Lattice Changes in Shape Memory CuZnAl Alloys on Aging at Room Temperature

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Abstract

The aging behavior of CuZnAl martensites (Cu-21.62 wt.% Zn-5.68 wt.% Al and Cu-24.98 wt.% Zn-4.43 wt.% Al) at about 297 K was studied by analyzing diffraction line profiles obtained by X-ray diffractometry. For the alloys, the change of the lattice parameters and the tetragonality associated with the aging time at room temperature were investigated. The habit planes versus the aging time at room temperature were calculated using the De Vos-Aernoundt-Delaey model, based on the crystallographic theory of Wechsler-Lieberman-Read(WLR), and from the $DO_3 \rightarrow 18R$ martensite transformation theory.

1. Introduction

Internally faulted martensites in CuZnAl alloys are characterized by a long period stacking order, such as the 9R or 18R type structures, depending on the number of close-packed layers in direction $[001]_{\beta'}$ in the unit cell. The faulted 18R martensite have long-period stacking order structures with a nearly close-packed basal plane $\{0018\}_m$, which originates from a $\{110\}_p$ plane of the parent phase. In the CuZnAl alloy system, a martensitic transformation from the B2 ordered parent phase to the 9R martensite occurs, whereas the DO_3-type ordered parent phase transforms into the 18R martensite. The stacking sequences of close-packed layers for the 9R and 18R martensite structures are $ABC/BCA/CAB$ and $AB'C/B'CA'/CA'B/A'BC'/BC'A/C'AB'$, respectively. For the 18R martensite in the CuZnAl alloys, it is known that the a-axis direction, and thus the actual structure, is not an ideal (or normal) 18R but a monoclinically modified 18R. The normal structure (N9R or N18R) is orthorhombic, whereas the modified version

(M9R or M18R) is monoclinic.

The distortion of the close-packed hexagon in the close-packed plane leads to a deviation from the ideal b/a and c/a ratios. The ratios between the lattice parameters in the case of an ideally close packed 18R structure are $a : b : c = 1 : 1.155 : 8.485$ [1,2]. Martensitic transformations do not permit a rearrangement of atoms on the martensitic lattice sites due to the diffusionless nature. The martensite is free, however, to adjust to the most favorable lattice spacing, provided the atomic volume remains nearly constant during the transformation, according to observations performed on CuZnAl alloys [3,4].

The deviation of tetragonality Ψ from the ideal value 1 cannot be explained by an ordered array of hard spheres of different sizes, since Ψ depends strongly on the stacking sequence of the basal plane, whereas Ψ for the 18R martensites in CuZnAl is approximately 1 [5]. The tetragonality Ψ is calculated from the lattice parameters of monoclinic 18R cell in the basal plane, according to $(2a/b) = \sqrt{1 + 2\Psi^2}$ [4].

In a previous report [6], the present authors investigated cycling effects on transformation behaviour in shape memory CuZnAl alloys. The purpose of the present paper is to investigate the lattice changes of the martensites vs. aging at room temperature. The lattice parameters of the martensite were calculated from X-ray diffraction peaks in the diffractograms.

The crystallography of the martensitic transformation from the DO_3-type structure to the modified monoclinic 18R structure in the alloys was calculated by computer using the De Vos-Aernoudt-Delaey model [7,8], based on the crystallographic WLR theory. Cakmak and Artunc [9] applied Suzuki's martensite crystallographic theory [10,11] to calculate the martensitic crystallography of $DO_3 \rightarrow 18R$ transformation in FeMnAlC [12]. In this paper, De Vos-Aernoudt-Delaey model is applied to calculate the martensitic crystallography for $DO_3 \rightarrow 18R$ transformation in CuZnAl alloys, to compare with the crystallography obtained from Cakmak-Artunc calculations [9].

2. Experimental Procedure

Two shape memory actuators of CuZnAl alloy were supplied by Delta Materials Research Ltd., Ipswich, England. These alloys originally have been given the closed-coil form deforming in martensitic condition after quenching from the β-phase region. The compositions of the alloys which are labeled as Alloy 1 and Alloy 2 are Cu-24.98 wt.%Zn-4.43 wt.%Al and Cu-21.62 wt.%Zn-5.68 wt.%Al, respectively. The electron concentrations of these alloys e/a are calculated to be 1.4286 and 1.4462, and M_s temperatures are measured to be $40.3°C$ and $32.4°C$ by means of electrical resistivity measurements, respectively.

Powder specimens for X-ray diffraction studies were prepared by filing some parts of alloys. The specimens were then heated in evacuated quartz capsules at 820°C for 20 minutes and immediately quenched into iced brine to produce martensite and remove the strain effect produced during the filing processes. The following post-quench heat treatments were applied on the quenched powder specimens:

(a) Aging at room temperature after quenching from 820°C

(b) Aging at room temperature after an intermediate anneal at 100°C for 30 minutes and quenching.

X-ray diffraction profiles were taken immediately after quenching and annealing treatments. The specimens were then kept at room temperature and the profiles were taken at intervals.

X-ray profiles were taken with cobalt K_α radiation with wavelength 1.7902 Å and automatically recorded on a Philips PW 1050 X-Ray Diffractometer. A nickel filter was used to eliminate the K_β radiation. The scanning speed of the Geiger counter was fixed at 2°, $2\theta/min$ for all the diffractograms.

3. Results and Discussion

In order to determine the crystal structure and lattice parameters of the alloys used in the present study, x-ray diffractograms were taken from the powder specimens of the alloys. The lines observed in the diffractograms given elsewhere [13] were identified as M18R martensite superlattice reflections and indexed on the monoclinic base. The experimental results obtained for lattice parameters of the monoclinic unit cell and stabilization treatments for each sample are given in Table 1. The lattice parameters a and b lie on the basal plane, the parameter c corresponding to the 18R close-packed layers, makes an angle β different from 90°. The lattice parameter a_β of the DO_3 parent phase used for the calculation was taken from Cakmak et al. [14], namely, $a_\beta = 5.87$ Å. This lattice constant was assumed to be invariant for CuZnAl alloys listed in Table 1.

The changes in tetragonality Ψ against the aging time at room temperature after quenching and post-quench aged treatments are plotted in Figure 1 for Alloy 1 and Alloy 2, respectively. They show a trend to increase with holding time at room temperature and this increase is larger in the initial stages of aging. However, changes in Ψ for both alloys are constant after aging for 48 h at room temperature. Another interesting observation is that as-quenched and post-quenched β-phase annealed specimens show the same trend in Ψ changes with the effect of aging at room temperature. Long-term aging (400 h or more) results in almost the same value of Ψ for both as-quenched and post-quenched aged specimens for both alloys.
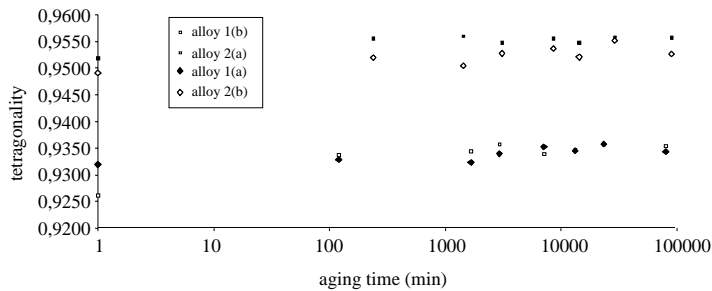

Figure 1. Change of the tetragonality of martensite vs aging time at room temperature

Table 1. Experimental results for the lattice parameters of the monoclinic unit cell and stabilization treaments in Cu-21.68Zn-5.68Al(wt.%) and in Cu-21.68Zn-5.68Al(wt.%) and Cu-24.98Zn-4.43Al(wt.%) alloys.

	e/a	C_{Zn} (wt.%)	C_{Al} (wt.%)	18R stabilization treatment	a (nm)	b (nm)	c (nm)	β (°)	a:b:c	Ψ	V ($10^{-3}\times$ nm³)
1 (a)	1.45	24.98	4.43	0 h-25°C	0.44752	0.53380	3.82066	88.6493	1:1.2090:8.6534	0.9318	909.9424
				2 h-25°C	0.44153	0.53344	3.82076	88.5856	1:1.2082:8.6535	0.9328	910.1826
				28 h-25°C	0.44157	0.53372	3.82099	88.4516	1:1.2087:8.6532	0.9322	906.2955
				48.5 h-25°C	0.44209	0.53372	3.82368	88.5626	1:1.2073:8.6491	0.9339	911.0934
				120.5 h-25°C	0.44224	0.53344	3.82779	88.5850	1:1.2062:8.6555	0.9352	913.3587
				220.5 h-25°C	0.44187	0.53328	3.82496	88.6634	1:1.2069:8.6563	0.9344	907.8868
				390 h-25°C	0.44080	0.53148	3.80103	88.4395	1:1.2057:8.6230	0.9358	903.4085
				1350 h-25°C	0.44159	0.53300	3.82143	88.6206	1:1.2070:8.6538	0.9342	907.7332
1 (b)	1.45	24.98	4.43	0 h-25°C	0.44735	0.53322	3.82004	89.1305	1:1.1926:8.5393	0.9519	900.2158
				3.5 h-25°C	0.44760	0.53252	3.81988	89.3118	1:1.1897:8.5341	0.9555	899.6285
				24 h-25°C	0.44685	0.53148	3.81288	89.0900	1:1.1894:8.5328	0.9559	900.1820
				52 h-25°C	0.44737	0.53252	3.81668	88.9149	1:1.1903:8.5314	0.9547	901.9221
				144 h-25°C	0.44803	0.53300	3.83303	89.1003	1:1.1897:8.5553	0.9556	902.7329
				239 h-25°C	0.44749	0.53268	3.81329	88.7651	1:1.1904:8.5215	0.9547	901.0700
				484 h-25°C	0.44694	0.53160	3.80588	88.9135	1:1.1894:8.5154	0.9559	890.1613
				1516 h-25°C	0.44774	0.53260	3.82082	89.0760	1:1.1895:8.5336	0.9557	899.1797
2 (a)	1.43	21.68	5.68	0 h-25°C	0.44077	0.53496	3.81453	88.0832	1:1.2137:8.6542	0.9261	898.9412
				2 h-25°C	0.44166	0.53328	3.82436	88.5912	1:1.2075:8.6591	0.9337	900.4733
				28 h-25°C	0.44175	0.53312	3.82117	88.3581	1:1.2068:8.6501	0.9345	899.5381
				48.5 h-25°C	0.44181	0.53272	3.81871	88.5239	1:1.2058:8.6443	0.9358	898.4772
				120.5 h-25°C	0.44169	0.53328	3.82248	88.4258	1:1.2074:8.6542	0.9338	900.0241
				220.5 h-25°C	0.44185	0.53316	3.82169	88.4670	1:1.2067:8.6493	0.9347	899.9791
				390 h-25°C	0.44128	0.53208	3.81205	88.2367	1:1.2058:8.6386	0.9358	894.6313
				1350 h-25°C	0.44173	0.53276	3.82104	88.4259	1:1.2061:8.6502	0.9354	898.8892
2 (b)	1.43	21.68	5.68	0 h-25°C	0.44674	0.53276	3.82365	89.1305	1:1.1926:8.5340	0.9491	911.6246
				3.5 h-25°C	0.44728	0.53276	3.82005	89.3118	1:1.1911:8.5406	0.9519	910.4255
				24 h-25°C	0.44705	0.53176	3.81321	89.0900	1:1.1895:8.5287	0.9504	905.4137
				52 h-25°C	0.44776	0.53252	3.82154	88.9149	1:1.1893:8.5348	0.9527	909.0979
				144 h-25°C	0.44783	0.53376	3.82159	89.1003	1:1.1919:8.5336	0.9537	915.2147
				239 h-25°C	0.44721	0.53200	3.81644	88.7651	1:1.1896:8.5339	0.9521	908.7589
				484 h-25°C	0.44662	0.53168	3.80536	88.9135	1:1.1905:8.5204	0.9552	904.0890
				1516 h-25°C	0.44712	0.53252	3.81323	89.0760	1:1.1910:8.5284	0.9526	911.0184

For each sample the electron concentration e/a and composition are given and are not repeated for all experiments with the same sample.

The calculated theoretical results of habit planes for the lattice parameters of the monoclinic unit cell and the stabilization treatments for each specimen are given in Table 2. As seen from this table, the solutions of habit plane from the calculation of martensitic crystallographic theories [7-9] are nearly equal each other in the theoretical and calculated cases. In the consequence of different thermal processes, in the alloys of the same composition of CuZnAl, we consider the stabilization treatments of the 18R, while the average value of the habit plane for alloy 1 becomes (1 4.304 ± 0.139 4.296 ± 0.208) at the result of the process a, this value becomes (1 3.383 ± 0.119 3.580 ± 0.194) at the result of the process b. Similar variations occur at the alloy 2. According to this data,

Table 2. Calculated values of habit plane using De Vos-Aernoudt-Delaey[7,8] and Cakmak-Artunc[9] crystallographic calculations in Cu-21.68Zn-5.68Al(wt.%) and Cu-24.98Zn-4.43Al (wt.%) alloys.

Alloy no	C_{Zn} (wt.%)	C_{Al} (wt.%)	18R stabilization treatment	(hkl) habit plane De Vos et al.			(hkl) habit plane S.çakmak et al.			Difference (°)
1 (a)	24.98	4.43	0 h-25°C	(1	4.376	4.395)	(1	4.330	4.338)	0.129
			2 h-25°C	(1	4.330	4.339)	(1	4.342	4.337)	0.139
			28 h-25°C	(1	4.395	4.414)	(1	4.323	4.331)	0.176
			48.5 h-25°C	(1	4.390	4.468)	(1	4.340	4.405)	0.140
			120.5 h-25°C	(1	4.554	4.675)	(1	4.501	4.609)	0.131
			220.5 h-25°C	(1	4.514	4.577)	(1	4.467	4.519)	0.120
			390 h-25°C	(1	3.801	3.527)	(1	3.749	3.465)	0.201
			1350 h-25°C	(1	3.644	3.467)	(1	4.378	4.367)	2.453
1 (b)	24.98	4.43	0 h-25°C	(1	3.437	3.685)	(1	3.425	3.669)	0.050
			3.5 h-25°C	(1	3.433	3.657)	(1	3.426	3.648)	0.030
			24 h-25°C	(1	3.360	3.463)	(1	3.344	3.446)	0.054
			52 h-25°C	(1	3.373	3.559)	(1	3.355	3.534)	0.065
			144 h-25°C	(1	3.743	4.135)	(1	3.729	4.115)	0.050
			239 h-25°C	(1	3.266	3.429)	(1	3.208	3.374)	0.204
			484 h-25°C	(1	3.164	3.167)	(1	3.147	3.191)	0.361
			1516 h-25°C	(1	3.440	3.680)	(1	3.427	3.662)	0.060
2 (a)	21.68	5.68	0 h-25°C	(1	4.221	4.181)	(1	4.131	4.070)	0.276
			2 h-25°C	(1	4.534	4.578)	(1	4.481	4.514)	0.134
			28 h-25°C	(1	4.377	4.388)	(1	4.309	4.304)	0.188
			48.5 h-25°C	(1	4.274	4.248)	(1	4.221	4.183)	0.156
			120.5 h-25°C	(1	4.441	4.468)	(1	4.378	4.390)	0.170
			220.5 h-25°C	(1	4.377	4.400)	(1	4.318	4.327)	0.164
			390 h-25°C	(1	4.124	3.985)	(1	4.052	3.897)	0.234
			1350 h-25°C	(1	4.389	4.383)	(1	4.327	4.307)	0.172
2 (b)	21.68	5.68	0 h-25°C	(1	3.642	3.883)	(1	3.629	3.865)	0.052
			3.5 h-25°C	(1	3.469	3.692)	(1	3.456	3.675)	0.051
			24 h-25°C	(1	3.338	3.459)	(1	3.317	3.430)	0.105
			52 h-25°C	(1	3.461	3.708)	(1	3.447	3.687)	0.068
			144 h-25°C	(1	3.416	3.702)	(1	3.401	3.862)	1.324
			239 h-25°C	(1	3.400	3.563)	(1	3.388	3.547)	0.053
			484 h-25°C	(1	3.181	3.217)	(1	3.159	3.188)	0.112
			1516 h-25°C	(1	3.309	3.455)	(1	3.287	3.425)	0.104

we have concluded that the habit plane of an alloy subjected to a direct quench and aging process will differ slightly from the habit plane of that same alloy subjected to an intermediate anneal before the aging process.

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