Phase transitions in an Fe–9Al–30Mn–2.0C alloy

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The as-quenched microstructure of Fe–9Al–30Mn–2.0C alloy is austenite phase containing fine $(Fe,Mn)_3AlC$ carbides. When the alloy was aged at 900–1100 °C and then quenched, both large and extremely fine $(Fe,Mn)_3AlC$ carbides could be observed simultaneously within the austenite matrix. This feature has never before been observed in FeAlMnC alloy systems. In addition, the Al and Mn concentrations in the coarse $(Fe,Mn)_3AlC$ carbides formed on the grain boundaries were found to vary drastically with the aging temperature.
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Phase transitions in austenitic FeAlMnC alloys, prepared by conventional casting process, have been widely studied [1–12]. The previous studies have found that when an alloy with a chemical composition in the range of Fe–(6–11) wt.% Al–(26–34) wt.% Mn–(0.54–1.3) wt.% C is solution heat-treated and then quenched rapidly, the microstructure is single-phase austenite (γ). After being aged at 500–750 °C for moderate times, fine and coarse $(Fe,Mn)_3AlC$ carbides were found to precipitate coherently within the austenite matrix and heterogeneously on the austenite grain boundaries, respectively. Both the fine and coarse $(Fe,Mn)_3AlC$ carbides have an $L'1_2$ structure [1–6]. For convenience, κ' carbide and κ carbide are used to represent the $(Fe,Mn)_3AlC$ carbide formed coherently within the austenitic matrix and heterogeneously on the γ/γ grain boundaries. With increasing aging time within this temperature range, the coarse κ carbides grew into adjacent austenite grains through a $\gamma \to \gamma_0$ (carbon-deficient austenite) + κ carbide reaction, a $\gamma \to \alpha$ (ferrite) + κ carbide reaction, a $\gamma \to \kappa$ carbide + β-Mn reaction, a $\gamma \to \alpha + \kappa$ carbide + β-Mn reaction, or a $\gamma \to \alpha + $ β-Mn reaction [4–9], depending on the chemical composition and aging temperature. In addition to extensive studies of FeAlMnC alloys with C $\leqslant$ 1.3 wt.%, the phase transitions in conventionally prepared FeAlMnC alloys with higher carbon content have also been examined by several workers [10–12]. Based on these studies, it is obvious

that the as-quenched microstructure of the Fe–(6–9) wt.% Al–(26–30.7) wt.% Mn–(1.5–2.8) wt.% C alloys was austenite phase containing fine κ' carbides [10,11]. This is quite different from what was observed in the austenitic FeAlMnC alloys with C $\leqslant$ 1.3 wt.%. These findings seem to imply that the carbon content may play an important role in the formation of fine κ' carbides within the austenite matrix during quenching. When the FeAlMnC alloys with $1.5 \leqslant$ C $\leqslant 2.8$ wt.% were aged between 800 and 1200 °C for longer periods, the stable microstructure was found to be a mixture of (austenite phase + κ carbide) [10–12]. In the previous studies, it is clearly seen that most examinations of the FeAlMnC alloys with higher carbon focused only on the alloys at 800 °C or above. Little information was available concerning the microstructural developments of the alloys at lower temperatures. Therefore, the purpose of this work is an attempt to study the phase transitions in the Fe–9 wt.% Al–30 wt.% Mn–2.0 wt.% C alloy heat-treated at 550–1200 °C.

The alloy, Fe–9 wt.% Al–30 wt.% Mn–2.0 wt.% C, was prepared in a vacuum induction furnace from 99.7% iron, 99.9% aluminum, 99.9% manganese and pure carbon powder. After being homogenized at 1250 °C for 12 h under a controlled protective argon atmosphere, the ingot was hot-forged and then cold-rolled to a final thickness of 2.0 mm. The sheet was subsequently solution heat-treated at 1200 °C for 2 h and rapidly quenched into room-temperature water. Aging processes were carefully performed at 550–1200 °C for various times in a muffle furnace under a controlled protective argon atmosphere and then quenched. Electron

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microscopy specimens were prepared by means of a double-jet electropolisher with an electrolyte of 60% acetic acid, 30% ethanol and 10% perchloric acid. Scanning transmission electron microscopy (STEM) was performed on a JEOL-2000FX microscope operating at 200 kV. Quantitative analyses of elemental concentrations for Fe, Al and Mn were made using the Cliff–Lorimar ratio thin section method.

Figure 1a is a bright-field (BF) electron micrograph of the as-quenched alloy, indicating that a high density of fine precipitates with a modulated structure was formed within the austenite matrix. Figure 1b, a selected-area diffraction pattern (SADP), demonstrates that the fine precipitates are $(Fe,Mn)_3AlC$ carbides (κ' carbides) having an $L'1_2$ structure [1–6,10,11]. Figure 1c, a dark-field (DF) electron micrograph taken with the $(100)_{\kappa'}$ superlattice reflection in the $[001]$ zone, reveals that the fine κ' carbides were formed along the $\langle 100 \rangle$ directions. This is consistent with the appearance of the satellites along the $\langle 100 \rangle$ reciprocal lattice directions in Figure 1b. Accordingly, the as-quenched microstructure of the alloy was austenite phase containing fine κ' carbides. The fine κ' carbides were formed by spinodal decomposition during quenching. The result is similar to that reported by other workers in the as-quenched FeAlMnC alloys with $1.5 \leqslant C \leqslant 2.8$ wt.% [10,11].

When the as-quenched alloy was aged at 550 °C for moderate times, the fine κ' carbides grew within the austenite matrix and a heterogeneous precipitation started to occur on the austenite grain boundaries. A typical microstructure is shown in Figure 2a. Figure 2b, an SADP taken from the coarse precipitate marked as "K" in Figure 2a, indicates that the grain boundary precipitate is also $(Fe,Mn)_3AlC$ carbide (κ carbide), which has an $L'1_2$-type structure. After prolonged aging at 550 °C, the coarse κ carbides grew into adjacent austenite grains through a $\gamma \rightarrow \gamma_0$ (carbon-deficient austenite) + κ carbide reaction. An example is shown in Figure 3a, which is a BF electron micrograph of the alloy aged at 550 °C for 32 h. With increased aging time at 550 °C, the $\gamma \rightarrow \gamma_0 + \kappa$ carbide reaction would proceed toward the whole austenite grains, as illustrated in Figure 3b. In Figure 3b, it can also be seen that only the κ carbides could be observed within the γ_0 phase.

TEM examinations indicated that the transition behavior could be preserved up to 850 °C. However, when the alloy was aged at 900 °C and then quenched, a high density of extremely fine precipitates could be detected within the remaining austenite matrix and within the γ_0 phase, as shown in Figure 4. Figure 4a, a BF elec-
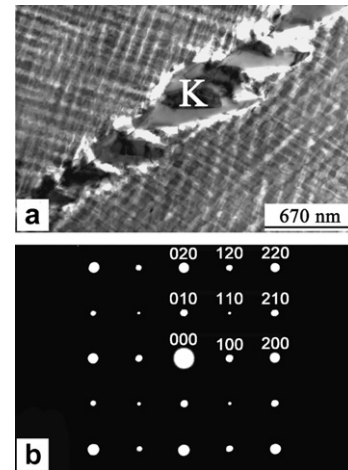

Figure 2. Transmission electron micrographs of the alloy aged at 550 °C for 12 h: (a) BF and (b) an SADP taken from the κ carbide marked "K" in (a).
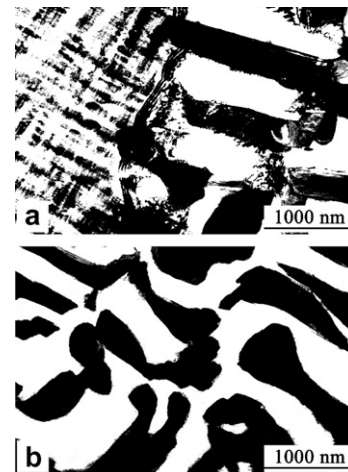

Figure 3. BF electron micrographs of the alloy aged at 550 °C for (a) 32 h and (b) 48 h.

tron micrograph of the alloy aged at 900 °C for 4 h and then quenched, clearly reveals that two types of κ' carbides can be observed within the austenite matrix: one is the larger κ' carbides (as indicated by arrows), which existed at the aging temperature, and the other is the extremely fine κ' carbides, which were formed during quenching from 900 °C. Figure 4b, an SADP taken from the region marked "A" in Figure 4a, reveals a satellite
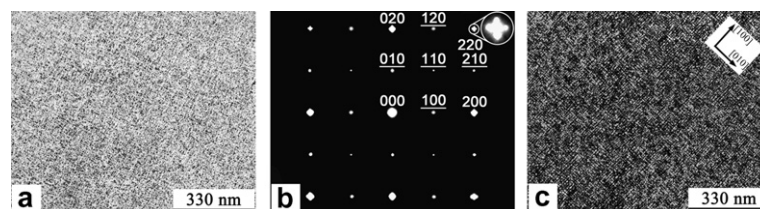

Figure 1. Transmission electron micrographs of the as-quenched alloy: (a) BF, (b) an SADP taken from the mixed region of austenite matrix and fine κ' carbides. The foil normal is $[001]$ (hkl: austenite matrix; $\underline{hkl}$: κ' carbide), and (c) DF obtained by use of the $(100)_{\kappa'}$ superlattice reflection in the $[001]$ zone.
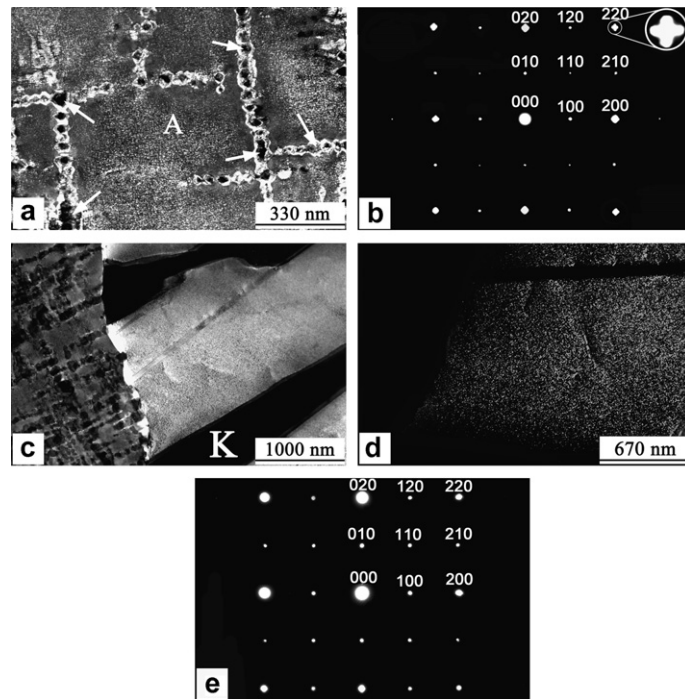
Figure 4. Transmission electron micrographs of the alloy aged at 900 °C for 4 h. (a) BF, (b) an SADP taken from the region marked "A" in (a), (c) BF, (d) $(100)_{\kappa'}$ DF and (e) an SADP taken from the coarse κ carbide marked "K" in (c).

lying along the $\langle 100 \rangle$ reciprocal lattice directions about the (200) and (220) reflection spots. This indicates that the extremely fine κ′ carbides having an L′l$_2$ structure were formed by spinodal decomposition during quenching, which is similar to what was observed in the as-quenched alloy. It is noteworthy that the presence of the large and extremely fine κ′ carbides simultaneously within the austenite matrix has not previously been observed by other workers in the FeAlMnC alloy system. Similarly, TEM examinations revealed that the presence of the coarse κ carbide and extremely fine κ′ carbides could also be detected within the γ_0 phase, as illustrated in Figure 4c and d. Figure 4e, an SADP taken from the coarse κ carbide marked "K" in Figure 4c, shows that the difference in the intensity between the (100) and (110) superlattice spots is only very slight. This is quite different from the pattern from the coarse κ carbide in the alloy aged at 550 °C (Fig. 2b).

Progressively higher temperature aging and quenching experiments indicated that the grain boundary precipitation of κ carbides could exist up to 1100 °C. However, as the aging temperature was increased to 1150 °C, only fine κ′ carbides were formed within the austenite matrix and no evidence of grain boundary precipitation could be detected, as shown in Figure 5. This indicates that the microstructure of the alloy present at 1150 °C or above should be single-phase austenite.

On the basis of the above results, it is evident that both the large and extremely fine κ′ carbides could be observed simultaneously within the austenite matrix in the alloy aged at 900 °C and then quenched. This feature has never before been observed by other workers in the FeAlMnC alloy system. In previous studies of the FeAlMnC alloy with C ⩽ 1.3 wt.% [1–9] the as-quenched
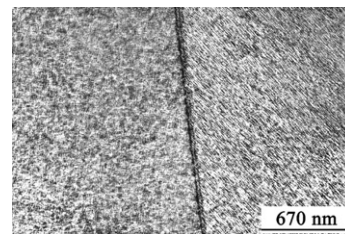

Figure 5. BF electron micrograph of the alloy aged at 1150 °C for 1 h.

microstructure was single-phase austenite. Therefore, it is reasonable to propose that although large κ′ carbides are present, the carbon concentration within the remaining austenite matrix in the alloy at 900 °C was still greater than 1.3 wt.%, which may lead to the formation of extremely fine κ′ carbides by spinodal decomposition during quenching. Based on the above proposition, it is also anticipated that in spite of the precipitation of coarse κ carbides on the grain boundaries, the carbon concentration within the γ_0 phase was still enough to result in the formation of the extremely fine κ′ carbides during quenching from 900 °C, as observed in Figure 4c and d.

Previous studies have reported that when the austenitic FeAlMnC alloys were aged at 550–750 °C for longer times, coarse κ carbides started to occur on the grain boundaries. The crystal structure of the coarse κ carbide is L′1$_2$, which is the same as that of the fine κ′ carbides formed within the austenite matrix [4,6,10]. According to structure factor $|F_{hkl}|$ calculations [10], the difference between $|F_{100}|$ and $|F_{110}|$ for the (Fe,Mn)$_3$AlC carbide with an L′1$_2$ structure is $2f_c$, where f_c is the electron
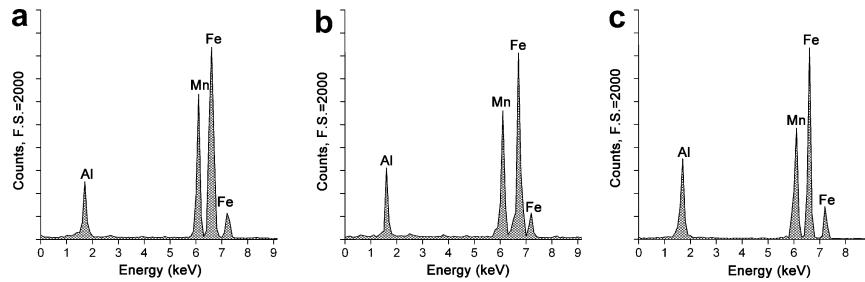
Figure 6. Three typical EDS spectra taken from the coarse κ carbide in the alloy aged at: (a) 550, (b) 750 and 900 °C, respectively.

Table 1. Chemical compositions of the κ carbide revealed by EDS

Aging temperature (°C)	Fe (at.%)	Al (at.%)	Mn (at.%)
550	47.2	14.2	38.6
750	49.3	16.5	34.2
900	51.7	19.8	28.5

scattering factor of a carbon atom. Since $2f_c$ represents a very large difference, the actual intensity of the (1 0 0) spot should much stronger than that of the (1 1 0) spot [10]. In the present study, it can clearly be seen in Figure 2b that the intensity of the superlattice (1 0 0) spot is indeed much stronger than that of the (1 1 0) spot, indicating that the coarse κ carbide formed in the alloy aged at 550 °C has an $L'1_2$ structure. However, the difference in the intensity between these two superlattice spots is only very slight for the coarse κ carbide in the alloy aged at 900 °C. In order to clarify this feature, an STEM energy-dispersive spectroscopy (EDS) study was undertaken. Figure 6a–c represents three typical EDS spectra taken from the coarse κ carbide in the alloy aged at 550, 750 and 900 °C, respectively. The average concentrations of substitutional alloying elements obtained by analyzing a number of EDS spectra are listed in Table 1. In Figure 6 and Table 1, it is obvious that the Al concentration of the κ carbide increased drastically with the aging temperature, and the reverse result was obtained for the Mn content. This result is similar to that determined by the present workers in the Fe–10.1Al–28.6Mn–0.46 C alloy [13]. Furthermore, in previous studies [11,12], it was found that in the κ carbide, the C concentration was always less than 20 at.% of the stoichiometric $(Fe,Mn)_3AlC$ composition, and that the C concentration would decrease markedly as Al concentration increased. For example, the C concentration in the κ carbide was 15.6 at.% with 15.9 at.% Al and only 13.1 at.% with 18.7 at.% Al [11]. The EDS examinations revealed that when the present alloy was aged at 900 °C, the Al concentration in the κ carbide was increased up to 19.8 at.%. Therefore, it is plausible to suggest that owing to the increase in the Al concentration, the C concentration in the κ carbide would be greatly lowered, which would significantly decrease the difference of the intensity between the (1 0 0) and (1 1 0) superlattice spots. Finally, it is worthwhile pointing out that EDS with a thick-window detector, as used in the present study, is limited to detecting elements of atomic number 11 or above, and therefore C cannot

be examined. Obviously, in order to further understand the transition behaviors in the FeAlMnC alloys, much more work is needed.

In summary, the as-quenched microstructure of the Fe–9 wt.% Al– 30 wt.% Mn–2.0 wt.% C alloy was austenite phase containing fine κ′ carbides. The fine κ′ carbides, which have an $L'1_2$ structure, were formed by spinodal decomposition during quenching. When the as-quenched alloy was aged at 550–1100 °C for moderate times, the fine κ′ carbides grew within the austenite matrix and a $\gamma \rightarrow \gamma_0 + \kappa$ carbide reaction started to occur on the austenite grain boundaries. The Al and Mn concentrations in the κ carbide vary drastically with the aging temperature. In addition, when the alloy was aged at 900 °C and then quenched, extremely fine $(Fe,Mn)_3AlC$ carbides could be formed within the remaining austenite matrix and within the γ_0 phase by spinodal decomposition during quenching.

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