

ORDER STATE AND STABILITY OF MARTENSITE IN AN AIR-QUENCHED Cu-Zr-Al ALLOY^①

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ABSTRACT The martensite structure and its order state of Cu-18Zr-14Al (atomic fraction) alloy were studied by X-ray diffraction experiment and its intensity analysis. It is convinced that the M18R martensite with fairly perfect long-range order can be obtained by air-quenching the alloy. The atomic ordering configurations are two kinds of nearest neighboring (nn) order ($K = \text{even}$, $H + K/2 = \text{odd}$), i. e., Al-Cu atoms ordering and Zr-Cu atoms ordering, and one kind of next nearest neighboring (nnn) order ($K = \text{odd}$), i. e., Al-Zn atoms ordering. The atomic distribution on the basic plane of the martensite is as follows: I —14/25Al+11/25Cu, II —Cu, III—18/25Zr+7/25Cu. The martensite stabilization occurs in the alloy even on perfect ordering condition.

Key words shape memory alloy Cu-Zr-Al alloy martensite ordering stabilization

1 INTRODUCTION

Cu-Zr-Al alloy is a low-price and high-quality shape memory alloy (SMA). Its shape memory effect (SME) comes from the thermoelastic martensite transformation and reversion. The stability of the transformation is directly related to its using properties which draws much attention in recently years. Many investigations were carried out on the martensite structure and its change, especially about its ordering state^[1-5]. The ordering state of as-prepared alloy depends at least on two factors, i. e., the composition of the alloy^[6] and the quenching rate, even though its work history, such as thermal-cycling, aging, action of stress, etc, is not considered. For the latter, it was known that the DO_3 ordering can be suppressed by quenching^[7]. So, different order states can be obtained in martensites for a definite composition alloy^[1, 4, 5]. This means that the martensite with nearly perfect long-range order can be obtained by reducing quenching rate. How is the atomic configuration in the perfectly ordering martensite? Whether or not

does the perfectly ordering martensite stabilize? Whether or not is the martensite stabilization related with its initial ordering state? These problems are not clear yet. In this paper, the problems mentioned above were studied with Cu-18Zr-14Al (atomic fraction) alloy. It was shown that the perfectly ordering M18R martensite can be obtained by air-quenching. But the stabilization phenomenon still occurred in the martensite. The results may have a help for us to further understand the martensite stabilization.

2 EXPERIMENTAL

The tested alloy, Cu-18Zr-14Al (atomic fraction) was induction melted, cast into flat ingots, homogenized at 1123 K for 24 h, then hot-rolled into sheets of 1 mm thickness after the surface defects of the ingots were cut off. The experimental samples for transformation temperatures measurement were cut from the sheets. The transformation temperatures and its variety were studied by $P-T$ curves measurement after the samples were subjected to different heat

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treatment. X-ray diffraction experiment and data processing were performed on a D-5000 diffractometer with powder sample, using $\text{Cu-}K_{\alpha}$ radiation with a Ni filter. In order to reduce solution time of powder sample for X-ray diffraction, a bulk sample was firstly subjected to a solution treatment at 1123 K for 10 min and quenched into iced brine, then filed into powder. The powder, roughly 100 μm in diameter, was rapidly heated to 1023 K in a sealed flat quartz tube back filled with argon, then air-quenched with the tube on cement floor.

3 RESULTS

3.1 Martensite structure and its order state of air-quenched Cu-18Zn-14Al alloy

Fig. 1 shows the X-ray diffraction spectrum of the tested alloy, which indicates that the martensite produced by air-quenching is M18R structure. Separation processing was carried out for overlapping peaks, then the d_{obs} values and the relative integrated intensities of all diffraction peaks were measured. The results were listed in Table 1. In order to more precisely obtain the intensity of superstructure diffractions which are very weak, the following measurement procedures were used for (111), (019), (108) and

(0018) diffractions^[8, 9]. ① Their integrated intensity was measured up to 10^5 counts of X-rays so that the statistical errors $\sigma = 1 / \sqrt{N} \leq 0.3\%$. ② The sample was measured several times, each time the powder was poured out off the sample box and filled in it again, in order to make the fluctuation $\leq 0.2\%$. The experimental results were also listed in Table 1. The lattice parameters, $a = 0.4419 \text{ nm}$, $b = 0.5331 \text{ nm}$, $c = 3.822 \text{ nm}$, $\beta = 88.64^\circ$, can be determined from the measured d_{obs} values. Using the lattice parameters, the calculated d_{cal} values can be obtained, which were listed in Table 1 as well. It can be seen that the d_{cal} coincides with the d_{obs} very well.

In order to determine the ordering state of the martensite, it is necessary to calculate and analyse its diffraction intensity according to its structure model. Fig. 2 shows the hard sphere atom structure model of the M18R martensite in which basic plane piles up along the C axis in sequence of $AB'CB'CA'CA'BA'BC'BC'AC'AB'$. There are only 4 kinds of different positions, i. e. I, II₁, III, II₂, on the basic plane (Fig. 2 (b)). No matter how many sort and much amount of atom is distributed on any positions, its structure factor can be expressed as:

Fig. 1 X-ray diffraction spectrum of air-quenched martensite of Cu-18Zn-14Al alloy

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

In which, $x = a/x'$,

$$x = c \cos \beta / 9 + a / 3^{10} \quad (2)$$

In formula (1) the first item is the structure factor of the basic plane, called as F_A . If the atom distribution is disorder, the atom on every position of the basic plane is an average one, whose scattering factor is called as f_{ave} .

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

Making $F_A = 0$, then the forbidden diffractions can be obtained.

$$K = \text{even}, H + K/2 = \text{odd}$$

$$K = \text{odd} \quad (4)$$

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

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

$$F_A = (f_{\text{I}} - f_{\text{II}}) + (f_{\text{III}} - f_{\text{II}}) \quad (5)$$

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

Table 1 X-ray diffraction data measured and data calculated of air-quenched martensite of Cu-18Zn-14Al alloy

hkl	d_{obs}	d_{cal}	$(I/I_{128})_{\text{obs}} \times 10^{-2}$	$(I/I_{128})_{\text{cal}} \times 10^{-2}$
111	0.339	0.3394	4.6 ± 0.2	3.89
019	0.332	0.3321	5.4 ± 0.2	4.54
$10\bar{8}$	0.321	0.3206	1.5 ± 0.2	1.11
1010	0.293	0.2925	1	0.86
020	0.267	0.2666	1	0.86
$12\bar{2}$	0.2265	0.2263	23	21.2
202	0.2200	0.2200	29	30.6
0018	0.2123	0.2123	70	70.1
$12\bar{8}$	0.2045	0.2049	100	100
208	0.2022	0.2023	28	29.7
1210	0.1970	0.1970	89	88.7
$201\bar{0}$	0.1895	0.1893	22	23.7
$121\bar{4}$	0.1732	0.1740	9	4.5
$201\bar{4}$		0.1737		3.8
$121\bar{6}$	0.1655	0.1660	7	7.4
$201\bar{6}$	0.1602	0.1603	9	10.4
$202\bar{0}$	0.1464	0.1462	12	7.6
$122\bar{0}$		0.1456		4.8
040	0.1331	0.1333	15	13.4
320	0.1289	0.1289	23	21.1
$202\bar{6}$	0.1236	0.1237	6	5.2
$122\bar{6}$	0.1227	0.1229	14	16.6
1228	0.1177	0.1178	14	14.7
$202\bar{8}$	0.1147	0.1149	5	4.2
242	0.1137	0.1140	7	6.4
0418	0.1127	0.1129	18	16.2
$24\bar{8}$	0.1108	0.1113	20	7.6
$321\bar{8}$		0.1112		13.7
$321\bar{8}$	0.1092	0.1092	14	13.2

Lattice parameters: $a = 0.4419 \text{ nm}$,
 $b = 0.5331 \text{ nm}$, $c = 3.822 \text{ nm}$, $\beta = 88.64^\circ$

When $K = \text{odd}$, the structure factor of the basic plane can be simplified as

$$F_A = (f_{\text{I}} - f_{\text{III}}) \quad (6)$$

It is the difference of scattering factor between atom on position I and that on position III. So, the diffractions with $K = \text{odd}$ represent the atomic ordering state of the next nearest neighboring (nnn).

With the structure model above and the composition of the alloy, the diffraction intensity of different ordering states can be calculated, in which the atomic configurations on the basic plane are different. In this experiment, the intensity of the *nnn* superlattice diffractions, such as (111) and (019), is obviously stronger than that of the *nn* superlattice diffractions, such as (108), (1010) and (020). On the other hand, among the difference of the scattering factor between every two kinds of the atoms of the three elements Cu, Zn and Al, the largest one is that between Zn atom and Al atom. So it can be supposed that the *nnn* related positions are preferentially occupied by the atoms Zn and Al, and insufficient part can be substituted by the atom Cu. Because the superstructure diffractions of the *nnn* and the *nn* are quite sharp, we suppose the structure of the experimental alloy is fully ordering. So, in Fig. 2(b), the atom on position I is $(14/25)\text{Al} + (11/25)\text{Cu}$, II is Cu, III is $(18/25)\text{Zn} + (7/25)\text{Cu}$. The structure factor of the basic plane is thus as follows.

For the fundamental diffractions, $F_A = (68/$

$$25)f_{\text{Cu}} + (18/25)f_{\text{Zn}} + (14/25)f_{\text{Al}} \quad (7a)$$

For the *nn* order diffractions, $F_A =$
 $(14/25)f_{\text{Al}} + (18/25)f_{\text{Zn}} - (32/25)f_{\text{Cu}} \quad (7b)$

For the *nnn* order diffractions, $F_A =$
 $(4/25)f_{\text{Al}} - (18/25)f_{\text{Zn}} + (4/25)f_{\text{Cu}} \quad (7c)$

With the lattice parameters obtained from the experiment, that $x = 2.808$ can be extracted. Using the formula (1) and considering the Lorentz-polarization and multiplicity factors, the relative diffraction intensities of the diffraction peaks concerned can be calculated (Table 1). It can be seen that the I_{cal} coincide satisfactorily with the I_{obs} , which means that the fully long-range ordering structure can be obtained by air-quenching the alloy.

3.2 The martensite stabilization of the air-quenched Cu-18Zn-14Al alloy

Fig. 3(a) shows the βT curve of the tested alloy which was firstly subjected to an air-quenching treatment. It can be seen that the temperatures of the first thermal-cycling reverse curve are higher than those of the second and the third. This means that the martensite stabilization occurred apparently in the as-air-quenched alloy, and that it can temporarily be eliminated by once reversion (see the second and the third reverse curves). When the air-quenched alloy was subjected to once reversion, then aged in the martensite state (343 K, just below the A_s temperature), the martensite stabilization took place again. Fig. 3(b) shows the increase of the A_s temperature with aging time. This result indicates that, for the tested alloy, the martensite stabilization can only be reduced but not be eliminated by heat treatment.

4 DISCUSSION

As mentioned above, the diffractions of (111) and (019) are the *nnn* ordering diffractions and that of (108) is the *nn* ordering diffraction. Their relative integrated intensities measured are 4.6 ± 0.2 , 5.4 ± 0.2 and 1.5 ± 0.2 respectively. They are larger than that obtained by calculating with fully long-range order structure model even though the fluctuations of the data are considerable. The difference

Fig. 2 Crystal structure model of M18R martensite

- (a) —viewed from [010] direction;
 (b) —the atomic configuration on the basic plane

Fig. 3 The martensite stabilization of air-quenched Cu-18Zn-14Al alloy

(a) — ρ - T curves of an air-quenched alloy. During measurement, the electrical current is constant, so $\rho \propto V$, then ρ can directly be expressed by V . The symbols “1”, “2” and “3” denote the first, the second and the third thermal cycling. (b) — Variation of A_s temperature with aging time in martensite state (at 343 K) of air-quenched alloy

between the measured data and the calculated data may be contributed to the primary extinction effect in X-ray diffraction^[11, 15]. In our X-ray diffraction experiment, in order to simulate the state of bulk sample with powder sample, the particles of the used powder is fairly coarse (about 100 μ m in diameter). For this fairly coarse powder, the primary extinction effect is involved unavoidably. The stronger the integrated intensity, the more remarkable the primary extinction effect. The intensity of the fundamental diffraction (0018) is far stronger than that of the superlattice diffractions, such as (111), (019) and (108). So the intensities of the superlattice diffractions might have thus been overestimated. The measured error of intensity may be brought into being for fairly coarse powder

because diffraction probability is not large enough. But this error can be reduced to ± 0.2 by pouring and filling sample then measuring it again and again. So, if the influence of the dynamics factor from the primary extinction effect is considered, the I_{obs} coincide fairly with the I_{cal} for the superlattice diffractions concerned. This means that both the nn order and the nnn order of the air-quenched alloy are completed. In addition, further calculation indicated that if we change atomic configuration on the basic plane, inconsistency between measured values and calculated values is brought into being not only for the diffraction intensities but also for the d values. So, the atomic distribution on the basic plane as shown in Fig. 2(b) for the air-quenched alloy is as follows. I — (14/25) Al + (11/25) Cu, II is Cu, III is (18/25) Zn + (7/25) Cu.

It is commonly held that the martensite stabilization in Cu-Zn-Al alloy is caused by reordering or disordering of atomic configuration of the martensite during aging^[4, 12–14]. Attempt was made at eliminating the martensite stabilization through enhancing order degree of the alloy. But the result shown in our experiment indicated that the martensite stabilization still occurred even though the nn order and the nnn order in the alloy were fairly perfect. So, the function is limited to suppress the martensite stabilization through enhancing order degree of the alloy. In fact, the reordering or disordering of atomic configuration during the martensite stabilization is a process of atom diffusion. So, one of the essential ways to suppress the martensite stabilization is to suppress atom diffusion during aging, such as alloying. One kind of Cu-base alloys whose thermoelastic reversion temperature is as high as 673 K even in as-quenching state was obtained through alloying in our lab. This work will be published elsewhere.

5 CONCLUSIONS

(1) For M18R martensite of Cu-base alloy, its structure factor analysing indicated that the diffractions with $K = \text{even}$, $H + K/2 = \text{odd}$ represent the nn atomic ordering state, and those with $K = \text{odd}$ represent the nnn atomic ordering

state.

(2) The fairly perfect *nn* order and *nnn* order exist in the air-quenched martensite of Cu-18Zn-14Al alloy whose atomic distribution on the basic plane is as follows. I —(14/25) Al+ (11/25) Cu, II is Cu, III is (18/25) Zn+ (7/25) Cu, as shown in Fig. 2(b).

(3) The martensite stabilization still occurred in the air-quenched alloy. The function is limited to suppress the martensite stabilization through enhancing order degree of the alloy.

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$$\begin{aligned}
 & z_{48} - \frac{z_{58} - z_{48}}{132}(y - 48)] M_3(3 + \frac{x}{80}) + \\
 & [2z_{56} + \frac{z_{62} - z_{56}}{81.5}(y - 17) - \\
 & z_{54} - \frac{z_{61} - z_{54}}{160}(y - 20)] M_3(-4 + \frac{x}{80})
 \end{aligned}
 \quad (18)$$

For the *fcc* region, the mathematical model for concentration distributions is

$$\begin{aligned}
 z &= S(x, y) \\
 &= [2z_1 + \frac{z_7 - z_1}{42.5}(y + 160) - \\
 & z_2 - \frac{z_9 - z_2}{99}(y + 160)] M_3(3 + \frac{x}{80}) + \\
 & [z_1 + \frac{z_7 - z_1}{85}(y + 160)] M_3(2 + \frac{x}{80}) + \\
 & [z_2 + \frac{z_9 - z_2}{99}(y + 160)] M_3(1 + \frac{x}{80}) + \\
 & [z_3 + \frac{z_{11} - z_3}{123}(y + 160)] M_3(\frac{x}{80}) + \\
 & [z_4 + \frac{z_{14} - z_4}{135}(y + 160)] M_3(-1 + \frac{x}{80}) + \\
 & [z_5 + \frac{z_{16} - z_5}{141}(y + 160)] M_3(-2 + \frac{x}{80}) +
 \end{aligned}$$

$$\begin{aligned}
 & [z_6 + \frac{z_{18} - z_6}{140}(y + 160)] M_3(-3 + \frac{x}{80}) + \\
 & \{[2z_6 + \frac{z_{18} - z_6}{70}(y + 160)] - \\
 & [z_5 + \frac{z_{16} - z_5}{141}(y + 160)]\} M_3(-4 + \frac{x}{80})
 \end{aligned}
 \quad (19)$$

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