In situ heating TEM observations of a novel microstructure evolution
in a low carbon martensitic stainless steel

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Abstract

A novel lath-shaped ω phase has been observed in the 0Cr13Ni4Mo low carbon martensitic stainless steel after quenching from high temperature. The orientation relationship is determined as: $[011]\alpha//[2\bar{1}\bar{1}0]\omega$ and $(2\bar{1}1)\alpha//(01\bar{1}0)\omega$. Using in situ heating transmission electron microscopy (TEM), we have investigated the microstructure evolution of the steel during heating. It has been found for the first time that the ω phase dissolves gradually during heating. Meanwhile, another newly identified nanometer scale λ phase precipitates homogeneously distribute within the martensite matrix. The λ phase precipitates have sizes of several nanometers and exhibit an orientation relationship with the matrix as follows: $[011]\alpha//[0001]\lambda$ and $(\bar{2}00)\alpha//(1\bar{2}10)\lambda$. The results are considered to contribute to a better understanding of the microstructure evolution of the martensitic steels during quenching and tempering.

Keywords: Alloy; Electron microscopy; Microstructure; Carbides

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1. Introduction

Since the hexagonal ω phase was first designated in the body-centered cubic bcc (β -phase) Ti alloys, it has attracted much attention because of its complex morphology, its effects on the mechanical properties and so on [1]. It is widely studied in a numerous group IV and V transition metals such as Ti, Zr, Hf and Ta and their alloys [2-9]. It has been reported that the ω phase can be formed either under quenching from a bcc β phase field or under dynamic pressures [1]. It is proposed that the ω phase appears by collapsing two neighboring (111) planes into one and leaving the adjacent (111) planes unaltered within bcc lattice [1]. The crystal lattices of the ω phase are coherent with the bcc lattices and has hexagonal lattice parameter of $a_{\omega} = \sqrt{2} a_{\text{bcc}}$ and $c_{\omega} = \sqrt{3} / 2 a_{\text{bcc}}$. The morphology of the ω phase is always considered to be as small cuboidal or ellipsoidal particles with a diameter of 10-20nm [9].

Recently, Ping [10,11] found and designated the ω phase in an oil-quenched martensite in spring steel with 0.6% C by means of transmission electron microscopy (TEM). He showed that the carbon helped to stabilize and promote the ω phase transformation [10]. The ω

phase could often be easily observed in the martensitic steel from the $[110]_{\alpha\text{-Fe}}$ and $[120]_{\alpha\text{-Fe}}$ zone axis, while their diffraction spots would be overlapped with those of the $\alpha\text{-Fe}$ from $[111]_{\alpha\text{-Fe}}$ or $[001]_{\alpha\text{-Fe}}$. However, till now, little attention has been paid on the ω phase in the low carbon martensitic steel. In the present study, we have found a novel lath-shaped ω phase in the 0Cr13Ni4Mo low carbon martensitic stainless steel after quenching from high temperature. Using in situ heating transmission electron microscopy (TEM), we investigated for the first time the evolution of the ω phase in the steel during heating.

2. Materials and experimental methods

The experimental material with the chemical compositions of 0.051C-12.34Cr-3.86Ni-0.45Mo-0.5Mn-0.022P-0.004S (wt.%) was used in this study. The alloy ingot was prepared by vacuum melting and casting. The cast ingot was forged to 35 mm thick and then hot rolled to 12 mm thick plate using several passes with an average reduction rate of 10% per pass. Samples cut from the hot-rolled plate were homogenized and austenitized at 1050 °C for 1 h and then water quenched. Samples were sectioned, mechanically polished and etched using Villella's reagent (picric acid 1g+HCl 5 ml +ethanol 100 ml) for observation in an optical microscope. TEM foils cut from the as-quenched sample were prepared by mechanical thinning and electropolishing with a twin jet polisher at -30°C, using a solution of 90% methanol +10% HClO₄ (in vol.%). In situ

heating TEM observations were carried out in a JEOL 2100 transmission electron microscope equipped with a Gatan double-tilt heating holder at 200 kV. The foils were heated at 10°C/min from room temperature to 750°C under a vacuum of 10^{-5} Pa and held at each targeted temperature for 5 min to keep the temperature stable. At each targeted temperature, the microstructures were observed from the same zone in the TEM foil.

3. Results

3.1 The microstructure characterization of the steel at the as-quenched state

Figure 1a shows the typical optical micrographs of the alloy after quenching from 1050 °C , demonstrating the large scale martensitic structural unites such as packets and blocks within the prior austenite grains. The previous investigations by the authors have proved that only the diffraction peak of the bcc martensite phase can be detected by X-ray diffraction (XRD) in the as-quenched sample [12]. A detailed structure of the sub-blocks was studied by TEM, as shown in Figure 1b. In the TEM bright-field (BF) image (Figure 1b), the structure of martensite laths is clearly visible and has a high density of dislocations. Figure 1c is a selected area elected diffraction (SAED) pattern taken from Figure 1b. It reveals the diffraction spots from the [011] zone axis of the martensitic matrix (bcc α -Fe). It is interesting to find another suit of diffraction spots from an unknown phase, which was never reported in this quenched steel.

According to Ping [10], the unknown phase can be identified to be a ω phase, which has a primitive hexagonal crystal structure with the lattice parameters $a = \sqrt{2}a_{\alpha-Fe} = 0.4052\text{nm}$ and $c = \sqrt{3}/2a_{\alpha-Fe} = 0.2482\text{ nm}$. The orientation relationship between the ω phase and the martensite matrix is determined to be: $[011]\alpha//[2\bar{1}\bar{1}0]\omega$ and $(2\bar{1}1)\alpha//(01\bar{1}0)\omega$. The dark field micrograph of the ω phase is imaged by using the $[01\bar{1}0]\omega$ diffraction spot as shown in Figure 1f. It can be seen that the ω phase precipitates are lath shaped and paralleled with the martensite laths. This is completely different from the observations in previous studied, which reported that the ω phase always occurs in bcc phase in a cuboidal or ellipsoidal shape [1, 5]. It is difficult to distinguish the ω phase from the martensite lath from the TEM BF image.

3.2 In situ observation of the microstructures at the temperature of 500-650°C

The as-quenched TEM sample was first heated to 500 °C. Figure 2a shows the in situ TEM-BF images recorded from the same area as shown in Figure 1 at this temperature. No obvious changes can be seen from the microstructure characterization compared with Figure 1b. The corresponding SAED result taken from Figure 2a is displayed in Figure 2b. However, different from the Figure 1c, three sets of diffraction spots can be identified in Figure 2b: the $[110]$ zone axis from the martensite

matrix, the $[2\bar{1}\bar{1}0]$ zone axis from the ω phase and another unknown phase. It is evident that the ω reflections present at $1/3$ (or $2/3$) $\{112\}\alpha$ -Fe locations, while some reflections from the unknown phase are located at the $1/2\{200\}\alpha$ -Fe locations. The hexagonal shaped diffraction spots of the unknown phase are pointed out by red arrows in Figure 2b. It can be calculated that the lattice parameter $a=0.57$ nm, which cannot match well with the well-known carbide precipitates in the steels such as ϵ carbide and so on. It is of great interest to find that the unknown phase can be indexed with a hexagonal close packed crystal structure based on the results of Tirumalasetty et al. [13], who have determined the crystal structure of this phase precipitate by TEM in a TRIP assisted steels. In this paper, we call the unknown phase the λ phase. Depending on their results [13], the lattice parameters of the λ phase are: $a=b\approx 5.73\text{nm}$, $c\approx 12.06\text{nm}$. The λ phase exhibits a definite Pitsch-Schraeder (P-S) orientation relationship with the matrix: $[011]\alpha // [0001]\lambda$ and $(\bar{2}00)\alpha // (1\bar{2}10)\lambda$. Figure 2c displays the dark field TEM image recorded from the ω phase by using the $[01\bar{1}0]\omega$ diffraction spot. Comparing with Figure 1d, we can find that the size of the ω phase became smaller and the quantity decreased. A detailed analysis of the morphology of the λ phase will be given in the below part, which indicates that the λ phase precipitates are several nanometers and dispersed in the martensite matrix. When the sample is heated up to 650°C , the TEM BF image of the in

situ area is shown in Figure 2d. It can be seen clearly that the dislocation density in the martensite matrix decreased. This means the dislocation recovery occurs during tempering. The ω phase and the λ phase are coexisted in the martensite matrix from the corresponding SAED pattern (Figure 2e), which can be indexed just like Figure 2b. The dark field TEM image of the ω phase by using the $[01\bar{1}0]\omega$ diffraction spot was shown in Figure 2f. Compared with Figure 2c, it can be found that more ω phase precipitates were dissolved.

3.3 In situ observation of the microstructures at the temperature of 700-750°C

On heating this TEM sample at the higher temperature of 700-750°C, it was observed that the ω phase precipitates had largely dissolved. These results are evident from Figure 3. Figure 3a-c are the in situ TEM images at the temperature 700 °C. It can be seen that the dislocation recovery still occurs. Compared with the SAED pattern shown in Figure 2e, the ω reflections at the $1/3$ and $2/3$ $\{112\}\alpha$ -Fe locations have disappeared substantially, clearly indicating the dissolution of these ω precipitates at this tempering temperature. Another two sets of diffraction spots can be observed: $[011]$ zone axis from the matrix and $[0001]$ zone axis from the λ phase. The dark field TEM image of the λ phase using $(11\bar{2}0)$ reflection was shown in Figure 3c. It can be seen clearly that the λ phase precipitates are very fine and spheroidal in nanometer size, dispersively

distributed in the matrix. Actually, we can find the morphology of the λ phase precipitates like sesame located in the martensite matrix clearly in Figure 3d, which shows the in situ TEM-BF image at the temperature 750 °C. It can be seen that a high density of nanoscale λ precipitates have nucleated from the martensite matrix. The corresponding SAED pattern (Figure 3e) can be indexed as the same as Figure 3b. The dark field micrograph (Figure 3f) shows the λ phase precipitates are still nanoscale and homogeneously distributed in the matrix. By comparison with Figure 3c, it is evident that the λ phase precipitates have not coarsened even at a higher temperature. It is considered that the low interface energy between the spheroidal λ phase precipitates and matrix is effective in stabilizing the nanoparticles.

3.4 In situ observation of the microstructures at room temperature cooled from 750°C

Figure 4 shows the microstructure of the sample cooled to room temperature after heating at 750 °C. From the in situ TEM-BF micrograph (Figure 4a), it can be found that dislocation arrays are formed during cooling. The corresponding SAED obtained from the same region was shown in Figure 4b. It is obvious that the electron diffraction patterns are from diffraction spots of the martensite matrix and the λ phase. The dark field TEM image of the λ phase using the $(\bar{1}\bar{1}20)$ reflection of the λ phase confirmed that it can be stable to room temperature during

cooling, as shown in Figure 4c.

4. Discussion

Actually, in addition to the ω and λ phase, other phases such as $M_{23}C_6$ carbides and the reversed austenite are also present in the microstructure during tempering [14]. However, the $M_{23}C_6$ carbides and the reversed austenite are not found from the in situ TEM area we observed. These ω precipitates are expected to be the results of an athermal transformation during the quenching. Hsiung et al. [9] proposed a dislocation mechanism for the ω phase transformation during shear deformation, where the ω phase can be produced by the glide of partial dislocations of the type $1/3[111]$, $1/6[111]$ and $1/12[111]$ dissociated from the $1/2[111]$ perfect dislocations in the bcc structure. In our case, when the 0Cr13Ni4Mo steels were quenched from the high temperature to room temperature, leading to the formation of martensite from austenite. Martensite is often referred to as a diffusionless and shear transformation, generated by a specific deformation of the austenite [15]. Meanwhile, a high density of dislocations of approximately the order of 10^{14} m^{-2} is introduced into the martensite matrix [16]. Thus, it is deduced that the ω phase is most likely formed by the gliding of partial dislocations.

The morphology of microstructures affects the mechanical properties. In the low carbon martensite stainless steels, it is thought that the high hardness and brittleness of the quenched steels is due to the formation of

martensite. There are several possible strengthening mechanisms to explain the origin of the high strength of martensite, such as substitutional and interstitial solid solution or dislocation strengthening and so on [17, 18]. In this study, the ω precipitates formed in the martensite matrix on quenching from the high temperature was observed. It has been generally supposed that the ω phase has a marked effect on the mechanical properties in alloys. The ω phase formation leads to increase in strength by precipitate-hardening with consequent loss of ductility [19, 20]. Tempering is necessary to modify mechanical properties of the martensite steels, where the ductility of the steels improves as the tensile strength falls usually. This has been attributed to some reasons such as the dislocation recovery [21]. From above results, it is found that tempering at higher temperatures leads to dissolution of the ω phase and formation of the nanoscale λ phase precipitates. The lattice coherency of the λ phase structure with the bcc matrix can make it easier for dislocation to cut through the nanoscale precipitates, which is thought to improve ductility [22].

5. Conclusions

In summary, a lath-shaped ω phase has been observed by TEM in the 0Cr13Ni4Mo low carbon martensite stainless steel. The ω phase exists in the as-quenched martensite matrix, with the orientation relationship: $[011]\alpha//[2\bar{1}\bar{1}0]\omega$ and $(2\bar{1}1)\alpha//(01\bar{1}0)\omega$. Tempering at higher

temperature leads to dissolution of ω phase gradually. Meanwhile, another nanometer-scale λ phase precipitates homogeneously distribute within the martensite matrix during heating. The λ phase precipitates have sizes of several nanometers and exhibit an orientation relationship with the matrix as follows: $[011]\alpha//[0001]\lambda$ and $(\bar{2}00)\alpha//(1\bar{2}10)\lambda$. The results help us better understand the microstructure evolution of the martensitic steels during quenching and tempering.

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Figure Captions

Figure 1 (a-b) The OM and bright field TEM images of the sample after quenching from 1050 °C; (c) A SAED pattern from [110] matrix and $[2\bar{1}\bar{1}0]$ ω phase taken from (b) and (d) The dark field TEM image from the same region of (b) using $(01\bar{1}0)$ ω phase reflection

Figure 2 (a-c) are the in situ bright field TEM image, the corresponding SAED pattern from $[2\bar{1}\bar{1}0]$ ω phase, [011] matrix and [0001] λ phase taken from (a) and dark field TEM image from the same region of (a) using $(01\bar{1}0)$ ω phase reflection at the temperature 500°C; (d-f) are the in situ bright field TEM image, the corresponding SAED pattern and the dark-field TEM image from the same region of (d) using $(01\bar{1}0)$ ω phase reflection at the temperature 650°C

Figure 3 The in situ TEM images at 700°C where (a) is the bright field image; (b) is the corresponding SAED pattern and (c) is the dark field image showing the distribution of λ phase precipitates using the $(11\bar{2}0)$ reflection of the λ phase; The in situ TEM images at 750°C where (d) is the bright field image; (e) is the corresponding SAED pattern taken from (d) and (f) is the dark filed image showing the distribution of λ phase precipitates using the $(11\bar{2}0)$ reflection of the λ phase

Figure 4 The in situ TEM images of the sample cooled to room temperature after heating at 750°C where (a) is the bright field image; (b) is the corresponding SAED pattern and (c) is the dark filed image

showing the distribution of λ phase precipitates using the $(\bar{1}\bar{1}20)$ reflection of the λ phase

Figure 1

Figure 2

Figure 3

Figure 4