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Effects of Aging Temperature on Microstructure and Thermal Properties of CuAlMn Shape Memory Alloys

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Abstract: The use of copper-based shape memory alloys is increasing rapidly. In this study, the aging effects of CuAlMn shape memory alloys were investigated. Three different alloys were produced during the work. These alloys were then aged for one hour at temperatures of 200 ° C, 300 ° C, 400 ° C and 500 ° C. DSC, XRD and microstructural investigations were carried out on samples which were not aged and aged at different temperatures. Experiments have shown that aging at high temperatures has an adverse effect on shape memory effect on alloys.

CuAlMn Şekil Hafızalı Alaşımların Yaşlandırılmasının Mikroyapı ve Termal Özelliklerine Etkileri

Anahtar Kelimeler
Şekil hafızalı alaşımlar,
CuAlMn,
DSC,
XRD,
Yaşlandırma

Özet: Bakır bazlı şekil hafızalı alaşımların kullanımı hızla gelişmektedir. Bu çalışmamızda, CuAlMn şekil hafızalı alaşımının yaşlandırma etkileri incelenmiştir. Çalışmalarda 3 farklı alaşım üretilmiştir. Daha sonra bu alaşımlar 200 °C, 300 °C, 400 °C ve 500 °C sıcaklıklarda bir saat yaşlandırılmıştır. Yaşlandırma yapılmamış ve farklı sıcaklıklarda yaşlandırılmış numunelerin DSC, XRD ve mikro yapı incelemeleri yapılmıştır. Deneyler sonucunda yüksek sıcaklıklarda yaşlandırma işleminin alaşımlar üzerinde şekil hafıza etkisine olumsuz etki ettiği görülmüştür.

1. Introduction

The development of shape memory alloys (SMA) occurs very quickly. Emerging industry has different needs. Therefore, different types of materials are needed [1, 2]. NiTi shape memory alloys are known, are used in the many field [3,4]. But the cost of NiTi production is expensive, and researchers have sought different alloys with the same capabilities. Today, there are three types of SMAs, marginally known as NiTi, copper based and iron based. Fe-based alloys from these alloys still do not achieve the desired qualities and capabilities [5]. Therefore, the most powerful competitor against NiTi alloys is Cu based SMAs. Cu-based SMAs are commonly used as a binary alloy with Al element. CuAlMn alloys exhibit ordered and disorder transitions in solid state phase transitions such as ß(A2) → ß2(B2) and ß2(B2)→ß2(L21) and ß phase exhibit insTable structure [6-8]. However, when the CuAl alloy is a metasTable phase, a third alloying element is required. That utilizes the sTable ß phase and improve the shape memory properties. This third element can be elements like manganese, nickel, zinc, etc.. Within these elements, manganese element alloying provides the highest damping and ductility [9]. A small change in the chemical composition affects the martensitic transformation temperatures very significantly [10,11]. Therefore, the proportions of the elements in the alloy are very important. At the same time, even if elements such as ferromagnetic Mn and Ni are present in Cu-based alloys, they are temperature-induced SMAs [12]. This will result in aging on the alloy subjected to temperature cycling in applications. As a result of the aging process, changes occur in the properties of the material [13]. Therefore, the end result of the aging process should be well known by the practitioners [14]. In this work, Mn element, which has very effective and useful properties on the binary CuAl alloy, is used. Aging experiments were carried out using three different CuAlMn alloy compositions. The results obtained from the experiments were analysed.

2. Material and Method

In this work, Cu, Al, Mn elements which are powder in 99% purity were used to make Cu-Al-Mn triple shape memory alloy samples with 3 different compositions.

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The weight chemical compositions of alloys are given in Table 1.

Table 1. Cu-Al-Mn chemical composition

Alloy id.	(wt. %)		
	Cu	Al	Mn
CAM-1	84.31	11.34	4.35
CAM-2	83.48	13.38	3.14
CAM-3	80.98	14.25	4.77

The powdery elements were scrapped to a total of 10 gr and homogenously mixed with the Clifton Cyclone brand vortex at predetermined compositions to prepare for pelleting. In the pelletizing process, 10 grams of powder mixtures were pressed under a pressure of 4 MPa with Graseby Specac pressing device. In the flat cylindrical form, 1 cm thick pressed samples were obtained. The pelletized powder mixture was melted and alloyed in an arc melting furnace (Edmund Buehler Arc Melter) shown in Figure 1 at a range of 12-24 V and 75-150 A in an argon gas atmosphere. Each of the three different alloys was cut into 5 equal pieces and prepared for experimental procedures. No aging process was applied to make a comparison to one sample cut from each alloy. 4 of the 5 samples were used for the aging process. One sample for each alloy type is separated as a reference sample.

Figure 1. Edmund Buehler Arc Melter furnace

The ingot was cut into small pieces and prepared for experimental procedures. After the cutting process, (Carbolite CWF-1200) muffle furnace at 900 ° C for 1 hour in the β-phase region. It was then cooled in salted ice water and martensite structures were formed on the sample. In aging experimental, the samples were aged in the ash furnace at 200 ° C, 300 ° C, 400 ° C, 500 ° C for 1 hour. The samples were then cooled in water at room temperature. Following thermal processes on samples, to determine the transformation temperatures of the test samples, measurements were made with differential scanning calorimeter (DSC) Shimadzu DSC-60A. Surface morphology and optical micrographs of materials were obtained by using an Nikon M200 optical micrograph. Furthermore, the crystallographic structural analysis measurements were made with the Rigaku RadB-DMAX II device.

3. Results

3.1. X-Ray Diffraction (XRD) analysis

In this study, X-ray analysis of aged and not aged samples were carried out with a computer aided X-ray diffractometer of Rigaku RadB-DMAX II using CuK_α (λ = 1.5405 Å). It was taken up from 30° to 75°. The planes in the measurements we took at room temperature were determined and plotted on the X-ray diffractogram (Figure 2.). The grain sizes are calculated by using these parameters and all specimens' grain sizes are given Table 2.

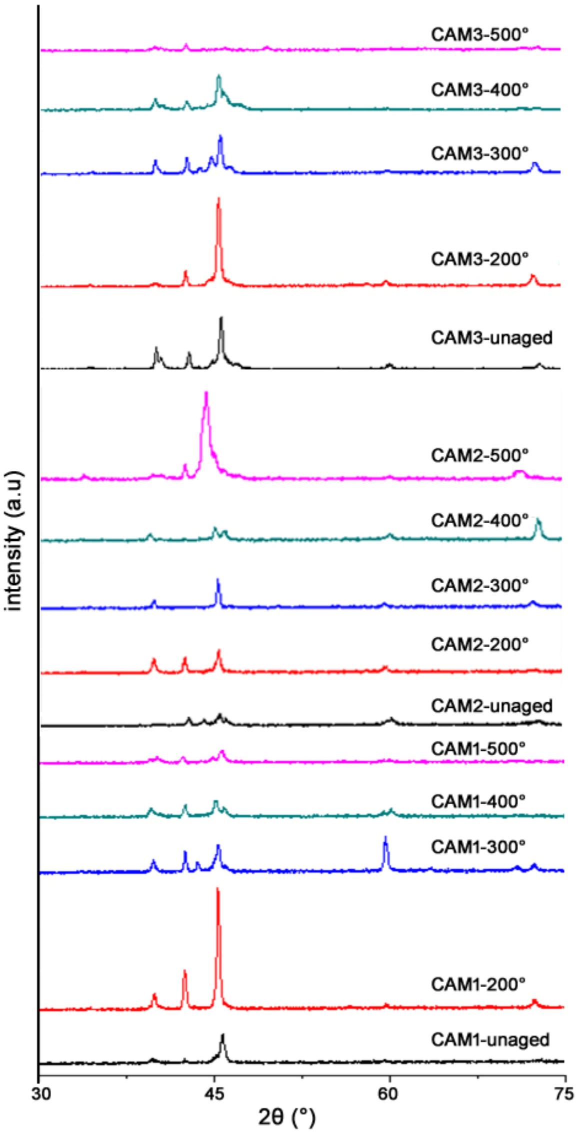

Figure 1. X-ray diffractograms obtained from specimens

The planes and intensities of the Cu-Al-Mn triple shape memory alloys giving the reflection in the X-ray diffractograms were determined. In X-ray measurements, depending on the aging temperature, the sharpness of the aging temperature residue peaks increases and at the same time the severity decreases. Large peaks were observed in the alloys prior to aging, and the peaks nested and not intercalate and split as in the form of halves.

Table 2. All specimens grain sizes obtained from X-ray diffractograms.

Alloy id.	Grain size (nm)
CAM1-unaged	19.37
CAM1-200°	28.70
CAM1-300°	19.74
CAM1-400°	16.69
CAM1-500°	22.89
CAM2-unaged	14.43
CAM2-200°	21.61
CAM2-300°	32.39
CAM2-400°	22.19
CAM2-500°	10.72
CAM3-unaged	20.73
CAM3-200°	24.27
CAM3-300°	22.61
CAM3-400°	16.42
CAM3-500°	12.80

However, the received X-ray diffractometer in the press after aging the alloy is applied at increased sharpness of the peaks and separation began with peaks in the intensity is also decreased. Literature studies have also confirmed that the sharp peaks of the planes obtained from the X-ray diffractometry are planes of the fundamental phases [15-17]. In this work, the basic peaks are (1210), (0022) and (202) planes in X-ray diractograms. The parameters of these reflecting planes are a = 4.494 Å; B = 5.189 Å; C = 46.610 Å. Therefore, it has been determined that these planes have orthorhombic crystal structure. As the aging temperature increases, the intensity of the main peaks decreases and peaks give different reflections. Furthermore, as the aging temperature of Cu-Al-Mn triple alloy increased, grain size changes were detected and these findings were also supported by optical micrograph displays.

3.2. Metallographic observations

Figures 2 shows optical micrographs taken at x100 magnifications of all experimental alloys. The microstructures at room temperature are completely martensitic. Some of these structures are V-type and some are needle-type martensite. In these surface photographs martensite structures also show different orientations. When the surface photographs of the parts of the alloys subjected to aging at temperatures of 200, 300, 400, 500 ° C are examined, the martensite surfaces began to disappear as the grain boundaries gradually became evident in the sample due to the aging temperature. There are also precipitate phases which affect the shape memory effect negatively. Here, the aging temperature increases the precipitation phases and that affects the shape memory effect.

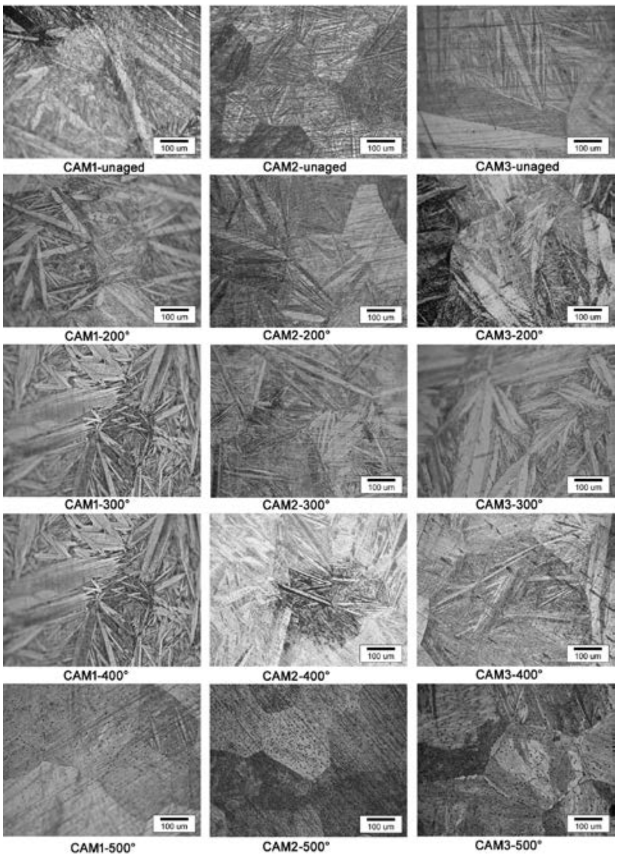

Figure 2. Microstructures of experiment specimens

When the micrographs of the samples aged at 500 ° C are examined, the precipitate phases are clearly visible. It was also found that martensite structures disappeared with increasing aging temperature. It has also been observed that the grain boundaries prior to the alloying aging process have widened and become more pronounced after aging.

These precipitation phases, which are caused by the increase in aging temperature in the alloy, also affect the transformation temperatures and kinetic parameters of the sample. Precipitate phases affect shape memory effect negatively. The shape memory effect is inversely proportional to the ratio of precipitate phases in the material. Therefore, it can be said that there is a relation between the aging temperature and the shape memory effect. As the aging temperature increases, the precipitate phases increase and as the precipitate phases increase, the shape memory feature decreases at that rate [18-20].

3.3. Thermal analysis

In this study, Cu-Al-Mn triple alloy with different composition; DSC (Differential Scanning Calorimetry) measurements were taken with different heating rates to obtain transformation temperatures, enthalpy values. Transformation temperatures were determined against heating rates of alloys 5° C/min. The DSC results are depicted in Table 3 and in Figure3.

Table 3. DSC results of the aging experiments

Alloy id.	**As**	**Af**	**Amax**	**T0**	**ΔHM→A**	**ΔSM→A (J/g°C)**	**Ms**	**Mf**	**ΔHA→M**	**ΔSA→M**
	(°C)	(°C)	(°C)	(°C)	(J/g)		(°C)	(°C)	(J/g)	(J/g°C)
CAM1-unaged	82.99	96.66	91.17	80.98	7.37	0.091	65.31	58.11	-10.77	-0.132
CAM1-200°	79.96	94.5	88.87	77.85	7.51	0.096	61.21	44.01	-9.15	-0.117
CAM1-300°	84.82	95.54	90.94	81.72	8.2	0.1	67.9	60.05	-12.07	-0.147
CAM1-400°	98.49	115	109.4	95.09	6.19	0.065	75.15	49.34	-10.7	-0.112
CAM1-500°	82.96	94.94	90.21	76.58	6.97	0.091	58.22	42.95	-8.7	-0.113
CAM2-unaged	101.5	116.5	109.5	97.41	7.89	0.08	78.35	65.14	-15.87	-0.162
CAM2-200°	101.2	116.5	110.1	97.15	5.94	0.061	77.84	62.89	-13.22	-0.136
CAM2-300°	102.2	118.8	111.2	98.52	7.46	0.075	78.23	64.59	-12.22	-0.124
CAM2-400°	77.53	94.02	86.88	77.92	6.62	0.084	61.82	51.92	-9.98	-0.128
CAM2-500°	95.83	108.9	104	92.28	5.25	0.056	75.66	65.97	-5.48	-0.059
CAM3-unaged	138.1	160.3	151.2	142.3	5.9	0.041	124.2	109.6	-9.82	-0.069
CAM3-200°	125.4	159.6	147	143.5	7.76	0.054	127.3	99.41	-12.82	-0.089
CAM3-300°	132.6	165.4	157	146.1	7.67	0.052	126.7	110.3	-12.45	-0.082
CAM3-400°	122.7	175.3	150.3	151.1	7.19	0.047	127	97.71	-13.87	-0.091
CAM3-500°	144.8	154.7	150.3	140.3	8.52	0.06	125.9	116.1	-10	-0.071

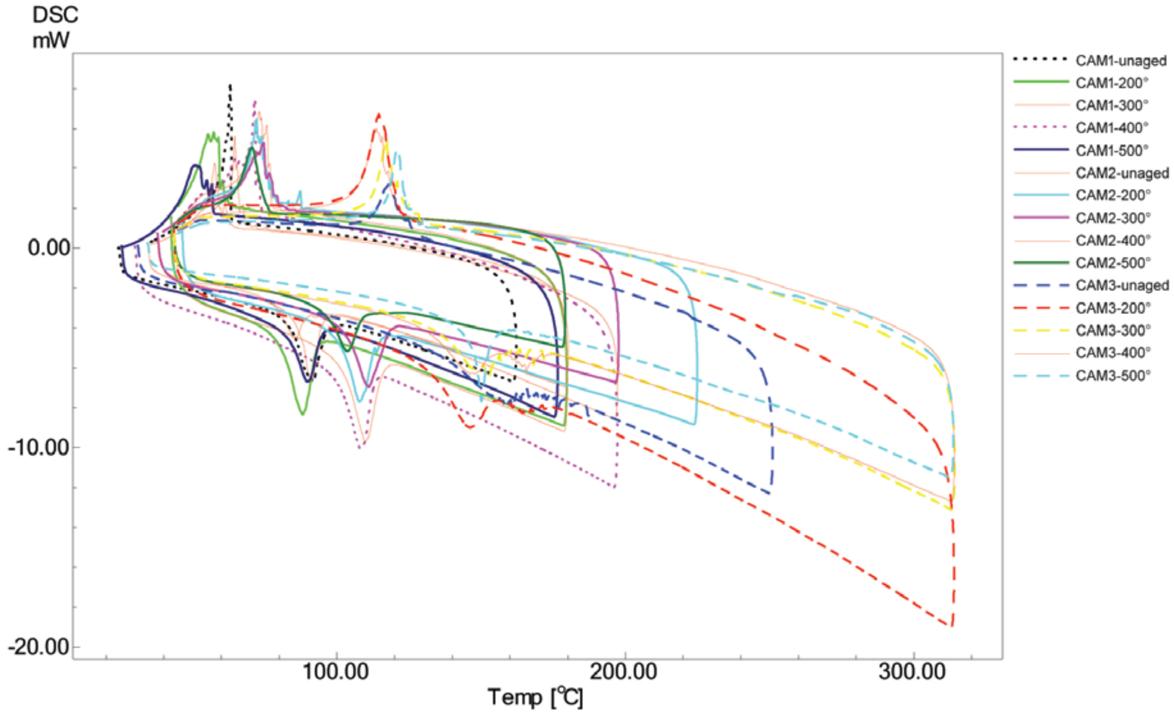

Figure 3. DSC plots of specimens at 5° C/min. heating rate.

DSC measurements of samples aged at 200, 300, 400 and 500 ° C at heating rate of 5° C/minute show that the transformation temperatures increase as aging temperature increasing. In addition to this, the aging temperature, shape memory effects decreases and transformation temperatures increase. This is because of the precipitate phases. This result is supported by optical micrograph images and literature searches. The precipitate phases affect shape memory in adverse ways as well as affect transformation temperatures [19-21].

4. Conclusion

In this study, shape memory alloys with at.% Cu23.01Al4.34Mn, Cu26.56Al3.06Mn and Cu27.96Al4.60Mn composition were obtained by arc melting method. The effect of aging on the transformation temperature (As, Af, Ms, Mf) and the physical properties of aged samples were investigated. At the same time, transformation temperatures before aging of samples and transformation temperatures after aging process were determined and effects of aging on transformation temperatures and physical properties were examined. As a result of the investigations, it was determined that the increase of the aging temperature increased the precipitates in the material, which was adversely affected by the shape memory characteristic.

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