatment they have the ordered structures. It can be observed that the maximum intensity of monoclinic (-1 1 15) hkl plane was kept. The aspect of diffraction lines were really narrow because the long period order and the coarse martensite specific this alloy.

The diffraction patterns from figure 3, reveal the same ordered structure and exhibit superlattice even after martensitic aging.

Anyway the maximum intensity was kept for the same monoclinic (-1 1 15) hkl plane and near that it can be observed the pick for the pair plan (-2 1 4) and both structures are monoclinic. It can be observed a flattening of diffraction picks corresponding to plan (2 0 2) and (0 0 18). The (2 0 2) habitus plan is an attribute of orthorhombic martensite.

The (0 0 18) habitus plan is an attribute of monoclinic martensite.

It turns out that the pick accordingly to diffraction plan (-1 2 5) was missing. The pick accordingly to diffraction plan (2 0 12) was reduced until flattening. The structure was partially ordered after martensitic aging time.

In cooper based SMAs as in Ti Ni, Ni Al or Fe Al alloy systems there can be observed a lot of aging process. Cooper based especially brasses are in general predisposition for aging even at room temperature [1].

The aging at high temperatures is determined for the precipitation from austenite phase in $Cu_9Al_4$ ($\gamma_2$) and NiAl ($B_2$) phases. In ternary Cu Al Ni alloy system the precipitation for $\gamma_2$ phase is inhibited by nickel addition.

It is considered that the precipitation brakes MT throw two mechanisms:

- Coherence of the fields around precipitations and/or destroyed potential germination centers in martensite state;
- Introducing vacations at quenching and precipitation process.

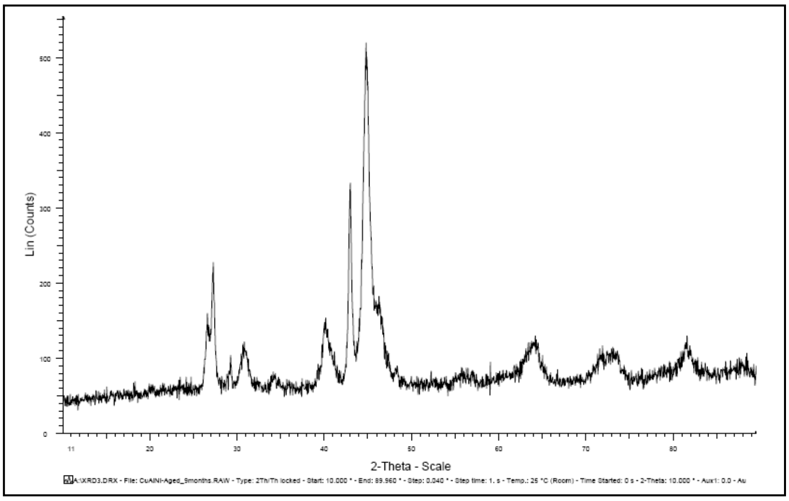


***Fig. 1.*** *X ray diffractogram of hot extruded sample*

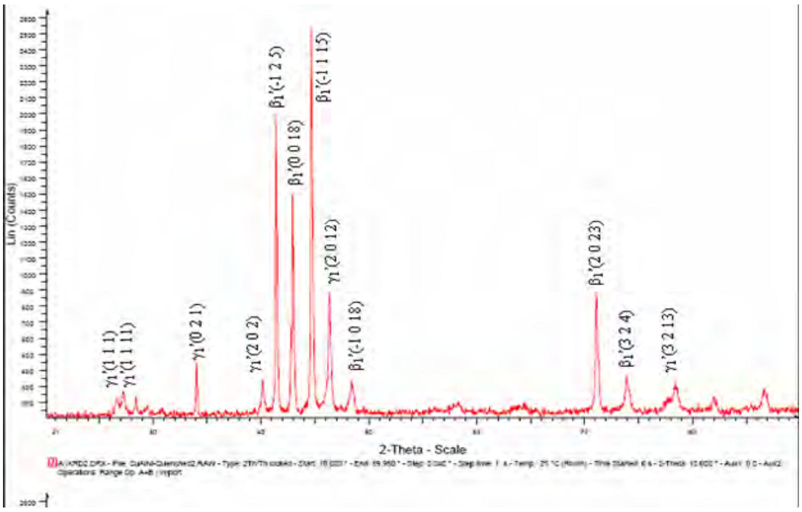


***Fig. 2.*** *X ray diffractogram of quenched sample*

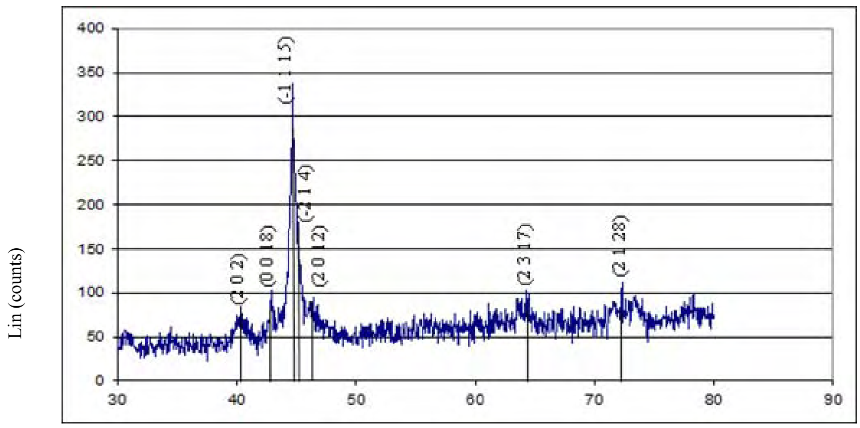


***Fig. 3.*** *X ray diffractogram of quenched and 14 months aged sample*

The increasing precipitates manage to changes in chemical composition of initial phase that modify transformation temperatures. In these conditions the shapes recovery becomes more difficult. Aging effect changes the memory characteristics for SMAs. The martensitic aging effect is accompanied by martensite stabilization process. The aging time in martensitic phase influences direct critical temperatures and sometimes the reverse martensitic transformation is canceled. The origin of the martensitic stabilization lies in two different mechanisms. One of them consists in internal crystalline structure changes. An atomic reorder takes place in martensite and that determined a relative stabilization between initial phase and martensite. It has been reported that the base plane of monoclinic martensite originates from one of $(0\ 0\ 1)_\beta$ planes of the matrix [3].

The reversible transformation occurs as:

$$\beta(DO_3)\underset{T\uparrow,\sigma=ct}{\overset{T\downarrow,\sigma=ct}{\Leftrightarrow}}\beta_1^{'}(18R)\underset{T\uparrow,\sigma=ct}{\overset{T\downarrow,\sigma=ct}{\Leftrightarrow}}\gamma_1^{'}(2H)$$

The mechanism is crystallographically describable by two steps. The transformation involves lattice deformation called Bain distortion and the second step called lattice invariant deformation when one of the close packed $(0\ 0\ 1)_\beta$ planes of matrix becomes martensite basal plan[8]. The martensite basal plan is distorted in case atom sizes are different and become sregular in case atom sizes are equal. Because of this deviation, the spacing differences $\Delta$d between the adjacent diffraction planes became different from null and it can be a measure of martensite order. It was observed that alloys from Cu Al Ni system undergo a partial order disorder transformation in primary aging stages so as in long term aging.

The second mechanism doesn't explain aging in single crystals but is valid for polycrystalline SMAs. One of SMAs properties behavior like rubber is determined by martensite stabilization. After quenching the alloy has the ordered structure and exhibits superlattice reflection.

## 4. Conclusions

The behavior of CuAl13Ni4 alloy, which exhibits shape memory properties, was evaluated by structural changes.

The alloy was studied, in different stages of deformation respectively extruded and quenched samples, using XRD analysis:

1. The memory characteristics are influenced by heat treatments history and aging phenomena in initial state but also in martensitic state.
2. The electron diffraction patterns of extruded alloy have a disordered structure with large widths of the characteristic lines. The structure was only partially premartensitic.
3. After quenching the alloy has the ordered structure and exhibit superlattice reflection. The aspect of diffraction lines were narrow because the long period order and the coarse martensite specific this alloy. In Cu Al13Ni4 SMA coexists two martensite types (monoclinic and orthorhombic).
4. The structure was partiallz ordered after martensitic aging time but it can be observed modification in accommodation of different habitus plans. Near the (-1 1 15) hkl plane it can be observed increasing the pick for the pair plan (-2 1 4) the both structures are monoclinic.

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