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# Investigation of Thermoelastical Martensitic Transformations and Structure in New Composition of CuAlMnTi Shape Memory Alloy.

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Shape memory alloys (SMAs) are a class of smart materials. These intelligent alloys have unique thermomechanical properties such as shape memory effect (SME) and superelasticity (SE) which enable them to utilize in numerous modern technological and industrial applications. Their macroscopic shape changing ability (SME) is based on their thermoelastical, isothermal and atomically non-diffusional martensitic phase transformations between low temperature phase (martensite) and high temperature phase (austenite). When these unusual alloys are mechanically deformed at low temperature (in martensite phase), they can return back to their first pre-deformed shape by heating and increasing their temperature up. In such processes the martensite phase changes into parent austenite phase. Conversely, when they are cooled down from high temperatures, the austenite phase converts into martensite phase, but at this time shape change does not occur and this one way shape changing ability is called one way shape memory effect (OWSME). SMAs are also acquired two way shape memory effect (TWSME) property by some trainings, and after once they are gained TWSME feature in them, then they can go and return between two different unauthentic shapes by heating and cooling them. In this work, the thermoelastical martensitic transformation phenomena of CuAlMnTi shape memory alloy with a new chemical composition was investigated by thermal and structural measurements and analyses including DSC, EDX, XRD and optical microscopy. The characteristic transformation phase start and finish temperatures, hysteresis, enthalpy and entropy change parameters were identified by DSC data analyses and calculations. The existing martensite phase forms on the alloy surface and in the alloy texture at room temperature were detected by XRD and optical measurements, respectively.

*Keywords:* Shape memory alloys, CuAlMnTi, Thermoelastical martensitic transformation, Martensite, Austenite.

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## 1. Introduction

Shape memory alloys (SMAs) are in the class of intelligent materials that regain their lost shape before deforming due to externally applied stresses and temperatures. Briefly, alloys that can remember the initial shape are called shape memory alloys [1]. When these unusual smart materials are exposed to physical forces like heat, mechanical stress, electric field exhibit non-diffusional, isothermal and reversible martensitic phase transformations.

Such martensitic phase transformations occur with sudden temperature reduction or stress applied to austenite structure. The temperature at which the austenite phase starts with the temperature applied to the alloy is $A_s$ and the austenite phase is the initial temperature. The temperature at the moment austenite phase is completed is $A_f$ and the austenite phase is the end temperature. After this stage, the temperature is reduced suddenly and after the critical temperature point, the martensite structure begins to form by reaching the starting temperature of $M_s$ martensite. The martensite phase transformations starting at $M_s$ temperature continue at certain temperatures and stop at $M_f$ temperature. $M_f$ is the end temperature of the martensite, the temperature at which the phase change ends. With the applied heating-cooling processes, the transitions between phases continue as indicated [2-7]. Macroscopic shape recalling mechanism that occurs by these phase transformations is called shape memory effect (SME). Also, another interesting property of these alloys is their superelasticity (SE) behavior which SMAs exhibit at a certain temperature region above $A_f$, so; if SMAs are kept deformed under stress at such temperatures they can completely return back to their predeformed austenitic shape when stress is removed [8, 9].

SMAs are mainly based on NiTi, Cu-rich and Fe-rich alloy systems. Mostly the NiTi ones are used in industrial applications due to their superior SMA properties. But, due to their high costs and hard processability drawbacks, researchers also have focused on the other possible alternatives and the closest candidate is Cu-based SMAs.

Copper is widely used in shape memory alloys. Copper based alloys are more advantageous in terms of low cost, easy forming, high conductivity and high strength. But they suffer from their problems of brittlement, lower strain recoverability or thermal instability. Therefore, one of the way to solve such problems and improve their properties is grain refinement and for this minor amounts of additive Ni, Mn and Ti or different elementsare added to improve the properties of Cu-based alloys [10-14].

## 2. Experimental details

In this research work, to prepare the quaternary Cu-Al-Mn-Ti alloy with 85Cu-11.28Al-3.36Mn-0.37Ti (at%) composition, the high purity (99.9 %) elements of Cu, Al, Mn and Ti powders were mixed and then compressed under pressure to form pellets and then these pellets were melted under argon atmosphere in an Edmund Buehler Arc Melter, thusly the alloy was casted as ingot. This ingot was cut into small alloy pieces (as ~30-60 mg and ~5x4x2 mm) and these alloy samples were all solution-treated at 900 °C for 1hto homogenize the atoms of alloying elements in the alloy texture and in order to bring SME property idest to form martensite phasein the alloy samples the hot samples were propmtly (rightafter at the end of this homogenization process) quenched in the conventional iced-brine water to prevent the formation of precipitations. A Bruker Model EDX (energy dispersive X-ray) was used at room temperature to determine the alloy's chemical composition i.e. the atomic fractions (at%) of the alloying elements. In order to characterize and determine thermo-operational and kinetic parameters of martensitic phase transformations of the alloy and alloy's behaviors at high temperatures several differential calorimetric (DSC and DTA) measurements were carried outon these post-quenched martensitic alloy in inert argon atmosphere at different heating/cooling rates by using Shimadzu DSC-60A and DTG-60AH model differential scanning calorimetry (DSC) and differential thermal analysis (DTA) instruments. To expose microstructural features of the alloy, XRD measurement was performed at room temperature by using a Rigaku RadB-DMAX II diffractometer with CuKα radiation to obtain diffraction pattern and the peaks on them that belong to the atomic planes indicating the martensite phases exist in the alloy. Furthermore, optical microscopy imaging result was obtained by using an OEM XJP-6A metal microscope at room temperature to pick out the morphological surface semblances that belong to the alloy's phases.

The activation energy ($E_a$) is a kinetic parameter of SMAs which designatethe reactions of martensitic phase

## 3. Results and discussion:

The forward down endothermic thermogram peaks indicating the martensitic phase transformations from martensite to austenite (M→A) on the all heating parts and reversibly their corresponding exothermic backward A→M peaks on the all cooling parts of the cycled curves of DSC measurements conducted on CuAlMnTi alloy sample at different heating/cooling rates can be seen in Fig.-1. These endo/exo peaks of reversible A↔M transitons [15-19] demonstrate a SME property must be present in this alloy. The tempretaure ranges of these peaks are at between ~90-155 °C, therefore this alloy can be defined as a high temterature shape memory alloy (HTSMA). The phase start, finish and maximum temperatures ($A_s$, $A_f$, $M_s$, $M_f$ and$A_{max}$), hysteresis values ( $A_f$-$M_s$) and some kinetic parameters such as equilibrium temperature ($T_0$), enthalpy (ΔH) and entropy (ΔS) change amounts of M→A and A→M transition peaks on each single DSC curve were listed in Table 1. Equilibrium temperature is the temperature at where the Gibbs free energies of A and M phases are equalized so that without a driver force at this point there is no any transition

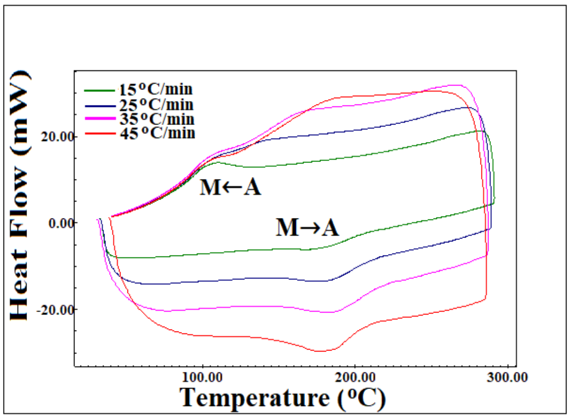


***Fig.-1:*** *Multiple DSCcurves of the CuAlMnTi alloy sample at different heating/cooling rates.*

procedes to any side. Here, $T_0$ values were calculated by using $T_0=(A_f+M_s)/2$ equation [20] and ΔS values during these transformations were calculated by using $\Delta S_{M\rightarrow A}=\Delta H_{M\rightarrow A}/T_0$ formula [17] for fordward transformations and by changing the M→A indices in this formula into A→M for backward transformations.transitions and crystallization behavior of the alloy. This energy treshold must be overcomefor a martensitic phase transition to occur. The value of $E_a$ parameter of the Cu-Al-Mn-Ti SMA was calculated here by using the equation of Kissinger [21] following as;

$$d\left[ln\left(\phi/T_m^2\right)\right]/d\left(1/T_m\right)=-E_a/R \qquad (1)$$

where; $\phi$ is heating/cooling rate, $T_m$ is maximum austenite peak temperature ($A_{max}$) and $R$ is the universal gas constant ($R$=8.314 J/mol.K). The left term in this equation was determined as a slope value by applying linear fiting on the $ln(\phi/T_m^2)$ v.s.$1000/T_m$ activation energy change plot given in Fig.-2. In this way, by putting this negative slope value in the Eq.-1, the activation energy of Cu-Al-Mn-Ti alloy was found as 96.06 kJ/mol.

**Table 1**: Transformation temperatures and kinetic parameters ofCu-Al-Mn-Ti alloy at different heating rates.

| Heating/ cooling rate (°C/min) | $A_s$ (°C) | $A_f$ (°C) | $A_{max}$ (°C) | $M_s$ (°C) | $M_f$ (°C) | $A_s$-$M_f$ (°C) | $T_0$ (°C) | $\Delta H_{M\rightarrow A}$ (J/g) | $\Delta H_{A\rightarrow M}$ (J/g) | $\Delta S_{M\rightarrow A}$ (J/g°C) | $\Delta S_{A\rightarrow M}$ (J/g°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 154.86 | 198.97 | 166.53 | 125.72 | 96.30 | 58.56 | 162.34 | 5.12 | -4.97 | 0.03154 | -0.03061 |
| 25 | 152.23 | 205.25 | 176.45 | 116.05 | 93.62 | 58.61 | 160.65 | 8.83 | -0.79 | 0.05496 | -0.00492 |
| 35 | 155.66 | 211.02 | 181.50 | 119.98 | 92.39 | 63.27 | 165.50 | 7.99 | -1.66 | 0.04828 | -0.01003 |
| 45 | 155.75 | 206.05 | 176.67 | 119.89 | 90.79 | 64.96 | 162.97 | 5.84 | -1.67 | 0.03583 | -0.01025 |

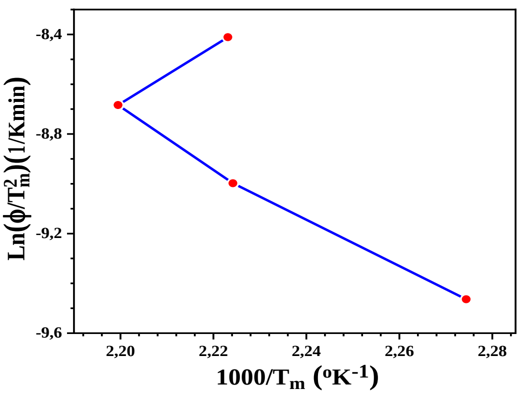


*__Fig.2:__The activation energy change plot of CuAlMnTi SMA.*

The DTA measurement result of the CuAlMnTi alloy sample obtained at the single heating/cooling rate of 25 °C/min was given in Fig.-3. As it can be seen in this figure, on the heating part of this DTA curve which started by heating from room temperature up to reach 900 °C (and then cooling back to room room temperature to complete the cycle) there is displayed a multiple phase transitions of M(β1'; 18R martensite) → A($DO_3$; $L2_1$) → B2 (disordered) → dissolution of α+γ2 precipitations → eutectoid recomposition →B2 (ordered) → A2 (disordered) and this result was found congruent with the results previously reported in the literature [16, 21, 22]. The reverse counterparts of these transitions also clearly seen on the backward cooling part of this curve.

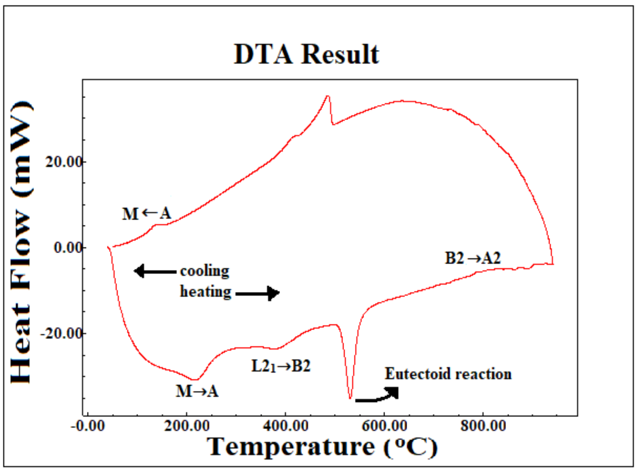


***Fig.-3:** DTA curve of the CuAlMnTi alloy sample at 25 °C/min of heating/cooling rate.*

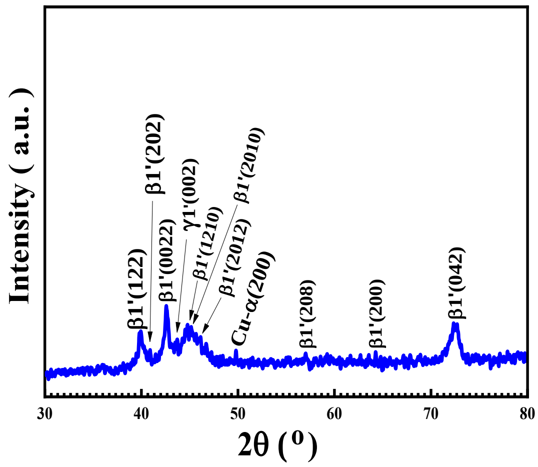


***Fig.-4:** X-ray diffraction result of CuAlMnTi alloy sample obtained at room temperature.*

X-ray diffraction pattern of CuAlMnTi alloy sample can be seen in Fig.-4. As seen in this figure, among the characteristic peaks thepeak of β1'(0022) martensite plane came out as the highest peak and the others with miscellaneous heights (intensities) are the peaks of β1'(122), β1'(202),γ1'(002), β1'(1210), β1'(2010), β1'(2012), α-Cu(200), β1'(208), β1'(200) and β1'(042) planes [16, 17, 19, 23]. These XRD peaks indicating these planes of martensite phases supported the aforementioned thermal results.

The average crystallite size ($D$) of the alloy sample was computed by the following Debye-Scherrer formula [34] as below;

$$D = \frac{0.9\lambda}{B_{1/2} cos\theta} \qquad (2)$$

where; λ is the X-ray wavelength of the CuKα radiation (λ=0.15406 nm) used in this XRD measurement, $B_{1/2}$ is full width at half maximum (FWHM) value of the highest peak and θ is the Bragg angle of diffraction. In this way, by substituting the values of θ angle and FWHM data of the highest peak in the Eq.-2the value of average crystallite size of the Cu-Al-Mn-Ti alloy sample was obtained as 21.71 nm.

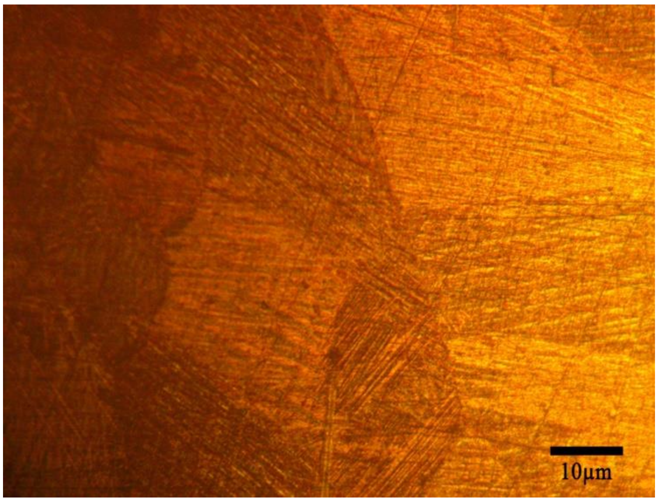


***Fig.-5:****The optical metallography imageshot on the surfaceCuAlMnTi alloy sampleat room temperature.*

Optical micrography imaging of the surface morphology of the alloy sample was given in Fig.-5. As to this metallograph, the microstructure of CuAlMnTi alloy on its surface include lamellar martensite plates ofmonoclinic β1'(18R) phase, lath typeγ1'(2H) martensites, α-Cu phase and dark spot like Ti precipitations [18, 19, 24, 25].

## Conclusions

The Cu-Al-Mn-Ti SMA produced by arc melting was undergone thermal and microstructural characterization analyses.The endo/exo peaks on the all thermal DSC curves demonstrated the reversible martensitic phase transitions which means that a SME property based on these solid solid phase transformations exist in the alloy. Kinetic parameters of these transition peaks were determined, too. High temperature DTA measurements displayed theconsecutive peaks indicatingmultiple phase transitions of β1′ → β1($DO_3$) → disordered β1(B2) →α+γ2 decomposition → eutectoid recomposition → ordered-B2 → disordered-A2 on the heating part of DTA curve and inversely on its cooling part. The X-ray and optical metallography resultsconfirmed the thermal findings idest the existence of 18R and 2H martensites in the alloy. In conclusion, this Cu-Al-Mn-Ti SMA with new composition maytake interest of its utility in variousSMA applications.

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