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 期中進度報告

鐵-鋁-鈦合金相變化
Phase Transformations in Fe-Al-Ti Alloys
第一年期中進度報告（精簡版）

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過去九個月中(2008年8月至2008年5月),本實驗室在國科會經費支持下對鐵-(20~25) at.%鋁-(6~9) at.%鈦合金的相變化進行研究,並已將其中部分研究成果整理成論文發表,其餘研究成果也正在整理準備發表中。較重要的成果為:(1) 在鐵-24.6 at.%鋁-7.5 at.%鈦合金中,發現鐵-24.6 at.%鋁-7.5 at.%鈦合金的淬火顯微結構為(A2 + D0₃),其乃在淬火過程中經由 A2 → B2 → (A2 + D0₃) 規律化變態所形成的。當此合金在 900°C 適當時間之時效處理後,發現 D0₃ 區域成長,並且由於原本的 D0₃ 區域成長時鈦及鋁原子會往 a/2<100>反相晶界擴散促使 A2 → B2 反應發生在 a/2<100>反相晶界上,故 B2 相會開始沿著 a/2<100>反相晶界析出。隨著時效時間的增加, D0₃ → (B2 + D0₃*) 相分離(phase separation)的現象會在 a/2<100>反相晶界處開始發生,並且持續相分離到先前完整的 D0₃ 區域。由於 D0₃* 中的鈦含量明顯較原本的 D0₃ 高而鋁含量稍低,而在鐵-鋁合金中 D0₃ 相僅在鋁含量 > 25 at.%、溫度低於 550°C 時才存在,故此現象也說明了鈦對 D0₃ 在高溫時的穩定有很重要的作用。此種 D0₃ → (B2 + D0₃*) 相分離的微觀結構變化至今從未被其他學者在鐵-鋁-鈦合金系統中發現過。這部分的結果我們已整理成論文 "Phase separation from D0₃ to (B2 + D0₃) in an Fe-24.6 at.% Al-7.5 at.% Ti alloy" 投稿至期刊 Materials Chemistry and Physics, 目前正在審查中。

(2) 我們發現在淬火狀態下,鐵-21 at.%鋁-7.8 at.%鈦合金的淬火顯微結構為經由 A2 → B2 → (A2 + D0₃) 規律化變態所形成的 A2 與 D0₃ 之混合相。當此合金在 750°C 作時效處理後其微觀結構為 (A2 + D0₃) 的混合相,其中 D0₃ 區域會沿著 <100> 特定方向成長,並隨著時效時間的增加 D0₃ 析出物的形貌會由立方體 (cuboidal) 轉變成粒狀 (granular)。當此合金在 850°C 作時效處理時其微觀結構為 (A2 + D0₃ + C14),除了在 (A2 + D0₃) 基地內有 C14 相析出外,還有三種不同形貌的 D0₃ 析出物被觀察到,分別是:因時效而成長的 granular D0₃ 相、隨著 C14 相析出而生成的 cuboidal D0₃ 以及在淬火過程中藉由規律化變態產生的極細微的 D0₃。當此合金在 900°C 作時效處理後其微觀結構為 (B2 + C14) 的混合相,並有極細微的 D0₃ 析出物被觀察到,此種極細微的 D0₃ 析出物為在淬火過程中經由 B2 → (A2 + D0₃) 規律化變態所形成的。當此合金在 900~1050°C 間作時效處理後其微觀結構為 (A2 + C14) 的混合相。當時效溫度提高至 1100°C 時,C14 析出物消失,僅餘淬火過程中產生的微小 D0₃ 和 B2 區域,說明在此溫度以上合金的微觀結構為單一的 A2 相。由實驗結果我們可知:當此合金在 750 至 1100°C 溫度範圍內做時效處理後其微觀結構之變化依序為: A2 + D0₃ → A2 + D0₃ + C14 → B2 + C14 → A2 + C14 → A2。這部分的研究結果我們正在整理中,即將寫成論文 "Phase Transformations in an Fe-21 at.% Al-7.8 at.% Ti Alloy" 投稿至期刊 Intermetallics。接下來除舉

出我們已投稿及正在進行投稿作業之兩篇論文外，另列出本研究群正執行中之數項技術轉移案、及已獲通過或正申請中的專利，本篇期中精簡報告內容則為本研究群對 Fe-24.6 at.% Al-7.5 at.% Ti 合金之研究成果。

一、論文：

1. 期刊名稱：Materials Chemistry and Physics (2007 Impact factor: 1.871)
計畫編號：NSC97-2221-E009-027-MY3
著作內容：K.M. Chang, C.S. Wang, C.W. Su, C.G. Chao and T.F. Liu, "Phase separation from $D0_3$ to $(B2+D0_3)$ in an Fe-24.6 at.% Al-7.5 at.% Ti alloy", submitted to Materials Chemistry and Physics (2009)
2. 期刊名稱：Intermetallics (2007 Impact factor: 2.219)
計畫編號：NSC97-2221-E009-027-MY3
著作內容：K.T. Tsai, C.S. Wang, K.M. Chang, C.W. Su, C.G. Chao and T.F. Liu, "Phase Transformations in an Fe-21 at.% Al-7.8 at.% Ti Alloy", preparing for submission to Intermetallics (2009)

二、技術轉移案：

- (1) 鐵鋁錳碳合金高爾夫球頭精密鑄造、鍛造和鑄鍛系列產品（復盛、明安、鉅明等三家公司，2005~2010）
- (2) 刀削式鰭片散熱器、刀具及其加工法（聚亨公司，2003~2009）

三、專利：

- (1) 低密度高強度高韌性合金材料及其製法（High Strength and High Toughness Alloy with Low Density and The Method of Making）（2007~2025，中華民國專利 I279448 號、美國專利 20070084528 公告中、日本專利正在審核中）
- (2) 刀削式鰭片散熱器、刀具及其加工法（2003~2018，中華民國專利 511449 號）
- (3) 低密度高韌性合金材料及其製法（Low Density And High Toughness Alloy And The Process For Making Same）（中華民國、美國、日本專利申請中）
- (4) 低密度合金材料及其製法（Low Density Alloy And The Method of Making）（中華民國、美國、日本專利申請中）

Phase separation from D0₃ to (B2+ D0₃) in an Fe-24.6 at.% Al-7.5 at.% Ti alloy

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Abstract

As-quenched microstructure of the Fe-24.6 at.% Al-7.5 at.% Ti alloy was a mixture of (A2+D0₃) phases. When the alloy was aged at 900°C, the D0₃ domains grew considerably and phase separation from well-grown D0₃ to (B2+D0₃*) occurred initially at a/2<100> anti-phase boundaries (APBs), where D0₃* is also a D0₃-type phase. With continued aging at 900°C, the phase separation would proceed toward the whole well-grown D0₃ domains. This microstructural revolution has not been reported in the Fe-Al-Ti alloy systems before.

Keywords : Iron alloys ; Phase transformations ; TEM ; Phase separation

Introduction

In previous studies [1-11], it is seen that the Ti addition in the Fe-Al binary alloys would (1) strongly increase the D0₃→B2 and B2→A2 transition temperatures [1-10], (2) significantly expand the (A2+D0₃) phase field [5-7], and (3) cause the D0₃ APBs to exhibit a tendency toward anisotropy [6]. In addition, a (B2+D0₃) two-phase field was reported to be existent at temperatures ranging from 800 to 1000°C in the Fe-Al-Ti ternary alloys [7-11]. It is noted that the (B2+D0₃) two-phase field has not been found by previous workers in the Fe-Al binary alloys before [12-13]. However, the existence of the (B2+ D0₃) two-phase field in the Fe-Al-Ti ternary alloys was determined principally by using X-ray diffraction and electron-probe microanalysis [7-11]. Recently, we have performed transmission electron microscopy (TEM) investigations on the phase transformations of an Fe-23 at.% Al-8.5 at.% Ti alloy aged at 900°C [14]. Consequently, it was found that when the alloy was aged at 900°C for longer times, the D0₃ domains grew considerably and an A2→(A2+D0₃)→(B2+D0₃) transition occurred at a/2<100>APBs. This feature has never been reported by other workers in the Fe-Al-Ti alloy systems before. Extending the previous work, the purpose of this study is an attempt to examine the microstructural developments of the Fe-24.6at.% Al-7.5at.% Ti alloy aged at 900°C.

Experimental Procedure

The Fe-24.6 at.% Al-7.5 at.% Ti alloy was prepared in a vacuum induction furnace by using Fe(99.9%), Al(99.9%) and Ti(99.9%). After being homogenized at 1250°C for 48 h, the ingot was sectioned into 2-mm-thick slices. These slices were subsequently solution heat-treated at 1100°C for 1 h and then quenched into room-temperature water rapidly. The aging processes were performed at 900 °C for various times in a vacuum heat-treated furnace and then quenched rapidly. TEM specimens were prepared by means of double-jet electropolisher with an electrolyte of 67% methanol and 33% nitric acid. Electron microscopy was performed on a JEOL JEM-2000FX scanning transmission electron microscope (STEM) operating at 200kV. 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, Al and Ti were made with the aid of a Cliff-Lorimer ratio thin section method.

Results and Discussion

Figure 1a is a selected-area diffraction pattern of the as-quenched alloy, exhibiting the superlattice reflection spots of the ordered D0₃ phase [14-16]. Figures 1b and c are (200) D0₃ (or, equivalently, (100) B2) and (111) D0₃ dark-field (DF) electron micrographs of the as-quenched alloy, showing the presence of the small B2 domains with a/4<111>

APBs and fine $D0_3$ domains with $a/2\langle 100 \rangle$ APBs, respectively [12,13]. In Figures 1b and c, it is seen that the sizes of both B2 and $D0_3$ domains are very small, indicating that these domains were formed by ordering transition during quenching [12,13]. In Figure 1b, it is also seen that a high density of disordered A2 phase (dark contrast) could be observed within the B2 domains. It is therefore concluded that the as-quenched microstructure of the alloy was a mixture of (A2+ $D0_3$) phases. This is similar to that observed by the present workers in the Fe-23at.% Al-8.5 at.% Ti alloy quenched from 1100 °C [14].

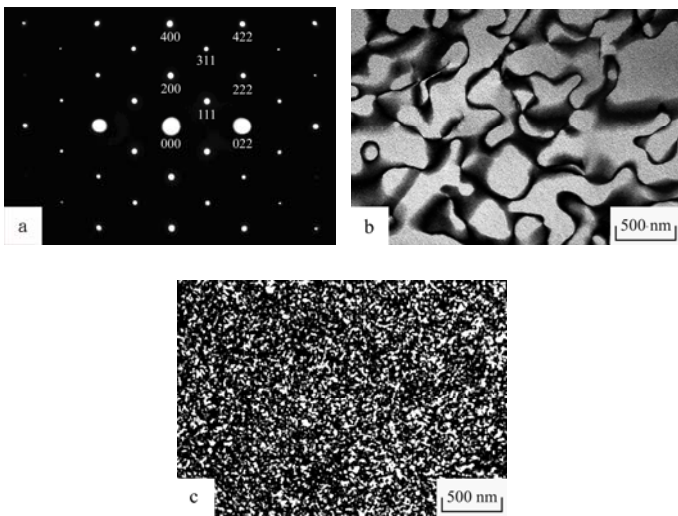


Fig. 1. Electron micrographs of the as-quenched alloy: (a) a selected-area diffraction pattern. The foil normal is $[01\bar{1}]$. (hkl = $D0_3$ phase); (b) and (c) (200) and (111) $D0_3$ DF, respectively.

Figure 2a shows a (111) $D0_3$ DF electron micrograph of the alloy aged at 900 °C for 6 h, indicating that the $D0_3$ domains grew significantly. Figure 2b, a (200) $D0_3$ DF electron micrograph of the same area as Figure 2a, reveals that the $a/2\langle 100 \rangle$ APBs were coated with the disordered A2 phase; otherwise there would be no contrast from these boundaries using a (200) reflection [12,13]. With continued aging at 900 °C, the disordered A2 phase disappeared and a phase separation started to occur basically at $a/2\langle 100 \rangle$ APBs of the $D0_3$ domains. A typical example is shown in Figure 3. Figure 3a is a (111) $D0_3$ DF electron micrograph of the alloy aged at 900 °C for 12 h, revealing that the $a/2\langle 100 \rangle$ APBs broadened and well-grown $D0_3$ domains decomposed into fine $D0_3$ domains (designated as $D0_3^*$ phase to be distinguished from the original $D0_3$

phase) separated by dark layers. Shown in Figure 3b is a (200) $D0_3$ DF electron micrograph taken from the same area as Figure 3a, clearly indicating that the whole region is bright in contrast. This indicates that the broadened dark lines on $a/2\langle 100 \rangle$ APBs and the dark layers around the periphery of the $D0_3^*$ domains should be of the B2 phase, since the (111) reflection spot comes from the $D0_3$ phase only; while the (200) reflection spot can come from both the $D0_3$ and B2 phases [6,7]. It is apparent that the B2 phase and the phase separation from $D0_3$ to (B2+ $D0_3^*$) started to occur initially at $a/2\langle 100 \rangle$ APBs. TEM examinations revealed that with increasing aging time at 900 °C, the phase separation from $D0_3$ to (B2+ $D0_3^*$) would proceed toward the inside of the whole well-grown $D0_3$ domains. A typical example is illustrated in Figure 4a. It is thus anticipated that the microstructure of the alloy in the equilibrium stage at 900 °C should be a mixture of (B2+ $D0_3^*$) phases, as indicated in Figure 4b.

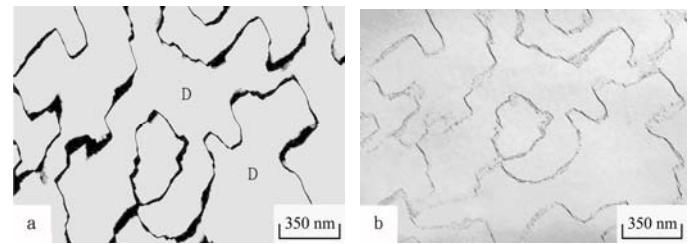


Fig. 2. Electron micrographs of the alloy aged at 900 °C for 6 h. (a) and (b) (111) and (200) $D0_3$ DF, respectively.

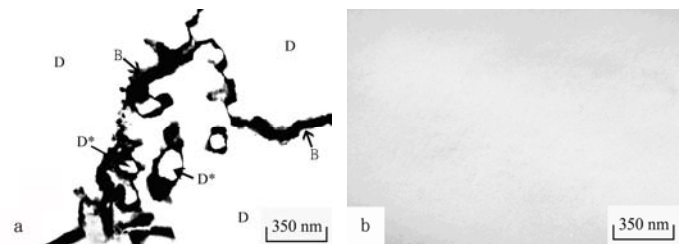


Fig. 3. Electron micrographs of the alloy aged at 900 °C for 12 h. (a) and (b) (111) and (200) $D0_3$ DF, respectively.

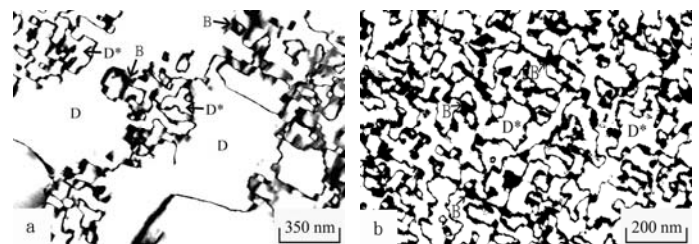


Fig. 4. (111) $D0_3$ DF electron micrographs of the alloy aged at 900 °C for (a) 24 h, and (b) 36 h.

Based on the above observations, two important experimental results are discussed below. (I) When the present alloy was aged at 900°C for longer times, the B2 phase and phase separation from well-grown D0₃ to (B2+ D0₃^{*}) occurred at a/2<100> APBs. This finding is different from that observed by the present workers in the Fe-23at.%Al-8.5at.%Ti alloy [14], in which we have demonstrated that when the Fe-23at.%Al-8.5at.% Ti alloy was aged at 900°C, the mixture of the (B2+ D0₃) phases occurred at a/2<100> APBs and no evidence of the phase separation could be observed. In order to clarify the apparent difference, an STEM-EDS study was undertaken. The EDS analyses were taken from in the middle of the D0₃ domains, B2 phase and D0₃^{*} domains marked as “D”, “B” and “D*” in Figures 2 through 4, respectively. The average concentrations of the alloying elements obtained by analyzing at least ten different EDS spectra of each phase are listed in Table 1. For comparison, the chemical composition of the as-quenched alloy is also listed in Table 1. It is noted here that since the size of the B2 phase (about 70 nm) examined is slightly larger than that of the electron beam spot (40nm) produced on the JEOL JEM-2000FX STEM, some errors in the exact percentage of elemental concentrations in the B2 phase are inevitable. However, it is seen in Table 1 that the Ti concentration in the B2 phase is much less than that in the D0₃ domains. Therefore, these analyses are still enough to permit an inference that the B2 phase is lacked in Ti. On the basis of the above analyses, it is found that the Ti concentration in the D0₃^{*} phase was distinctly higher than that in the D0₃ domains. In the previous studies, it is well-known that the D0₃ phase could be found to exist in the Fe-Al binary alloys only at temperatures below 550°C [12,13], and the Ti addition in the Fe-Al binary alloys could pronouncedly expand the D0₃ phase field [6-11]. Obviously, the Ti concentration would be the predominant factor for the stabilization of the D0₃ phase at high temperature. In our previous study of the Fe-23at.%Al-8.5at.%Ti alloy aged at 900°C for longer times [14], it was found that the Ti concentration in the well-grown D0₃ domains was up to about 11.1at.%, and no evidence of the phase separation could be detected. In the present alloy, however, the Ti concentration was found to be only about 8.2 at.%, which is noticeably lower than that detected in the previous alloy. Therefore, it is plausible to suggest that the

insufficient concentration of Ti would cause the well-grown D0₃ domains to become unstable. Consequently, the well-grown D0₃ domains would separate to the mixture of the Ti-riched D0₃^{*} and Ti-lacked B2 phase, as observed in Figures 3 and 4. (II) Compared to our previous study [14], it is clearly seen that the a/2<100> APBs of the well-grown D0₃ domains in the previous alloy exhibited more pronounced anisotropy than those observed in the present alloy. The reason is probably that the well-grown D0₃ domains in the previous alloy had significantly higher Ti concentration.

Table1. Chemical compositions of the phases revealed by EDS.

Heat Treatment	Phase	Chemical composition (at. %)		
		Fe	Al	Ti
as-quenched	A2+D0 ₃	67.9	24.6	7.5
900°C, 6 h	D0 ₃	65.7	26.1	8.2
	D0 ₃ [*]	66.4	25.6	8.0
900°C, 12 h	D0 ₃	65.7	25.2	9.1
	D0 ₃ [*]	65.7	25.2	9.1
	B2	69.4	24.1	6.5
900°C, 24 h	D0 ₃	66.6	25.5	7.9
	D0 ₃ [*]	65.2	25.8	9.0
	B2	69.4	24.3	6.3
900°C, 36 h	D0 ₃ [*]	65.2	25.7	9.1
	B2	69.5	24.2	6.3

Finally, it is worthwhile to point out that, compared with the previously established isothermal sections of the Fe-Al-Ti ternary alloys at 900°C [9-11], the chemical compositions of both the previous Fe-23at.%Al-8.5at.%Ti alloy and the present Fe-24.6at.%Al-7.5at.%Ti alloy are just located in the (B2+D0₃) region. TEM examinations revealed that at 900°C, the stable microstructure of both alloys was indeed the mixture of (B2+D0₃) phases, which is in agreement with that reported by the previous workers[9-11]. However, the microstructural revolutions for the formation of the (B2+D0₃) phases between the two alloys are quite different.

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