SEM and X-Ray Diffraction Studies on Microstructures in Cu–26.04%Zn–4.01%Al Alloy

E. Aldirmaz[a,*], H. Celik[b] and I. Aksoy[c]

[a]Department of Physics, Faculty of Science and Arts, Amasya University, Ipekkoy, 05000 Amasya, Turkey
[b]Department of Elementary Education, Education Faculty, Kırıkkale University, Yahsihan 71450, Kırıkkale, Turkey
[c]Department of Physics, Science and Arts Faculty of Kırıkkale University, Yahsihan 71450, Kırıkkale, Turkey

Due to fact that Cu-based alloys are very sensitive to the thermal treatments, in scanning electron microscopy and X-ray diffraction observations, according to the different quenching techniques Cu–26.04%Zn–4.01%Al alloys can display different product phases such as martensite and precipitation. Rapidly cooling sample was formed as M18R structure from the ordered DO_3 phase and in the monoclinic case, $\beta = 89.1°$ determined for sample. It was seen that a α-precipitation (fcc) phase in the matrix is slowly cooling.

1. Introduction

Because of copper-based shape memory alloys have a good shape memory effect, they indicates the advantage of a lower price than Ni–Ti shape memory alloys [1]. Copper-based shape memory alloys are very sensitive to the thermal effects before and after the transformation. Therefore these effects may cause important changes on crystallographic properties or the other transformation parameters of the alloys [2]. Cu-based shape memory β-phase alloys exhibit order-disorder transformation at elevated temperatures. Although the β_1-phase is metastable, it remains stable at room temperature upon quenching from the high temperature β-phase [3]. Metastable parent β_1 (B2 or DO_3) and martensitic β_1' (M9R or M18R) phases are transformed to bainitic α_1 (9R), complex cubic γ_2, or fcc α phases by thermally activated processes [4–6]. In the majority of copper-based alloys such as Cu–Zn–Al the bainitic precipitation has been observed. Bainitic transformation occurs in these copper-based alloys, and β-phase forms diffusionally [7]. Since it has a diffusionless nucleation and a diffusion-controlled growth, even so its formation is accompanied by a geometry change characterized as reverse shape memory effect, bainitic transformation is irreversible, in contrast to martensitic transformation [8].

Among various Cu-based ternary shape memory alloys (SMAs), single crystals of Cu–Zn–Al, Cu–Al–Ni and Cu–Al–Mn alloys were most thoroughly investigated. Although there are many studies reporting some physical properties of copper-based alloys, literature reveals no studies on the effects of thermal on microstructure and properties of microstructures for the related composition of alloys. In our study microstructures of martensites and precipitates formation in the related alloys were reported in detail.

2. Experimental details

The composition of the alloy used in the present study was Cu–26.04%Zn–4.01%Al (wt%) which were prepared by vacuum induction melting under an argon atmosphere from pure (99.9%) alloying elements. After this alloying, product alloy was used in the form of cylindrical bars with 1 cm diameter and 10 cm length. Samples cut from the alloy were heated in evacuated quartz tubes in an Ar atmosphere and immediately quenched into iced-brine rapidly cooling or in furnace cooled slowly cooling for homogenization. First group of samples were homogenized at 850 °C for 30 min and quenched into iced-brine water (sample A), the second group of samples were homogenized at 850 °C for 30 min and furnace cooled to 25 °C at a rate of approximately 2 °C/min and then air cooled (sample B). Bulk samples used in the scanning electron microscopy (SEM) observations were mechanically polished and etched into a solution composed of 2.5 g $FeCl_3 \cdot 6H_2O$ and 48 ml methanol in 10 ml HCl. SEM observations were made under a JEOL 5600 scanning microscope operated at 20 kV. X-ray diffraction patterns of the powder samples were taken by a Bruker D8 Advance diffractometer. For these examinations, the monochromatic copper K_α radiation with wavelength of 1.5418 Å was used, a step size of 0.02°.

3. Results and discussion

The microstructures of the sample A that were quenched directly into iced-brine water are shown in Fig. 1a–c. The sample that were quenched into iced-brine water show a microstructure that is fully martensitic. Martensites appear to the typical morphology of β_1' martensite. Martensite plates are formed in a V-shape

*corresponding author; e-mail: ealdirmaz@gmail.com

in some grains while they occur needle-like in others (Fig. 1a) [9]. This kind of needle-like martensite in Cu–Zn–Al alloy has been reported until now (Fig. 1b) [2]. As seen from Fig. 1c SEM micrograph shows self-accommodating martensite plate groups. The fundamental grade of the shape memory effect can be illustrated by self-accommodation mechanism. Self-accommodating martensitic transformation involves plate groups, and each of them contains four "cooperating" martensite variants [10, 11]. Figure 1d shows α-precipitation (fcc) phase in the matrix, the morphological structures about surface observation which has got over by cooling gradually Cu–Zn–Al shape memory alloy (sample B). The precipitation kinetics of Cu–Zn–Al alloys are very sensitive to zinc and aluminum content. Moreover, the precipitation of α or other phases causes a degradation in the shape memory capability and decreases of the forward--transformation temperatures. This effect is related to the interaction of martensite interfaces with the precipitates and defects. Decrease of aluminum content in shape memory Cu–Zn–Al alloys accelerates the formation of both α and α_1 phases. The high shape-memory life of Cu–Zn–Al alloys at high temperatures can be obtained by increasing the Al content. These results are in agreement with the observations made previously [12–14].
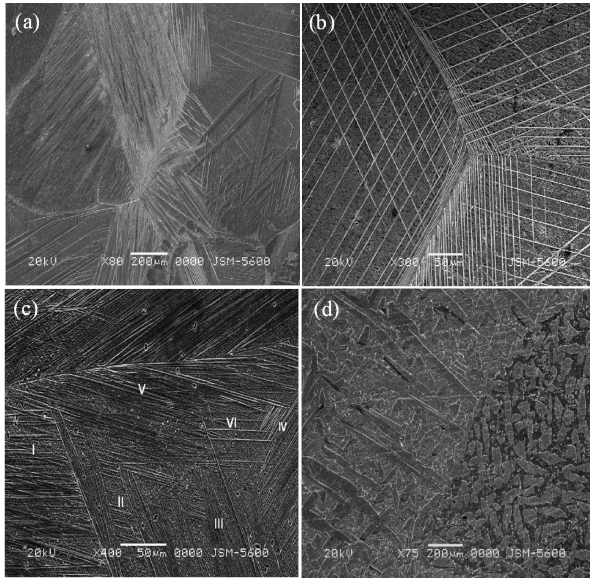

Fig. 1. SEM micrographs showing the microstructures of the alloy 2: (a) V-type and needle-like martensites in different grain, (b) needle-like martensites, (c) β_1' martensite self-accommodating variants, and (d) α precipitates in parent phase.

In order to determine the crystal structure of the Cu–Al–Zn alloys in the martensite state, X-ray diffraction (XRD) samples were taken. Typical X-ray powder diffraction profiles taken from the samples of alloy are shown in Fig. 2. The measured d values (d_m) of each diffraction peak, its relative integrated intensities and hkl planes measured are shown in Tables I and II, respec-
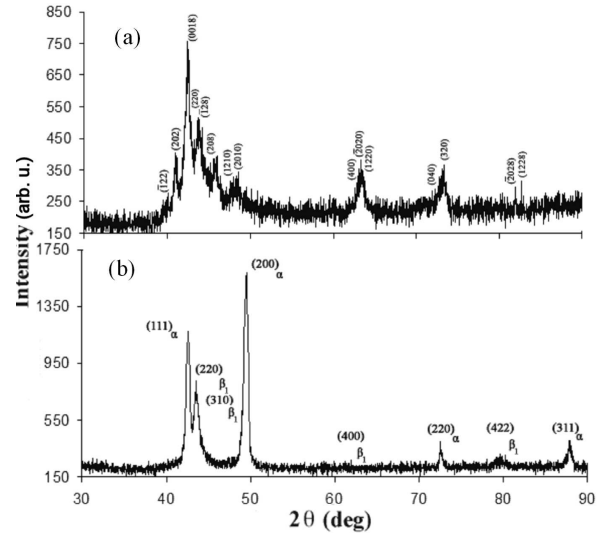

Fig. 2. X-ray powder diffractograms of the samples of alloy: (a) sample A, (b) sample B.

tively, for sample A and B. As seen from these diffractograms, the alloys exhibit superlattice reflections in the quenched case. Sample A, only β_1' martensite is formed, γ_1' martensite phase was not detected (Fig. 2a).

TABLE I

The values of the 2θ angles, intensities of X-ray diffraction and the Miller indices of the crystal lattice planes that contribute to the X-ray peaks for sample A.

2θ [°]		d [Å]		I/I_0		(hkl)	
M18R	DO$_3$	M18R	DO$_3$	M18R	DO$_3$	M18R	DO$_3$
40.18	43.60	2.2442	2.0758	278	442	$(\bar{1}22)$	220
40.96	63.36	2.2033	1.4679	407	343	(202)	400
42.44		2.1298		758		(0018)	
44.20		2.0490		483		$(\bar{1}28)$	
45.28		2.0026		373		(208)	
46.88		1.9379		285		(1210)	
47.64		1.9088		308		(2010)	
63.54		1.4462		305		$(\bar{2}020)$	
64.00		1.4549		285		(1220)	
72.10		1.3099		262		(040)	
73.42		1.2896		320		(320)	
82.00		1.1750		297		$(\bar{2}028)$	
82.76		1.1662		317		(1228)	
DO$_3$	$a = 5.871$ Å						
M18R	$a = 4.445$ Å, $b = 5.240$ Å, $c = 38.350$ Å, $\beta = 89.1°$						

The martensitic phase in copper based β-phase alloys is based on one of the $\{110\}_\beta$ basal planes. In the case where the constituent atoms are randomly distributed in the basal plane, the ratio a/b of the lattices parameters should be equal to $\sqrt{3}/2$, while the value of this ratio is less than $\sqrt{3}/2$ in the ordered case due to the atomic sizes of the constituent atoms for 18R martensite [15–17]. The ratio of a/b for sample A was determined as 0.84. As a result of this ratio, product martensite with 18R structure was formed from the ordered DO$_3$ phase [3]. Thus, the sample A has an ordered state inherited from the or-

TABLE II

The values of the 2θ angles, intensities of X-ray diffraction and the Miller indices of the crystal lattice planes that contribute to the X-ray peaks for sample B.

Precipitation-phase (fcc) α-phase				Parent-phase (bcc) β_1-phase			
2θ [°]	d [Å]	I/I_0	(hkl)	2θ [°]	d [Å]	I/I_0	(hkl)
42.54	2.1250	1104	(111)	43.62	2.0749	771	(220)
49.54	1.8399	1479	(200)	49.08	1.8561	625	(310)
72.66	1.3012	293	(220)	63.38	1.4675	213	(400)
88.02	1.1095	320	(311)	80.08	1.1983	237	(422)
$a = 3.68$ Å				$a = 5.87$ Å			

dered parent phase existing prior to the transformation. Monoclinic distortion takes place in some cases, and 18R structure is modified as M18R [15]. The normal structure is orthorombic samples, whereas the modified version is monoclinic [18].

In the monoclinic case, $\beta = 89.1°$ determined for sample A. The deviation observed in the angle is very little and shows that the long range order has a excellent DO_3 order. If the monoclinic angle of the quenched martensite, β, is 90° (orthorhombic) or very close to 90°, the transition from monoclinic to orthorhombic would be restrained, but it would be difficult for the martensite stabilization to occur during aging in the martensite state, these results are in agreement with the observation made by other work [19]. The lattice parameters calculated from these profiles of sample A were $a = 4.43$ Å, $b = 5.67$ Å and $c = 4.85$ Å. XRD observations showed that phase transformation occurred in sample B (Fig. 2b). Figure 2b shows that the precipitates are seen that in sample B were observed as α-phase. The α-phase is the cubic fcc copper-rich solid solution [20]. It was detected as fcc α-phase with parameter $a = 3.68$ Å.

Although all of the diffractograms exhibit similar characteristics, some changes have been observed in peak locations on the diffractograms with thermal treatment and the differences in lattice constants [15]. These changes are attributed to new transitions which have diffusive character. It can be explained that some neighbour atoms change locations and also some of the neighbour peak pairs have moved toward each other [21].

4. Conclusions

It can be concluded from the above results that the copper based shape memory alloys are very sensitive to the thermal treatments. In the present work, mono-

clinic martensitic structure M18R was observed in step--quenched samples of alloy. Direct quenching into an iced-brine water results in the formation of 100% martensite, whereas quenching into other slowly, such as furnace cooled, results in the conversion of some amount of austenite into α precipitates.

References

[1] F.J. Gil, J. Pena, J.M. Guillemany, *J. Mater. Synth. Proc.* **7**, 127 (1999).

[2] Ş.N. Balo, M. Ceylan, M. Aksoy, *Mater. Sci. Eng. A* **311**, 151 (2001).

[3] A. Aydoğdu, Y. Aydoğdu, O. Adıgüzel, *Mater. Res. Bull.* **32**, 507 (1997).

[4] N.F. Kennon, D.P. Dunne, L. Middleton, *Metall. Trans.* **13A**, 551 (1982).

[5] Y.S. Han, Y.G. Kim, *J. Mater. Sci.* **21**, 2711 (1986).

[6] M.M. Reyhani, P.G. McCormick, *Scr. Metall.* **20**, 571 (1986).

[7] Y.S. Han, Y.G. Kim, *Scr. Metall.* **21**, 947 (1987).

[8] H. Pops, in: *Shape Memory Effects in Alloys*, Ed. J. Perkins, Plenum Press, New York 1975, p. 525.

[9] F. Dagdelen, T. Gokhan, A. Aydogdu, Y. Aydogdu, O. Adiguzel, *Mater. Lett.* **57**, 1079 (2003).

[10] T. Saburi, C.M. Wayman, K. Takata, S. Nenno, *Acta Metall.* **28**, 15 (1980).

[11] T. Saburi, C.M. Wayman, *Acta Metall.* **27**, 979 (1979).

[12] S.S. Leu, C.T. Hu, *Metall. Trans.* **22A**, 25 (1991).

[13] V. Sampath, *Mater. Manufac. Proc.* **22**, 9 (2007).

[14] N.B. Pugacheva, *Metal Sci. Heat Treatment* **49**, 67 (2007).

[15] O. Adıgüzel, *Mater. Res. Bull.* **30**, 755 (1995).

[16] Q. Xuan, J. Bohong, T.Y. Hsu, *Mater. Sci. Eng.* **93**, 205 (1987).

[17] N. Kayali, S. Ozgen, O. Adiguzel, *Mater. Res. Bull.* **32**, 569 (1997).

[18] O. Adıgüzel, *Commun. Fac. Sci. Ankara, Series A2, A3* **36**, 47 (1987).

[19] J. Van Humbeeck, M. Chandrasekaran, L. Delay, *ISIJ Int.* **29**, 388 (1989).

[20] J. Hirsch, K. Lucke, M. Hatherly, *Acta Metall.* **36**, 2905 (1988).

[21] O. Adiguzel, *J. Mater. Proc. Technol.* **185**, 120 (2007).