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Coarsening of nanoscale (Ti,Mo)C precipitates in different ferritic matrixes

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ABSTRACT

Coarsening of nanoscale (Ti,Mo)C precipitates within quasi-polygonal ferritic (QPF) matrix and polygonal ferritic (PF) matrix is studied via HRTEM and In-situ heating TEM. Influenced by different nucleation processes, inverse coarsening process showing dissolution of large clustered precipitates and growth of small interphase precipitates is directly observed in the PF matrix. However, due to the evolution of high-density subboundaries, coarsening of precipitates in QPF matrix is mainly characterized by the subboundary migration assisted coarsening process, during which arch-like coarsened precipitates form after the sweeping of subboundaries. Analysis of atomic structure clarify that "imposts" of the arch-like coarsened precipitates are established by the re-precipitation of solute atoms from movable subboundary to the close packed planes {111} of (Ti,Mo)C precipitates, and that the "key stones" are constructed due to the change of re-precipitation planes to {200}. Geometric phase analysis (GPA) illustrates that not only the change of re-precipitation direction during the formation of arch-like precipitates, but also the selective coarsening of clustered precipitates in PF matrix, is caused by the highly anisotropic strain field around (Ti,Mo)C precipitates.

1. Introduction

Precipitation strengthening plays an important role in various alloying systems, such as low alloy steels [1,2], heat resist steels [3] and even high-entropy alloys [4]. Formation of high-density and nanoscale precipitates (< 10 nm) has been persistently studied due to the attractive improvement on mechanical properties. Nowadays, although precipitation status can be controlled through different approaches, the other important aspect, stability of precipitates, needs to be further studied. That is because the strengthening effect is sensitive to the precipitation status. Additionally, stability control through alloying design [5–7] and microstructure optimization [8,9] has achieved great improvement on various service conditions.

According to the Orowan strengthening theory, coarsening process could significantly weaken the strengthening effects. As for the coarsening mechanisms, reduction of interfacial energy for the whole system is generally regarded as the driving force [10]. Based on the lattice diffusion process, Lifshitz, Slyozov and Wagner proposed a theoretical model (LSW theory) to illustrate the detail of coarsening process, it has been widely used and been proved to be reliable [3,9,11–13]. Pipe diffusion mechanism of dislocation is then adopted to account for the relatively fast coarsening process in matrix with high-density dislocations [14,15]. Additionally, since subboundaries are mainly consisted of geometric necessary dislocations, subboundary assisted coarsening (sBAC) process is mainly discussed by assuming a precipitate is traversed by numerous dislocations [10]. Moreover, influenced by the Zener dragging effect, coarsening of precipitates during the sBAC process is generally analyzed by assuming the migration of subboundary is restricted [16,17]. However, as for the matrix with high-density substructures, motion and annihilation of (sub)boundaries is inevitable and even regarded as the dominant phenomenon during the recovery process [13]. Therefore, effects of microstructures on the coarsening of precipitates have yet to be investigated.

Movable precipitates driven by the migration of grain boundary had been reported by Ashis et al. [18,19], related process was investigated through the phase-field method. Nourbakhsh [20] discussed the formation of deformable precipitates considering the interfacial tension and grain boundary diffusion. Additionally, interaction between precipitates and grain boundaries during recrystallization process was also reported [10,21–24]. However, although several researchers have predicted the evolution of precipitates with theory analysis [21] or computational simulation [25], experiment results linking to microstructural information, especially for the coarsening process, are rarely reported. Moreover, dualism of precipitation status [26] within a ferrite grain was reported, but related coarsening process of this mixed precipitation status has not been discussed so far. Accordingly, in this

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study, polygonal ferrite (PF) matrix and quasi-polygonal ferrite matrix (QPF) with different precipitation status, are used to investigate the influence of microstructures. In-situ heating transmission electron microscope (TEM) and high resolution TEM (HRTEM) are adopted to get more accurate information during related coarsening of precipitates.

2. Experiment

The low carbon low alloy steel with composition Fe-0.067C-0.064Ti-0.32Mo-0.039Al-1.5Mn-0.2Si-0.012 N-0.003S-0.006P was used in this research and a heavy plate 35 mm in thickness was achieved after controlled rolling and controlled cooling process, related manufacturing process was presented in our previous research [27]. Specimens cut from QPF matrix and PF matrix were used to conduct investigation. The former has small grains containing numerous substructures and the latter mainly features substructure-free large grains. In order to investigate the coarsening process, these specimens were reheated to 600 °C in a furnace at a heating rate of ~5 °C s^{-1} and held for 60 min. After that, they were quenched to room temperature with water and observed with electron back-scattered diffraction (EBSD, Zeiss Ultra 55) and transmission electron microscopy (TEM, FEI Tecnai F20). Corresponding EBSD specimens were firstly ground with silicon carbide paper and then electro-polished with 10 vol% perchloric acid +90 vol% ethanol at 15 V at room temperature for 10–15 s. Specimens for TEM were thinned to 50 ± 10 μm by silicon carbide paper and then polished in a twin-jet electro-polisher using a solution of 10 vol% perchloric acid +90 vol% ethanol at 20 V at −20 °C for 60–120 s.

In-situ heating experiment was conducted recurring to a heating in-situ holder from Gatan corporation. Since contrast of TEM image can be significantly influenced by the recovery process, evolution of nanoscale precipitates in QPF matrix was hard to trace, therefore the in-situ heating TEM experiment was only carried out for the samples with PF matrix. Additionally, continuous shooting was used to record the coarsening process. HRTEM images were analyzed by the Digital Micrograph software and related geometric phase analysis (GPA) was involved to depict the strain fields around precipitates, which was conducted based on a script file that can be installed in the software [28]. Additionally, size of the virtual aperture was set to be about 1/2a_{ref} to get more accrete results during the GPA process [29].

3. Experimental Results

3.1. Microstructure Evolution

Microstructures before and after the isothermal process are presented in Fig. 1. It illustrates the PF matrix was mainly consisted of high angle boundaries, and after the isothermal process the average grain size slightly increased from ~14 μm to ~16 μm. On the contrary, in the QPF matrix, the microstructure was mainly featured with low angle boundaries (LABs). Migration and annihilation of (sub)boundaries (i.e. LABs) occurred and several subboundary-free regions formed after the isothermal process. Area fraction of these regions was measured to be about 27% after the isothermal process. Our previous research had illustrated that the different kinds of matrixes are mainly determined by the cooling rate within the phase transition stage [27]. Additionally, recovery is of great importance for the appearance of subboundary-free regions. However, although the microstructure evolution in different ferrite matrixes is simple, related precipitation status change significantly within the first hour of the isothermal process according to the statistical results [27]. Therefore, evolution of precipitates in the first hour is studied in detail and related coarsening mechanisms are discussed in the following sections.

3.2. Coarsening in QP Matrix

In-situ heating TEM results are listed in Fig. 2 and different marks are used to trace the evolution of specific precipitates. The selected area is characterized by a mixed precipitation status which contains the typical interphase precipitation region and clustered precipitation region, where the interphase precipitates are small and distributed compactly, but the clustered precipitates are large and distributed sparsely. It is deduced that the large clustered precipitates are generated in the substructures through heterogeneous nucleation before γ-α transition and the interphase precipitates are formed during the γ-α transition process [26]. The precipitation status kept stable within the first 30 min, however, obvious inverse coarsening process was observed after isothermal for 60 min. Related statistical results are presented in Fig. 3a and Fig. 3b, where small precipitates in the interphase precipitation region grow up, but large precipitates in the clustered precipitation region shrink or even disappear.

For better understand the inverse coarsening process, detailed analysis is conducted respectively for the two kinds of regions. With respect to the interphase precipitation region, although most precipitates grow up, several unstable interphase precipitates disappear and leave white dots, one of which is marked with a yellow arrow in Fig. 2d. It means the conventional coarsening process actually happen in the local interphase precipitation region. In the clustered precipitation region, most precipitates shrink and the average diameter decreases from ~6.1 nm to ~5.1 nm. In addition, as shown in the enlarged windows C1 and D1, the precipitate 1 grow larger along with the dissolution of precipitate 2. It needs to be noticed that the shape of precipitate 1 is slightly extended approaching the direction of precipitate 2, which indicates the occurrence of selective coarsening phenomenon that solute atoms diffuse along specific directions. Additionally, as presented in Fig. 3, reduction of area fraction of both the two kind precipitates indicates the dissolving of precipitates.

Extra attention about TEM focusing process verified the change of contrast was not caused by the under-focused condition or over-focused condition [30]. The contrast change around the shrunk or disappeared precipitates is related to the diffusion process, during which alloying atoms gradually dissolve into the matrix, which is induced by the increased solubility of ferrite matrix under the isothermal temperature. Thus, the thickness of the original regions containing dissolved precipitates become thin and finally lead to the reduction of mass thickness contrast of TEM image. Moreover, HRTEM image of a typical interphase precipitates is presented in Fig. 4a, corresponding diffraction pattern achieved through fast fourier transform (FFT) is presented in Fig. 4b, in which the diffraction points marked with red circles are used to conduct inverse FFT to demonstrate the (Ti,Mo)C precipitate. Actually, the selected points should have vanished because of the structure extinction condition of ferrite matrix [32]. However, due to the strain field caused by alloying atoms, the Bragg condition is released so that the coherent precipitates can be distinguished as shown in Fig. 4c. It manifests that the precipitate keeps good coherency with ferrite matrix except few dislocations. Additionally, as shown in Fig. 4d, lattice parameter of the (Ti,Mo)C precipitate measured from Fig. 4a is 4.3 Å, which is in coincidence with previous researches [6,31].

3.3. Coarsening in QPF Matrix

Precipitation status before and after the isothermal process are presented in Fig. 5. As shown in the TEM bright field (BF) image (Fig. 5a), precipitates in the initial stage are tangled with lots of dislocations. Corresponding TEM dark field (DF) image is presented in Fig. 5b. Despite some relatively large precipitates that distributed randomly, distribution of numerous precipitates that smaller than 2 nm is compact, part of them can be regarded as unstable precipitation nucleuses. After isothermal treatment at 600 °C for one hour, precipitates grow up and distribute randomly with a very high density, as