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STUDY OF ULTRA-FINE PRECIPITATES IN LOW ALLOY STEELS

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Abstract - Precipitates formed before and at the peak stage of secondary hardening in tempered low alloy steels were examined by atom probe - field ion microscopy. The present AP analysis confirmed the existence of Mo₂C, NbC, and V₄C₃ even before and at the peak stage of secondary hardening. In addition to alloy carbides, existence of Mo clusters and Nb clusters were found. Formation of such clusters may play an important role in secondary hardening of Mo and Nb steels.

1. Introduction

Remarkable secondary hardening observed on tempering of low alloy steels which contain Mo, V, and Nb has been considered to be due to precipitation hardening caused by the formation of needle-like Mo₂C, plate-like V₄C₃, and plate-like NbC, respectively. However, decisive evidence for the existence of these carbide phases before and at the peak stage of secondary hardening has not been obtained yet, because high density of dislocations are retained in the matrix, and precipitates, if exist, are too small to be analyzed by electron microscopy. In addition, it is quite difficult to determine the morphology and chemical compositions of ultra-fine precipitates less than about 10nm in size even by modern analytical electron microscopy.

AP-FIM is a much more powerful technique for the characterization of such ultra-fine precipitates than electron microscopy. It has been applied to the analysis of precipitates in isothermally transformed steels, nitrided steels, and quenched and tempered low alloy steels. Davies and Ralph suggested the formation of three kinds of precipitates before the peak stage of a tempered Mo steel by FIM observations, but the nature of the precipitates were left unknown.

In the present study, morphology and chemical compositions of the precipitates formed at the early stage of tempering of several low alloy steels containing Mo, Nb, V, and V plus N, respectively, were examined by TEM and AP-FIM. Particular emphasis was placed on the characterization of the precipitates formed at the peak stage of secondary hardening.

2. Experimental procedure

The chemical compositions of the steels used are given in Table 1. 20kg ingots of each steel were vacuum-melted. Main alloying element in each steel was Mo, Nb, V and V plus N,
respectively. Excepting the V-N steel, N content was limited to less than 15ppm. Carbon content in all steels used was approximately 0.15wt.%. After hot rolling, two samples were cut from each steel plate and sealed in evacuated silica capsules. They were solution treated at 1473K for 3.6ks, quenched into iced water, and tempered at 973 or 873K for 3.6ks. For FIM observations and AP analysis, needle-shape specimens (with about 50nm tip radius) were prepared by electropolishing using a mixed solution of CrO3, H3PO4 and H2O at 20v dc. The imaging gas (99.99%Ne) pressure was 10⁻⁴ Pa during FIM observations and the background pressure was approximately 10⁻⁶ Pa. The specimen temperature was kept at 20-30K during AP analysis which was performed at the pulse fraction of 16% and the pulse frequency of 250Hz.

3. Results and discussion

3-1. 0.15C-1.0Mo steel

Figure 1 shows TEM and FIM images of a specimen tempered at 973K for 3.6ks (corresponding to an averaged stage). The TEM image demonstrates the existence of needle-like Mo2C precipitates along the ⟨100⟩α-Fe directions. In the FIM image, a precipitate is recognized as the bright area indicated by the arrow. A ladder diagram of analysis of the precipitate is given in Figure 2, where the total number of ions detected by AP analysis is represented on the abscissa and the number of ions of each element on the ordinate. Concentration of the elements contained can be calculated from the average slopes of the lines for the respective elements. The concentration ratio of Mo to C obtained from Figure 2 is approximately 2:1 and indicates that the precipitate is Mo2C. Thus, the results of AP-FIM is in good agreement with that of TEM observation.

Figure 3 is a TEM image of the steel tempered at 873K for 3.6ks (corresponding to the peak stage of secondary hardening). The precipitates in the matrix can not be distinguished from dislocations. On the other hand, they can be easily revealed by FIM as shown in Figures 4 and 5. It can be concluded that the precipitate in Figure 4 is a needle-like Mo2C based on the evidence that its longitudinal axis is parallel to ⟨100⟩α-Fe direction and that it disappears after field evaporation of only a few atomic layers. According to the results of AP analysis, the detection ratio of Mo to C is 2:1 (Figure 6). The precipitate is thus evidently needle-like Mo2C as in the case in Figure 1. The AP-FIM analysis, therefore, demonstrates that Mo2C precipitates are undoubtedly present at the peak stage of secondary hardening. The Mo2C precipitates are about 20nm long and 3nm wide on the average.

It is to be noted that the present AP-FIM analysis has made clear the existence of another precipitate phase at the peak stage of secondary hardening. This precipitate phase is observed as a row of several atoms and is finer than Mo2C as evident from Figure 5. It is definitely different from Mo2C in two points. First, crystallographically, the row of atoms is observed to be parallel to the [100]α-Fe direction and its location does not change during field evaporation of a few tens atomic layers when the tip axis is parallel to the [001]α-Fe direction. This implies that the precipitate has not a needle-like but a plate-like shape lying parallel to [100]α-Fe planes. Second, in the atom probe analysis, only Mo ions are detected (Figure 7). Namely, it does not contain any C and N at all. Absence of N in the precipitate exclude the possibility of a plate-like Mo nitride (8,9). Thus the precipitate is believed to be a cluster of Mo atoms that does not contain either C or N. Hornbøgen(12) has reported the formation of Mo-rich clusters parallel to [100]α-Fe planes in Fe-Mo binary system. The formation of Mo-rich zones in a tempered Mo steel was suggested by Irani et al.(13) from TEM observations, although the size of their zones is bigger than the Mo cluster found in the present study. The plate-like precipitate reported by Davies et al.(9) may correspond to the present Mo cluster.

Results of FIM observations in the present study showed that the Mo cluster is not present either in the as-quenched martensite structure or in a specimen tempered at temperatures above 923K. It is thus considered as a transient precipitate formed only around the peak hardening stage at 873K. Since the Mo cluster is finer and more densely distributed than Mo2C, its presence may significantly contribute to the secondary hardening of Mo-steel.

3-2. 0.16C-0.03Nb steel
As shown in the FIM image (Figure 8), precipitate phase is extremely fine even after the specimen was tempered at 973K (overaged stage). It is difficult to observe such precipitates by electron microscopy. On the contrary, the FIM image clearly reveals the atomic arrangement of the precipitate. The reason why distinct FIM images are obtained may be due to the stability of the precipitate at the tip surface after field evaporation. The average size of the precipitates is several nm in diameter. AP analysis indicates that the precipitate is NbC (Figure 9).

At the peak stage, many ultra-fine precipitates smaller than 1 nm in diameter are observed (Figure 10). Based on the results of AP analysis, it was confirmed that there are two types of precipitates, one being NbC and another being Nb cluster. The former usually contains nearly the same amount of Nb and C ions as indicated in Figure 11. On the other hand, the latter does not contain C and N at all. Figure 12 shows a linked ladder diagram obtained from several Nb clusters after the probe hole area was aimed at them. Increase in Nb ions without change in C ions is evident at the points B and C in Figure 12. Therefore, the result of Figure 12 indicates the formation of Nb clusters at the peak stage of secondary hardening. This result may be the first report of the formation of Nb clusters in Nb-bearing steels. Such Nb clusters are supposed to be formed on the \( \text{100} \alpha\text{-Fe} \) planes, although crystallographic analysis was not carried out. It may be deduced that Nb cluster will play an important role at the secondary hardening like Mo cluster.

3-3. 0.14C-0.20V and 0.14C-0.008N-0.20V steels

In the case of the 0.14C-0.20V steel, V carbide is found at the peak stage of secondary hardening (Figure 13). According to the AP-FIM analysis, the size of V carbide formed at the peak stage is larger than the Nb cluster or NbC described before, and the average ratio of C to V in the carbides is around 0.75, which indicates that its composition may be represented by \( V_4C_3 \) (Figure 14). It is in good agreement with the analysis by electron microscope observations at overaged stages. The size of \( V_4C_3 \) platelets is usually larger than NbC platelets formed at the same tempering condition. This may be attributed to the difference in the diffusion rate of V and Nb.

In the V-N steel, precipitates were V carbonitrides having a wide range of C to N ratio. Figure 15 shows the results of compositional analysis of a precipitate formed in the V-N steel after tempering at 873K, representing the presence of \( VN^{2+} \) ion as well as \( N^+ \) ion. Furthermore, it was confirmed that N-rich vanadium carbonitride is formed in this stage. For example, Figure 16 was a typical histogram obtained from a V carbonitride. The chemical composition of the precipitate shown in Figure 16 may be represented by \( V_{0.57}(N_{0.33},C_{0.10})_2 \). This fact indicates that N-rich V carbonitride is preferentially formed in spite of a smaller amount of N contained in the steel compared with C. On the other hand, at overaged stages, only \( V_4C_3 \) which contains a small amount of N was observed. These findings suggest that the affinity of V for N is stronger than that of V for C at a relatively low temperature range below 873K.

4. Conclusion

In the present study, precipitate phases formed at the fourth stage of tempering in low alloy steels were examined by atom probe - field ion microscopy. The main results may be summarized as follows; (1) Mo steel: Existence of not only needle-like Mo\(_2\)C along \( \{100\}\alpha\text{-Fe} \) directions but also plate-like Mo clusters parallel to \( \{100\}\alpha\text{-Fe} \) planes was confirmed. (2) Nb steel: Many ultra-fine precipitates were observed. They were either NbC or Nb cluster. (3) V steel: V cluster was not found in this steel. The composition of precipitates was represented by \( V_4C_3 \). (4) V-N steel: Precipitates were mainly composed of V and N, namely \( V(N,C) \) at the peak hardening stage. At overaged stages, \( V_4C_3 \) containing a small amount of N was predominant.

Existence of a large number of ultra-fine Mo clusters or Nb clusters may significantly contribute to the hardening of Mo- or Nb-containing steels.
References

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Table 1 Chemical composition of the low alloy steels used (wt.\%)

<table>
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<tr>
<th>steel</th>
<th>C</th>
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</tr>
<tr>
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<td>----</td>
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</tbody>
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Figure 1 TEM and FIM images of the Mo steel tempered at 973K for 3.6ks.
Figure 2. Ladder diagram representing AP analysis of the needle-like Mo2C shown in Fig.1.

Figure 4. FIM image of a needle-like Mo2C in the Mo steel tempered at 873K for 3.6ks.

Figure 6. AP analysis of needle-like Mo2C.

Figure 8. FIM image of NbC in the Nb steel tempered at 973K for 3.6ks.

Figure 3. TEM image of the Mo steel tempered at 873K for 3.6ks (peak stage).

Figure 5. FIM image of a Mo cluster found in the Mo steel tempered at 873K for 3.6ks.

Figure 7. AP analysis of a Mo cluster.

Figure 9. Ladder diagram representing AP analysis of the NbC shown in Fig.8.
Figure 10 FIM image of a Nb cluster in the Nb steel tempered at 873K for 3.6ks.

Figure 11 AP analysis of NbC in the Nb steel tempered at 873K for 3.6ks.

Figure 12 Linked ladder diagram representing AP analysis of NbC(A) and Nb clusters (B and C) shown in Fig.10.

Figure 13 FIM image of V carbide in the V steel tempered at 873K for 3.6ks.

Figure 14 Ladder diagram representing AP analysis of V$_4$C$_3$ in the V steel tempered at 873K for 3.6ks.

Figure 15 AP analysis of V$_4$C$_3$ which contains N in the V-N steel tempered at 873K for 3.6ks.

Figure 16 AP analysis of MN type precipitates in the V-N steel tempered at 873K for 3.6ks. Composition of the precipitate is V$_{0.57}$(N$_{0.33}$,C$_{0.10}$)