# Study on the microstructure of Fe-C(-Mn) alloys during early stages of ageing using atom probe

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A small age-hardening peak during early stages of ageing for ferritic Fe-C(-Mn) alloys was observed. The microstructural and C distribution analyses by using transmission electron microscopy and 3 dimensional atom probe technique suggest that the early stage age-hardening was associated with the aggregation of C atoms and the formation of clusters and precipitates.

## 1. Introduction

The microstructure and mechanical properties of most commercial ferritic (α) Fe-C(-X) alloys have been studied extensively [1-3]. These alloys showed age-hardening characteristics that involved a monotonic increase towards a peak hardness after a certain time of ageing, ranging from a few minutes to several hours. Peak hardness is always associated with the formation of precipitate particles (e.g. $MC_3$). However there is relatively little systematic work on the very early stages of ageing using direct nanostructural analysis and some questions remain on the potential for clustering of interstitial C atoms prior to the precipitation reaction.

In this paper, we report a small hardness peak within 5 minutes of ageing at 550°C for Fe-C(-Mn) ferritic alloys, with a second large hardness peak appearing after ageing for 50 hours. The microstructural and compositional distribution analyses for the small peak condition samples using transmission electron microscopy (TEM) and high resolution TEM (HRTEM), combined with 3 dimensional atom probe (3DAP) are presented, and the possible mechanisms of the initial hardening phenomenon is discussed.

## 2. Experimental

Alloy compositions are given in Table 1. Ingots were homogenized at 1200°C for 15 h in vacuum furnace. Samples cut from the ingots in the form of 0.7 mm thick slice were first austenitized at 1050°C for 0.5 h, followed by water quenching, then solution saturation heat treated at 700°C for 1 h, followed by water quenching, and finally aged at 550°C for various time. The microstructure was examined using TEM (Philips CM20) and HRTEM (JEM-3000F). 3DAP analysis was conducted in ultrahigh vacuum at a tip temperature of 50–60 K using a local electrode atom probe (LEAP, Imago). The pulse fraction was 0.20. Samples for atom probe analysis were prepared by cutting the slice into square rods of $0.7\times0.7\times12$ mm$^3$ and electropolishing the square rod to a sharp tip.

Table 1. Compositions of the Fe-C and Fe-C-Mn alloys (at.%).

| Alloy | C | Mn | Si | Mo | Ti, N | Ni, Cr | Cu, Nb | Fe |
|---|---|---|---|---|---|---|---|---|
| Fe-C | 0.05 | <0.02 | <0.04 | <0.006 | <0.01 | <0.01 | <0.01 | balance |
| Fe-C-Mn | 0.05 | 0.90 | <0.04 | <0.006 | <0.01 | <0.01 | <0.01 | balance |

## 3. Results and Discussions

The mechanical properties of the Fe-C(-Mn) alloys was measured as a function of ageing time and selected samples around the first peak condition were subjected to TEM and HRTEM observations, combined with 3DAP analyses.

Figure 1 is the age-hardening curves of the Fe-C and Fe-C-Mn alloys. The two alloys have similar age-hardening curves, both showing a small peak hardness at about 5 min and a second large peak hardness at about 50 h, with the hardness of Fe-C-Mn alloy being consistently higher than that of Fe-C alloy. The hardness increase for the first small peak is about 25% of the second peak. A similar trend for the yield strengths was also observed for these two alloys.

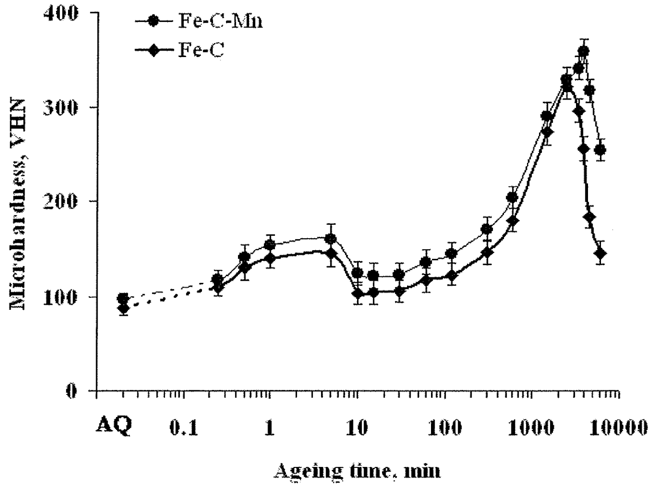

Fig. 1. Hardness versus ageing time curves for the Fe-C and Fe-C-Mn alloys.

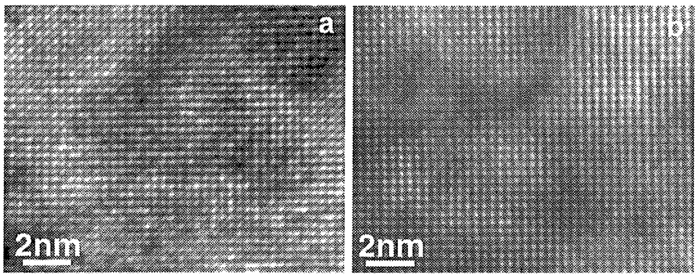

Fig. 2. HRTEM micrographs of (a) Fe-C and (b) Fe-C-Mn alloys aged for 0.5 min at 550°C. Zone axis is [100].

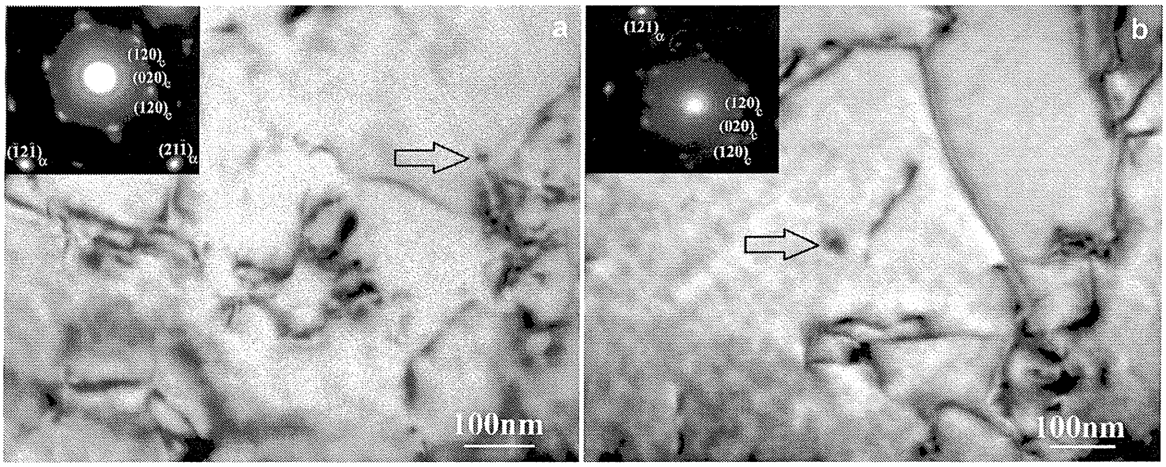

Fig. 3. TEM micrographs for (a) Fe-C and (b) Fe-C-Mn alloys aged for 5 min at 550°C. Zone axis is [135]. The insets are SAD patterns. The arrows indicate precipitates.

Microstructural observations showed coarse ferrite grains before ageing for both alloys, with average grain sizes of 190 ± 110 μm and 130 ± 70 μm for the Fe-C and Fe-C-Mn alloys. No precipitates were observed in these samples. Dislocations observed in the Fe-C alloy were more uniformly distributed than in the Fe-C-Mn alloy. The Fe-C-Mn alloy showed tangled dislocations and some large dislocation-free areas. After ageing for 0.5 min, no significant change in the microstructure could be observed in both alloys. HRTEM observations also confirmed that no precipitate appeared in the matrix at this stage, although some strain may be present, shown in Fig. 2. After further ageing for 5 min (the first peak hardness condition), the ferrite grains grew only a little, with average grain sizes of 200 ± 100 μm for the Fe-C alloy and 135 ± 70 μm for the Fe-C-Mn alloy, however, some precipitates could be observed in the ferrite matrix in both alloys, shown in Fig. 3 (marked by arrows). The insets are selected area electron diffraction (SAD) patterns, showing extra spots superimposed on the ferrite matrix spots. These extra spots could be indexed using cementite ($Fe_3C$) structure. The precipitates were very small, being about 5 nm in diameter in the Fe-C alloy. In the Fe-C-Mn alloy, some slightly larger precipitates could be observed. The number density of the precipitates was estimated to be about $10^{21}/\mathrm{m}^3$.

To investigate the evolution of the precipitates in these alloys during the early stage of ageing, 3DAP has been used to examine the C and Mn atom distributions and possible segregation of C and Mn atoms in these alloys. By taking the advantage of the new LEAP's capacity of high data acquisition rate, much effort had been put in collecting a large number of data for both alloys in the as-quenched state and aged for 0.25, 0.5, 1 and 5 min respectively, and more than 90 million atoms were successfully collected with a total length of about 2000 nm. For all tested tip samples (except one of the Fe-C-Mn alloy aged for 0.5 min), the C atoms were observed to be uniformly distributed in the whole matrix, only some Mn aggregations could be identified in the Fe-C-Mn alloy. This result is not very surprising, as the number density of the precipitate or cluster present in the peak hardness condition revealed by TEM was so low that the opportunity to hit one by atom probe analysis was too small. Nevertheless, the exceptional one sample of the Fe-C-Mn alloy aged for 0.5 min did show some sign of the presence of C segregation, although this run did not last long due to fracture and only about 241,000 atoms was collected. The apparent C concentration was 0.17 at.%, much higher than other data sets. Figure 4 is the mass spectrum for this tip. As seen in Fig. 4, a large portion of C atoms evaporated in the form of cluster ions of the type $C_2^+$ and $C_3^{2+}$, composed of about 52% of C atoms detected. This fact that C atoms evaporated in the cluster form supports the view that C atoms form clusters during the early stage of ageing, although the effect of surface diffusion process cannot be completely ruled out. The atom map also showed C atom aggregation. The addition of Mn to the alloy seemed not to affect the aggregation of C atoms. The contingency table analysis suggested that there was no interaction between C and Mn atoms. In addition, it is found that the Mn aggregations did not change much with increasing the ageing time. Hence the aggregation of Mn atoms does not probably contribute to the formation of C clusters. The increase in the hardness with the Mn addition may be attributed to the uniform distribution of the Mn clusters in the matrix, which results in some degree of cluster strengthening. The small age-hardening peak is believed to be associated with the formation of precipitates evolved from the clustering of C atoms.

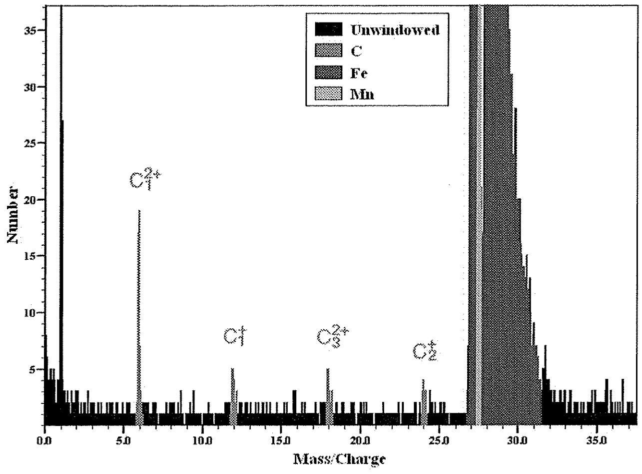

Fig. 4. Mass spectrum of the Fe-C-Mn alloy aged for 0.5 min.

## 4. Summary

The ferritic Fe-C(-Mn) alloys exhibited age-hardening during early stages of ageing. Before the peak hardness, the age-hardening was associated with the formation of C atom clusters and Mn atom clusters. The addition of Mn to the alloy did not change the microstructure of the alloy, but had cluster strengthening effect. No interaction between the added Mn atoms and C atoms was observed in the alloy, therefore, the added Mn atoms may have no effect on the clustering of C atoms during ageing.

## Acknowledgments

This work was supported by ARC Large Grant scheme. We also acknowledge the technical, scientific and financial assistance from the NANO-MNRF.

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