

行政院國家科學委員會補助專題研究計畫成果報告

PHASE TRANSFORMATIONS IN FE-9.0AL-30.0MN-4.0CR ALLOY

計畫類別：個別型計畫 整合型計畫

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行政院國家科學委員會補助專題研究計劃成果報告

PHASE TRANSFORMATIONS IN FE-9.0AL-30.0MN-4.0CR ALLOY

鐵-9.0 鋁-30.0 錳-4.0 鉻合金相變化

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1.中文摘要

經由 OM、SEM、TEM 及 X-ray 來分析 Fe-9.0Al-30.0Mn(wt.%) 合金的相變化，在淬火狀態下為肥立鐵及沃斯田鐵的混合相。且不論在任何溫度的時效處理後，在沃斯田鐵基地內都不會發現析出物，不過隨著溫度的提升在肥立鐵的晶粒內卻可發現許多不同的析出物。在肥立鐵晶粒內隨著溫度提高完整的相變化過程為 $(\alpha + A12 \alpha\text{-Mn} + D0_3) \rightarrow (\alpha + A12 \alpha\text{-Mn}) \rightarrow (\alpha + A13 \beta\text{-Mn}) \rightarrow \alpha$ 。

關鍵字：鐵鋁錳鉻合金、相變化、 $D0_3$ 、 $A12 \alpha\text{-Mn}$ and $A13 \beta\text{-Mn}$

Abstract

Phase transformations in the Fe- 9.0 wt. % Al -30.0 wt. % Mn alloy with 4.0 Cr has been investigated by means of optical microscopy, scanning transmission electron microscopy and energy-dispersive X-ray spectrometry. In the as-quenched condition, the microstructure in the Fe- 9.0 wt. % Al-30.0 wt. % Mn-4.0 wt. % Cr alloy was α (ferrite) + γ (austenite) duplex phases. When the alloy was aged at various temperatures, no precipitate could be found within the austenite matrix. However, different kinds of precipitates could be observed within the ferrite grains with increasing the aging temperature. In the alloy, the phase transformation sequence in the ferrite grains as the aging temperature increased were found to be $(\alpha + A12 \alpha\text{-Mn} + D0_3) \rightarrow (\alpha + A12 \alpha\text{-Mn}) \rightarrow (\alpha + A13 \beta\text{-Mn}) \rightarrow \alpha$.

Keywords: Fe-Al-Mn-Cr alloy, phase transformation, $D0_3$, $A12 \alpha\text{-Mn}$ and $A13$

$\beta\text{-Mn}$

2. INTRODUCTION

Recently, a considerable amount of interest has focused on developing Fe-Al-Mn alloys as the substitutes for conventional stainless steels [1-9]. Results concerning corrosion resistance and high temperature oxidation resistance have been given in several publications [3,4,5]. In order to improve the corrosion resistance and high temperature oxidation resistance, chromium or silicon has been added to the Fe-Al-Mn alloys [6-9]. Whereas, the phase transformations in a Fe-9.1 wt.% Al-29.9 wt.% Mn-2.9 wt.% Cr alloy have been studied principally by the present workers [10-12]. After solution heat-treated at 980°C for 1 hour and then quenched into room-temperature water rapidly, the microstructure of the Fe-9.1wt.% Al-29.9wt.% Mn-2.9wt.% Cr alloy was the mixture of the γ (austenite) + α (ferrite) phases. When the alloy was aged at temperatures ranging from 350°C to 560°C for moderate times, no precipitates could be detected within the austenite phase. However, there are three kinds of precipitates, namely $D0_3$ phase, $A12 \alpha\text{-Mn}$, and $A13 \beta\text{-Mn}$, could be observed within the ferrite phase. The $D0_3$ phase has an ordered face-centered cubic structure with lattice parameter $a=0.5785\text{nm}$. The orientation relationship between the $D0_3$ phase and ferrite matrix was $(002)_{D0_3} // (002)_{\alpha}$ and $[110]_{D0_3} // [110]_{\alpha}$ [10]. The $A12 \alpha\text{-Mn}$ precipitate has a body-centered cubic structure with lattice parameter $a=0.8889\text{nm}$. The orientation relationship between the $A12 \alpha\text{-Mn}$ and ferrite matrix

was $(110)_{\alpha\text{-Mn}}// (110)_{\alpha}$, $[001]_{\alpha\text{-Mn}}// [001]_{\alpha}$. It is noted that the A12 $\alpha\text{-Mn}$ precipitates formed within the ferrite matrix has a dohecahedral shape, which is bounded by six sets of $\{110\}$ interface planes^[11]. The A13 $\beta\text{-Mn}$ precipitate has a simple cubic structure with lattice parameter $a=0.63\text{nm}$. The orientation relationship between the A13 $\beta\text{-Mn}$ and ferrite matrix was determined to be $(001)_{\beta\text{-Mn}}// (001)_{\alpha}$ and $[120]_{\beta\text{-Mn}}// [100]_{\alpha}$. The axis/angle pair of rotation between the A13 $\beta\text{-Mn}$ and the ferrite matrix is $\langle 100 \rangle / 26^{\circ}$ ^[12].

Up to date, most examinations were focused on the Fe-Al-Mn alloy with $\text{Cr} \leq 2.9 \text{ wt}\%$. Little information concerning the Fe-Al-Mn alloy with higher chromium content has been provided. Therefore, the purpose of the present study is an attempt to examine the effect of the higher chromium content on the microstructural developments of the Fe-9wt.% Al-30.0wt.% Mn alloy by using optical microscopy, scanning transmission electron microscopy and energy-dispersive X-ray spectrometry.

3. EXPERIMENTAL PROCEDURE

(A) Alloy Preparation

The alloy, Fe-9.0wt.% Al-30.0wt.% Mn with 4.0 wt.% Cr was prepared in an air induction furnace by using electrolytic iron (99.5%), electrolytic aluminum (99.7%), electrolytic manganese (99.9%), electrolytic chromium (99.9%). After being homogenized at 1150°C for 24 hours under a protective argon atmosphere, the ingots were hot-forged and then cold-rolled to a final thickness of 2.0 mm. The sheets were subsequently solution heat-treated at 1050°C for 2 hours in a vacuum furnace and quenched into room-temperature water rapidly. The aging processes were performed at the temperatures ranging from 350°C to 950°C for various times in a vacuum furnace and then quenched into water rapidly.

(B) Microstructure Observations and

Diffraction Analyses

(1) Optical Microscopy (OM)

The specimens were prepared by the following steps: sectioning, mounting, rough polishing, fine polishing and finally etching with 40% nitric acid, 40% glycerine and 20% hydrochloric acid.

(2) Transmission Electron Microscopy (TEM)

Specimens for electron microscopy were prepared by means of a double-jet electropolisher with an electrolyte of 13% perchloric acid, 35% acetic acid and 52% ethanol. Electron microscopy was performed on a 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 analysis of elemental concentrations for Fe, Mn, Al and Cr were made with the aid of a Cliff-Lorimer Ratio Thin Section method.

4. RESULTS

Figure 1(a) is an optical micrograph of the alloy after being solution heat-treated at 1050°C for 2 hours and then quenched. It reveals a two-phase microstructure. The small grains (i.e., marked as A) with annealing twins are austenite (γ) phase and the large grains are of the ferrite (α) phase (i.e., marked as F). Figure 1(b) is a bright-field (BF) electron micrograph of the as-quenched alloy. Figures 1(c) and 1(d) are two selected-area diffraction patterns (SADPs) taken from the grains marked "A" and "F" in Figure 1(b), respectively. It indicates that the microstructure of the alloy in the as-quenched condition was a mixture of austenite and ferrite phases^[2,6-12].

Figure 2(a) is a BF electron micrograph of the alloy aged at 350°C for 48 hours, revealing that fine precipitates were formed within the ferrite matrix. Figure 2(b) is an SADP taken from an area covering the fine precipitates and their surrounding matrix. It is seen in this SADP that in addition to the reflection spots of the disordered ferrite phase^[10-12], the

diffraction pattern also consist of two sets of reflection reciprocal lattices. It is found that one set was of the $D0_3$ phase having an ordered B.C.C. structure with lattice parameter $a=0.5785\text{nm}$ ^[10] and another was of the A12 α -Mn having a complexed B.C.C. structure with lattice parameter $a=0.8889\text{nm}$ ^[11]. Figure 2(c) is a (111) $D0_3$ dark-field (DF) electron micrograph, showing that a high density of $D0_3$ precipitates was formed within the ferrite matrix. Figure 2(d), an ($\bar{1}10$) A12 α -Mn DF electron micrograph of the same area as Figure 2(a), clearly revealing that the presence of the fine A12 α -Mn particles.

When the alloy was aged at 450°C , cuboidal-shaped particles were always observed within the ferrite phase, as illustrated in Figure 3(a). Figures 3(b) demonstrates SADP taken from the particle marked as “D” in Figure 3(a). It is found that the cuboidal-shaped particles are also of the A12 α -Mn ^[11]. Figure 3(c) is an SADP taken from an area covering the particle marked as “D” and its surrounding matrix, clearly reveal that in addition to the reflection spots of the A12 α -Mn and ferrite phase, another kind of reflection spots could be observed in the SADP. It is found that the reflection spots belong to the $D0_3$ phase. Figures 3(d) and (e) are ($\bar{1}10$) A12 α -Mn and ($\bar{1}11$) $D0_3$ DF electron micrographs, showing the presence of the A12 α -Mn particles and the $D0_3$ precipitates, respectively. It is clear in Figure 3(e) that the $D0_3$ precipitates were formed not only within the ferrite matrix with a spherical-shaped but also at the regions surrounding the A12 α -Mn particles. This result indicates that the microstructure of the ferrite grains at 450°C was still a mixture of ($\alpha + \text{A12 } \alpha\text{-Mn} + D0_3$) phases.

Transmission electron microscopy examinations of thin foils indicated that the ($\alpha + \text{A12 } \alpha\text{-Mn} + D0_3$) phases could be preserved up to 500°C . However, when the aging temperature was increased to 550°C , no evidence of the $D0_3$ precipitates could be detected within the ferrite phase, as shown

in Figure 4(a). Figure 4(b) is a ($\bar{1}10$) A12 α -Mn DF electron micrograph, revealing that the morphology of the A12 α -Mn particles was gradually changed from cuboidal to irregular-shaped.

When the alloy was aged at 650°C , the A12 α -Mn particles disappeared and plate-like precipitates started to occur within the ferrite grains, as illustrated in Figure 5(a). Figure 5(b) shows a BF electron micrograph of the alloy aged at 650°C for 6 hours. Figures 5(c) was performed to include only the precipitate marked as “P” in Figure 5(b). The crystal structure of the precipitate was determined to be a simple cubic structure with a lattice parameter $a = 0.630 \text{ nm}$, which is consistent with that of A13 β -Mn ^[12]. Figures 4(d) demonstrates SADP taken from the precipitate marked as “P” and its contiguous region, displaying that the orientation relationship between the A13 β -Mn and the ferrite matrix was $(012)_{\beta\text{-Mn}}// (001)_\alpha, (02\bar{1})_{\beta\text{-Mn}}// (010)_\alpha, (100)_{\beta\text{-Mn}}// (100)_\alpha$. Figure 4(e), a (001) A13 β -Mn DF electron micrograph, shows the presence of the plate-like A13 β -Mn precipitates. Accordingly, the microstructure of the ferrite grains at 650°C was a mixture of ($\alpha + \text{A13 } \beta\text{-Mn}$) phases.

Progressively higher temperature aging and quenching experiments indicated that the ($\alpha + \text{A13 } \beta\text{-Mn}$) phases were present up to 800°C . However, when the alloy was aged at 850°C for 2 hours and then quenched, no evidence of any precipitates could be observed within the ferrite grains. This indicates that the microstructure within the ferrite grains present at 850°C or above is a single ferrite phase.

Based on the above observations, the phase transformation sequence in the ferrite grains was found to be $(\alpha + \text{A12 } \alpha\text{-Mn} + D0_3) \rightarrow (\alpha + \text{A12 } \alpha\text{-Mn}) \rightarrow (\alpha + \text{A13 } \beta\text{-Mn}) \rightarrow \alpha$.

5. DISCUSSION

On the basis of the observations, it is clear that the phase transition sequence in the ferrite grains was found to be $(\alpha + A12 \alpha\text{-Mn} + D0_3) \rightarrow (\alpha + A12 \alpha\text{-Mn}) \rightarrow (\alpha + A13 \beta\text{-Mn})$, in which the precipitation of A12 $\alpha\text{-Mn}$ could be observed in the present alloy aged at temperatures ranging from 350°C to 550°C. In the past, however, the A12 $\alpha\text{-Mn}$ precipitates have never found in the Fe-Mn-Al system alloys. In addition, a kind of ordered $D0_3$ precipitates could be detected in the ferrite grains at aging temperatures ranging from 350°C to 450°C, the coexistence of A12 $\alpha\text{-Mn}$ and ordered $D0_3$ precipitates have also never been found in the Fe-Mn-Al system alloys by other workers. In order to clarify these observations, an STEM-EDS study was undertaken. The average weight percentages of alloying elements examined by analyzing at least ten different EDS spectra of each phase as listed in Table 1. It is seen in Table 1 that the manganese and chromium contents of the A12 $\alpha\text{-Mn}$ precipitates is much greater than those of the ferrite matrix in the as-quenched condition, and the reverse result is obtained for the concentration of aluminum. Therefore, it is reasonable to believe that the addition of 4.0 wt% chromium to the Fe-9Al-30Mn alloy would cause the formation of (Cr, Mn)-riched A12 $\alpha\text{-Mn}$ precipitates and the surrounding ferrite matrix of A12 $\alpha\text{-Mn}$ precipitates would be enriched in aluminum. Form the previous studies^[10], it is concluded that the higher aluminum concentration in the Fe-Mn-Al alloys would enhance the formation of order $D0_3$ phase. Thus, the enrichment of aluminum content in the ferrite phase would enhance the formation of Al-riched $D0_3$ phase at the region contiguous to the A12 $\alpha\text{-Mn}$ precipitates.

Furthermore, it is well-known that the solubility of aluminum in the ferrite phase increases with increasing the aging temperature. For the reason, it is therefore suggested that since the solubility of aluminum in the ferrite phase would increase as in increasing the aging

temperature from 450°C to 550°C, the Al-riched $D0_3$ phase would be absent in the ferrite matrix.

6. CONCLUSIONS

The phase transformations in Fe- 9.0 wt. % Al –30.0 wt. % Mn alloy with 4.0 wt. % Cr have been investigated in the present study.

- (1) The phase transitions sequence of the present alloy was found to be $(\alpha + A12 \alpha\text{-Mn} + D0_3) \rightarrow (\alpha + A12 \alpha\text{-Mn}) \rightarrow (\alpha + A13 \beta\text{-Mn}) \rightarrow \alpha$.
- (2) Adding 4.0 wt% chromium to the Fe-Al-Mn alloys would enhance the precipitations of the A12 $\alpha\text{-Mn}$ phases. Along with the precipitation of Al-lacked A12 $\alpha\text{-Mn}$, the Al-riched $D0_3$ precipitates were formed in the vicinity of the A12 $\alpha\text{-Mn}$ precipitates at temperatures between 350°C and 450°C.
- (3) When the aging temperature was increased to 550°C, the absence of the $D0_3$ phase contiguous to the A12 $\alpha\text{-Mn}$ would be found, which was attributed to the result of the higher aluminum solubility in the ferrite matrix at higher temperature.

7. ACKNOWLEDGEMENTS

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Table 1. Chemical Compositions of the Phase Revealed in Alloy A by Energy-Dispersive X-ray Spectrometer (EDS)

Heat Treatment	Phase	Chemical Composition (Wt.%)			
		Al	Mn	Cr	Fe
As-quenched	γ	6.10	31.78	2.24	59.88
	α	8.79	27.13	6.06	58.02
450°C 48hrs aging	α	5.94	20.19	3.18	70.69
	D0 ₃	9.13	24.68	5.09	61.1
800°C 2hrs aging	A12 α -Mn	5.26	48.21	17.26	39.27
	α	9.56	24.95	8.62	56.87
	A13 β -Mn	4.11	36.85	13.21	45.83

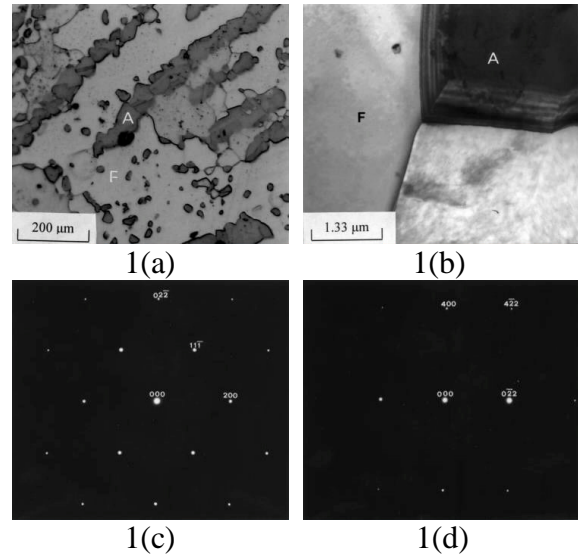


Fig.1 (a) An optical micrograph of the as-quenched alloy A. Electron micrographs of the as-quenched alloy A (b) BF, (c) SADP taken from the grain marked "A" in (b). The foil normal is [011]. (d) SADP taken from the grain marked as "F" in (b). The foil normal is [011].

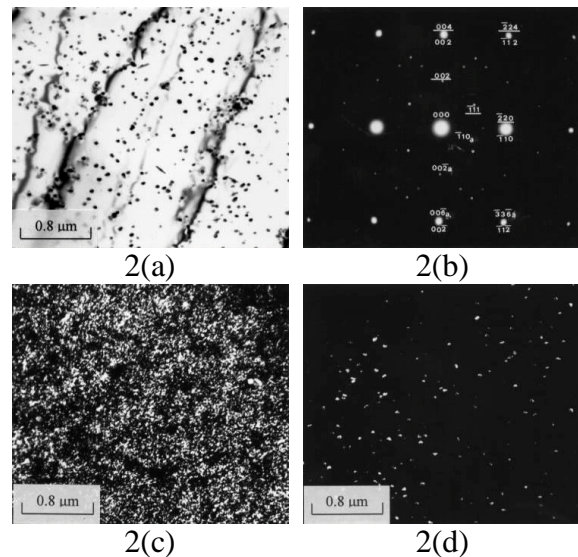


Fig.2 Electron micrographs of the alloy A aged at 350°C for 48 hours. (a) BF, (b) an SADP taken from an area covering the fine particles and their surrounding matrix. The foil normal is [110]. (hkl = ferrite matrix; \underline{hkl} = D0₃; hkl_a = α -Mn). (c) ($\bar{1}11$) D0₃ DF, (d) ($\bar{1}10$) A12 α -Mn DF.

