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Microstructure and Properties of Low Al Content Cu-Al-Cr and Cu-Al-Cr-Mn Shape Memory Alloys Produced by Arc Melting

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In this study, low Al content (<5 at.%) Cu-Al-Cr and Cu-Al-Cr-Mn shape memory alloys (SMAs) were fabricated by using the arc melting technique, which can be produced as high-purity alloys with various compositions. Due to the low aluminum content, the phase transformation behavior and shape memory properties of these alloys have not been sufficiently investigated in the literature. This study aimed to characterize the microstructure, phase transformation temperatures, and shape memory properties of the arc-melted CuAlCr and CuAlCrMn alloys and compare them with the data in the literature. The effect of Mn addition and arc melting process on the performance of Cu-Al-Cr SMAs was also discussed. The results showed that the arc-melted alloys had a homogeneous microstructure and that Cr addition improved the phase transformation temperatures and shape memory properties. Mn addition was found to lower the phase transformation temperatures but increase the shape memory properties.

Keywords: *Shape Memory Alloys, Arc Melting, Microstructure, Phase Transformation, Mechanical Properties*

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1. Introduction

Shape memory alloys (SMAs) are a class of functional materials that exhibit the ability to recover their original shape after being deformed by applying heat or stress. This phenomenon is known as the shape memory effect (SME) and is caused by a reversible solid-solid phase transformation between austenite and martensite phases [1]. Austenite is a face-centered cubic (FCC) structure that exists at high temperatures or low stresses. Martensite is a body-centered cubic (BCC) or body-centered tetragonal (BCT) structure that exists at low temperatures or high stresses. The transformation between austenite and martensite can occur either thermally or mechanically. The thermal transformation is induced by changing the temperature across certain critical values, such as M_s (martensite start), M_f (martensite finish), A_s (austenite start), and A_f (austenite finish). The mechanical transformation is triggered by applying stress above a certain level, such as σs (stress-induced martensite start) and σf (stress-induced martensite finish). The phase transformation of SMAs is also influenced by the alloy composition, microstructure and processing history [2]. SMAs have attracted considerable attention for their potential applications in various fields, such as aerospace, biomedical, robotics and actuators [3]. Among the SMAs, Cu-based alloys are of particular interest due to their low cost, high thermal and electrical conductivities, excellent processability and adjustable transformation temperatures [4]. However, Cu-based SMAs also suffer from some drawbacks, such as low mechanical strength, poor thermal stability and large hysteresis [1].

One way to improve the performance of Cu-based SMAs is to introduce alloying elements that can modify the phase transformation behaviour and microstructure. However, the effect of Cr addition on the shape memory properties of Cu-Al-Ni SMAs is not well understood, especially for low Al content alloys. Moreover, most of the studies on Cu-Al-Ni-Cr SMAs have been conducted using conventional fabrication methods, such as casting and hot rolling, which may introduce defects and inhomogeneities in the microstructure. In this study, we fabricated CuAlCr and CuAlCrMn shape memory alloys with low Al content (<5 at.%) by using arc melting, a technique that can produce high-purity alloys of various compositions. In this study, the microstructure, phase transformation and shape memory properties of the arc-melted CuAlCr and CuAlCrMn alloys were investigated and compared with those of the literature. The effect of Mn addition and arc melting process on the performance of Cu-Al-Cr SMAs was also discussed.

2. Experimental

In this study, CuAlCr and CuAlCrMn SMA alloys respectively named M1 and M2 with different elemental contents were fabricated by arc melting technique. High-purity elemental metals of Cu, Al, Cr and Mn were used as the starting materials. The alloys had a nominal composition of 5 wt.% Al and 0-2 wt.% Cr in Cu base. The arc melting process was carried out in a vacuum chamber filled with high-purity argon gas to prevent oxidation. The vacuum level was maintained at approx. 7.5 x 10^{-3} Torr during the process. The specimens for the experiments were cut from the arc-melted ingots and adjusted to have a mass of ~40-60 mg. After then, the specimens were subjected to a homogenization treatment at 900 °C for 1 hour and then quenched in salted iced-brine water to obtain a uniform microstructure.The phase transformation behavior of the alloys was investigated by differential scanning calorimetry (DSC) using Shimadzu DSC-60A equipment. The DSC experiments on both M1 and M2 alloys were performed at a same heating and cooling rate of 25 °C/min. The microstructure of the alloys was characterized either by XRD and optical microscopy at room temperature. CuKα X-rays were utilized in the XRD diffraction tests that were made by using a Bruker D8 Advance X-ray diffractometer. Before the optical microscopy observations were performed by using a XJP-6A model optical metallographic microscope, the alloy specimens were polished and etched with ($FeCl_3$ $6H_2O$)-H_2O with HCl solution to reveal the grain boundaries.

3. Results and Discussion

The chemical compositions of the CuAlCr and CuAlCrMn SMAs are shown in Table. 1. The phase transformation temperatures of the alloys were determined from the DSC curves as the onset points of the exothermic and endothermic peaks. The phase transformation temperatures of the alloys are listed in Table 1.

Table 1. The chemical composition of the CuAlCr and CuAlCrMn alloys.

Alloy ID	Cu % wt.	Al % wt.	Cr % wt.	Mn % wt.
M1	90.75	5.28	3.98	*
M2	88.61	5.05	3.54	2.8

The DSC results of the fabricated M1 and M2 alloys are presented in Fig.1 and Fig.2. On both left side heating parts of these DCS curves there are seen a downward endothermic reverse martensite to austenite (M→A) phase transformation peak emerged at around 200 °C and 300 °C. But, the corresponding upward exothermic direct austenite to martensite (A→M) transition peaks expected on the right side back cooling parts of the curves were not observed, or they are so small to be noticed. The reason for this is the use of low Al content in both alloys which content is or should be normally used in the range of 9-14 wt.% in usual CuAl-based shape memory alloys such as CuAlMn or CuAlNi [3,9,10,11,12,13,14] to achieve more ideal shape memory properties. The characteristic reverse (M→A) transformation temperatures and enthalpy change values for both alloys determined from DSC peak analyses applying the tangent differentiation method via DSC software are presented in Table 2.

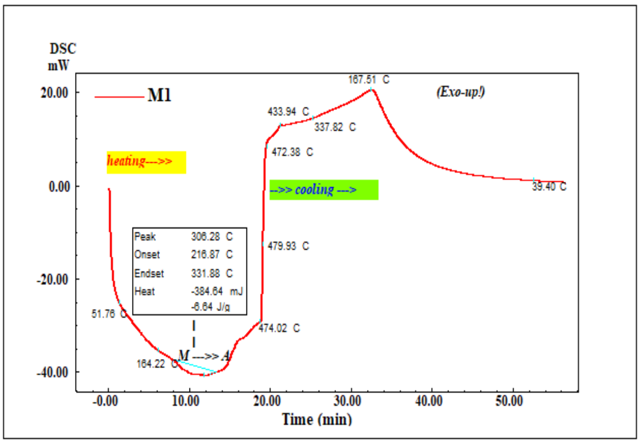


Fig.1. The DSC heating+cooling curve of M1 alloy.

It can be seen that the phase transformation temperatures of the alloys increase with increasing Cr content. This is because Cr atoms substitute for Cu atoms in the Cu-based SMAs and increase the lattice parameter of the austenite phase [5]. The lattice parameter difference between austenite and martensite phases is a driving force for phase transformation [3]. Therefore, increasing the lattice parameter of the austenite phase by Cr addition increases the phase transformation temperatures of the alloys.

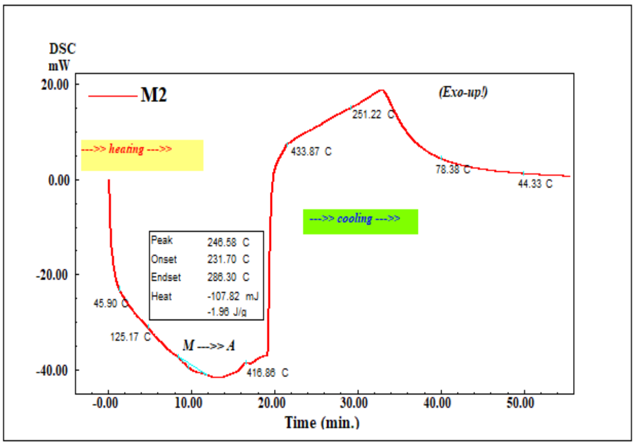


Fig.2. The DSC heating+cooling curve of M2 alloy.

Table 2. The transformational temperatures and enthalpy change values of M→A phase transition in SMAs.

Alloy ID	**Heating /cooling rate (°C/min)**	**A_s (°C)**	**A_f (°C)**	**A_{max} (°C)**	**$\Delta H_{M\rightarrow A}$ (J/g)**
M1	25	216.87	331.88	306.28	6.64
M2	25	231.70	286.30	246.58	1.96

The DSC results also show that the heat treatment at 900 °C for 1 hour and quenching in iced-brine water affects the phase transformation behavior of the alloys. The heat treatment causes a homogenization of the alloy composition and microstructure, which reduces the segregation and precipitation of Cr-rich phases [6]. The quenching process induces a high cooling rate, which suppresses the formation of equilibrium phases and stabilizes the martensite phase at room temperature [7]. The heat treatment and quenching process also affect the enthalpy change of the phase transformation, which is proportional to the area under the DSC peaks. The enthalpy change of the phase transformation reflects the degree of reversibility and stability of the phase transformation [1]. The enthalpy change of the phase transformation decreases after the heat treatment and quenching process, indicating that the phase transformation becomes less reversible and stable.

The use of low Al content (5% at.) in CuAlCr SMA alloys also influences their phase transformation and shape memory properties. Low Al content results in make higher martensitic transformation temperature [8]. In thermoelastic Cu-Al-based SMAs such as CuAlMn; with low (<14 at.%) Al content the parent phase can be one of two different $\beta(A2)$ and $\beta1(L2_1)$ phases and the martensite can be $\alpha1'(3R)$, with intermediate (14-17 at.%) Al content only $\beta1(L2_1)$ austenite phase exists and martensite is $\beta1'(18R)$ which results in more ideal shape memory properties, and with higher Al content ranges the $\gamma1'(2H)$ martensite becomes dominant martensite phase [9]. This knowledge are also coincide with or supported by the knowledge obtained by assessments made upon the magnitude of average electron conduction ratio (e/a ratio) of the Cu-based alloys taking values within a certain e/a ratio values range (1.45 and 1.50) as a condition to have good shape memory properties and giving clues about which types of martensite phases should form in the alloy depending its e/a ratio [3,13]. Here, the presence of two parent phases forming with low Al content leads to a more complex phase transformation behavior and a less ideal shape memory effect. This resulted in low shape memory capacity with low transformational enthalpy change amounts and a non-noticeable direct transition from austenite to martensite seen in the above-given DSC results.

The addition of Mn has been shown to decrease the martensitic transformation temperatures of CuAlMn alloy and provide a wider range of shape memory effects for the alloy [10]. Additionally, it has been found that the addition of Mn plays an important role in the phases and phase transitions in the alloy [11]. With the addition of Mn, two different parent phases (β and β1) formed in the alloy, and these phases transformed into different martensitic phases (18R and 2H) during martensitic transformation [11, 12]. These phases were found to appear as distinct peaks in the XRD diffraction pattern [13]. DSC measurements revealed that direct and reverse martensitic phase transformations in the alloy were shown as clear peaks in the thermograms [13]. These results indicate that the addition of Mn significantly improves the thermal and structural properties of CuAlCrMn alloy. It has been reported in the literature that the addition of Mn reduces the grain size of the alloy, which increases its mechanical strength and ductility [11], too.

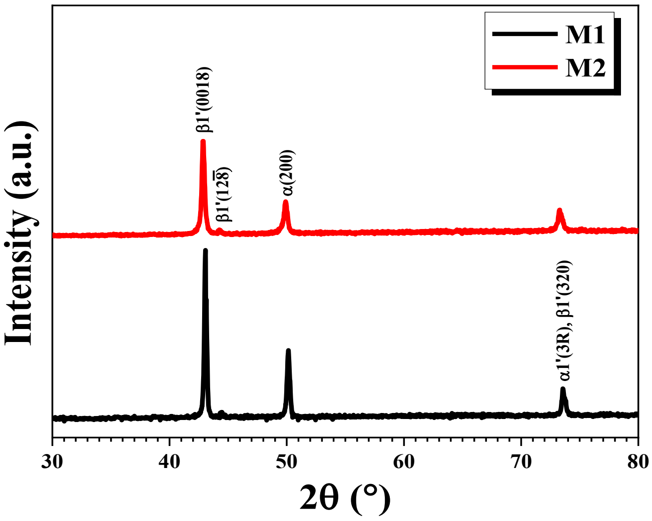


Fig.3. The X-ray diffraction patterns of the alloy samples.

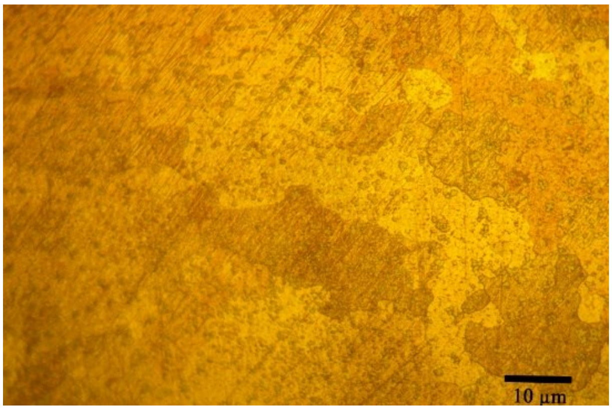
The X-ray diffraction patterns of the alloy samples are presented in Fig.3 in order to get informed about the microstructural features of them. The same main peak observed in both alloys' patterns is β1'(0018), and the other observed peaks are β1'(12$\bar{8}$), β1'(320), α1'(3R) and Cu-α(200) determined by comparing with those in the literature [14,15,16]. The intensity of the mean martensite peak of M1 (CuAlCr) alloy sample is seen reduced by adding Mn element to M2 (CuAlCrMn) alloy sample. Therefore, it can be said that the polycrystallinity of M2 alloy became higher than M1 alloy due to the increased configurational atomic complexity in the M2 alloy matrix by the addition of Mn additive, which might have also consequently led to the average crystallite size of the M2 alloy to be smaller than that of M1 alloy. Let's see this by finding the average crystallite size values for the alloys by using the well-known Debye-Scherrer formula [13] given as below;

$$D = \frac{0.9\lambda}{B_{1/2} cos\theta} \tag{1}$$

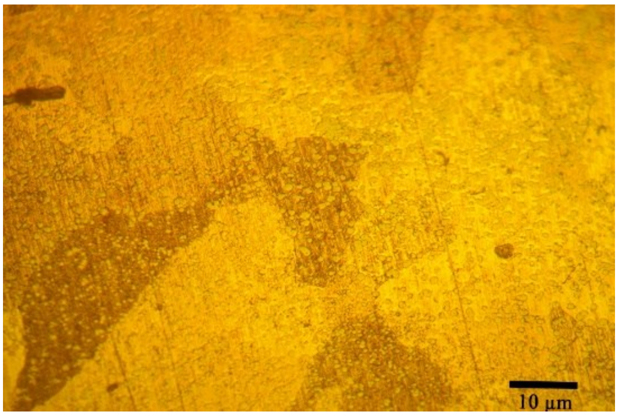
where; λ stands for the X-ray wavelength of the CuKα radiation (λ=0.15406 nm) used in the XRD test, θ is the Bragg angle of the diffraction and $B_{1/2}$ refers to the full width at half maximum (FWHM) value of the maximum intensity peak (the main peak). The average crystallite size, D values of the alloy samples were found as 55.34 nm for the M1 alloy, and 40.79 nm for the M2 alloy. As expected, the D value of M2 was found some lower than the D value of M1 alloy, which confirms the above-mentioned prediction conducted over the effect of Mn addition to M2 alloy.

The optical microscopy images of the alloy samples are presented in Fig.4. As these micrographs of the alloy samples were examined, no columnar structures encountered in shape memory alloys were observed. It has been observed that there are different phases in different colour tones on the structure. The structure is generally in the austenite phase and this appearance is considered to be normal in structures that exhibit unidirectional phase change. In addition, it is thought that there are coherent precipitate phases that were formed due to Cr addition. Cr addition has been reported to improve the mechanical and functional properties of Cu-based shape memory alloys (SMAs) by forming a coherent precipitate phase [17,18].

The coherent precipitate phase is a phase that has the same crystal structure and atomic order as the matrix phase, resulting in low interfacial energy. However, the coherent precipitate phase also causes elastic strain due to the lattice mismatch with the matrix phase, which increases with the growth of the precipitate phase and leads to coherency loss at a certain threshold size. The coherency loss is accompanied by the formation of interfacial defects and an increase in interfacial energy [19].



(a)



(b)

Fig.4. Micrographs of; a) M1 (CuAlCr), and b) M2 (CuAlCrMn) SMA specimens.

The effect of Cr addition on Cu-based SMAs depends on the alloy composition and processing conditions. For example, in Cu-Al-Ni SMAs, Cr addition can enhance the strength and stability of the alloys [20]. However, Cr addition can also reduce phase transformation temperatures [21]. Therefore, Cr addition can have both positive and negative effects on Cu-based SMAs with coherent phases, depending on the balance between the elastic strain energy and interfacial energy of the precipitate phase, as well as the alloy composition and processing conditions. Phase transformation analysis revealed that Cr addition increased the phase transformation temperatures and Mn addition decreased the phase transformation temperatures. These results were consistent with the data in the literature and indicated that arc melting technique was a suitable method for producing low Al content Cu-Al-Cr and Cu-Al-Cr-Mn SMAs.

4. Conclusions

In this study, it was aimed to investigate the microstructure, phase transformation and shape memory properties of low Al content CuAlCr and CuAlCrMn shape memory alloys. For this purpose, low memory alloys with low Al (~5 wt.%) and different Cr and Mn contents were successfully produced by using the arc melting technique. The obtained results are as follows: Cr addition and low Al content increased the phase transformation temperatures of the alloys. This is assumed to be due to Cr atoms replacing Cu atoms in Cu-based SMAs and increasing the lattice parameter of the austenite phase. Mn addition decreased the phase transformation temperatures of the alloys. This is due to Mn addition causing two different parent phases (β and β1) to form in the alloys and these phases transform into different martensitic phases (18R and 3R) during martensitic transformation. Low Al content (5 wt.%) also affected the phase transformation and shape memory properties of CuAlCr SMA alloys. Low Al content caused the martensitic transformation temperature to be high. In low Al content Cu-Al-based SMAs, a thermoelastic martensitic transformation occurs between martensite (3R or 18R) and the parent β (A2) or β1 (L21) phases, while in those with high Al content, only β1 (L21) phase exists and this phase can also transform to martensite but the dominant 2H type. This study shows that the arc melting technique is a suitable method for producing low Al content Cu-Al-Cr and Cu-Al-Cr-Mn SMAs. It also reveals that Cr and Mn addition significantly affects the thermal, structural and mechanical properties of these alloys.

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