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Effect of cooling rate on the order in martensite of a Cu-Zn-Al alloy

LI ZHOU, WANG MINGPU, GUO MINGXING, CAO LINGFEI, JIANG XIANLIANG
School of Materials Science and Engineering, Central South University, Changsha 410083, People's Republic of China
E-mail: lizhou6931@sina.com

The martensite structure and order state of Cu-18Zn-14Al alloy was studied by means of X-ray diffraction. The alloy was subjected to four different quenching treatments. As the quenching rate decreased, the nnn order degree of the alloy increased and the nn order degree remained almost unchanged. The splitting parameter $\rho = |\sin^2\theta_1 - \sin^2\theta_2|$ and the monoclinic angle β changed very little. In addition, the order state of the alloy was calculated according to its crystal structure model. It is suggested that only the Zn and Al atoms exchange along the *b*-axis as the nnn order decreases, which slightly influences crystal symmetry and lattice constant.

1. Introduction

Cu-based alloy has shape memory effect (SME), which comes from the thermoelastic martensite transformation and reversion. Many investigations have been carried out on the martensite structure and its change, especially on its order state [1–10]. The order state of the as-prepared alloy depends on at least two factors, the composition of the alloy and the quenching rate, regardless of its work history such as thermal cycling, aging and action of stresses. The order state of the martensite structure in the Cu-based shape memory alloy is expressed in two ways [11–14]: (1) the relative integrated intensity of (111), (019), (108), (1010), (020) super-structure diffraction peaks of the martensite; (2) the splitting parameter of (12L) and $(20\bar{L})$, (04L) and (32L), or $(32\bar{L})$ diffraction pairs: $\Delta d = (d_1 - d_2)$, $\rho = |\sin^2\theta_1 - \sin^2\theta_2|$, or the monoclinic angle β. Whether there is an inherent relation between the two ways is not yet clear. The above mentioned parameters of the Cu-18Zn-14Al (at%) alloy were subjected to four different quenching treatments and measured by X-ray diffraction. The order state of the martensite structure and its characterization will be discussed in this paper.

2. Experimental

The test alloy Cu-18Zn-14Al (in atomic fraction) was first melted in an induction furnace, then cast into flat ingots, homogenized at 1123 K for 24 h, and finally hot-rolled into sheets of 1 mm thick after the surface defects of the ingots were cut off. X-ray diffraction experiments and data processing were performed on a D-5000 diffractometer using powder specimens, the powders of which had passed through 200-mesh sieve. The powder specimens were solution-treated at 1073 K for 10 min in a sealed quartz tube filled with argon, followed by four different quenching treatments, (1) quenching into 0°C-salt water (fast-quenching), (2) quenching into 0°C-salt water then putting into 100°C water immediately and holding for 30 min (fast-quenching/aging), (3) quenching into 100°C water (slowly-quenching), (4) air-quenching. In order to precisely obtain the intensity of (111), (019), (020) peaks superstructure diffractions, the following measurements were taken. Their integrated intensity was measured up to 10^5 X-ray counts so that the statistical errors $\sigma = 1/\sqrt{N} \leq 0.3\%$. The sample was measured several times. Each time the powder was poured out of the sample box and filled in it again in order to make the fluctuation $\leq 0.2\%$.

3. Results

Fig. 1 shows the X-ray diffraction patterns of the test alloy, with four different quenching treatments. The figure indicates that the martensite produced by these treatments has an M18R structure. The position of the peak-pairs of (12L) and $(20\bar{L})$ as well as (04L) and (32L) vary slightly. The experimental values d_{obs} and the relative integrated intensities of all the diffraction peaks were measured and listed in Table I. The lattice parameters, determined using the measured values d_{obs}, were given in Table I. Using the lattice parameters, the calculated values d_{cal} are obtained, which were also listed in Table I. It can be seen that the d_{cal} coincides with the d_{obs}.

The relative integrated intensity of the (111), (019), (020) super-structure diffraction peaks of the martensite, with four different quenching treatments was measured and listed in Table II. With the decrease of quenching rate, the relative integrated intensity of the (111), (019) increases slowly, but the relative integrated intensity of the $(10\bar{8})$, (1010), (020) peaks remain unchanged, within the test error.

The change of Δd $(=(d_1 - d_2))$, and $\rho(=|\sin^2\theta_1 - \sin^2\theta_2|)$ between (1210) and (2010), (1216) and (2016), (040) and (320) and the monoclinic angle β with the

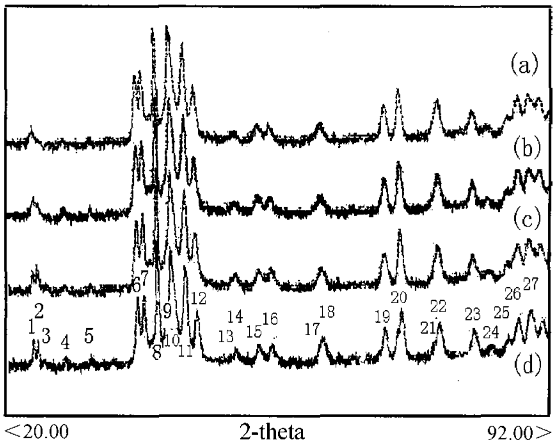


Figure 1 X-ray diffraction spectrum of air-quenched martensite of Cu-18Zn-14A1: (a) Fast-quenching, (b) Fasr-quenching/aging, (c) lowly-quenching, and (d) Air-quenching.

variation of quenching rate were measured and listed in Table III. Within the test error, the Δd value of each peak-pair remains unchanged and the ρ value and the monoclinic angle β change slightly.

4. Discussion

With the decrease of cooling rate, the relative integrated intensity of the (111) and (019) super-structure diffraction peaks of the martensite given in Table II increases, but the Δd values between (1210) and (2010), (1216) and (2016), (040) and (320) listed in Table III remain unchanged. Therefore the order degree change of the martensite of the alloy that is expressed by the change of the relative integrated intensity of the (111), (019) super-structure diffraction peaks, can not be represented by Δd values. For the Cu-Zn-Al alloys, such as Cu-17.4Zn-13.0Al (at%) alloy [15], Cu-10.0Zn-19.0Al (at%) alloy [16] and Cu-20.99Zn-5.35Al (wt%) alloy [17], the stabilization of martensite occurred when they were aged in the martensite state for some time, and the Δd value of each peak-pair between (1210) and (2010), (1216) and (2016), (040) and (320) changed obviously, i.e., the peak-pairs of (12L) and $(20\bar{L})$ as well as (04L) and (32L) of the martensite were separated, then their Δd values of each peak-pair above tended to be zero during aging in the martensite state for some time. Hereby, the change of the nnn order degree of the

TABLE I The X-ray diffraction data of M18R martensite in the Cu-18Zn-14Al alloy

	Station Lattice parameter (mm)	Quick-quenching $a = 0.4427, b = 0.5337, c = 3.826, \beta = 88.1°$		Quick-quenching/aging $a = 0.4423, b = 0.5333, c = 3.826, \beta = 88.71°$		Slowly-quenching $a = 0.4423, b = 0.5333, c = 3.826, \beta = 88.71°$		Air-quenching $a = 0.4419, b = 0.5331, c = 3.822, \beta = 88.64°$	
No.	Diffraction index	*d* (mm) measurement	*d* (mm) calculation	*d* (mm) measurement	*d* (mm) calculation	*d* (mm) measurement	*d* (mm) calculation	*d* (mm) measurement	*d* (mm) calculation
1	111	0.340	0.3398	0.340	0.3396	0.339		0.339	0.3394
2	019	0.332	0.3325	0.332	0.3324	0.332		0.332	0.3321
3	108	0.321	0.3215	0.321	0.3211	0.321		0.321	0.3206
4	1010	0.293	0.2924	0.293	0.2926	0.293		0.293	0.2925
5	020	0.267	0.2669	0.267	0.2667	0.267		0.267	0.2666
6	122	0.2266	0.2266	0.2265	0.2264	0.2265		0.2265	0.2263
7	202	0.2201	0.2204	0.2201	0.2202	0.2201		0.2200	0.2200
8	0018	0.2125	0.2125	0.2125	0.2125	0.2125		0.2123	0.2123
9	128	0.2048	0.2053	0.2047	0.2051	0.2047		0.2045	0.2049
10	208	0.2025	0.2024	0.2024	0.2024	0.2024		0.2022	0.2023
11	1210	0.1975	0.1971	0.1972	0.1971	0.1972		0.1970	0.1970
12	2010	0.1901	0.1899	0.1898	0.1896	0.1898		0.1895	0.1893
13	1214	0.1735	0.1744	0.1734	0.1742	0.1734		0.1372	0.1740
14	2014	0.1658	0.1737	0.1656	0.1738	0.1656		0.1655	0.1737
15	1216		0.1661		0.1661				0.1660
16	2016	0.1606	0.1607	0.1604	0.1605	0.1604		0.1602	0.1603
17	2020	0.1464	0.1462	0.1464	0.1463	0.1464		0.1464	0.1462
18	1220	0.1332	0.1459	0.1331	0.1458	0.1331		0.1331	0.1456
19	040	0.1291	0.1334	0.1290	0.1333	0.1290		0.1289	0.1333
20	320		0.1291		0.1290				0.1289
21	2026	0.1236	0.1237	0.1236	0.1238	0.1236		0.1236	0.1237
22	1226	0.1229	0.1231	0.1228	0.1230	0.1228		0.1227	0.1229
23	1228	0.1180	0.1178	0.1179	0.1178	0.1179		0.1177	0.1178
24	2028	0.1154	0.1152	0.1150	0.1151	0.1149		0.1147	0.1149
25	242	0.1140	0.1141	0.1139	0.1140	0.1139		0.1137	0.1140
26	0418	0.1128	0.1130	0.1128	0.1129	0.1128		0.1127	0.1129
27	248(3218)	0.1112	0.1114	0.1112	0.1113	0.1112		0.1108	0.1113

TABLE II Relative integrated intensity of the super-structure diffraction peaks of the M18R martensite

	111 + 019		020	
	Measured-value	Calculated-value	Measured-value	Calculated-value
Fast-quenching	5.4 ± 0.2		1.1 ± 0.2	
Fast-quenching/aging	5.7 ± 0.2		1.2 ± 0.2	
Slowly-quenching	8.5 ± 0.2		1.2 ± 0.2	
Air-quenching	10.0 ± 0.2	8.43	1.1 ± 0.2	0.86

TABLE III X-ray diffraction data of M18R martensite

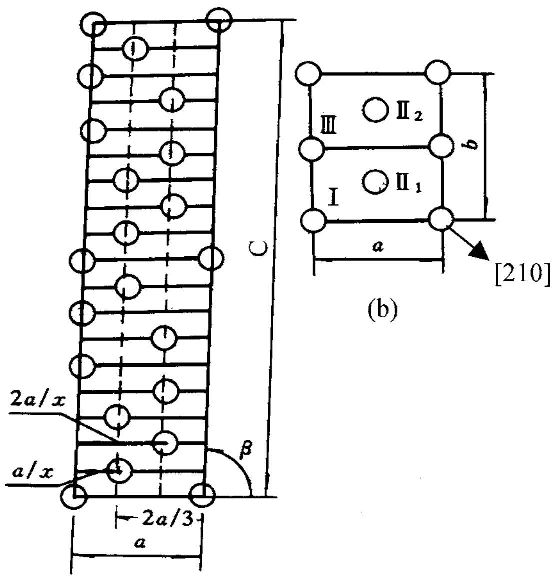
Conditions		Fast-quenching	Fasr-quenching/aging	Slowly-quenching	Air-quenching
Monoclinic angle β		88.81°	88.71°	88.71°	88.64°
1210	Δd mm	0.0074	0.0074	0.0074	0.0075
2010	$\rho \times 10^{-3}$	12.09	12.15	12.15	12.36
1216	Δd mm	0.0052	0.0052	0.0052	0.0053
2016	$\rho \times 10^{-3}$	14.23	14.28	14.28	14.59
040	Δd mm	0.0041	0.0041	0.0041	0.0042
320	$\rho \times 10^{-3}$	21.61	21.66	21.66	22.22

martensite has little effect on the Δd value, but the degree of the martensite stabilization has remarked effect on the Δd value.

As the test alloy was subject to two different heat treatments (fast-quenching followed by aging at 100°C; quenching into 100°C water), the relative integrated intensity of the (111), (019) super-structure diffraction peaks show obvious differences (Table II), but within test error, the ρ value and the monoclinic angle β remain unchanged (Table III), which is not similar to that of the Cu-12.5Zn-19.4Al (at%) alloy [12], for it, the difference of monoclinic angle β was 0.39 deg during its thermal cycling from 1st (the β was 88.85°) to 10^4th (the β was 89.24°). Consequently the order degree change of martensite of the tested alloy caused by cooling rate also can not be reflected by β value.

The relative integrated intensity of the (020) $(10\bar{8})$, (1010) super-structure diffraction peaks of the martensite in the test alloy remains almost unchanged, indicating that the nn order degree of the martensite of the alloy is hardly affected by the quenching rate.

The points as discussed above, can be described by the martensite structure model of Cu-Zn-Al alloy. Fig. 2 [18] shows the model hard sphere atom structure of the M18R martensite in which the basic plane piles up along the C axis in sequence of AB′CB′CA′CA′BA′BC′BC′AC′AB′. There are only four kinds of different positions, *i.e*, I, II_1, III, II_2 on the basic plane (Fig. 2b). Crystal structure factor of the monoclinic M18R martensite can be expressed as follows.



(b)

(a)

Figure 2 (a) The unit cell of the M18R martensite viewed from the (010) direction and (b) The atomic configuration in the basal plane of the M18R martensite.

$$\begin{aligned} F = \{ & f_{\text{I}} + f_{\text{III}} e^{2\pi i(K/2)} + f_{\text{II}_1} e^{2\pi i(H/2+K/4)} \\ & + f_{\text{II}_2} e^{2\pi i(H/2+3K/4)} \} \cdot \{ 1 + e^{2\pi i(H/x+K/2+L/18)} \\ & + e^{2\pi i(2H/x+L/9)} \} \cdot \{ 1 + e^{2\pi i(H/3+K/2+L/6)} \\ & + e^{2\pi i(2H/3+L/3)} \} \cdot \{ 1 + e^{2\pi i(K/2+L/2)} \} \end{aligned} \tag{1}$$

where,

$$x = a/x', \quad x' = c\cos\beta/9 + a/3 \text{ [19]} \tag{2}$$

In Equation 1, the first item is the structure factor of the basic plane, called F_{A}. If the atom distribution is random, the atom in any position of the basic plane has an average value. Its scattering factor is called as f_{ave}.

$$\begin{aligned} F_{\text{A}} = f_{\text{ave}} \{ & 1 + e^{2\pi i(K/2)} + e^{2\pi i(H/2+K/4)} \\ & + e^{2\pi i(H/2+3K/4)} \} \end{aligned} \tag{3}$$

$F_{\text{A}} = 0$, forbidden diffractions occur:

$$K = \text{even}, H + K/2 = \text{odd} \quad K = \text{odd}. \tag{4}$$

If the atom distribution on the basic plane is ordered, the diffractions expressed in formula (4) may occur. Their intensities are determined by the order state of atom distribution. This is fundamental to the calculation of the order state of the martensite .

When $K = \text{even}$, $H + K/2 = \text{odd}$, the structure factor of the basic plane can be simplified to:

$$F_{\text{A}} = (f_{\text{I}} - f_{\text{II}}) + (f_{\text{III}} - f_{\text{II}}) \tag{5}$$

where the two items connected by the plus sign are the difference of scattering factors between atoms in position I and in position II, and the difference between atoms in position III and in position II respectively. According to the experimental data of the lattice parameters, we can obtain $1\big/2b > 1/2\sqrt{a^2 + (b/2)^2}$. This means that the atoms between position I and position II, and those between position III and position II are the closest, respectively. Therefore, the diffractions with $K = \text{even}$ and $H + K/2 = \text{odd}$ represent the atomic order state of the nearest neighbors (nn) when the martensite structure is ordered.

When K is odd, the structure factor of the basic plane can be simplified to:

$$F_A = (f_I - f_{III}) \qquad (6)$$

because the difference of scattering factors between atoms in position I and II, the diffractions with $K =$ odd represent the atom order state of the next closest neighbor (nnn).

It is important to know the exact atom sites on the basic plane of the martensite in order to understand the change of the order degree. Recently, Nakata Y and his coworkers [20] investigated the configuration on the basic plane of the martensite in the alloy Cu-11.4Zn-18.7Al (at%) by means of electron channeling enhanced microanalysis. They paid special attention to the site occupancies of the Cu and Zn atoms. This technology is called ALCHEMI (Atom Location by Channeling Enhanced Microanalysis). By this technology, the atoms on the basic plane of the martensite of the Cu-11.4Zn-18.7Al alloy in position I are Al + Cu, II are Cu + Zn, and III are Zn + Cu. Although the difference of the atomic scattering factor of Cu and Zn is small, the configuration on the basic plane of the martensite of the Cu-18Zn-14Al (at%) alloy can be determined exactly by X-ray diffraction. In this experiment, the intensity of the "nnn" order diffraction peaks of (111) and (019), is obviously higher than that of the "nn" order diffraction peaks of $(10\bar{8})$, (1010) and (020). Among the difference of the scattering factor between every two kinds of the atoms of the three elements of Cu, Zn and Al, the largest difference is between Zn atom and Al atom. Thus, it can be supposed that Zn and Al atoms preferentially occupy positions I and III, and the Cu atom can fill other positions. Because the diffractions peaks of the superstructure nnn and nn are quite sharp under the air-quenching state, it can be said that the structure of the test alloy is fully ordered. According to formula (5) and (6), the atoms in position I are (14/25)Al + (11/25)Cu, II is Cu, III are (18/25)Zn + (7/25)Cu. The structure factor of the basic plane is given as follows:

For the fundamental diffractions,

$$F_A = (68/25)f_{Cu} + (18/25)f_{Zn} + (14/25)f_{Al} \qquad (7a)$$

For the nn order diffractions,

$$F_A = (14/25)f_{Al} + (18/25)f_{Zn} - (32/25)f_{Cu} \qquad (7b)$$

For the nnn order diffractions,

$$F_A = (4/25)f_{Al} - (18/25)f_{Zn} + (4/25)f_{Cu} \qquad (7c)$$

Using formula (1) for the ordered state and considering the Lorenz-polarization and multiplicity factors, the relative diffraction intensities of the diffraction peaks concerned, in the fully ordered state can be calculated. The relative diffraction intensities of (111), (019) and (020) diffraction peaks are calculated and listed in Table II. Taking into account of the influence of the primary extinction, the calculation coincides with experimental results very well.

TABLE V Atom configurations on the basic plane of the M18R Martensite

I-position			III-position			
Cu	Zn	Al	Cu	Zn	Al	II-position
11/25	1.9/25	14/25	7/25	16.1/25	1.9/25	Cu
11/25	1.7/25	12.3/25	7/25	16.3/25	1.7/25	
11/25	0.6/25	13.4/25	7/25	17.4/25	0.6/25	
11/25	0	14/25	7/25	18/25	0	

It is concluded that the quenching rate only affects the nnn order state. In other words, with the increase of quenching rate, the order degree of the nnn decreases, which is relative to the exchange between Al and Zn atom on positions I and III respectively. The relative diffraction intensities of (111), (019) and (020) superlattice diffraction peaks were calculated by formula (1) when Al and Zn atom exchange each other. Calculation results are given in Table IV. It can be seen that while the nnn order degree decreases, the nn order degree remains unchanged as the Al and Zn atoms exchange with each other. Using the data in Table IV and the interpolation method, the atom configuration on the basic plane for different quenching rates can be calculated, and the results are given Table V. According to Y. Nakatand [20], there were the atoms rearrangement in the martensite stabilization process in the Cu-Zn-Al alloy too, but the atoms rearrangement were the interchange between Cu-Zn "nn" atom pair.

When Al and Zn atoms exchange with each other along the b-axis, the nnn order degree changes. Because the atom type along with the b-axis is invariable, the lattice parameter of the b-axis and the length of [210] orientation are invariable, according to the hard sphere atom structure model of M18R martensite. Now, it is generally accepted that the martensite possesses a long period order structure of the M18R type that is constructed by the basic plane stacking along in the order of AB′CB′CA′CA′BA′BC′BC′AC′AB′. The unchanged lattice parameters (a, b, c and monoclinic angle β) of the martensite indicate that Δd value, the ρ value and the monoclinic angle β remain unchanged when the nnn order state varies. This implies that the change of the nnn order degree of the martensite of the test alloy cannot be simply represented by Δd value, the ρ value and the monoclinic angle β.

5. Conclusions

(1) For the M18R martensite of the Cu-18Zn-14Al alloy, the diffractions with $K(=$ even) and $H + K/2$ (=odd) represent the atom ordered state of the closest neighbors (nn). The diffractions with K(=odd) represent the atom order state of the next closest neighbors (nnn).

(2) Only the nnn order degree of the martensite of the Cu-18Zn-14Al alloy is affected by the cooling rate. As the cooling rate decreases, the nnn order degree of the martensite increases while the nn order degree remains unchanged.

(3) For the Cu-18Zn-14Al alloy, the change of the nnn order degree has little effect on the Δd value of

TABLE IV Relation between the intensities of superlattice diffraction and Al-Zn atom location

Atoms location	I			II			Calculation of the relative insensity	
Atom	Cu	Zn	Al	Cu	Zn	Al	$111 + 019$	020
	11/25	0	14/25	7/25	18/25	0	8.43	
	11/25	0.5/25	13..5/25	7/25	17.5/25	0.5/25	7.28	
	11/25	1/25	13/25	7/25	17/25	1/25	6.24	
Allotment of the atoms	11/25	1.5/25	12.5/25	7/25	16.5/25	1.5/25	5.26	
	11/25	2/25	12/25	7/25	16/25	2/25	4.37	0.86
	10/25	3.5/25	11.5/25	8/25	14.5/25	2.5/25	3.45	
	10/25	4.5/25	10.5/25	8/25	13.5/25	3.5/25		
	9/25	6.5/25	9.5/25	9/25	11.5/25	4.5/25		
	9/25	9/25	7/25	9/25	9/25	7/25		

each peak-pair between (1210) and (2010), (1216) and (2016), (040) and (320) and the monoclinic angle β, the change of the order degree of martensite, expressed by the change of the relative intensity of (111), (019) super-structure diffraction peaks, not can be simply represented by Δd value (the splitting parameter of the (12L) and (20L), (04L) and (32L) or (32L) diffraction pairs, ρ value (=$\sin^2\theta_1$-$\sin^2\theta_2$), $\Delta d = (d_1 - d_2)$, or the monoclinic angle β simply.

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