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Magnesium Effect on Characteristic Properties of Cu-based Smart Materials

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Cu-based shape memory alloys feature high transformation temperature, low cost of production simplicity in manufacturing processes and ability to vary the achieved properties through alloy additions. In this work Cu-based SMAs were produced by arc melting. In an attempt to understand the effect of Mg addition in Cu-based SMAs, different percentages of Mg was added to Cu-based ternary alloy system. The characteristic transformation temperatures of the alloys were determined with different thermal mesurements. We observed the main diffraction planes of martensite forms in the fabricated alloys by XRD analysis at room temperature. The sizes of all XRD peaks found to be sensitively affected by the small changes of the Mg content.

Keywords: *CuAlMnMg Shape memory alloy, Transformation temperatures, Martensite, DSC, XRD*

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1. Introduction

Shape memory alloys (SMAs) are functional materials that are the distinctively important in modern technological industrial applications mainly because of their unique thermomechanical shape memory effect (SME) and superelasticity (SE) properties [1, 2]. Generally SMAs consist of 3 alloy base systems. These alloy base systems are NiTi- based, Cu-based and Fe-based SMAs [1,2,3,4] which have been found to be commercially attractive for the practical applications of superelasticity (SE), the shape memory effect (SME) and two-way memory (TWME), and are drawing attention as high damping materials [1,3,4]. Although the NiTi alloys are the most commercial SMAs due to their superior SMA properties they have disadvantages of high costs and hard processing. The much lower costs and simpler fabrication of Cu-based shape memory alloys, regarded as the closest alternative to NiTi SMAs, draw researchers' attention to study and improve them according to their reduced cost and excellent superelasticity properties. They have reversible martensitic transformation mechanism, which is a solid-solid phase transformation and accompained by deformations. These can be recovered by heating or applying stress [5]. Cu-based SMAs exhibit a martensitic transformation on cooling and austenite transformation on heating and during cooling process, close-packed structures are characterized by long period stocking order such as 6R, 18R, and 2H type structure [6]. In Cu-based alloys, the high temperature parent phase with an ordered $L2_1$ structrure ($\beta 3$) can transform at lower temperatures to the 18R or 2H type martensite. The type of martensite structure and transformation temperatures depend mainly on the chemical composition [7]. Advantages of Cu based SMAs include amongst other features, high transformation temperatures, low cost of production, ease in manufacturing, processes and ability to vary the achieved properties through alloying additions. However, Cu-based alloys are generally brittle originated from coarse grain sizes in their alloy matrices. A frequently used way to decrease grain size and increase alloys' ductility, or improve or modify their SMA properties such as transformation temperatures is to add extra elements such as Ti, Mg, Cr, Co, V [1,3,4,9,10] in minor amounts. By this way, the changes or improvements can be achieved due to such additions in terms of microstructural changes, hardness, phase precipitation and transformation temperatures. Attempts have been made to analyze the changes in properties achieved in the based Cu-Al-Mn alloys due to the quaternary additions [4, 8, 9,10]. In this study, the microstructure and martensitic transformation as being the base of the shape memory effect of Mg-doped Cu-Al-Mn shape memory alloys were investigated.

2. Experimental

The quaternary Cu-Al-Mn-Mg (at.%) polycrystalline shape memory alloys was produced by using high purity (99.9%) elements of copper, aluminum, manganese and magnesium powders. After blending these elements powders according to the each alloy composition, each mixture was pelletized under pressure. Then, these pellets were melted by an Edmund Buehler Arc Melter under inert argon atmosphere and the alloys were casted as ingots. Then, the ingots were cut into small alloy samples and these samples were solution treated at 900 ℃ for 1 h, and quenched in the iced-brine water to obtain β1' martensite.

The characteristic martensitic transformation peaks and analyzed data for each alloy were determined by thermograms obtained by a Shimadzu DSC-60A model differential scanning calorimetry (DSC) equipment cycled at varied heating/cooling rates of 15, 20, 25, 30 and 35 °C/min and with the help of liquid nitrogen cooling support. The alloys' behavior in high temperature β-phase region was observed by using a Shimadzu DTG-60AH model differential thermal analysis (DTA) instrument run at a single heating rate of 25 °C/min for each alloy from room temperature to 900 °C. The X-ray measurements (with CuKα radiation) at room temperature were carried out by a Rigaku RadB-DMAX II diffractomer to reveal the diffraction peaks of the martensite structure in the alloys.

Table-1: The chemical compositions (at.%) of the alloy samples detected by EDX test.

Alloy ID	Cu	Al	Mn	Mg
Mg1	77.69	19.56	2.74	0.02
Mg2	76.03	20.83	3.00	0.07
Mg3	78.39	17.92	3.42	0.29
Mg4	78.05	18.45	3.07	0.42

The chemical compositions of the alloys as atomic percentages (at.%) were determined by a Zeiss Evo MA10 model EDX (energy dispersive X-ray) instrument at room temperature. The alloys were coded as Mg1, Mg2, Mg3 and Mg4 based on the increase of Mg additive content. Each alloy composition can be seen in Table-1.

3. Results and Discussion

The DTA heating curves of the Mg1, Mg2, Mg3 and Mg4 alloys can be seen in Fig1. On this heating DTA curves of the Mg1, Mg2, Mg3 and Mg4 alloys, at first the endothermic downside martensite to austenite (M→A) transformation peaks can be seen on the far left of the curves and then the ripples of β1($L2_1$) → β2(metastable)→ precipitating (α+γ2) transitions, then the deep eutectoid recomposition (at ~500-600°C) peaks and finally the ripples of B2(stable)→A2(disordered) transitions appear, respectively and this multistage phase transition chain is a characteristic common thermal behavior of Cu-Al based SMAs.

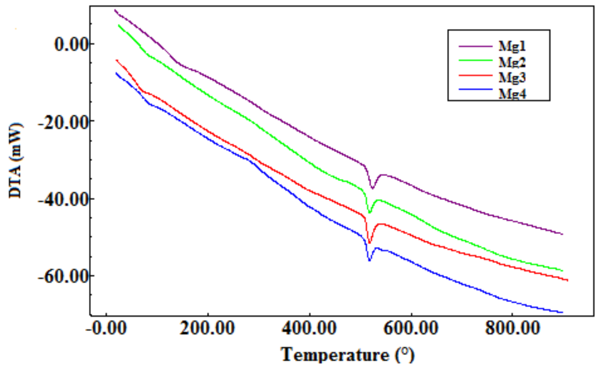

Fig.1. The DTA curves of CuAlMnMg alloy taken at the single heating rate of 25 ° C/ min.

The forward heating and backward cooling curves of the alloy samples displayed on time *x*-axis obtained from DSC measurements at different heating/cooling curves of the alloys can be seen Fig 2, Fig 3, Fig 4 and Fig 5. The sign of characteristic onward-heating martensite to austenite martensitic phase transformation were observed down-endothermic peaks on the heating parts of the DSC loops of the curves for each sample of Mg1, Mg2, Mg3 and Mg4 SMA. Contrarily, the sign of characteristic backward-cooling austenite to martensite (A→M) phase transformation were observed up-exothermic peaks on cooling parts of the DSC loops of the curves for each sample Mg3 and Mg4. The (A→M) peaks were not observed on the DSC curves of Mg1 and Mg2 alloys and this may happened due to the relatively low Mg contents that were used in these alloys.

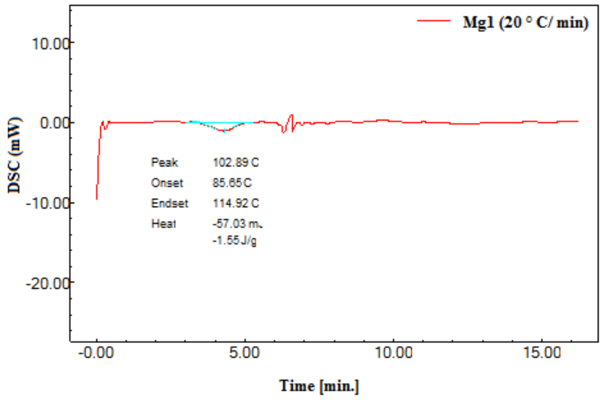

Fig.2. The DSC curve obtained for Mg1 alloy for heating at the heating / cooling rate of 20 °C/ min.

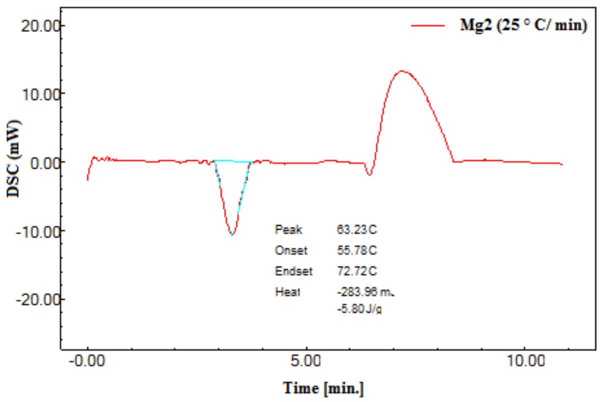

Fig.3. The DSC curve obtained for Mg2 alloy for heating at the heating / cooling rate of 25 ° C/ min.

It is seen from the DSC curves that even the small amount of Mg addition into the Cu-Al-Mn alloy has much effect on the transformation temperatures, so that by the small increase of Mg content the A_s temperature of Mg1 alloy decreased at least 30 °C and A_f lowered nearly 40 °C. Moreover, the peaks of martensite to austenite transformation appeared on the heating parts of the DSC curves enlarged and deepened by the change of Mg content, too. The characteristic transformation temperatures and some other thermodynamical parameters of the produced alloys are presented in Table 2.

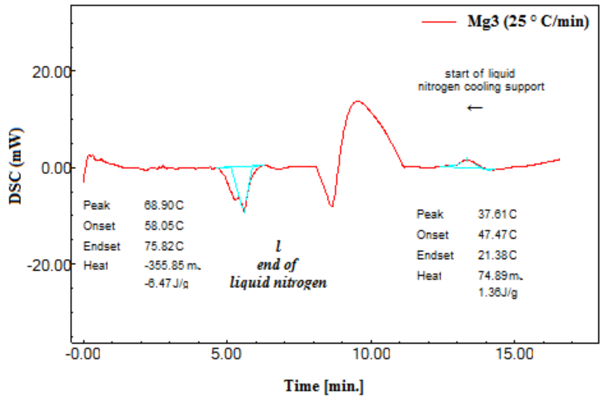

Fig.4. The DSC curve obtained for Mg3 alloy for heating at the heating / cooling rate of 25 °C/ min.

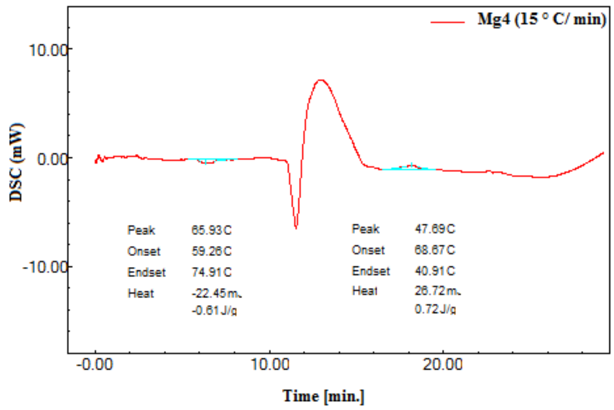

Fig.5. The DSC curve obtained for Mg4 alloy for heating at the heating / cooling rate of 15 °C/ min.

Table-2. Transformation temperatures and thermodynamical parameters of CuAlMnMg alloy at different heating rates.

	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)
Mg1	85.65	114.92	102.89	-	-	-	-	1.55
Mg2	55.78	72.72	63.23	-	-	-	-	5.80
Mg3	58.05	75.82	68.90	47.47	21.38	36.67	61.65	6.47
Mg4	59.26	74.91	65.93	68.67	40.91	18.35	71.79	0.61

The equilibrium temperature, T_0 was calculated from $T_0=(M_s+A_f)/2$ formula of Tong and Wayman [11]. At this point of equilibrium temperature, the chemical (Gibbs) free energy amounts of two interconverting phases are equal, and for that matter there is no any driving force to transform a phase into another.

Fig.6 shows the XRD paterns of the CuAlMnMg alloy samples. The structural analysis was made by X-ray observations at room temperature. The diffractions planes are β1′(122), γ1′(111), β1′(128),β1′ (0018), β1′(1210) and β1′(042) martensites peak [5, 10, 11, 12, 13]. The Mg1, Mg2, Mg3 and Mg4 alloys martensitic conditions have mainly 18R-type structure as seen from Fig.6. As seen on these diffraction patterns, among these polycrystalline alloys the Mg3 is seen to have the the most single crystallinity due to its single high peak of β1' martensite and this result becomes interestingly matching with the largest enthalpy change of Mg3 (see in Table-2), which indicate that the Mg3 alloy can have the most powerful shape memory effect among the others. The sizes of all XRD peaks so the microstructures of the alloys seem to be sensitively affected and changed by the little changes of the Mg content.

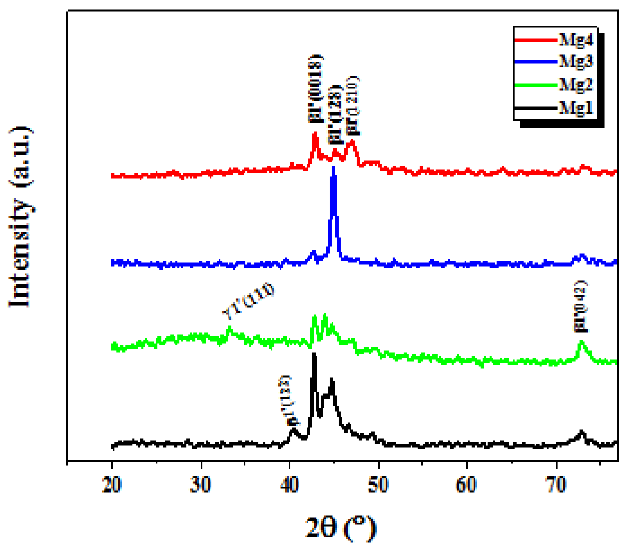

Fig.6. The XRD results for Mg1, Mg2, Mg3 and Mg4 alloys showing different planes of martensite phases.

4. Conclusion

In this study, the quaternary CuAlMnMg alloys with increasing minor Mg contents were succesfully produced by arc melting method. The characteristic martensitic temperatures of the alloys determined by the DSC tests taken at different heating/cooling rates were found to change by the change of minor Mg additive. DTA curves of the alloys exhibited eutectoid recomposition (at ~400-600°C). Furthermore, the structural X-ray diffraction measurements taken at room temperature revealed the formed martensite phase in the fabricated alloys, which is a condition and provide a basis for the alloys to have a shape memory effect property. The results show that the transformation temperatures and the lattice structure of CuAlMn SMA can be sensitively modified by tuning the quaternary Mg additive.

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