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THE EFFECT OF CHROMIUM ADDITION ON PHYSICAL PROPERTIES OF Cu-Al BASED HIGH TEMPERATURE SHAPE MEMORY ALLOY

Cu-Al-based high temperature shape memory alloys are preferred commonly due to their cheap costs and shape memory properties. In recent years, studies have been conducted on developing and producing a new type of Cu-Al based shape memory alloy. In this study, the CuAl-Cr alloy system, which has never been produced before, is investigated. After production, the SEM-EDX measurements were made in order to determine the phases in the $Cu_{84-x}Al_{12}Cr_{x+4}$ (x = 0, 4, 6) (weight %) alloy system; and precipitate phases together with martensite phases were detected in the alloys. The confirmations of these phases were made via *x*-ray measurements. The same phases were observed by XRD diffractogram of the alloys as well. The values of transformation temperature of alloys were determined with Differential Scanning Calorimetry (DSC) at 20°C/min heating rate. According to the DSC results, the transformation temperature of the alloys varies between 320°C and 350°C. This reveals that the alloys show high temperature shape memory characteristics.

Keywords: Cu-Al based, shape memory alloy, transformation, phase

1. Introduction

There is a great demand on shape memory alloys (SMAs) since they have a large working area in industry, robotics, automotive, aerospace and other industrial applications with high-temperature alloys and could transform over 120°C. Generally, Co-, Fe-Mn-Si, Cu-Al-Ni, Ni-Al, Ni-Al-Ti-core Pt, and Ni-Ti-based high temperature shape memory alloys have been studied [1-4].

The advantages of copper based high temperature shape memory alloys compared to other SMAs can be explained as follows: These alloys can transform at high temperature, also the production is cheap and properties of alloys may change significantly by the addition of various elements. In addition, Cu-based alloys like Cu-Al-Ni, Cu-Al-Zn and Cu-Al-Mn alloys have mostly been studied [5,6]. Copper based alloys are also highly demanded in industrial applications because of having high thermal and electrical conductivity, and they show good resistance to corrosion. In particular, aluminum bronze (Cu-Al) shows good strength and corrosion resistance [7]. Binary $Cu_{76}Al_{24}$ (atomic%) has β phase and exhibits eutectoid transformation at more than 565°C. DO3 order phase (β1) transition transforms to orthorhombic martensite phase in which shape memory effect is seen with the reducing of temperature. The transformation temperature of CuAl alloy is reduced to the available temperature by adding elements such as Ni, Zn and Be [8,9].

The transformation temperature of shape memory alloy is largely dependents on the composition of alloys. A small change in composition leads to a serious change in the transition temperature. This feature is used for achieving in desired transformation temperature. The researchers have tended to achieve some advantages in order to increase the transformation temperature and improve the mechanical properties of Cu based alloys. Some of these achievements could be creating a new class of shape memory alloys, producing an efficient SMA, improving performance of shape memory effects due to changing the composition and the transformation temperature, and producing shape memory thin film [10].

Being cost-effective on production, the high temperature shape memory alloys such as CuAlNb, CuAlTa, CuAlFe and especially CuAlAg have been produced as an alternative to NiTi based high temperature shape memory alloys at the past decade [9,11-17]. Furthermore, adding Chromium to alloys, could increase the hardness, and hence wear resistance and corrosion resistance. Morever, Chromium increases the critical temperature of heat treatment applications [1,6]. Cr element is used to metallurgical application as an alloys element. Because, this element has corrosion resistant properties [18]. Masahiro et al. used Cr element to improve of NiTi shape memory alloys. They found that Cr element decrease transformation temperature of alloy and improve rigidity [19]. Cu-Al-Cr alloy which is used in this study has not been handled in literature yet, hence it is the unique investigation.

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Accordingly, SEM-EDX and XRD measurements and crystal structural analysis of the produced Cu-Al-Cr alloy group was carried out, afterward thermo-elastic transformation was checked out by DSC measurements and the obtained results were assessed.

2. Experimental

The Cu-Al-Cr alloy group was produced by following the $Cu_{84-x}Al_{12}Cr_{x+4}$, where x is the molar fraction of Cr with 0, 4 and 6 values, which is ordered in a systematic way. The Cu-Al-Cr alloy system consists of a mixture of Cu, Al and Cr elements in high purity level. The pelletized mixtures are produced by melting several times in arch melting furnace. The alloys that were put in the bulk form were kept at 900°C for 24 hours and then fast-cooled in icy, salty water to ensure homogenization. The x-ray measurements of the alloys, which were at room temperature in martensite phase, were performed by Rigaku X-ray measurement system through CuKα radiation with 2°/min scanning rate. In order to determine the micro-structure and the phases in the mechanically polished alloy system, the alloys were kept in 5g Fe_2Cl-H_2O/96 ml ethanol/20 ml HCl acid etching solution. Then the SEM-EDX measurements were made. The SEM-EDX measurements and the elemental analyses of the alloys, that were homogenized, were made at room temperature. Differential Scanning Calorimetry (DSC) was calibrated with pure indium and was handled to determine the transformation temperatures of the alloys in nitrogen gas atmosphere with 20°C/min heating/cooling rate between 100-450°C temperature ranges. In addition, melting point and enthalpy change of indium were found as 156.6°C and 28.4 J/g respectively. Furthermore, the Vickers Hardness measurement of alloys was done for 0.5 g/f value to characterize the effect of the Cr addition on the micro-hardness of the CuAl-based alloy.

3. Results and discussion

The x-ray measurement results were evaluated according to the literature and JCPDS cards no: 050-1477, 28-0005 [11,12] (Fig. 1). All of the alloys are in martensite phases, which are known as monoclinic $\beta_1{}^1$ phase, orthorhombic $\gamma_1{}^1$ phase, and in Cu_9Al_4 precipitation phase No Cr-based precipitation phases were detected, since the x-ray peak values of the CuAlCr are very close to each other. CuAl shape memory alloy – which include, 40 wt% Aluminum — shows β_1' martensite phase with an 18R long-period ordered super lattice structure after quenching. Otherwise, some other effects cause to be new martensite phase like as α' martensite with 6R structure or γ_1' martensite with 2H structure and precipitates phase. The precipitates can be occurring in the martensite matrix. The precipitates can be blocked moving interface and modified retransformation temperatures [20,21].

After polishing, general EDX analysis was carried out on their surfaces, and desired values most consistency were specified. According to the general EDX results, it is observed that the results are consistent. As it was expected, the aluminum

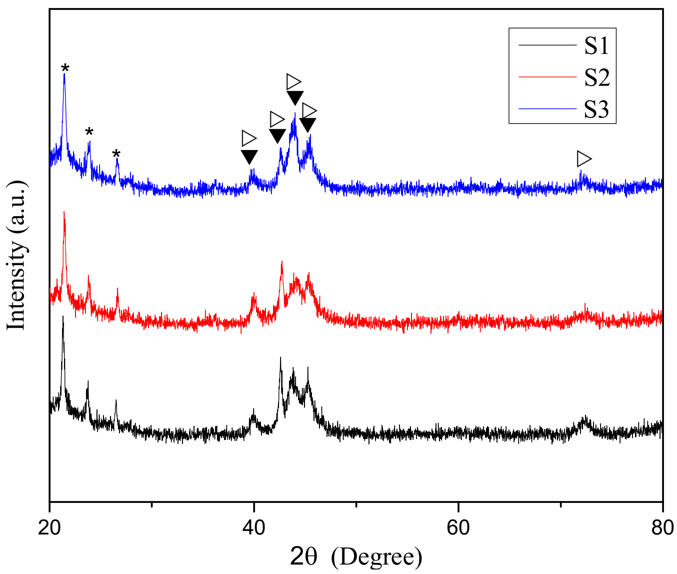

Fig. 1. Xray difractograms of Cu-Al-Cr shape memory alloy systems at room temperature (*: Cu_9Al_4, ▷: $\gamma_1{}^1$ martensite phase, ▼: $\beta_1{}^1$ martensite phase)

rate was nearly stable, while the Cu rate diminished and Cr rate increased (Table 1).

TABLE 1

EDX results of Cu-Al-Cr shape memory alloy systems

Samples Code	Cu (% wt.)	Al (% wt.)	Cr (% wt.)
S1	83.2	12.0	4.8
S2	80.4	12.1	7.5
S3	77.7	11.6	10.7

The SEM images of the CuAlCr alloy group are given in Figure 2. The martensite plates and the precipitation areas are clearly seen in SEM images.

The EDX measurements from the different precipitation areas and from the martensite phase areas, which are clearly seen, were made in a point or regional manner according to the form of the image by using the SEM images. The EDX results of martensite phases with the precipitations and corresponding spectrum number are given in Table 2. The analyses of the phases for the chemical compounds were made in accordance with the literature [11,12]. Correlation between EDX results and SEM images show a most martensite phase on the alloy, where these phases consist of β_1' (18R) thin martensite and γ_1' (2H) thick martensite for Cu-Al-based alloys [12,22]. β_1' martensite phase has a very high thermo-elastic behavior. These martensite plates include self-accommodation plates [13]. When the chemical analysis of the precipitations on martensite plates are concerned, it is observed that some of the precipitations are Cr-based Cr(Al,Cu) and Cr or Cu-based (Cu,Cr)Al phase. The other precipitation phase was determined to be the Cu_9Al_4 phase, which is observed frequently in Copper-Aluminum-based alloys. These results are in accordance with the x-ray measurement results.

The DSC curves and results of the $Cu_{84-x}Al_{12}Cr_{x+4}$ (x = 0, 4, 6) (weight %) alloy system are given in Figure 3. and Ta-

TABLE 2

EDX result of CuAlCr alloy systems

Sample Code	Spectrum No and phases	Cu (%wt.)	Al (% wt.)	Cr (% wt.)	Cu (% at.)	Al (% at.)	Cr (% at.)
S1	**12:** Cu_9Al_4	83.7	10.9	5.4	72.2(±%2)	22.1(±%0.5)	5.7(±%0.2)
	13:Cr(Al,Cu)	20.0	3.8	76.2	16.4(±%0.5)	22.1(±%0.2)	76.2(±%0.2)
	14:Martensite	87.1	12.0	0.9	74.8(±%2.1)	24.3(±%0.5)	0.9(±%0.1)
	15:Martensite	86.8	12.5	0.7	74.1(±%2)	25.2(±%0.5)	0.7(±%0.1)
	16:(Cu,Cr)Al	49.1	7.3	43.7	41.0(±%1.1)	14.3(±%0.3)	44.7(±%1)
S2	**17**:Martensite	85.9	12.9	1.2	73.0(±%1.9)	25.7(±%0.5)	1.3(±%0.1)
	18: Cr(Cu,Al)	3.3	2.8	93.9	2.6(±%0.1)	5.3(±%0.2)	92.7(±%2.3)
	19:(Cu,Cr)Al	36.7	6.8	57.1	30.3(±%0.9)	12.0(±%0.3)	57.7(±%1.4)
	20: Cu_9Al_4	84.6	13.4	2.0	71.3(±%1.8)	26.6(±%0.5)	2.1(±%0.1)
S3	**25**:Martensite	84.9	13.8	1.3	71.3(±%1.8)	27.4(±%0.2)	1.3(±%0.1)
	26:Cr(Al,Cu)	5.7	3.7	90.6	4.6(±%0.2)	6.9(±%0.2)	88.5(±%2.1)
	27:Cu_9Al_4	78.7	12.1	9.4	66.3(±%1.8)	24.0(±%0.5)	9.7(±%0.2)

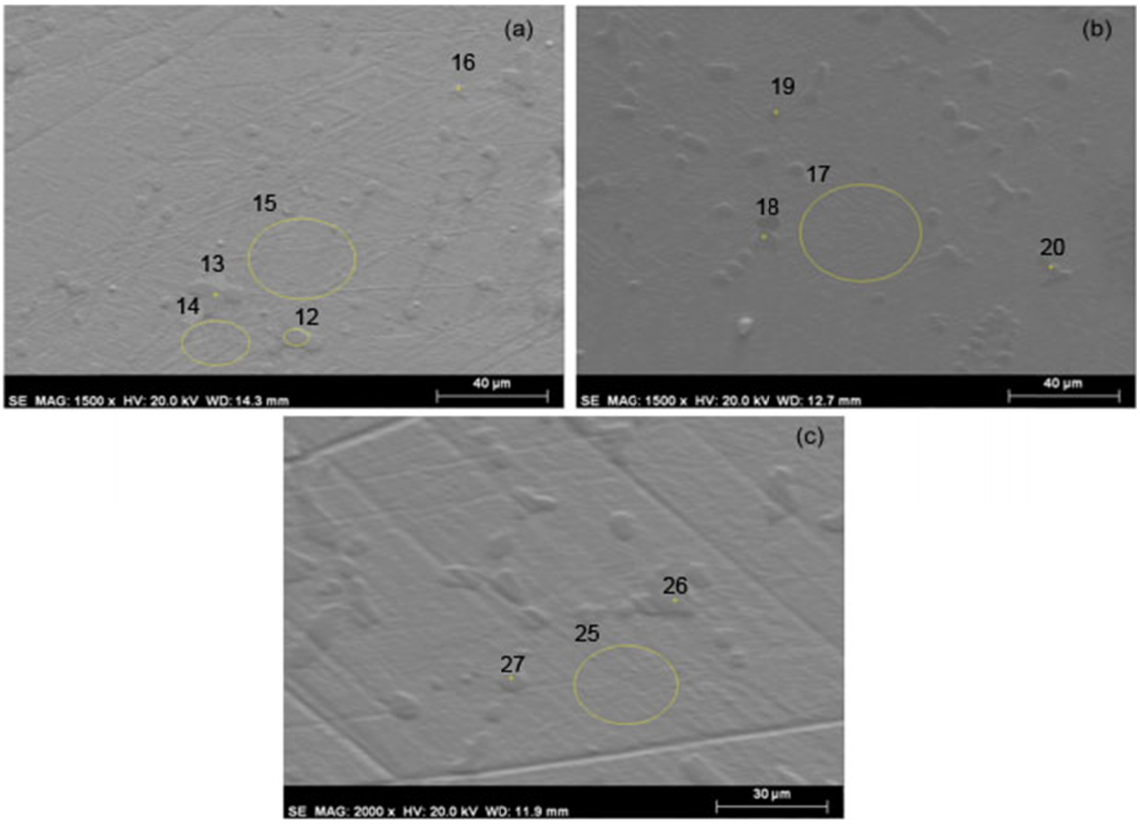

Fig. 2. SEM images of CuAlCr Alloy systems, (a) for S1, (b) for S2, and (c) for S3

ble 3. In alloys containing $x = 0$ and $x = 4$ chromium element, the austenite, martensite transformation temperature value increases with the increase in x value; however, the transformation temperature value decreased for $x = 6$. The enthalpy value also decreased. The 88 wt% Cu-12 wt% Al binary alloy shows the eutectoid phase transformation at nearly 565°C. This transformation causes another transformation into martensite phase with the decrease in the temperature. Due to the transformation of the Eutectoid phase transformation into martensite phase in CuAl-based alloy, the alloy shows a shape memory effect [8].

The eutectoid phase transformed into martensite phase, is an indicator of shape memory effect. It was also determined that the martensite phase transformation temperature is between 320°C to 350°C with the contribution of chromium. Thus, it can be noticed that the CuAlCr, which is produced, is a new type of a high temperature shape memory alloys. According to the thermal analyses results, the austenite phase transformation temperature increased with the increase of the chromium in the alloy system which included 4 wt% and 8 wt% chromium in total weight, and a decrease in the transformation temperature and the enthalpy value was observed in the alloy which contained 10 wt% chromium. Therefore, the reasons for this might be the increase in the Cr-based precipitation phases in Cu-Al-based alloys after a certain amount of chromium is added. Likewise, the results (Table 3) illustrated that the hardness value of CuAlCr alloy is enhanced by increasing Cr. Soliman et al investigated the effect of ageing on the hardness value of the 88 wt% Cu-12 wt% Al alloy, and reported that the hardness value in an alloy, that was not exposed to any ageing, was 132 HV [23]. When this result is compared with the alloy group in the current study, it can be concluded that chromium generally increases the hardness value, and hence the addition of chromium increases the hardness penetration [6]. By so-doing, the endurance of the alloy increases as well. In other words, since the chromium element forms precipitation in some areas in the alloy, the endurance increases. These precipitations were analyzed with EDX.

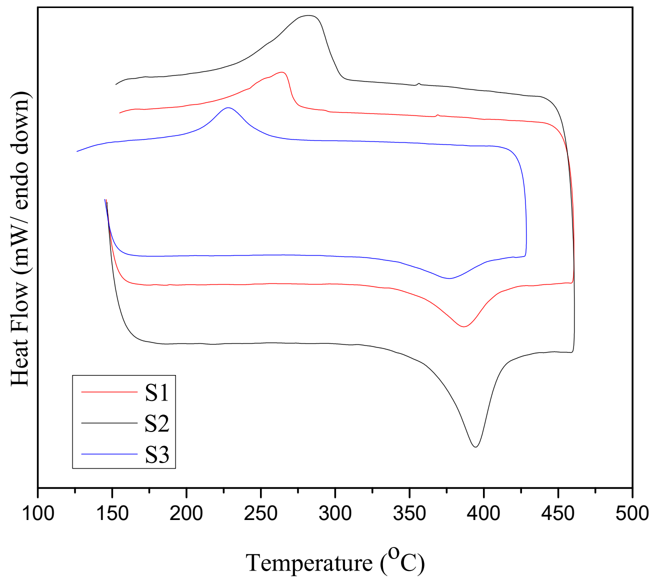

Fig. 3. DSC thermograms of CuAlCr shape memory alloy systems

4. Conclusions

Thick and thin martensite phase together with different precipitation phases were determined in the alloy By using the SEM-EDX measurements. This result is in coherences with the *x*-rays, *X*-ray measurement results showed that the crystal structure of the alloy in martensite phase was 18R monoclinic (thick plate), and 2H orthorhombic (thin plate) martensite phase. In addition, the Cu_9Al_4 phase, which is precipitation phase, was also detected. DSC results showed that all of the CuAlCr alloy systems show high temperature shape memory alloy characteristics. It was observed that the micro-hardness of CuAl-based alloy increased by increasing the rate of Cr.

TABLE 3

Transformation Temperature and hardness values of CuAlCr alloy systems

Sample	A_s/°C	A_p/°C	A_f/°C	M_s/°C	M_p/°C	M_f/°C	ΔH/J.g^{-1}	Vickers Hardness (HV)
S1	349.9	386.3	409.4	273.4	264.7	233.4	8.06	230.8
S2	358.6	394.4	412.9	302.0	283.9	239.2	9.69	235.6
S3	329.6	377.0	405.7	252.0	228.3	202.2	7.31	256.4

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