Ultrafine Ferrite Grains Produced by Tempering Cold-rolled Martensite in Low Carbon and Microalloyed Steels

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Ultrafine ferrite grains as small as a few hundred nano meters were obtained, without severe plastic deformation, by tempering cold-rolled martensite in a low carbon and a microalloyed steel. A multilevel subdivision mechanism responsible for the formation of ultrafine ferrite grains in cold-rolled martensite was discussed. It involves subdividing firstly a prior austenite grain into several martensite packets by phase transformation and then further subdividing the martensite structure into ultrafine cell blocks by plastic deformation. The relatively large misorientation between the ultrafine cell blocks achieved at a moderate strain level in martensite may be attributed to the interaction between the transformation introduced and the deformation introduced dislocations. Ultrafine ferrite grains were developed from the cell blocks during tempering at the temperature range from 500 to 600°C for 60 min. It was also demonstrated that the microalloying precipitates can effectively pin down the movement of dislocations and grain boundaries and thus, can increase the thermo stability of the ultrafine grained microstructure.

KEY WORDS: ultrafine grains; cold rolled martensite; tempering; microalloyed steel.

1. Introduction

Ultrafine grained (UFG) materials and their production methods have received extensive attention from material scientists during the past decades. This is because grain refinement is the only known approach that can improve strength and toughness at the same time. Most existing methods for producing UFG structure are based on severe plastic deformation (SPD), such as equal channel angular pressing (ECAP), accumulative roll-bonding (ARB), and high pressure torsion (HPT). Although these methods are capable of obtaining submicron or nano-scaled microstructure, the need of using special equipments to achieve the necessary huge accumulative strain makes them inadequate and uneconomic in mass production of UFG materials.

In recent years, alternative methods has been investigated to obtain ultrafine ferrite grains, e.g. from cold-rolled martensite in low carbon steels and from warm-rolled 17Ni-0.2C martensite steel. Since no severe plastic strain and special equipment are needed, these methods are believed to be superior for mass production of UFG steels. The first method mentioned above has drawn particular attention from metallurgists because it allows to takes the advantage of the interaction between the transformation introduced and the plastic introduced dislocations, which may promote the formation of the cell blocks with large misorientation. However, the forming mechanisms of the cell blocks during the process are still not fully understood.

In the present study, the formation of ultrafine ferrite grains by tempering the cold-rolled martensite in a low carbon and in a microalloyed steel was studied. Particular attentions were paid to the mechanisms of the formation of the cell blocks in martensite during deformation and the formation of the high angle grain boundaries during tempering, as well as the feasibility of using microalloying elements to improve the thermal stability of the obtained ultrafine ferrite grains.

2. Experimental Materials and Procedure

Two steels were tested; their compositions are shown in Table 1. Steel No. 1 contains microalloying elements (Nb, Ti and V) and No. 2 is microalloy free. Both steels contain Si in the concentration range of typical TRIP steel. The two steels received as hot-rolled plates with thickness of 12 mm were cut into several 70 mm × 150 mm blocks. After austenitizing at 1 200°C for 40 min, the blocks were further hot rolled to sheets with thickness of 3 mm and then directly quenched in 10% saltwater at the finish rolling temperature of 940°C, which is well above the A3 temperatures of 914°C and 900°C calculated respectively for steel No. 1 and No. 2 using the thermo-calc software.

| Table 1. Composition in Wt Pct of experimental steels. |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Steel          | C   | Si  | Mn  | Nb  | Ti  | V   | P   | S   |
| No.1           | 0.16| 1.76| 1.75| 0.050| 0.065| 0.095| <0.016| <0.006|
| No.2           | 0.17| 2.31| 1.58| —   | —   | —   | <0.006| <0.004|

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The hot-rolled sheets were cut into 250 mm × 30 mm pieces and went through a 15 pass cold rolling with a total reduction of 50%. Some of the cold-rolled sheets were subsequently tempered at temperature range from 450 to 650°C for 60 min.

Optical and scanning electron microscopy (SEM) specimens were prepared from as-quenched, cold-rolled and tempered sheets using standard polishing and etching techniques. SEM observations were carried out using JEOL JSM-5900 Scanning Electron Microscope at 20 kV. Thin foils were prepared using the usual twin-jet electropolishing and were observed in Philips CM200 TEM at 200 kV. The microstructure in the transverse direction (TD) was observed on SEM and that in normal direction (ND) was observed on TEM. Carbide precipitation in steel No. 1 was investigated using carbon replica using a JEOL2100 FE-TEM with EDX analysis. The high-resolution electron backscattered diffraction (EBSD) in FE-SEM (HITACHI S-4300E) equipped with a TSL-OIM software was employed for automatic orientation mapping acquisition. Data for producing misorientation angle distributions were obtained by EBSD scanning over a 50×50 μm² area with a 0.2 μm step size. Microhardness of the tempered sheets was measured using a FM 700 micro Vickers hardness tester with a testing force of 300 g and loading time of 10 s.

3. Results

Figure 1 shows the SEM micrograph of the as-quenched martensite in steel No. 1 and No. 2. Typical lath morphology of martensite in low carbon steels is observed. The prior austenite grain boundaries can also be seen clearly, e.g. that marked with arrows. In this way, the prior austenite grain size was estimated to be about 19 μm in steel No. 1 and 23 μm in steel No. 2, respectively. They are considerably smaller than that reported by Ueji et al. in a similar study where experimental sheets were quenched directly after reheating without hot deformation.9)

The lath structure of the as-quenched martensite in steel No. 1 is detailed in Fig. 2. It can be seen that martensite laths about 0.2 μm in width contain high density of dislocations. Similar lath structure was also observed for the as-quenched martensite in steel No. 2.

The SEM micrograph of the cold-rolled martensite in steel No. 1 is shown in Fig. 3. In comparison with the martensite structure shown in Fig. 1, the majority of the martensite laths in Fig. 3, which are randomly orientated originally after quenching, are turned to the rolling direction (RD) after a 50% cold-rolling. The corresponding TEM micrograph of the microstructure is given in Fig. 4(a) showing the detailed structure of the deformed laths. It can be seen that dark contrast caused by dense dislocations makes the martensite laths bamboo-like even though they remain largely parallel to each other. The dislocation structure, which has an apparent cell size of 300 nm in average, suggests that shear banding and severe sliding have taken place within and between martensite laths during cold rolling. The selected area diffraction (SAD) patterns taken from the circled area in Fig. 4(a) using an aperture with a diameter of 1.6 μm are ring-like indicating that different crystal orientations had been developed during cold rolling.

On the other hand, as shown in the circled region A in Fig. 3, a small fraction of laths are roughly perpendicular to RD and/or severely bended. The corresponding TEM micrograph of the bended martensite laths is given in Fig. 4(b). No individual martensite lath can be distinguished, but dense dislocation structures with a mean cell diameter of 300 nm can be observed. The disappearance of lath boundaries under TEM indicates that the martensite laths in this region underwent a more severe and uniform deformation. This explanation is in line with the SAD taken from the circled area in Fig. 4(b), which shows better developed ring-
like patterns in comparison with that associated with Fig. 4(a). Finally, the corresponding TEM micrograph of the martensite laths perpendicular to RD as shown in region A in Fig. 3 is given in Fig. 4(c). It can be seen that even though dense micro shear bends were introduced into the martensite laths by the cold rolling, the morphology of the laths retains more or less unchanged. The associated SAD patterns, as also shown in Fig. 4(c), are spot-like indicating that only a single crystal orientation exists in the selected area. It suggests that the martensite laths perpendicular to RD had received relatively small straining than that bended or parallel to RD.

Microstructure changes of the cold-rolled martensite after 60 min. tempering at different temperatures are shown in Fig. 5 for both steels. As can be seen in Figs. 5(a) and 5(f), after 60 min tempering at 450°C, the lath morphology had almost completely been erased in the microstructure. However, both dislocation density and the size of dislocation cells do not seem to be changed even though the dislocation cell walls had apparently better developed (to compare with Figs. 4(a) and 4(b)). At 500°C (Figs. 5(b) and 5(g)), some dislocation cell walls were converted into grain or subgrain boundaries, especially in steel No. 2 (see Fig. 5(g)). At 550°C, equiaxed grains with sharp boundaries in the size range from 200 to 500 nm started to appear in steel No. 1 as shown in Fig. 5(c). By contrast, as shown in Fig. 5(h), equiaxed grains with similar size had fully developed in steel No. 2 at the same temperature. In addition, as indicated by the arrows in Figs. 5(c) and 5(h), fine cementite particles of several nanometers in diameter started to appear at 550°C in both steels. At 600°C, most of the dislocation cell walls in steel No. 1 had been converted into sharp grain boundaries as shown in Fig. 5(d) even though dislocation dense areas can still be found. By contrast, grains in steel No. 2 had coarsened as large as a few micrometers as shown in Fig. 5(i). It can also be seen that cementite particles (indicated by arrows) had coarsened slightly in steel No. 1 (see Fig. 5(d)) but significantly in steel No. 2 (see Fig. 5(i)). As can be seen in Fig. 5(e), significant growth of both ferrite grains and cementite particles in steel No. 1 occurred when the tempering temperature was increased to 650°C.

Microhardness of the cold-rolled martensite in both steels after tempering for 60 min at different temperatures was measured and plotted in Fig. 6. It can be seen that the hardness decreases slowly as temperature is below 550°C, but quickly when the tempering temperature exceeds 550°C. The decline of hardness with tempering temperature is a consequence of the reduction of dislocation density and grain coarsening. As can be seen in Fig. 5, at tempering temperatures below 550°C, the microstructure of the cold-rolled martensite underwent mainly dislocation rearrange-
4. Discussion

4.1. Mechanism of the Formation of Ultrafine Grains in Cold-rolled Martensite

It has been demonstrated clearly in Fig. 5 that ultrafine grains as small as a few hundred nm in diameter were formed. The ultrafine grains started to grow rather quickly in steel No. 1 when the tempering temperature exceeded 600°C and in steel No. 2 when the tempering temperature exceeded 550°C. Combining the information given in Figs. 5 and 6, it seems reasonable to conclude that the strength of the cold-rolled martensite may be largely retained up to the formation of the ultrafine grains, but it will be lost quickly as the grain coarsens begins.

4.1.2. Subdivision by the Formation of Cell Blocks in Martensite during Cold Rolling

Like the microstructure change in ferrite undergoing severe plastic deformation (SPD), cell blocks and dislocation cells with large crystal misorientation form in martensite during deformation. However, there are important differences between the mechanisms of forming high angle cell blocks in ferrite and that in martensite that is of a body-centered tetragonal (BCT) crystal structure. First of all, the strain required for forming such cell blocks in martensite is much smaller than that in ferrite. The former, as indicated in the present study, is only 50% reduction, or an equivalent true strain of 0.8. By contrast, the latter is usually 4 or larger. The dramatic difference is likely caused by the high density of accommodation dislocations and block/packet boundaries introduced by martensite transformation. It has been demonstrated that dislocation density in martensite transformed at 300°C can be as high as \(7.4 \times 10^{15} \text{ m}^{-2}\). It is in the same order of dislocation density in severely cold-deformed ferrite. More importantly, the accommodation dislocations are likely sessile making them strong barriers to moving dislocations and thus, can accelerate the formation of dislocation cell structures. Usually, such a high density of sessile dislocations can only be obtained in ferrite after severe plastic deformation. In addition, martensite block/packet boundaries are well known to be high misorientation and thus can effectively affect dislocation movement and multiplication. Furthermore, due to the high concentration...
of silicon in both the steels tested, a considerable volume fraction of retained austenite phase is likely to present in martensite matrix resulting in additional barriers to the movement of dislocations. Because of the high density of the transformation introduced accommodation dislocations, martensite block/packet boundaries and the second phase particles of retained austenite, more dislocations are stored in the crystal for a given macro plastic strain and in turn dislocation cells are formed with increased rate. As dislocation density increases, cell blocks with large misorientation are developed. The ring-like patterns of the selected area diffraction (SAD) given in Figs. 4(a) and 4(b) indicate that cell blocks with large misorientation exist in martensite after 50% cold-rolling. This can be seen more clearly in Fig. 8 where the number fraction of misorientation angle of cell blocks in cold-rolled martensite measured for steel No. 1 and No. 2 are plotted. It shows that more than 50% of the detected crystal area have a misorientation larger than 15°.

The second difference, which is worthy of notice as well, is that the boundaries between high angle cell blocks in cold-rolled martensite are more chaotic than that in ferrite undergone severe plastic deformation. As shown in Figs. 4(a) and 4(b), such boundaries are actually regions with dense dislocations. This indicates the rate of dynamic recovery, which determines the dislocation rearrangement and annihilation rate, is slower in deformed martensite than that in deformed ferrite. This may be attributed to the fact that accommodation dislocations do not generally sit in a slip plane and thus make no contribution to the population of recovery sites, which control the mechanical dynamic recovery rate17) and in turn result in a slower dynamic recovery.

4.1.3. Transformation from Martensite Cell Blocks to Ultrafine Ferrite Grains during Tempering

The tempering process of the ‘regular’ as-quenched martensite involves the decomposition of supersaturated single BCT phase into ferrite and cementite phases and the subsequent recovery and recrystallization of the ferrite phase. During recovery, the dislocations within the ferrite laths are rearranged and annihilated, but the lath boundaries, which are essentially low angle, retain stable up to about 600°C. The lath-shaped ferrite grains are usually changed to equiaxed grains between 600°C and 700°C as a result of recrystallization.12) Although the phase change of the cold-rolled martensite during tempering should be comparable to that of the as-quenched martensite, the resulting microstructures are totally different. As shown in Fig. 5, ultrafine grained ferrite phase is obtained in the cold-rolled martensite after tempering. The difference in the resulting microstructure is originated from the starting microstructure of the cold-rolled martensite where ultrafine cell blocks with high angle misorientation were formed during plastic deformation (see Fig. 4). The interior of cell blocks, which is relatively dislocation free, is separated by dislocation dense areas or cell walls from each other. At the recovery temperature range 450–600°C, dislocations within the cell walls are rearranged and annihilated. As a result, the cell walls become thinner or the cell blocks grow while rotating. This phenomena is similar to the phenomena usually observed during continuous recrystallization.13,14) When two cell blocks grow into impingement, a sharp grain boundary is formed between them. As shown in Fig. 5, such sharp grain boundaries started to appear at 500°C in both steels. The majority of the cell walls had been transformed into sharp boundaries at 550°C in steel No. 2 and at 600°C in steel No. 1. As indicated by the distribution of the grain boundary misorientation measured for the both steels at 550°C (Fig. 9), most of the boundaries are high angle. In comparison with Fig. 8, it is clear that the tempering process may increase the population of high angle grain boundaries.

It is important to note that the underlying mechanism of the formation of ultrafine ferrite grains from deformed martensite is still under debate. More experimental evidences are required to differentiate the contribution from
each possible mechanism suggested so far such as the effect of block/packet boundaries, solute carbon, initial dislocation density and second phase particles.

4.2. Effect of Microalloying Elements

It has been observed in Fig. 5 that the temperatures at which clear grain boundaries (thus the ultrafine grains) started to form and at which the ultrafine grains started to coarsen in the microalloyed steel No. 1 are at least 50°C lower than that in steel No. 2. The retardation of the ultrafine grain formation and their subsequent coarsening in steel No. 1 can be attributed to the pining effect of microalloying precipitates on dislocation and grain boundary movement. Using carbon replica, carbide particles were detected in samples of cold-rolled martensite undergone tempering at 550°C for steel No. 1. As shown in Fig. 10, the precipitates are combined carbide phase containing Nb, Ti and V and are as small as a few nano meters in diameter. Such a carbide phase is supposed to be thermodynamically stable in ferrite and are very effective in retarding grain growth according to Zener.\(^\text{15}\) Thus, the present results have suggested a practical approach of increasing the thermal stability of ultrafine grained microstructure in steels.

5. Conclusions

(1) Ultrafine ferrite grains as small as a few hundred nanometers can be obtained from 50% cold-rolled martensite after 60 min tempering at temperatures from 500 to 600°C.

(2) The ultrafine ferrite grains formed in cold-rolled martensite are induced by multilevel subdivisions of microstructure, including the subdivision by martensite transformation and the subdivision by the formation of dislocation cell blocks.

(3) The dislocation cell blocks formed in martensite during cold rolling are separated by thick dislocation walls of which more than 50% are with a misorientation greater than 15°.

(4) Sharp grain boundaries are developed from cloudy cell block walls during tempering as a result of dislocation rearrangement and annihilation.

(5) The rates of the development and the subsequent coarsening of the ultrafine ferrite grains can be significantly retarded by the carbide precipitation of microalloying elements during tempering.

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