BAINITE STRUCTURE IN Cu-Zn-Al ALLOY OBSERVED BY SCANNING TUNNELING MICROSCOPE①

Li, Chunming Fang, Hongsheng Feng, Qingling Zheng, Yankang
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084
Yan, Junjue
Beijing University, Beijing 100871

ABSTRACT

The bainite structure in a Cu-25.9Zn-4.0Al-0.1Re (wt.-%) alloy was investigated by STM for the first time. The fine structure of the bainite-subunits were discovered under the STM. It had been found that the subunits of the bainite take on a regular shape and distribution. Structural roughness exists on the surface of the subunits.

Key words: Cu-Zn-Al alloy scanning tunneling microscope bainite subunit

1 INTRODUCTION

Reverse shape memory effect of shape memory alloys has close relationship with bainitic transformation of them[1, 2]. The study of fine structure of bainite in these alloys will benefit not only the research on bainitic transformation but also the understanding of the mechanism of reverse shape memory effect. So far, SEM and TEM are the main instruments to observe and analyse the structures of alloys. These instruments can not resolve the fine structure of alloys because of their insufficient resolution ability. For example, although the lateral resolution ability of TEM can reach as high as 0.3 nm, the vertical one of it is relatively very low and can not resolve the structural difference along the vertical direction.

Scanning tunneling microscope is a new type of surface analysis instrument developed in 1980s[3]. It has many advantages such as the high resolution ability, simple structure, convenience for sample preparing, no destruction to samples, etc. Especially, it has an excellent vertical resolution ability. The lateral and vertical resolution power of it can reach as high as 0.1 nm and 0.01 nm, respectively. So it is suitable to reveal the surface microstructure of materials[4]. The present authors have succeeded in observing the lower bainite structure by STM, and revealed the sub-subunit structure which has not been reported before[5]. In this paper, STM is employed to observe the bainite structure in a Cu-Zn-Al alloy. Furthermore, the fine structure of bainite is also investigated.

2 EXPERIMENTAL

The experimental alloy is Cu-25.9Zn-4.0Al-0.1Re (wt.-%). The alloy was homogenized for 12 h at 850 ℃, solutioned 3 min at 750 ℃ and then isothermally reacted at moderate temperature for a short time to obtain bainite. As it is the first time to investigate the bainitic structure in a nonferrous alloy with STM, the constitution of alloy structure becomes the first problem to be solved. If there are few precipited phases, they will impede the observation. On the other hand, however, if there are too many phases, they will mingle each other and be difficult to distinguish under STM. The most appropriate construction is only the bainite phase with suitable quantity distributed in the matrix phase. This makes it easy to confirm the reality of structures. Upon a large number of repeat-

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ed tests, the optimum parameter of treatment has been found. Having been milled and polished, the samples were etched in a solution of 5 g $FeCl_3$ + 100 mL C_2H_5OH + 2 mL HCl. The specimen was revealed by STM in the air at ambient temperature. Special surface protection measures have been taken to prevent the oxidizing. STM was operated under constant current mode. The tip, which is made of tungsten filament, is electrically etched in a NaOH solution and connected to ground under operation. The biased pressure imposed on the sample is 200 mV and the tunneling current is 0.5 nA.

3 RESULTS AND ANALYSIS

The optical micrograph of the specimen is shown as Fig. 1, in which the typical bainites with "V" shape distribute in the matrix phase. The length and width of these bainite plates are ca. 10 μm and 0.2～0.8 μm, respectively. Fig. 2 is the SEM micrograph of the specimen showing the bainite structures near a grain boundary. It can be seen that the bainite plate is also 0.2～0.8 μm wide. The interfacial boundary between the bainite and matrix is not even (as illustrated by the arrows), as if the plate were uncontinuous. As the resolution ability of SEM is very limited, the fine structure of the bainite can not be distinguished.

Fig. 3 is the etched surface microstructures of the specimen under STM. The tip of STM scanned 2.0, 1.92μm and 2.4, 1.92μm on the surface of specimen along the *X* and *Y* direction, respectively. 200 data were collected in each line along the *X* direction and 200 lines were adopted along the *Y* direction in each image. So the corresponding point resolution power along *X* and *Y* direction is 10.0, 9.6 nm and 12.0, 9.6 nm. It should be pointed out that this lateral resolution power is lower than that of TEM, but the vertical one is far higher than that of TEM.

Fig. 3a is the three-dimensional morphology of the surface near a corner part of a bainite plate which demonstrates the "V" shape morphology of the plate, as indicated by the arrows. Fig. 3b is the 3-D morphology of the front part of two bainites *P* and *Q*. It can be seen that the bainite plates are also 0.2～0.8 μm wide, equal to that under optical, SEM and TEM micrograph and that they have similar plate-like morphologies. As the structural constitution of the specimen is definite in advance, i.e., there is only one phase(bainite) in the matrix, the structure observed under STM in Fig. 3 is bainite.

It can be seen from Fig. 3 that bainite is composed of small subunits. The subunits are of regular shape, arranged in proper order from the origin to the tip of the bainite plate along the growth direction and decrease progressively in size. The biggest subunit is near the original part of the plate which is ca. 800 nm × 300 nm while the smallest one is the tip of the plate with the size of ca. 60 nm × 60 nm, as shown by *a* and *b* in Fig. 3b.

It can be found in Fig. 3 that there exists tiny roughness on the surface of subunits. In order to detect the surface corrugation, the bainite in Fig. 3c was sectioned along the *OS* direction. The result

Fig. 1 Optical micrograph of the specimen(306 ℃, 45 s)

Fig. 2 SEM micrograph of the specimen(306 ℃, 45 s)

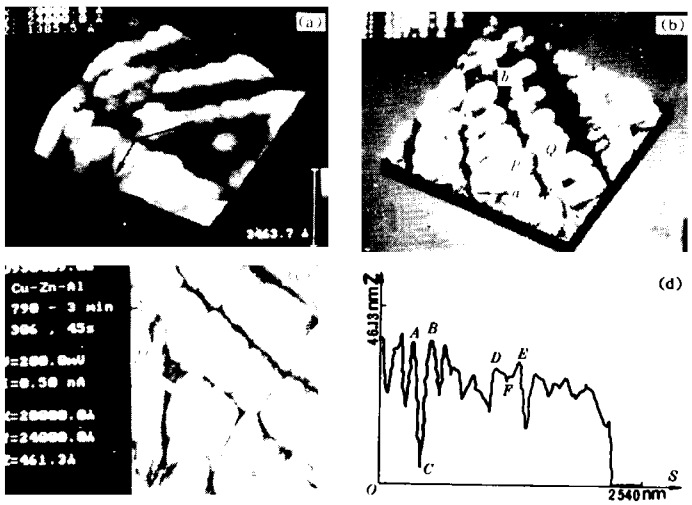

Fig. 3 STM micrograph of the specimens(306 C, 45s)
(a)—corner part of a bainite; (b)—3-D morphology of the front part of a bainite plate; (c)—middle part of a bainite plate; (d)—surface profile of the bainite indicated by *OS* in (c)

was indicated by Fig. 3d, in which the maximum height of coordinate *Z* is 46.13nm. This is the maximum depth of the etched surface of the specimen detected. It reveals that there exist hollows between subunits, as shown by the valley zone. The roughness of the curve implies that the etching rate of the bainite and matrix is different, thus there exists height difference between them. In Fig. 3d, the lowest point *C* between subunit *A* and *B* is about 30 nm lower than *A* and *B*. This is the maximum depth between the subunit and the boundary of two subunits under the present etching conditions. It can also be seen from Fig. 3d that, there exists roughness on the surface of subunit. In Fig. 3d, the lowest point *F* between point *D* and *E* is about 3 nm lower than *D* and *E*. This means the tiniest corrugation on the surface of subunit is only 3 nm.

Up to now, bainitic transformation in Cu-Zn-Al alloys has been studied widely but there is no report about the fine structure inside bainite plates. This is because that formerly used TEM and SEM have a relatively low resolution power(especially a low vertical resolution power) and can not reveal the subunit of bainite. However, STM has superior vertical resolution ability(in this paper, the vertical resolution power of STM has actually reached 0.01 nm), can make up the deficit of SEM and TEM effectively and distinguish the subunits with their boundaries 10~30nm lower than themselves. This makes good progress in revealing the fine structure of bainite in non-ferrous alloys. Similarly, the tiny corrugation which is only about 3 nm on the surface of subunit can not be resolved by TEM and SEM. The fine structure of subunit and the relationship between the subunit and the reverse shape memory effect remains to be studied further.

4 CONCLUSIONS

(1) It is feasible to investigate the bainite

structure of nonferrous alloys by STM in the air at ambient temperature under appropriate heat treatment and surface protection measures.

(2) The fine structure of bainite in the Cu-Zn-Al alloy-subunit has been found for the first time. The subunits take on a regular shape and range in proper order. The maximum subunit is about 800 nm × 300 nm while the minimum one is 60 nm × 60 nm or so.

(3) The maximum depth between the subunit and the boundary of two subunits is ca. 30 nm and the corrugation on the surface of subunit is ca. 3 nm.

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(*From page 86*)precisely predicted.

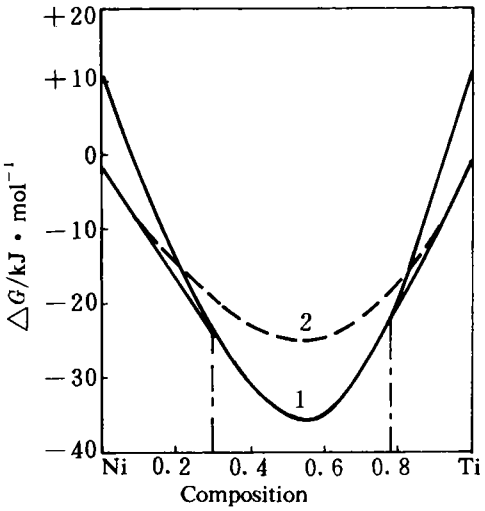

Fig. 8 Free energy of formation for amorphous phase and solid solution in Ni-Ti system at 227 ℃
1—amorphous phase; 2—solid solution

4 CONCLUSIONS

(1) Mixed elemental Ni-Ti powders formed composite powders with layered structure at the starting milling stage; on further milling, the layered structure refined, the crystallite size of nickel crystal diminished, and microstrain increased with the increasing plastic deformation. After 1 h milling, the hardness and size of powders reached saturation values.

(2) For Ni50Ti50 samples, the fraction of amorphous phase increased very rapidly during 0.5 ~2 h milling period, because the deformation-fracturing-welding process made the reaction interface between nickel and tiatnium increase. At the final milling stage, amorphization rate decreased, after 7 h milling, amorphization process completed.

(3) Ni_xTi_{100-x} ($40 \leqslant x \leqslant 60$) amorphous alloys were obtained, which is basically in agreement with the result calculated by thermodynamics method.

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