ORDERING OF BAINITE IN A Cu—Zn—Al ALLOY [1]

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ABSTRACT

The ordering of bainite is studied and compared with that of martensite in a Cu—20Zn—6Al(wt —%) alloy by X-ray analysis. Experimental results show that in contrast with the diffraction pattern for $9R$ or $18R$ martensite, in which the (115) diffraction peak is distinguishable from the ($\bar{2}$ 0 5), and the (1 2 10) from the (2 0 10), the (1 1 5) and ($\bar{2}$ 0 5) or the (1 2 10) and ($\bar{2}$ 0 10) diffraction peaks in the bainites formed from high temperature $B2$ or low temperature $L2$ parent phase overlap, and these phenomena do not change after prolonged aging or slow-cooling. The bainite structure is quite different from that of the martensite, i. e., the inheritance of the ordering of the parent phase would not occur, during bainite formation.

Key words: Cu—Zn—Al alloy   marensite   bainite   ordering

1 INTRODUCTION

Investigation into whether bainite inherits the ordering of the parent phase or not is significant for clarification of the mechanism of bainite formation. Takezawa et al [1] determined from the electron diffraction in a Cu—29.8Zn—6.1Al (wt.—%) alloy that the stress-induced bainite possesses a $9R$ disordered structure. Wu et al [2] found that the bainite has an ordered structure in a Cu—Zn—Al alloy and indicated that the bainite formed from the low temperature $L2_1$ parent phase inherits the parent phrase ordering, and the bainite formed from the high temperature $B2$ parent phase also inherits the nearest-neighbor (NN) ordering of the parent phase, supporting the idea that the bainitic transformation possesses the characteristic of the martensitic transformation. Doing and Flewitt [3] reported that the composition of bainite plate at its growing edge is no different from that of the matrix in Cu—Zn and Cu—Zn—Al alloys and suggested that the bainite grows by a martensitic shear mechanism at the early stage of its formation.

However, Wu and Wayman [4] and Nakata et al [5] detected a definite composition difference between the very thin (30 nm) bainite plate and the adjacent matrix in Cu—Zn—Al alloys. Tadaki et al [6] also found the composition difference between the thin bainite plate and the matrix in Cu—Zn—Al alloys and proposed that bainite formed by partially inheriting the ordering of the parent phase. Our previous investigation [7] revealed that the bainite formed from $B2$ and $DO3$ parent phase possesses an almost orthorhombic long period structure in a Cu—Zn—Al alloy and the martensite in the same alloy is monoclinic in structure, showing a lower degree of ordering in the bainite than in the martensite. According to the results of a thermodynamic study of Cu—Zn—Al alloy [8], the long range diffusion of atoms must occur during the formation of bainite, and the disordered bainite may undergo ordering during continuing aging or slow-cooling. In this investigation, the ordering of bainite formed at different transformation stages was systematically studied and compared with that of martensite so as to clarify whether the bainite inherits the

ordering of the parent phase.

2 EXPERIMENTS AND RESULTS

The critical transition temperature of $B2 \to L2$ in a Cu−20Zn−6Al(wt.−%) alloy about 265 $°C^{[9]}$. The plate specimen was held at 800 $°C$ for 3 min for solution treatment, then quenched to 150 $°C$ for 15 min and finally quenched to 0 $°C$ ice water to obtain the martensitic structure. Its X-ray diffraction pattern is shown in Fig. 1. The spacing $\triangle l$ between diffraction peaks (1 2 10) and ($\bar{2}$ 0 10) is 0.006.6 nm. In order to obtain a higher ordering of $L2_1$ parent phase, the specimen was held at 150 $°C$ for 2 h to obtain martensite with $\triangle l$ = 0.007.9 nm. For the martensite formed from the $B2$ parent phase through quenching from 800 $°C$, the (1 1 5) peak also seperated from the ($\bar{2}$ 0 5) diffraction peak. The plate specimens with higher ordering of the $L2$ parent phase formed through holding the specimen at 150 $°C$ for 2 h were respectively up-quenched to 300 $°C$ and 250 $°C$ for various durations and then quenched to 0 $°C$ brine to get bainites formed from $B2$ to $L2$ parent phase. For each isothermal process, two kinds of bainite plates were observed by X-ray diffraction the primary non-degraded bainite plate formed after a short holding time and the prolonged aging bainite plate formed after a long holding time. The primary bainites up-quenched to 300 $°C$ and 250 $°C$ were slowcooled in a furnace to room temperature rather than quenched to 0 $°C$ brine to observe the influence of this slow-cooling on bainite structure. And a continuing observation of the bainite formation at 300 $°C$ in different states mentioned above was made with powder specimen by using SIEMENS D500 and D · MAX−IIIA automatic X−ray diffractometers.

The bainite plates formed by holding the specimens at 300 $°C$ for 15, 25, 40 min, 1, 1.5 and 2 h were inspected by metallography. Bainite plates formed by holding for 25 min are regarded as examples of the primary non-degraded bainite which exhibits even sizes and straight boun-

daryies, as shown in Fig. 2, and bainite plates formed by holding for 1 and 1.5 h are chosen as the prolonged aging bainite. The bainite plates formed through slow-cooling were obtained by cooling the primary bainite to 200 $°C$ at a rate of 1 $°C$ / min and then to room temperature at a rate of 0.5 ~ 0.7 $°C$ / min. After prolonged aging and slow-cooling treatment, the bainite plates become coarser and developed irregular boundaries as shown in Fig. 3, which illustrates the bainite structure in a specimen through holding for 1 h, as an example. X-ray diffraction results show that the (1 1 5) and ($\bar{2}$ 0 5) diffraction peaks all overlapped in the kinds of bainite mentioned above, as shown in Fig.4.
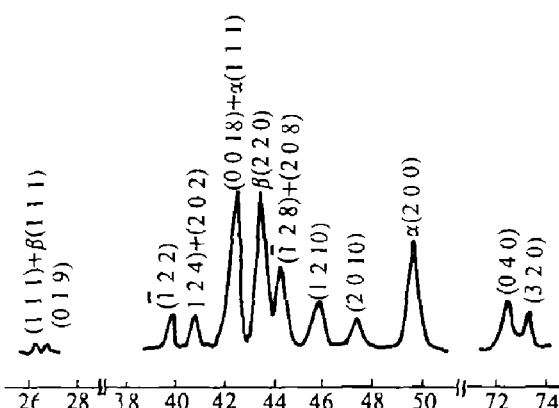

Fig. 1 The X-ray diffraction pattern of martensite formed from $L2$ parent phase by quenching to 0 $°C$ ice water after an isothermal holding at 300 $°C$ for 15 min

Metallographic inspections of the bainite plates formed by holding the specimens at 250 $°C$ for 30, 50 min, 1 h +10 min, 1.5, 2 and 3 h showed that the structure of the specimen held for 30 min was only martensite, all the rest exhibited the mixed transformation products consisting of bainite and martensite. The typical microstructure of martensite lying between sparely dispersed bainite plates is shown in Fig. 5 from the specimen held at 250 $°C$ for 1.5 h. With the increase of the holding time, the amount of bainite increases and that of martensite decreases gradually. Different transformation products were obtained by the two slow-cooling treatments, i. e.,

(1) holding for 1 h followed by cooling to 200 ℃ at a rate of 1 ℃ / min and then to room temperature at a rate of 0.7~0.5 ℃ / min, a mixture of bainite and martensite was obtained; (2) holding for 1 h and 20 min followed by cooling to 200 ℃ at a rate of 0.6 ℃ / min and then to room temperature at a rate of 0.4 ℃ / min, the only product was bainite. X-ray diffraction patterns in Fig. 6 show that in the martensite structure, the diffraction peaks of (1 2 10) are separate from those of ($\bar{2}$ 0 10). As the holding duration increases, the bainite diffraction intensity increases and the martensite diffraction intensity decreases. There only exists the bainite diffraction peaks after holding for 1h+20 min and then slow-cooling. In all these processes, the diffraction peak (1 2 10) overlaps with ($\bar{2}$ 0 10) in the bainite structure (Fig. 6).

Fig. 2   The microstructure of bainite plates formed from $B2$ parent phase by an isothermal holding at 300 ℃ for 25 min(× 400)

An experiment of the high temperature X-ray diffractometry was conducted as follows. The powder specimen with the martensitic state was heated to 150 ℃ for 2 min to convert the martensite to $B2$ parent phase. After the disappearance of the diffraction peak with the highest intensity ($\bar{1}$ 2 8) in the martensite structure, as shown in Fig. 7(a), the specimen was quickly heated to 300 ℃ until the appearance of the diffraction peak with the highest intensity ($\bar{1}$ 1 4)

in the bainite structure was detected, as shown in Fig. 7(b), and then the (1 1 5) and ($\bar{2}$ 0 5) diffraction peaks were recorded during the periods of 20~30, 35~45 and 55~65 min by slow scanning. Fig. 7(c) shows that the (1 1 5) and ($\bar{2}$ 0 5) diffraction peaks overlapped with each other. After being held at 300 ℃ for 65 min, the specimen was slow-cooled to room temperature at an average rate of 2.5 ℃ / min. The diffraction patterns at 200 ℃, 100 ℃ and room temperature can be seen in Fig. 7(d) and 7(e), showing the overlap of the (1 1 5) and ($\bar{2}$ 0 5) diffraction peaks. Therefore, the result from the powder specimen is analogous to that from the plate specimen.

Fig. 3   The microstructure of bainite plates formed from $B2$ parent phase by an isothermal holding at 300 ℃ for 60 min(× 400)

3 DISCUSSION

In the 9R or 18R bainite and martensite structure, the spacing $\triangle l$ between diffraction peaks (1 1 5) and ($\bar{2}$ 0 5) or (1 2 10) and ($\bar{2}$ 0 10) is directly proportional to the degree of ordering[10]. The values of $\triangle l$ were 0.006,6 and 0.007,9 nm for the martensites formed by quenching with the 0 ℃ ice water after holding the specimens at 150 ℃ for 15 min and 2 h respectively. It is evident that the martensite with $\triangle l$ = 0.007,9 nm corresponds to the higher ordering of the $L2_1$ parent phase compared with the martensite with $\triangle l$ = 0.006,6 nm. The bainite formed by up-quen-

ching to 300 ℃ or 250 ℃ from the higher $L2_1$ ordering parent phase(150 ℃ +2h) is chosen so as to detect its greater ordering.
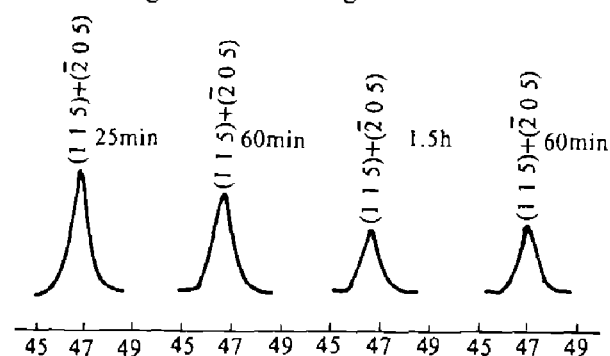

Fig. 4 The (1 1 5) and ($\bar{2}$ 0 5) diffraction peaks for bainite formed by an isothermal holding at 300 C for various duration and slow-cooling treatment

In the bainite formed from the $B2$ parent phase through a holding at 300 C , the (1 1 5) peak overlapped with the ($\bar{2}$ 0 5) diffraction peak. The prolonged aging and slow-cooling treatment may not affect this phenomenon and only convert gradually converted the bainite plates to the f c c α phase. In contrast with the diffraction pat-

tern in bainite. these two diffraction peaks separated in the martensite formed from the $B2$ parent phase. The bainite and martensite formed from the same $L2_1$ parent phase may coexist on a 250 C holding, and it can be inferred from Fig. 5 that the bainite grows very sluggishly at this temperature. because only sparely distributed

Fig. 5 The microstructure of mixed products of bainite and martensite formed from the $L2_1$ parent phase by an isothermal holding at 250 C for 1.5 h(> 500)
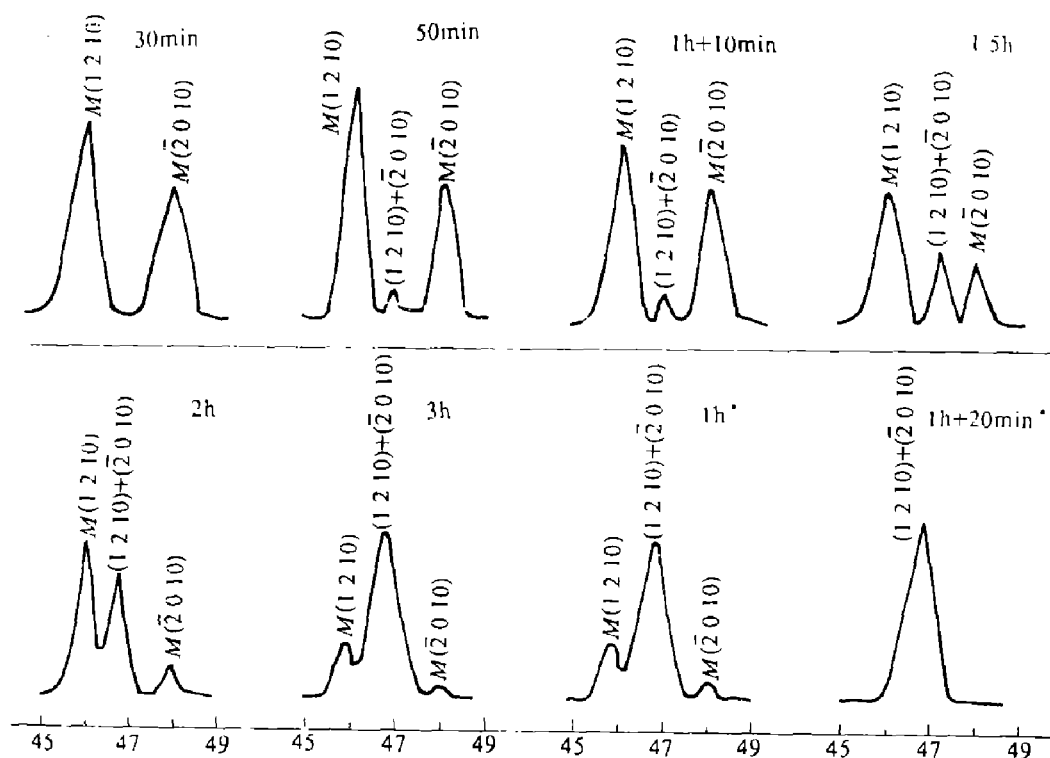

Fig. 6 The (1 2 10) and ($\bar{2}$ 0 10) diffraction peaks for bainite and martensite formed from the $L2$: parent phase by an isothermal holding at 250 C for different times and then slow cooled
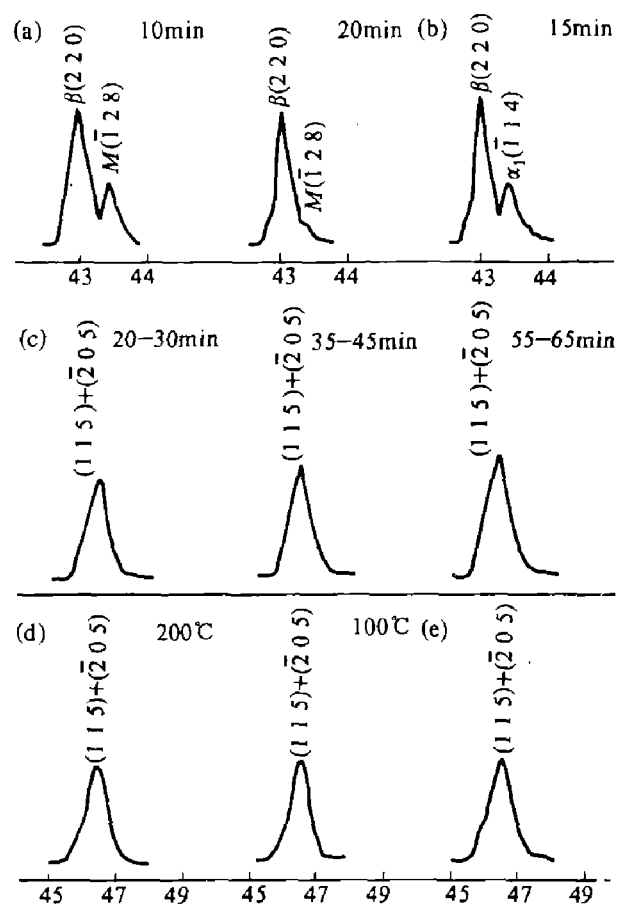
Fig. 7　Experimental results of X-ray diffraction

a—on holding at 150 C. the disappearance of (1 2 8) diffraction peak in the martensite structure;

b—on holding at 300 C. the disappearance of (1 1 4) diffraction peak in the martensite structure;

c—on holding at 300 C, the disappearance of (1 1 5) and (2 0 5) diffraction peaks in martensite structure;

d—diffraction at about 200 C and 100 C for specimen after slow-cooling from 300 C, showing the (1 1 5) and (2 0 5) diffraction peaks in bainite;

e—diffraction at room temperature for specimen after slow-cooling from 300 C, showing the (1 1 5) and (2 0 5) diffraction peaks in the bainite structure

bainite plates were formed after a 1.5 h holding. Thus, holding at 250 C is very suitable for observation of the course of bainite formation and comparision with the diffraction of the martensite. The (1 2 10) and (2 0 10) diffraction peaks constantly overlap in bainite and separate in martensite. As the aging duration was prolonged,

the intensity of the bainite diffraction peaks increased and finally left only the overlapping (1 2 10) and (2 0 10) diffraction peaks after a very slow-cooling. Therefore, the degree of ordering in bainite structure is totally different from that of martensite.

According to the hard sphere model, it can be computed that the spacing $I_{115} = I_{205} = I_{1210} = I_{2010} = I_0 = 0.193.4$ nm for the disordered $N9R$ or $N18R$ bainite in the alloy used, that is to say, the $(1\ 1\ 5)$ and $(\bar{2}\ 0\ 5)$ or $(1\ 2\ 10)$ and $(\bar{2}\ 0\ 10)$ diffraction peaks overlap exactly, i.e. $\triangle I = 0$[11]. Experiments show that for the $9R$ or $18R$ bainite formed through a holding at 300 C or 250 C, the I_1 and I_2, respectively standing for the spacing of the overlapping $(1\ 1\ 5)$ and $(\bar{2}\ 0\ 5)$ peak as well as the $(1\ 2\ 10)$ and $(\bar{2}\ 0\ 10)$ diffraction peaks, are all larger than I_0, and $\bar{I}_1 = 0.194.84$ nm, $\bar{I}_2 = 0.194.26$ nm. The computation of X-ray diffraction intensity indicates that the comparative intensity between $(1\ 1\ 5)$ and $(\bar{2}\ 0\ 5)$ or $(1\ 2\ 10)$ and $(\bar{2}\ 0\ 10)$ is $I_{205} / I_{115} = I_{2010} / I_{1210} = 47\%$. When the bainite possesses ordering, $I > 0$. $I_{115} > I_0 > I_{205} >$ or $I_{1210} > I_{2010}$, and the overlapping peak shifts towards I_{115} or I_{1210} because of the higher intensity of $(1\ 1\ 5)$ and $(1\ 2\ 10)$ diffraction peaks. i.e. $I_{115} > I_1 > I_0 > I_{205}$ or $I_{1210} > I_2 > I_0 > I_{2010}$ Hence, it can be concluded here that $9R$ and $18R$ bainite possess a low degree of ordering.

The present experimental results reveal that the degree of ordering in bainite is markedly different from that in martensite. Unlike martensite, bainite can not inherit the ordering of the parent phase. Experiments[1-6] revealed the change in composition associated with the formation of bainite, in conformity with the results of thermodynamics study[8]. The change of composition involves the long range diffusion of atoms which may destroy the ordering structure, and thus, the bainite formed can not even partially inherit the ordering of the parent phase. Wu and Wayman[2] and Tadaki et al[6] found by means of TEM that the bainite possesses NN and NNN ordering.

but in their work, the results did not show the degree of ordering. In the present results, the overlapping of (1 1 5) and (2 0 5) or (1 2 10) and (2 0 10) diffraction peaks in all $9R$ and $18R$ bainite structure, and the $I > 0$ obviously show the low degree of ordering in bainite. Referring to the result of the thermodynamic study, it may be conceived that the bainite formed at the early stage of the transformation is disordered and will become ordered on prolonged aging or slow-cooling.

4 CONCLUSION

In a Cu—20Zn—6Al (wt.—%) alloy, the (1 1 5) and (2 0 5) or the (1 2 10) and (2 0 10) diffraction peaks in bainite formed from $B2$ or $L2_1$ parent phase overlap, but these peaks separate in martensite formed from $B2$ or $L2_1$ parent phase. These phenomena seen in the bainite structure were not changed by a prolonged aging or slow-cooling treatment. The ordering in the bainite structure is different from that in the martensite structure, and the bainite can not inherit the or-

dering of the parent phase. The low degree of ordering in the bainite structure obtained in the experiments may be derived through the ordering of the freshly disordered bainite by continued aging or slow-cooling.

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