

## Grain Boundary Precipitation in Fe-30Mn-9Al-5Cr-0.7C Alloy

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The as-quenched microstructure of the Fe-30%Mn-9%Al-5%Cr-0.7%C (in mass%) alloy was single-phase austenite. When the as-quenched alloy was aged at 550°C–750°C, fine (Fe,Mn)<sub>3</sub>AlC carbides were formed within the austenite matrix. In addition, as the aging temperature increased, a M<sub>7</sub>C<sub>3</sub> carbide + D0<sub>3</sub> → M<sub>7</sub>C<sub>3</sub> carbide + B2 → M<sub>7</sub>C<sub>3</sub> carbide + α (ferrite) phase transition had occurred on the grain boundaries. This grain boundary precipitation behavior has never before been observed in FeMnAlC and FeMnAlCrC alloy systems.  
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### 1. Introduction

Phase transformations in austenitic FeMnAlC alloys have been extensively studied by many workers.<sup>1–8)</sup> These studies have shown that in the as-quenched condition, the microstructure of the alloy with a chemical composition in the range of Fe-(26–34)%Mn-(6–11)%Al-(0.54–1.3)%C was single-phase austenite (γ). After being aged at 500–750°C for moderate times, fine and coarse (Fe,Mn)<sub>3</sub>AlC carbides (κ carbides) having an L'1<sub>2</sub>-type structure were observed to precipitate coherently within the austenite matrix and also heterogeneously on the austenite grain boundaries, respectively. With increasing aging time within this temperature range, the coarse κ carbides grew into the adjacent austenite grains through a γ → γ<sub>0</sub> (carbon-deficient austenite) + κ carbide reaction, a γ → α + κ carbide reaction, a γ → κ carbide + β-Mn reaction, or a γ → α + κ carbide + β-Mn reaction,<sup>5–8)</sup> depending on the chemical composition and aging temperature. In order to improve the corrosion resistance, chromium has been added to the austenitic FeMnAlC alloys.<sup>9–12)</sup> In their studies, it was concluded that the chromium addition could effectively improve the corrosion resistance of the alloys. However, to date, information about the influence of Cr addition on the microstructural developments of the austenitic FeMnAlC alloys is very deficient. Therefore, the purpose of this work is an attempt to study the phase transformations in the Fe-30%Mn-9%Al-5%Cr-0.7%C alloy.

### 2. Experimental Procedure

Fe-30%Mn-9%Al-5%Cr-0.7%C alloy, was prepared in an induction furnace by using commercial 99.9% Fe, Mn, Al, Cr and pure carbon powder under a controlled protective argon atmosphere. After being homogenized at 1250°C for 12 h, the ingot was hot-forged and then cold-rolled to a final thickness of 3.0 mm. The sheet was subsequently solution heat-treated (S.H.T.) at 1050°C for 2 h and then rapidly quenched into

room temperature water. Isothermal aging was performed at 550–850°C for various times in a vacuum furnace and then quenched. Specimens for electron microscopy were prepared by means of a double-jet electropolisher with an electrolyte of 65% ethanol, 20% acetic acid and 15% perchloric acid. Electron microscopy was performed with JEOL 2000FX scanning transmission electron microscope (STEM) operating at 200 kV. This microscope was equipped with a Link ISIS 300 energy-dispersive X-ray spectrometer (EDS) for chemical analysis. Quantitative analyses of elemental concentrations for Fe, Mn, Al and Cr were made using the Cliff-Lorimer ratio thin section method.

### 3. Results and Discussion

Transmission electron microscopy examinations indicated that in the as-quenched condition, the microstructure of the alloy was single-phase austenite. Figure 1(a) is a bright-field (BF) electron micrograph of the alloy aged at 550°C for 6 h, revealing that fine precipitates with a modulated structure were formed along the ⟨100⟩ directions within the austenite matrix and no evidence of precipitates could be detected on the grain boundary. A selected-area diffraction pattern (SADP) taken from a mixed region covering the austenite matrix and fine precipitates (Fig. 1(b)), demonstrates that the fine precipitates are (Fe,Mn)<sub>3</sub>AlC carbides (κ carbides) having an L'1<sub>2</sub> structure.<sup>4–7)</sup> After prolonged aging at 550°C, a heterogeneous reaction started to occur on the grain boundaries. A typical microstructure is illustrated in Fig. 2(a). Figures 2(b) and (c) are two SADPs taken from the precipitates marked as “D” and “M” in Fig. 2(a), indicating that the two kinds of coarse precipitates were of D0<sub>3</sub> phase and (Fe,Mn,Cr)<sub>7</sub>C<sub>3</sub> (designated as M<sub>7</sub>C<sub>3</sub>) carbide, respectively.<sup>3,13)</sup> This result indicates that the precipitation of (M<sub>7</sub>C<sub>3</sub> carbide + D0<sub>3</sub> phase) had occurred on the grain boundaries. By increasing the aging time at the same temperature, the precipitation would proceed toward the inside of the austenite grains, as illustrated in Fig. 3. Figure 3(a) is a BF electron micrograph of the alloy aged at 550°C for 48 h, revealing that the precipitation of (M<sub>7</sub>C<sub>3</sub> carbide + D0<sub>3</sub> phase) has a lamellar structure. Figure 3(b) is a (100)<sub>κ</sub> dark-field (DF) electron micrograph, revealing the

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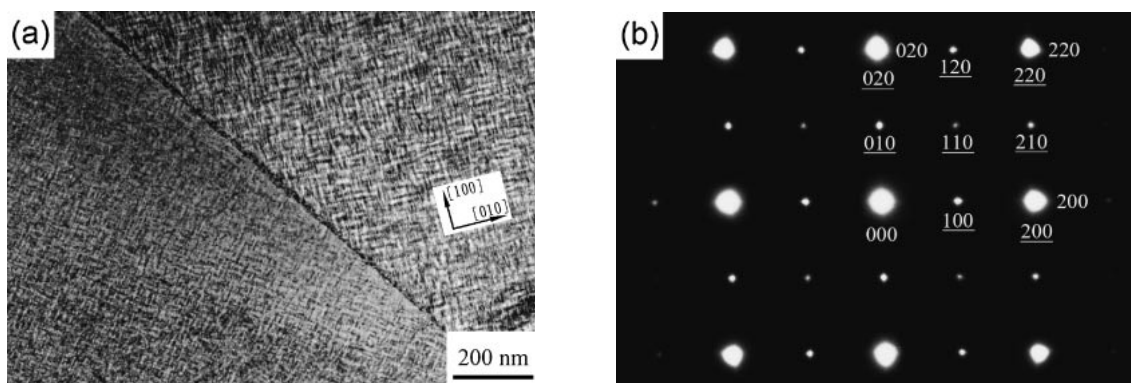


Fig. 1 Transmission electron micrographs of the alloy aged at 550°C for 6 h. (a) BF, and (b) an SADP taken from a mixed region covering the austenite matrix and fine  $\kappa$  carbides. The zone axis is  $[001]$  ( $hkl$ : austenite matrix;  $\underline{hkl}$ :  $\kappa$  carbide).

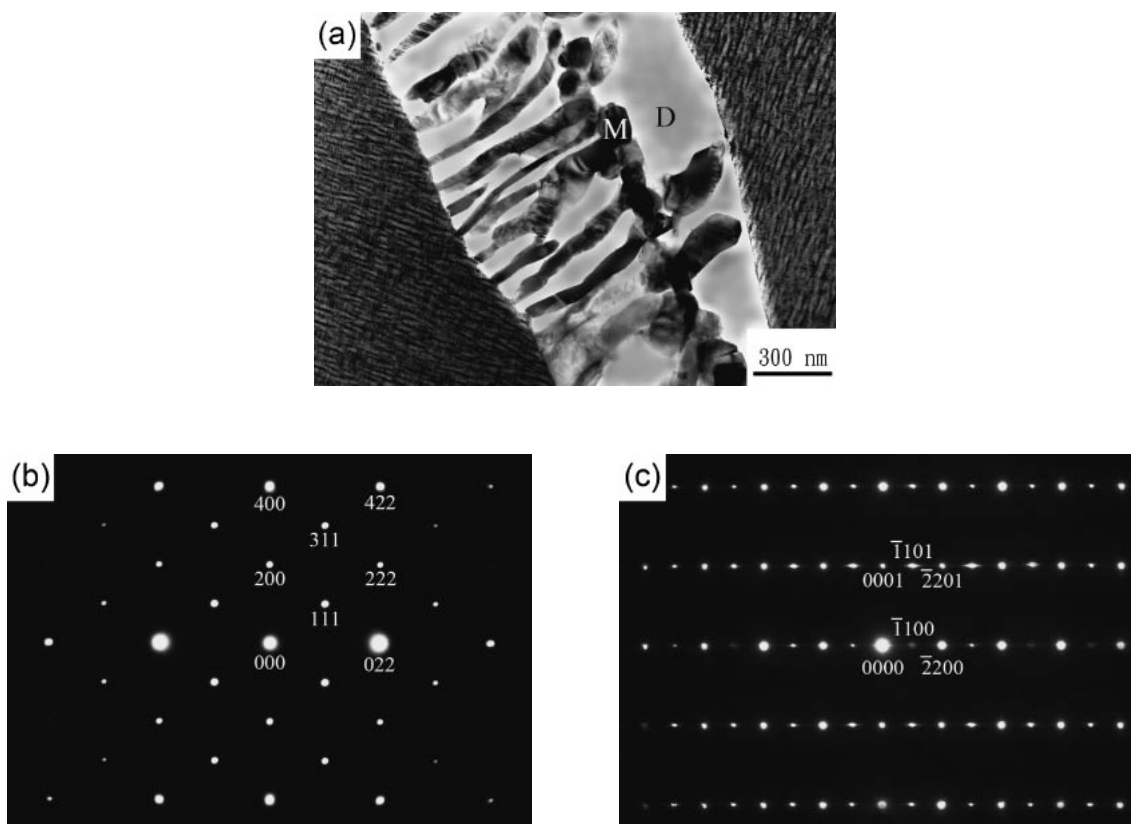


Fig. 2 Transmission electron micrographs of the alloy aged at 550°C for 24 h. (a) BF, (b) an SADP taken from the  $D0_3$  phase marked “D” in (a). The zone axis is  $[01\bar{1}]$ , and (c) an SADP taken from the  $M_7C_3$  carbide marked “M” in (a). The zone axis is  $[11\bar{2}0]$ .

presence of fine  $\kappa$  carbides within the austenite matrix. Figures 3(c) and (d) are (111) and (200)  $D0_3$  enlarged DF electron micrographs, clearly revealing that the (111)  $D0_3$  DF image and (200)  $D0_3$  DF image are morphologically identical. Since the (200) reflection spot comes from both the B2 and  $D0_3$  phases, while the (111) reflection spot comes only from the  $D0_3$  phase,<sup>14)</sup> the bright precipitates presented in Figs. 3(c) and (d) are considered to be  $D0_3$  phase.

When the alloy was aged at 650°C, the morphology of the grain boundary  $M_7C_3$  carbides changed from plate-like to granular shape, as shown in Fig. 4(a). Figure 4(b) is a BF electron micrograph taken from the austenite matrix, showing that the amount of the fine  $\kappa$  carbides within the austenite matrix was drastically decreased. Figures 4(c) and (d) are

(111) and (200)  $D0_3$  enlarged DF electron micrographs of the grain boundary, revealing the presence of the extremely fine  $D0_3$  and large B2 domains, respectively. Since the size of the  $D0_3$  domains is extremely fine, it is plausible to suggest that the extremely fine  $D0_3$  domains were formed by a B2  $\rightarrow$   $D0_3$  ordering transition during quenching from the aging temperature.<sup>14)</sup> It means that the grain boundary microstructure of the alloy present at 650°C was a mixture of ( $M_7C_3$  carbide + B2). Transmission electron microscopy of thin foils indicated that the precipitation of ( $M_7C_3$  carbide + B2) was preserved up to 700°C. Figures 5(a) through (c) are BF, (111) and (200)  $D0_3$  DF electron micrographs of the alloy aged at 750°C for 6 h and then quenched, revealing that besides the presence of the  $M_7C_3$  carbide (marked as “M” in

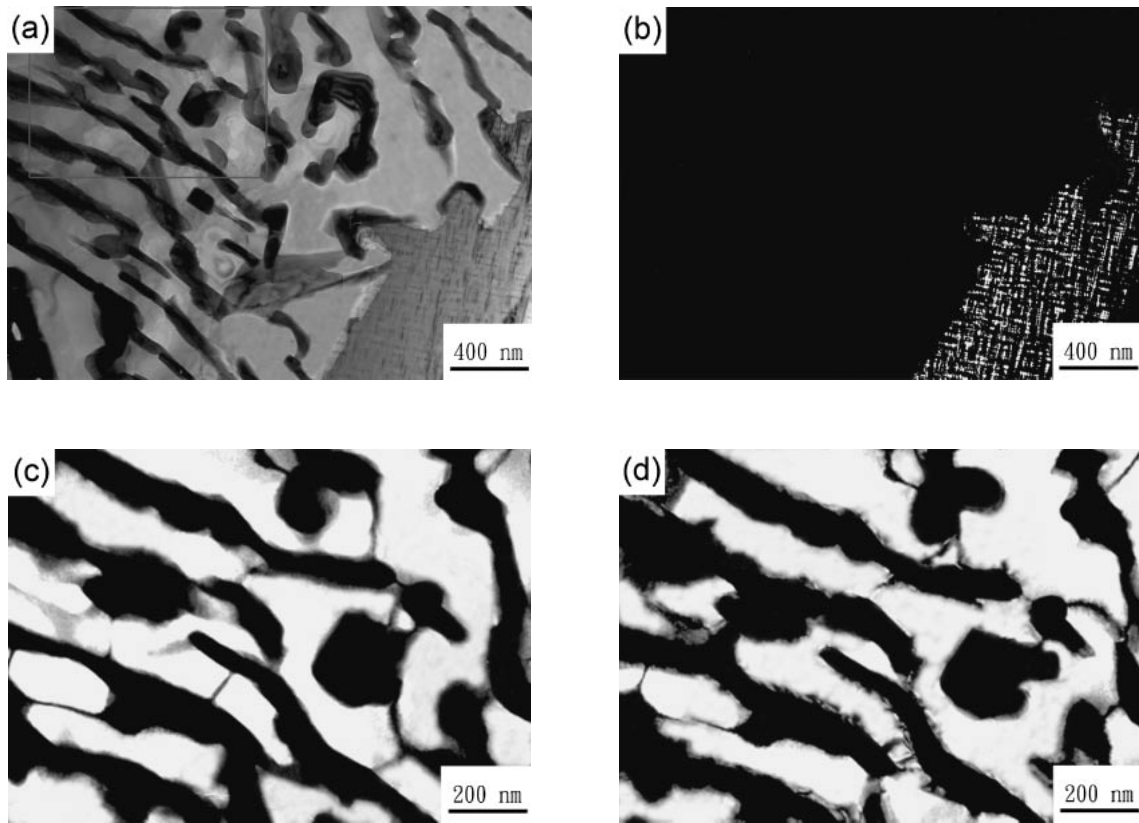


Fig. 3 Transmission electron micrographs of the alloy aged at 550°C for 48 h. (a) BF, (b) (100) $\alpha$  DF, (c) and (d) (111) and (200) D0<sub>3</sub> DF, respectively.

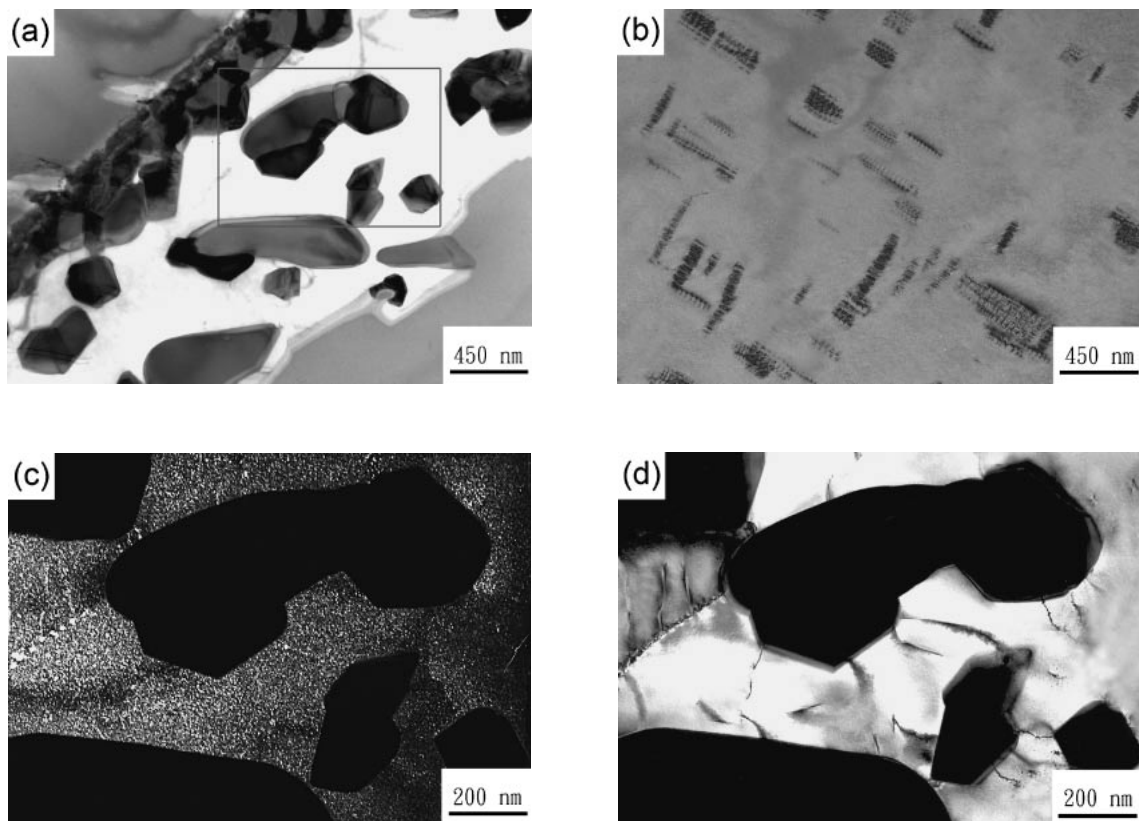


Fig. 4 Transmission electron micrographs of the alloy aged at 650°C for 12 h. (a) and (b) BF taken from the grain boundary and austenite matrix, respectively, (c) and (d) (111) and (200) D0<sub>3</sub> DF, respectively.

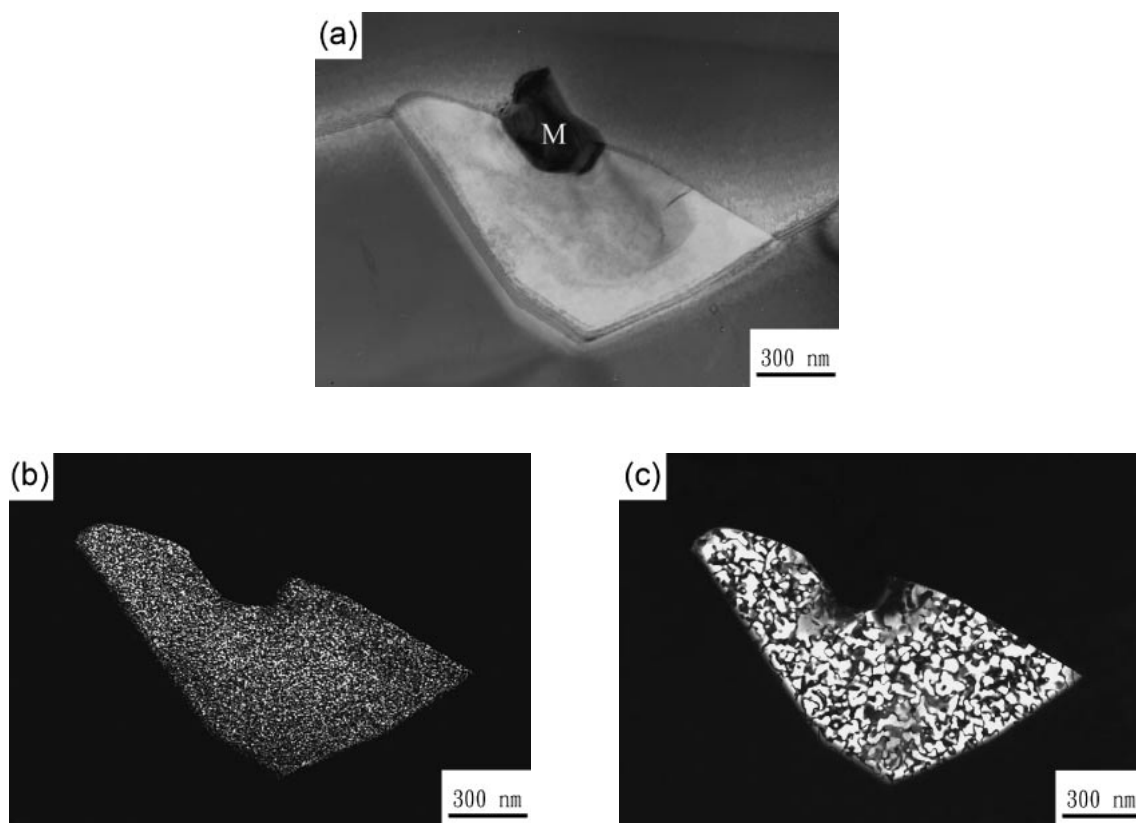


Fig. 5 Transmission electron micrographs of the alloy aged at 750°C for 6 h. (a) BF, (b) and (c) (111) and (200) D0<sub>3</sub> DF, respectively.

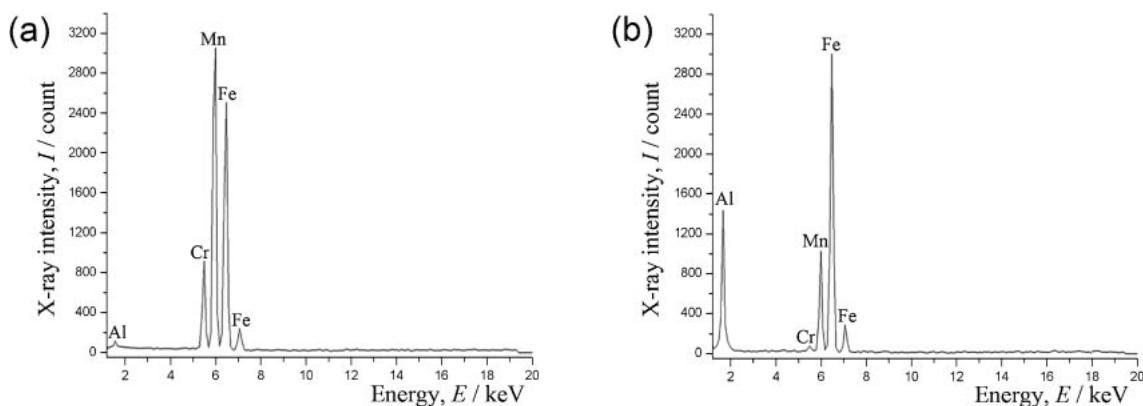


Fig. 6 EDS spectra taken from (a) M<sub>7</sub>C<sub>3</sub> carbide, and (b) D0<sub>3</sub> phase in the alloy aged at 550°C for 48 h.

Fig. 5(a)), only extremely fine D0<sub>3</sub> domains and small B2 domains could be observed on the grain boundaries. This indicates that the grain boundary microstructure of the alloy present at 750°C should be a mixture of (M<sub>7</sub>C<sub>3</sub> carbide + α), and the extremely fine D0<sub>3</sub> domains and small B2 domains were formed by a α → B2 → D0<sub>3</sub> continuous ordering transition during quenching.<sup>14)</sup> Progressively higher temperature aging and quenching experiments indicated that the grain boundary precipitation of (M<sub>7</sub>C<sub>3</sub> carbide + α) could be observed up to 800°C. However, when the aging temperature was increased to 850°C, only single-phase austenite could be observed and no evidence of the grain boundary precipitation could be detected.

The fact that the phase transition of M<sub>7</sub>C<sub>3</sub> carbide + D0<sub>3</sub> → M<sub>7</sub>C<sub>3</sub> carbide + B2 → M<sub>7</sub>C<sub>3</sub> carbide + α had oc-

curred on the grain boundaries in the alloy aged at 550–750°C is a remarkable feature in the present study. This grain boundary precipitation behavior has never before been observed in FeMnAlC and FeMnAlCrC alloy systems. In order to clarify this feature, an STEM-EDS study was made. Figures 6(a) and (b) represent two typical EDS spectra taken from a M<sub>7</sub>C<sub>3</sub> carbide and the D0<sub>3</sub> phase in the alloy aged at 550°C for 48 h, where the Fe, Mn, Al, and Cr peaks were examined (EDS with a thick-window detector is limited to detect the elements of atomic number of 11 or above; therefore, carbon cannot be examined by this method). The quantitative chemical compositions of M<sub>7</sub>C<sub>3</sub> and D0<sub>3</sub> phases from Figs. 6(a) and (b) are listed in Table 1. For the comparison, the chemical compositions of the M<sub>7</sub>C<sub>3</sub> carbide, B2 and α phases in the alloy aged at different temperatures

Table 1 Chemical compositions of the phases identified by energy-dispersive X-ray spectrometer (EDS).

Heat treatment	Phase	Chemical composition (at%)			
		Fe	Mn	Al	Cr
S.H.T.	$\gamma$	50.68	27.60	16.86	4.86
550°C, 48 h	D0 <sub>3</sub>	56.78	15.84	26.31	1.07
	M <sub>7</sub> C <sub>3</sub>	37.91	47.69	1.83	12.57
650°C, 12 h	B2	55.62	16.17	26.95	1.26
	M <sub>7</sub> C <sub>3</sub>	37.87	46.76	1.75	13.62
750°C, 6 hr	A2	53.57	17.12	27.13	2.18
	M <sub>7</sub> C <sub>3</sub>	37.09	46.15	1.63	15.13

are also listed in Table 1. In Fig. 6 and Table 1, it is clearly seen that when the alloy was aged at 550°C, the Mn and Cr contents in the M<sub>7</sub>C<sub>3</sub> carbide are much higher than those of the as-quenched alloy, and the reverse result is obtained for the Al content. Since it is known that the Mn is an austenite former in the FeMnAlC alloy system, the precipitation of coarse Mn-rich M<sub>7</sub>C<sub>3</sub> carbide on the grain boundary would cause the austenite phase in the vicinity of the coarse M<sub>7</sub>C<sub>3</sub> carbides to become unstable. Furthermore, it is seen in Table 1 that the Al content in the M<sub>7</sub>C<sub>3</sub> carbide is only about 1.83 at.%, which is much less than that in the as-quenched alloy. It is thus anticipated that along with the precipitation of the M<sub>7</sub>C<sub>3</sub> carbides, the surrounding regions would be enriched in Al. In Fe-Al phase diagram,<sup>14</sup> it is seen that when an Fe-26.31 at.%Al alloy is heated at 550°C, the microstructure was a D0<sub>3</sub> phase. Therefore, it is reasonable to believe that owing to the enrichment of Al, the unstable austenite phase would be transformed into the D0<sub>3</sub> instead of the  $\alpha$  phase. Similarly, when the alloy was aged at 650°C as well as 750°C and then quenched, the Al-rich B2 and  $\alpha$  phases could be formed at the regions contiguous to the M<sub>7</sub>C<sub>3</sub> carbides, and B2  $\rightarrow$  D0<sub>3</sub> as well as  $\alpha$   $\rightarrow$  B2  $\rightarrow$  D0<sub>3</sub> ordering transitions would be expected to occur during quenching.<sup>14</sup> This is in agreement with the experimental observations in Figs. 4 and 5, respectively. Finally, it is worthwhile pointing out that the coarse Mn-rich  $\kappa$  carbides were always observed on the grain boundaries in the austenitic FeMnAlC alloys aged at 500–750°C for longer times.<sup>5–8,15</sup> However, only (Mn,Cr)-rich M<sub>7</sub>C<sub>3</sub> carbides were formed, and no evidence of coarse  $\kappa$  carbides could be detected on the grain boundaries in the present alloy aged

at 550–750°C. Obviously, the chromium addition in the austenitic FeMnAlC alloys would bring about for the formation of the (Mn,Cr)-rich M<sub>7</sub>C<sub>3</sub> carbides and suppress the precipitation of the coarse Mn-rich  $\kappa$  carbides on the grain boundaries.

#### 4. Conclusions

As-quenched microstructure of the Fe-30%Mn-9%Al-5%Cr-0.7%C alloy was single-phase austenite. When the as-quenched alloy was aged at 550–750°C, fine  $\kappa$  carbides were formed within the austenite matrix, and a M<sub>7</sub>C<sub>3</sub> + D0<sub>3</sub>  $\rightarrow$  M<sub>7</sub>C<sub>3</sub> + B2  $\rightarrow$  M<sub>7</sub>C<sub>3</sub> +  $\alpha$  phase transition had occurred on the grain boundaries.

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