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Thermo-structural Shape Memory Effect Characterization of Novel CuAlCoMg HTSMA with Ternary Co and Quaternary Mg Additititions

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The second largest world-wide commercial functional materials group in smart materials class is the shape memory alloys (SMAs). Among SMAs, Cu-based SMAs thanks to their good shape memory effect properties, capable of high transformation temperatures, cost-effective and relative simplicity of production/processing and achievable desired properties by tuning their alloying compositions by additions are described as the closest alternative to the superior NiTi SMAs. In this work, the novel quaternary CuAlCoMg high temperature shape memory alloy (HTSMA) by the additions of minor amount of Co as the ternary and trace amount of Mg as the quaternary additive alloying elements was fabricated by arc melting method. The martensitic transformation temperatures and other properties of the alloy were characterized by carrying out several thermal and structural measurements of DTA and XRD analysis and the magnetization status of the alloy was also investigated by measuring with a vibrating sample magnetometer (VSM). The DTA results showed that the alloy is a high temperature shape memory alloy (HTSMA) exhibiting reverse martensitic transformations in a temperature range between 208.95°C and 394.32°C. The VSM test showed that the alloy shows a diamagnetic behavior with a weak ferromagnetic coersivity. The XRD result revealed the diffraction peaks observed at room temperature indicating the martensite phases existing in the alloy, formed by the end of quenching the alloy. The produced alloy can be useful in HTSMA research and applications.

Keywords: *Shape memory alloy, CuAlCoMg HTSMA, DTA, X-ray diffraction, VSM*

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1. Introduction

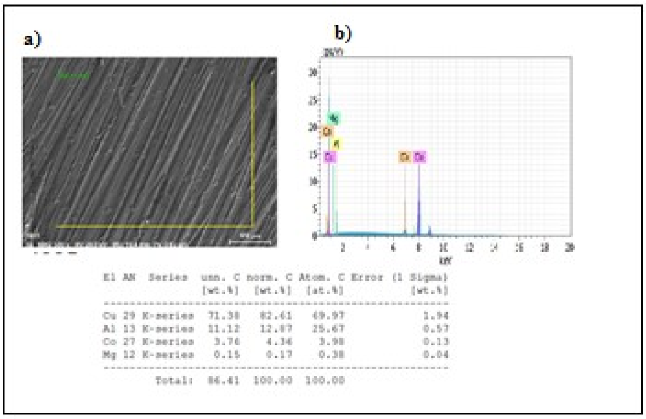
Shape memory alloys (SMAs) are smart materials that after plastically deformed while they were in martensite phase have the ability to recover back to their original shape -the so-called shape memory effect (SME) property of them- when they reach at high temperatures [1]. Such shape changes happen when they are stimutaled by external effects (heat, stress, electric/magnetic field; etc.) which effects force to their crystal lattices by creating internal stresses in them and thus lead to form a new type solid phase lattice that is seen as a total macroscopic shape change in these smart materials [1,2]. SMAs that are kept in bended or deformed shape by a mechanical load in a temperature region [3] also have the ability to return to their original shape when load is removed and this property of them is called as superelacticity (SE) [1,4,5]. SMAs exhibit two phases: the low temperature phase called martensite (M) and also the high temperature phase called austenite (A). But also austenite phase is referred to as the β phase. This two unique properties (SME and SE) are based on these reversible and interconvertible solid phase changes (called as martensitic transformation) between martensite and austenite phase [1,4–6].

Among SMAs, the NiTi SMAs consist the majority of commercial SMAs due to their superior SME and SE properties. But, they are expensive and their production and processing are difficult. The Cu-based SMAs [7–9], regarded as the closest alternative to NiTi SMAs, are much cheaper and have relative easiness of production and processing, and what's more is their higher thermal and electrical conductivities [10,11]. But, Cu-based SMAs have also some disadvantages such as brittleness due to their coarse grains, poor workability or thermal instability [12–14]. A simple and common way used to refine grain size, improve SME, SE and mechanical properties, modify the martensitic transformation temperatures etc. is to add some minor amounts of ternary or more (grain refining) elements like Ti, Cr, Be, Fe, Mg, Co, etc. [13–17] into the binary Cu-based alloys.

In this research paper, a novel Cu-based quaternary high temperature shape memory alloy (HTSMA) with an unprecedented alloying composition of 69.97Cu-25.67Al-3.98Co-0.38Mg (at%) consisting the additive elements of Co as the ternary and Mg as the quaternary alloying elements fabricated by arc melting method is presented. The thermal, structural and related shape memory effect characteristics of the fabricated CuAlCoMg HTSMA were investigated by DTA, EDS (or EDX) and XRD analyses. Also, the magnetic status and coercivity of the alloy was determined by making VSM test.

2. Experimental

In the experimental stage of this work, to prepare the CuAlCoMg alloy with its quaternary composition of 69.97Cu-25.67Al-3.98Co-0.38Mg (at%), at first mixing the powders of high purity (99.9%) elements of Cu, Al, Co and Mg was completed. Then, by applying pressure the powder mixture was taken into pellet forms. Then, these pellets were together melted in an arc melter under argon atmosphere and thus the as-cast ingot CuAlCoMg alloy was obtained. Then, the small sized alloy pieces obtained by cutting from the ingot proper to be tests samples were all solution-treated at 900 °C for 1 hour and then immediately quenched in iced-brine water medium to form β1'martensite phase in the alloy samples. The chemical composition of the alloy was determined by using a Zeiss Evo MA10 model EDS (energy dispersive X-ray spectrum). The EDS result of the alloy is given in Fig. 1. To observe the martensitic and other phase transitions at high temperatures, the differential thermal analysis (DTA) tests were carried out consecutively in between room temperature and 900 ˚C at the same 25 ºC/min of heating/cooling rate via using a Shimadzu DTG-60AH model DTA instrument under a constant argon flow [18–20]. The characteristic martensitic transformation temperatures (A_s, A_f, A_{max}, M_s and M_f) and the heat (enthalpy change, ΔH) amount took in the alloy sample during the reverse M→A phase transformation were detected directly by DTA software [19,20]. By using a Rigaku RadB-DMAX II diffractomer with CuKα radiation the structural X-ray diffraction (XRD) pattern of the alloy was obtained at room temperature (300 °K) in order to determine the martensite phases formed in the CuAlCoMg alloy. The vibrating sample magnetometer (VSM) measurement was also taken at room temperature by using a Quantum Desing Physical Properties Measurement System (PPMS) with VSM equipment in the magnetic field range of ±3T.



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                 [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------------
Cu 29 K-series   71.38   82.61   69.97             1.94
Al 13 K-series   11.12   12.87   25.67             0.57
Co 27 K-series    3.76    4.36    3.98             0.13
Mg 12 K-series    0.15    0.17    0.38             0.04
------------------------------------------------------------
         Total:  86.41  100.00  100.00
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Fig. 1. a) SEM image, and **b)** EDX measurement result of the CuAlCoMg alloy.

3.Results

The consecutive DTA heating/cooling cycled curves of the produced CuAlCoMg HTSMA are given in Fig.2.

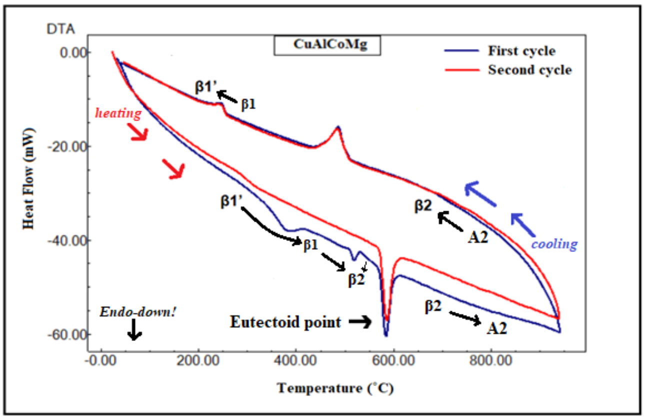

Fig. 2. The consecutive looping DTA curves of the CuAlCoMg HTSMA taken at the same single 25 ˚C/min of heating/cooling rate.

On both of the two DTA curves (the first and second cycles) of the CuAlCoMg alloy seen in Fig.2, there are some successive downward endothermic peaks seen on the lower parts of these curves each time on heating the alloy. These endothermic peaks indicate a multiple stage of phase transition array. From far left to the far right of the curves, this phase transition array is as; martensite (β1'(18R)+γ1'(2H)) → austenite β1($L2_1$) → β2 (metastable) → formation of precipitations → eutectoid reaction (dissolution of precipitations) → β2 (ordered) → A2 (disordered), and this phase transitions array is seen as a common behavior in Cu-based SMAs [17,19,21–24]. The phase transition from martensite to austenite (M→A) at the beginning of this array is the reverse martensitic transformation. Upon cooling the alloy, all of this multi-staged phase transitions turn back to the martensite phase again (seen as the upward exothermic peaks on the up cooling fragments of the curves). The characteristic temperatures of martensitic transformations (both M→A and A→M) and some related thermodynamic parameters related to M→A transformation were determined and are given in Table 1. Among these parameters, the equilibrium temperature (T_0), the Gibbs free energies of both phases are equal i.e. no driving force exist at this temperature point to induce a martensitic transformation, was determined by using $T_0=(A_f+M_s)/2$ formula [21]. The value of the entropy change ($\Delta S_{M\rightarrow A}$) was calculated by using $\Delta S_{M\rightarrow A}=\Delta H_{M\rightarrow A}/T_0$ relation [21,25]. The determined M→A transformation temperatures seen in Table 1 are all above 100 ºC and this classifies the produced CuAlCoMg alloy as a high temperature shape memory alloy (HTSMA) [21,26,27]. While the up direct A→M peaks observed on the up cooling parts of both DTA curves are almost exact-matched, there is seen a martensite stabilization effect [28,29] in the reverse M→A transition peak (thermal instability of M→A transformation peak) discerned on the second cycle curve as compared with that on the first cycle curve. The M→A peak or the austenite phase is seen partially completed on the second cycle due to some of martensites remained stabilized and not transformed to austenite. The high enthalpy change value ($\Delta H_{M\rightarrow A}$) indicate the powerful reverse transformation and thus a powerful shape memory effect property of the CuAlCoMg HTSMA. The superior NiTi SMAs can exhibit enthalpy values more than 30 j/g [3].

Table 1. The martensitic transformation temperatures and thermodynamic parameters of the CuAlCoMg HTSMA.

A_s (ºC)	A_f (ºC)	A_{max} (ºC)	M_s (ºC)	M_f (ºC)	A_s-M_f (ºC)	T_0 (ºC)	$\Delta H_{M\rightarrow A}$ (j/g)	$\Delta S_{M\rightarrow A}$ (j/g)
343.02	394.32	368.28	257.45	208.95	134.07	325.89	12.09	0.037

The XRD result of CuAlCoMg HTSMA obtained at room temperature is given in Fig.3. The peaks observed on this diffraction pattern demonstrate the existence of both β1' and γ1' type martensite structures in the produced alloy. Here, the highest XRD peak belongs to the atomic plane of β1'(0018) martensite, the second highest peak close to this highest peak belongs to the plane of γ1'(002) martensite, and the other observed peaks indicate the martensites of β1'(202), β1'(12$\bar{8}$), β1'(128), β1'(1210), β1'(320), β1'(042), γ1'(012) and γ1'(211) [20,21,30–32].

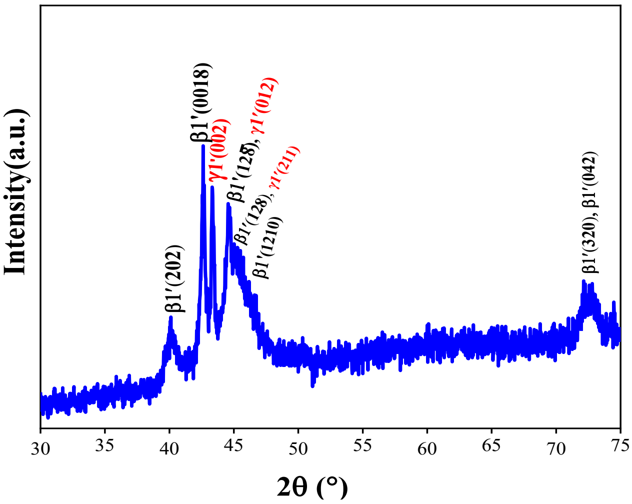

Fig.3. The XRD pattern of the CuAlCoMg HTSMA obtained at room temperature.

The ratio of valence or conduction electron per atom (e/a ratio) of the CuAlCoMg alloy was calculated by using $e/a=\Sigma f_i v_i$ formula [21], where f_i represents the atomic fractions of the alloying elements and v_i represents their valence electron numbers. Thus, the e/a ratio of the CuAlCoMg HTSMA was found as 1.55, and this value indicates a volumetric dominancy of γ1' martensite over the β1' and the co-existence of these two martensite phases in the alloy [21], just as confirmed by the XRD result given above.

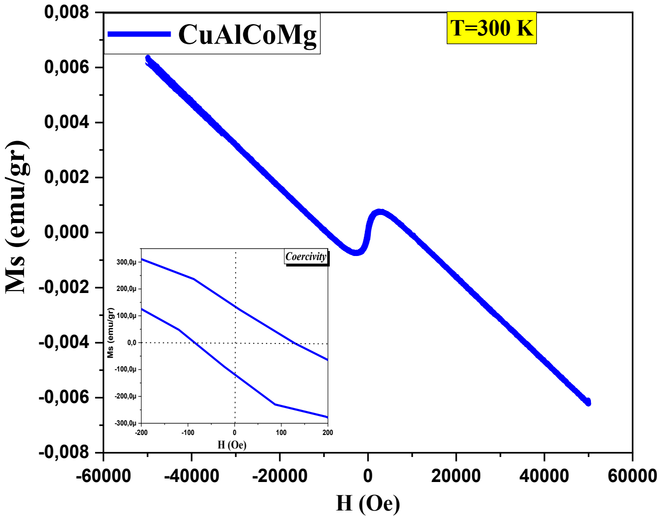

Fig.4. Vibrating sample magnometer (VSM) hysteresis loop and inset coercivity profile of the CuAlCoMg HTSMA at room temperature.

The magnetic hysteresis loop of CuAlCoMg HTSMA obtained at room temperature by vibrating sample magnometer (VSM) test is given in Fig.4. The magnetic hysteresis of CuAlCoMg HTSMA indicates that the magnetic contexture of the alloy has a diamagnetic contribution (due to Cu) and a small ferromagnetic coercivity contribution [33–35]. This small ferromagnetic contribution might have stemmed from the contribution of the secondary crystalline phases and ferromagnetic Co-rich precipitates in the grain boundaries [33].

4. Conclusion

In this study, the CuAlCoMg HTSMA was succesfully produced by arc melting method. the DTA results showed that the alloy is a high temperture alloy with characteristic martensitic transformation temperatures in the range of between 208.95°C and 394.32 °C. It was observed on the reverse transformation peak appeared on the second DTA test curve that the alloy showed a bit of martensite stabilization due to that peak was found as some shifted left, elongated and shallowed by the second DTA cycle, after the first DTA cycle. The XRD test confirmed the formation of martensite phases which constitute the base mechanism of shape memory effect property of novel alloy. The VSM test showed the diamagnetic and a weak ferromagnetic coercivity contributions, the diamagnetic contribution is due to the copper and the ferromagnetic one is most probably stemmed from the precipitation of cobalt in the grain boundaries. The obtained results showed that the produced alloy can be useful in related HTSMA research and related applications.

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