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Behavior of precipitation in bainitic steel during relaxation processing of RPC technique

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Abstract: Thermal simulation test, TEM (Transmission Electron Microscope) and nanobeam EDS (Energy Dispersed x-ray Spectrum) techniques were used to investigate the precipitation behavior of Nb, Ti, Mo *etc.* in HSLA (High Strength Low Alloy) steel. The strain induced precipitation occurred during the isothermal relaxation stage after deformed in the non-recrystallization temperature region. After 30% predeformation at 850 and 900°C, there are two kinds of particles, (Ti,Nb)(C,N) and a few Nb(C,N), to precipitate during holding. The content of Nb in particles rises with the relaxation time increasing. During the final holding stage, some Nb and Ti atoms in the lattice sites of the precipitates would be replaced by Mo atoms, and the Mo content in the precipitates increases with the relaxation time. The results were compared with the refinement effect of microstructures caused by relaxation-precipitation controlling transformation (RPC) processing.

Key words: RPC technique; microalloyed element; (Ti,Nb)(C,N); nanobeam EDS

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1 Introduction

It has been well known that the combination of microalloying and TMCP (Thermal Mechanical Controlled Process) technique is a very promising way to develop HSLA steel in recent years [1,2], and the precipitation behavior in deformed austenite containing one or more microalloying elements is of primary importance in controlling the properties of HSLA steels. During the last decades, most of the investigations in this subject area have been concerned with Nb, Ti, Nb-V and Nb-Mo steels. However, the effect of Ti and Nb is still uncertain and controversial, even if in simple Nb and Ti bearing steels [3-5]. The former work [6] has showed that with combination of TMCP and newly-developed RPC technique, the ultra-refined bainitic microstructure can be obtained in low carbon steel, and the formation of dislocation substructure and the stain induced precipitation behavior during relaxation process play a key role to the refinement. The purpose of present paper was using thermal-simulation tests to investigate the precipitation behavior in multi-microalloyed steel during the relaxation stage. The particle size was measured and the evolution of chemical composition of carbonitrides was surveyed.

2 Materials and experimental procedures

The experimental steel used in this study was fabricated by vacuum induction melting, homogenized at 1200°C and forged into bars of ϕ14 mm. The chemical composition of the material (mass fraction, %) is: C, 0.035; N, 0.0033; Mn, 1.54; Si, 0.22; Nb, 0.076; Ti, 0.080; Cu, 0.32; Ni, 0.33; Mo, 0.33; B, 0.0020. The bars were machined into cylinders of ϕ8 mm×12 mm for thermal-simulation tests. Prior to the deformation, the samples were preheated at 1250°C for 20 min, and then cooled at the rate of 2°C /s to 850°C and 900°C respectively. Finally, the specimens deformed up to 30% were held for different time and followed by water quenching.

The quenched specimens were cut vertically to the compression axis. The carbon replica technique was employed to extract the precipitates from the specimens. The distribution of particle size was determined by using JEOL-100CX TEM. To do the measurement, the magnification was selected as 100000, followed by magnifying 3 times mechanically to determine the size of individual particles. From 200 to 400 particles were measured for each specimen. The type of precipitates

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and the variation of composition were identified by using JEM-2010F and nanobeam technique.

3 Results and discussion

3.1 Morphology of precipitates and variation of particle size during relaxation time

The results of stress relaxation experiment shows that [7] the start time and finish time of precipitation are 20 s and 200 s respectively for the tests steel after pre-deformed for 30% at 850°C. The investigation of the amount of precipitates and the variation of morphology after different relaxation time were carried out in the water quenching specimens. The relaxation time was chosen as 0, 30, 60, 200 and 1000 s.

Figure 1 shows the morphologies of precipitates in the specimens relaxed for different time after deformed for 30% at 850°C. No particles can be observed in non-relaxation specimens (figure 1(a)), except few large inclusions. It can be concluded that, after solution treatment at 1250°C for 20 min, the pre-existed precipitates in the steel have fully dissolved in austenite, and none of the new precipitates formed during the water quenching process. Very small precipitates with a mean particle size of about 4 nm are occasionally observed after relaxation for 30 s (figure 1(b)), they display a chain-like distribution. It seems that the dense dislocations and deformed bands are the preferred nucleation sites for precipitates during relaxation [8]. As the relaxation time prolongs to 200 s, the distribution of precipitates becomes uniformly and the average particle size is up to 10 nm, as shown in figure 1(d). When the relaxation time is further increased to 1000 s (figure 1(e)), the mean size of the precipitates increases continuously and some particles start to coarsen. Meanwhile, the density of particles decreases evidently. The finer particles formed in the early stage of precipitation are elliptical. With the relaxation time increasing, the morphology of precipitates develops gradually into the polygon.

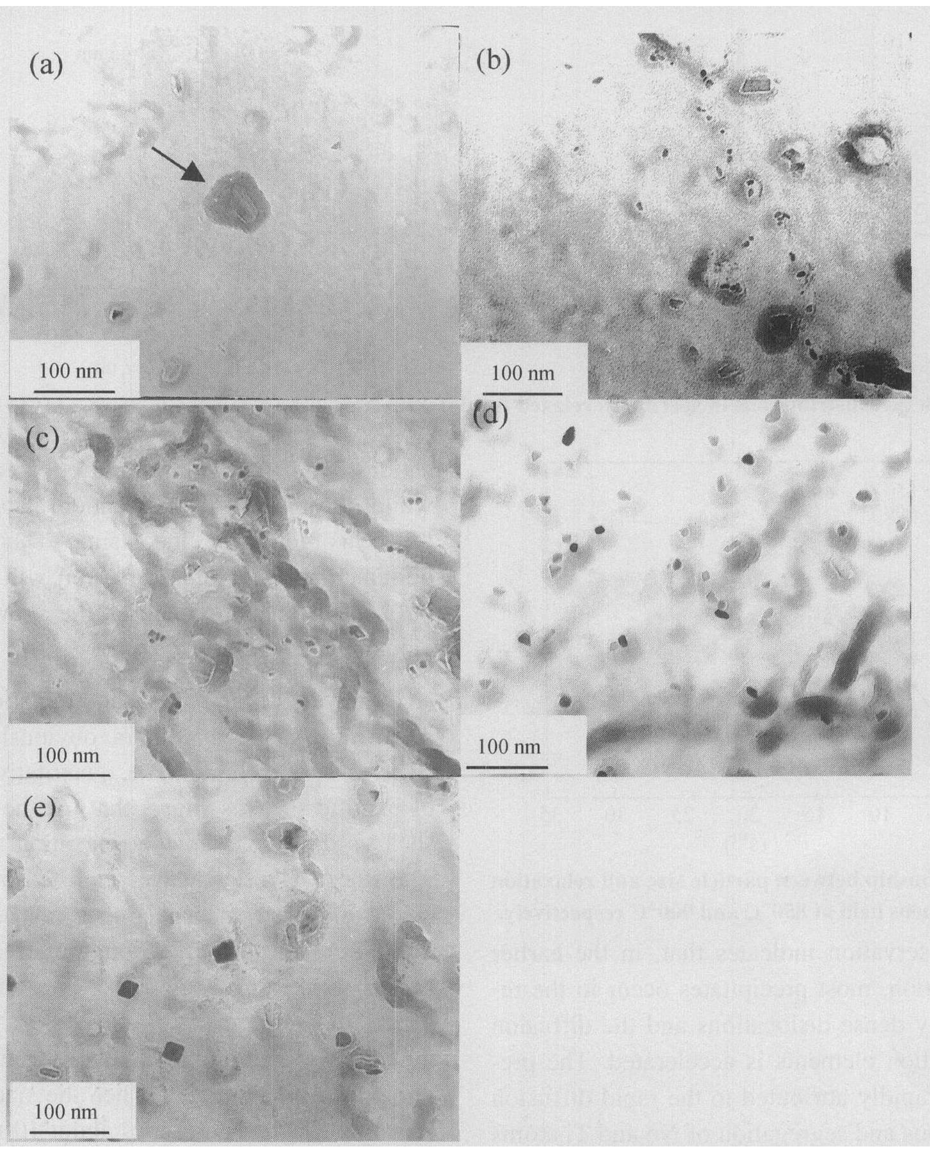

Figure 1 Precipitates in the specimens relaxed for different time after deformed for 30% at 850°C: (a) 0; (b) 30 s; (c) 60 s; (d) 200 s; (e) 1000 s.

The size distribution and the mean values are shown in **figure 2**, which are based on the measured results made on replicas using a quantitative analysis. The particle size distribution corresponds to the normal distribution with all relaxation time, the peak shifts to the right gradually with the relaxation time increasing and the peak location is nearly equal to that of the mean values. The mean particle sizes change from 4 nm to 10 nm during holding periods from 30 s to 200 s. When the relaxation time increases to 1000 s, the mean particle size reaches about 13 nm. The results show that the progress of precipitates during relaxation can be divided into three stages: nucleation, growth and coarsening. At the earlier stage of relaxation, the particle size grow rapidly, however, it grow slowly at the final stage, as shown in **figure 3**.

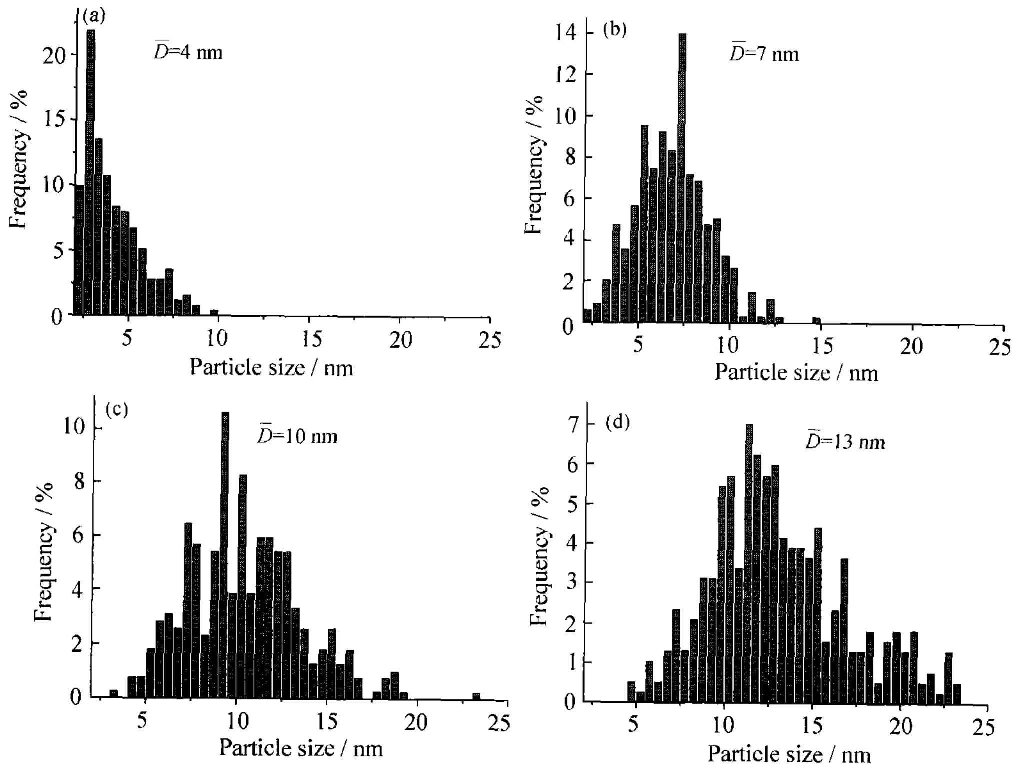

Figure 2 Particle size distributions in specimens relaxed for different time after deformed at 850°C: (a) 30 s; (b) 60 s; (c) 200 s; (d) 1000 s.

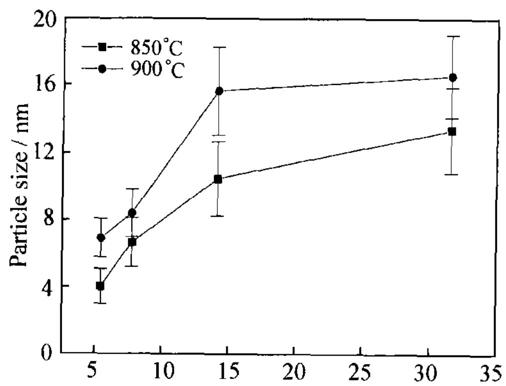

Figure 3 Relationship between particle size and relaxation time while specimens held at 850°C and 900°C respectively.

All these observation indicates that, in the earlier stage of nucleation, most precipitates occur in the region with highly dense dislocations and the diffusion process of solution elements is accelerated. The precipitates grow rapidly attributed to the rapid diffusion along dislocations and segregation of Nb and Ti atoms to the dislocations. In the coarsening stage, the dislocations gradually get rid of the precipitates, meanwhile, the density of dislocation also decreases with the relaxation time increasing. Therefore, the predominant roles of pipe diffusion will be replaced by bulk diffusion which causes the growth rate of precipitates to decrease.

Using the similar thermal-simulation test, the experimental steel can obtain obviously finer bainitic sheaves after cooling. The quantitative measurement of bainitic sheaves shows that [6] the size of bainitic sheaves declines with the relaxation time increasing. The finest bainitic sheaves can be obtained by water quenching after the specimens relaxed for 200 s at 850°C. For further relaxation, the effect of refinement begins weakening. Compared with the results of this paper, the refinement effect of RPC processing involves the distribution density, average size and morphology of precipitates. When the size of precipitates (containing Nb, Ti) reaches about 10 nm in austenite, the finest bainitic sheaves can be obtained.

3.2 Composition evolution of precipitates with different relaxation time

Most investigations on the precipitation behaviour of carbonitrides have focused on Nb, Ti and Nb-Ti steels, and concluded that the most common precipitation found in hot-worked austenite are carbides and nitrides of Ti, Nb, or more complex carbonitrides, such as (Ti,Nb)(C,N). The heterogeneous nucleation of NbC or Nb(C,N) can base on pre-existed undissolvable TiN in Nb-bearing steel [9]. In microalloyed steel containing Nb and Ti, Ti-rich precipitates are observed in a higher temperature while Nb-rich precipitates occur in a lower temperature. During the isothermal holding, the youngest nuclei tend to be Ti-rich, but as they grow, the Ti/Nb ratio decreases [10].

The experimental steel in this paper contains Mo, Ni, Cu, B, *etc.* and the influence of each of them on precipitation process is remarkable. The TEM of JEM-2010F and nanobeam EDS technique are used to investigate the precipitates type and the composition evolution. After predeformation for 30% at 850°C, no finer particles can be found in direct water quenching specimens. Only some coarse inclusions containing Ti along with less Nb are observed which are undissolved particles before hot deformation. **Figure 4** shows the composition evolution of precipitates with relaxation time in the specimens deformed for 30% at 850°C. The relaxation time is 60, 200 and 1000 s, respectively. The results indicate that there are two types of particles, Nb(C,N) and (Nb,Ti)(C,N) in the sample. The former is elliptical with particle sizes less than 5 nm, as shown in figure 4(a), indicated by arrow marks. The particles shown in figure 4(b) are (Nb,Ti)(C,N). Compared with Nb(C,N) precipitates, (Nb,Ti)(C,N) particles are larger and appear as the polygon. Semi-quantitative composition analysis demonstrates that the number of Nb(C,N) particles are much less than (Nb,Ti)(C,N). When the relaxation time increase to 200 s, no Nb(C,N) particles can be found. Figure 4(c) and figure 4(d) indicate that Mo atoms can present in the precipitates during relaxation from 200 s to 1000 s. With the increasing of relaxation time, the fraction of Nb and Ti changes obviously, that is, the content of Nb in particles rises and the Ti/Nb ratio decreases. At the same time, the content of Mo also increases with the relaxation time increasing.

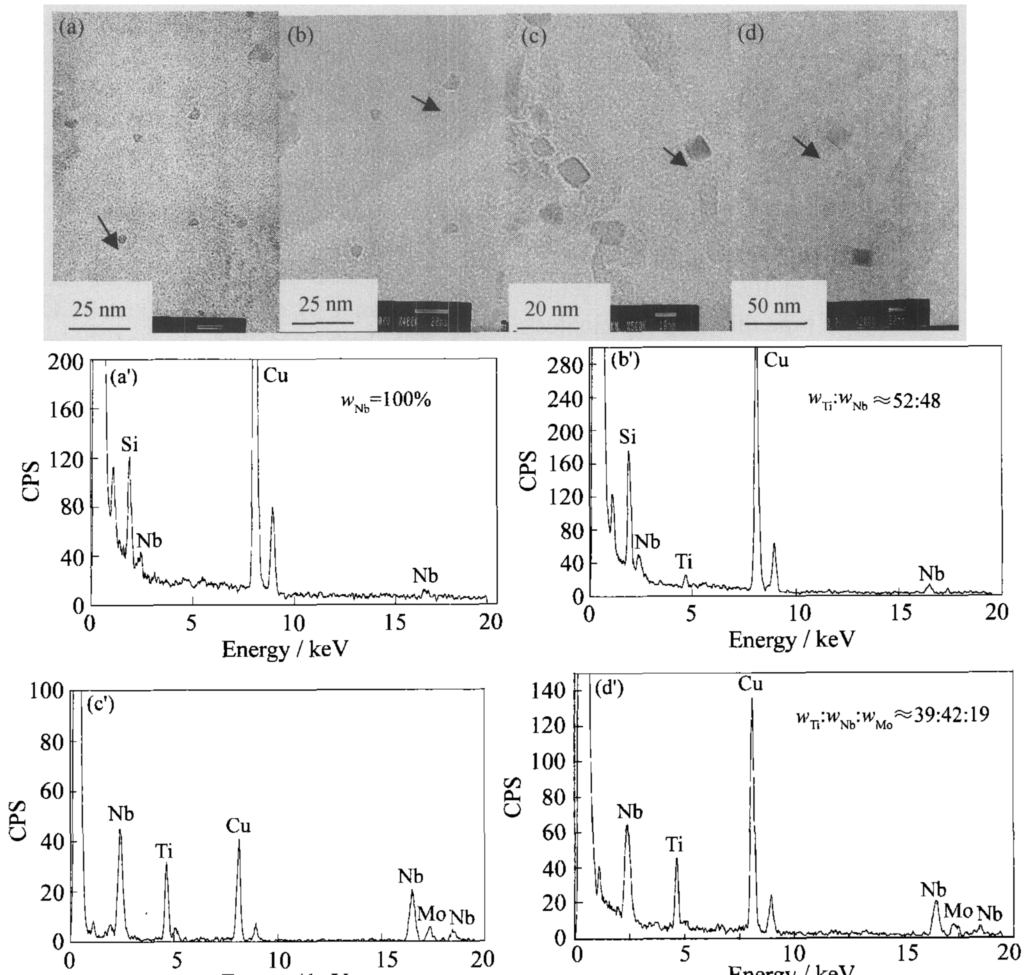

Figure 4 Composition evolution of precipitates with relaxation time in the specimens deformed for 30% at 850°C: (a) and (a') 60 s; (b) and (b') 60 s; (c) and (c') 200 s; (d) and (d') 1000 s.

When the relaxation time increased to 1000 s, the Ti/Nb ratio almost keeps unchanged, but the content of Mo increases as well.

It deserves to be noted that no investigation has been reported about Mo atoms presenting in carbonitrides in hot worked austenite steel. Some works have indicate that Mo carbides of could not form in the austenite temperature region [11,12]. However, the present work shows that Mo can co-exist with Nb and Ti as carbonitrides. The diffraction pattern of precipitates in specimen relaxed for 1000 s at 850°C (**figure 5**) indicates that the precipitates remain the same crystal structure as that of Nb(C,N). Obviously, some Nb and Ti atoms in the lattice of the precipitates are replaced by Mo atoms because Mo carbides can not exists at this experimental temperature. In terms of the variation of Ti/Nb ratio during the holding from 200 s to 1000 s, Mo would replace Nb atoms rather than Ti atoms to some extent.

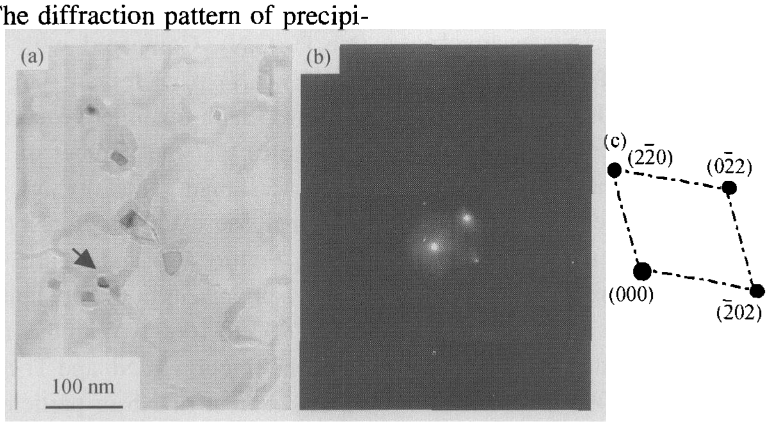

Figure 5 Precipitates in the specimen relaxed for 1000 s: (a) TEM image; (b) diffraction pattern; (c) indexed pattern.

4 Conclusions

(1) During the relaxation period of RPC processing, the strain induced precipitation of carbonitrides can be divided into three stage: nucleation, growth and coarsening. But the particle size distributions in the specimens with different relaxation time overlap significantly.

(2) The precipitates grow rapidly in the early stage of precipitation, it seems that pipe diffusion dominates in the early stage while the growth rate declines due to bulk diffusion playing an important role during coarsening.

(3) The precipitates are complex carbonitrides of Nb and Ti. In the early stage of relaxation, precipitates consists of complex (Ti,Nb)(C,N) along with a few Nb(C,N). With the relaxation increasing, the Ti/Nb ratio declines. In the final holding stage, some Nb and Ti atoms in the lattice of the precipitates are replaced by Mo atoms, but the Ti/Nb ratio does not change obviously.

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