Stable and metastable phases in some quaternary Al-Si-Mn-Fe alloys

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Abstract. Metastable and stable phases in rapidly quenched and quenched and annealed quarternary Al–Si–Mn–Fe alloys have been identified using electron and x-ray powder diffraction techniques. It has been found that the constituent phases in rapidly quenched specimens a (Al_6Mn), b $(Al_{82}Mn_{17}Fe_1)$, c $(Al_{86}Si_4Mn_{10})$, d $(Al_{75}Si_7Mn_{14}Fe_4)$, e $(Al_{78}Si_4Mn_{12}Fe_6)$ and f $(Al_{75}Si_6Mn_{10}Fe_9)$ are metastable icosahedral and decagonal phases and stable crystalline Al, Al_6Mn, α-AlMnFeSi and $Al_{13}Fe_4$ phases. The constituent phases in the quenched-and-annealed Al–Si–Mn–Fe specimens are crystalline Al, Al_6Mn, $Al_{11}Mn_4$, α-AlMnFeSi and $Al_{13}Fe_4$ phases. The relative contents of these phases are dependent on the composition of each alloy.

1. Introduction

Since the discovery of the icosahedral phase (I-phase) in rapidly quenched binary Al–Mn alloys (Shechtman *et al* 1984) efforts have been made to produce stable I-phases with good quality. For this purpose, different alloy systems and, in particular, ternary and quarternary systems have been tried (see, e.g., Yamane *et al* 1987, Tsai *et al* 1987, 1988, 1989, He *et al* 1990). Moreover, it is important to study the crystallisation process and the products of quasicrystals to examine the stability and to investigate the atomic structure of quasicrystals (see, e.g., Fung and Zhou 1986, Wang *et al* 1986, Yamane *et al* 1987). In the present work, we report our identification of the metastable and stable phases in rapidly quenched quarternary Al–Si–Mn–Fe alloys a (Al_6Mn), b $(Al_{82}Mn_{17}Fe_1)$, c $(Al_{86}Si_4Mn_{10})$, d $(Al_{75}Si_7Mn_{14}Fe_4)$, e $(Al_{78}Si_4Mn_{12}Fe_6)$ and f $(Al_{75}Si_6Mn_{10}Fe_9)$ and their crystallisation products.

2. Experimental details

Ingots with six chemical compositions were induction melted from high-purity (better than 99.95%) raw materials in vacuum. Thin ribbons were prepared from these ingots by the melt-spinning technique using a copper wheel 35 cm in diameter rotated at 1200 rev min^{-1}. The main compositions of these ribbons were determined by an energy-dispersive x-ray analysis (EDXA) facility attached to a Hitachi X-650 scanning microprobe

and are listed in table 1. Most of the quenched ribbons were annealed at 623, 673, 723, 753, 823, 873, 923 and 953 K for 1 h. Specimens for transmission electron microscopy (TEM) were prepared by ion milling and then examined with a JEOL JEM-100CX(II) electron microscope operated at 120 kV and with a double-tilting stage. All the rapidly quenched and the annealed specimens were examined using powder x-ray diffraction and selected-area electron diffraction (SAED) at room temperature. The crystallisation process of specimen a (Al_6Mn) was pursued *in situ* with a high-temperature attachment fitted to the x-ray diffractometer. Phases which exist in each specimen have been identified by combining both SAED patterns and powder x-ray diffraction patterns.

3. Results and discussion

Table 1 lists the compositions of the specimens studied in this work, determined by EDXA, and summarises the main results of this work, which are described in detail as follows.

3.1. Phase identification of the rapidly quenched alloys

Figure 1 shows parts (2θ from 35° to 50°) of x-ray powder diffraction patterns of six rapidly quenched Al–Si–Mn–Fe alloys at room temperature. In order to arrive at a precise phase identification, some series of SAED patterns obtained by tilting the specimen around a spot row were photographed for each main phase and minor phase in the specimen. The reciprocal lattice corresponding to each series of SAED patterns was then reconstructed and compared with those reported in the literature. In this way, six phases have been identified in the rapidly quenched Al–Si–Mn–Fe alloys. They are as follows.

(1) I-phase (Schechtman *et al* 1984), for which the SAED patterns for the fivefold, threefold and twofold axes are shown in figures 2(*a*), 2(*b*) and 2(*c*), respectively. The x-ray powder reflections of the I-phase are denoted by I in figure 1. The I-phase is the main phase in rapidly quenched alloys a (Al_6Mn), b ($Al_{82}Mn_{17}Fe_1$), c ($Al_{86}Si_4Mn_{10}$) and d ($Al_{75}Si_7Mn_{14}Fe_4$). When more manganese is substituted by the element iron, the content of the I-phase decreases. For example, the I-phase becomes a minor phase in alloy e ($Al_{78}Si_4Mn_{12}Fe_6$) and a trace phase in alloy f ($Al_{75}Si_6Mn_{10}Fe_9$).

(2) Decagonal phase (Bendersky 1985), for which the D SAED pattern is shown in figure 2(*d*). This phase has only been identified in the rapidly quenched alloy b ($Al_{82}Mn_{17}Fe_1$).

(3) Crystalline aluminium (c-Al) as denoted by A in figure 1. The content of c-Al is rather more in rapidly quenched Al_6Mn and $Al_{86}Si_4Mn_{10}$ and less in the other alloys because the composition of the I-phase is $Al_{78}Mn_{22}$ (Yamane *et al* 1987).

(4) Crystalline Al_6Mn (Murry *et al* 1987), an orthorhombic phase with space group $C_{mcm}^{2\ 2\ 2}$ (No. 63), $a = 0.755\,18$ nm, $b = 0.649\,78$ nm and $c = 0.887\,03$ nm. The principal reflection conditions of *Cmcm* are *hkl* ($h + k = 2n$), *h0l* ($h, l = 2n$) and 00*l* ($l = 2n$) which are in agreement with the series of SAED patterns for which the [010] zone axis pattern is shown in figure 3(*a*). This phase is only a minor phase existing in quenched alloy Al_6Mn and its x-ray reflections are indicated by M in figure 1.

(5) Crystalline α-AlMnFeSi (Cooper and Robinson 1966, Cooper 1967), a cubic phase consisting of Mackay icosahedra. Its space group is $Pm\bar{3}$ (200) with $a = 1.268$ nm for α-$Al_9Mn_2Si_{1.8}$ and $Im\bar{3}$ (204) with $a = 1.256$ nm for α-$Al_{19}Fe_4MnSi_2$. The SAED

Table 1. Compositions, constituent phases and crystallisation temperatures of the investigated Al–Si–Mn–Fe alloys.

Alloy	Composition	Constituent phases in rapidly quenched alloys			Crystallisation temperature (K)	Constituent phases in annealed alloys		
		Main	Minor	Trace		Main	Minor	Trace
a	Al_6Mn	I, Al	$c\text{-}Al_6Mn$		683–723	$c\text{-}Al_6Mn$		
b	$Al_{82}Mn_{17}Fe_1$	I	D	Al	873–953	α-AlMnFeSi	$c\text{-}Al_6Mn$	$Al_{11}Mn_4$
c	$Al_{86}Si_4Mn_{10}$	I, Al	α-AlMnSi		753–823	Al, α-AlMnSi	$c\text{-}Al_6Mn$	
d	$Al_{75}Si_7Mn_{14}Fe_4$	I	α-AlMnFeSi, $Al_{13}Fe_4$	Al	753–823	α-AlMnFeSi		$Al_{13}Fe_4$
e	$Al_{78}Si_4Mn_{12}Fe_6$	α-AlMnFeSi	I, $Al_{13}Fe_4$	Al	753–823	α-AlMnFeSi		$Al_{13}Fe_4$
f	$Al_{75}Si_6Mn_{10}Fe_9$	α-AlMnFeSi	$Al_{13}Fe_4$	Al, I	753–823	α-AlMnFeSi		$Al_{13}Fe_4$

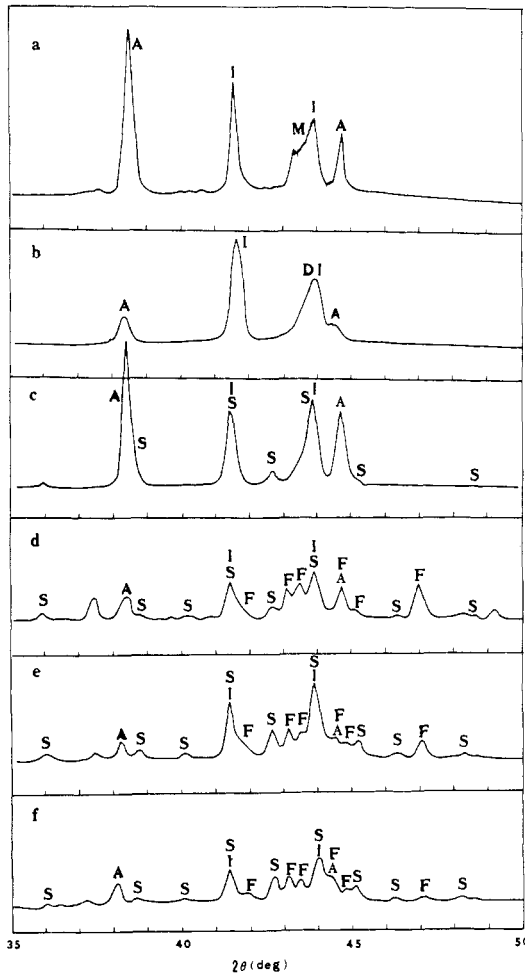**Figure 1.** Parts of the powder x-ray diffraction patterns (Cu Kα) of rapidly quenched ribbons for the compositions (a) Al_6Mn, (b) $Al_{82}Mn_{17}Fe_1$, (c) $Al_{86}Si_4Mn_{10}$, (d) $Al_{75}Si_7Mn_{14}Fe_4$, (e) $Al_{78}Si_4Mn_{12}Fe_6$ and (f) $Al_{75}Si_6Mn_{10}Fe_9$: I, icosahedral phase; D, decagonal phase, A, c-Al; M, c-Al_6Mn; S, α-AlMnFeSi; F, c-$Al_{13}Fe_4$.

patterns photographed from one of the important phases in rapidly quenched $Al_{75}Si_7Mn_{14}Fe_4$, $Al_{78}Si_4Mn_{12}Fe_6$ and $Al_{75}Si_6Mn_{10}Fe_9$ specimens, for which the [001] zone axis pattern is shown in figure 3(*b*), reveal the reflection condition $h + k + l = 2n$. This shows that the space group of this phase is $Im\bar{3}$ (204) and not $Pm\bar{3}$ in accordance with the fact that these specimens contain some Fe substituting for Mn. Moreover, this phase has been identified also in the rapidly quenched $Al_{86}Si_4Mn_{10}$ alloy as a minor phase. Because the α-AlMnSi phase in the rapidly quenched alloy c cannot possess the ordering of the α-$Al_9Mn_2Si_{1.8}$ phase, it remains a body-centred phase even when it does not contain Fe. The x-ray reflections of the α-AlMnFeSi phase are indicated by S in figure 1. Hoier *et al* (1973) identified the α-$Al_{12}Mn_3Si$ phase even in as-cast Al-1.8 wt% Mn alloy with Fe (0.03 wt%) and Si (0.03 wt%) being only impurities. Because of this, the existence of the α-phase in rapidly quenched Al–Si–Mn–Fe alloys is not surprising.

(6) Crystalline $Al_{13}Fe_4$ (Black 1955), a monoclinic phase with space group $C2/m(12)$, $a = 1.5489$ nm, $b = 0.8083$ nm, $c = 1.2476$ nm and $\beta = 107.71°$. The reflection condition for this space group is $h + k = 2n$. The series of SAED patterns obtained from one phase
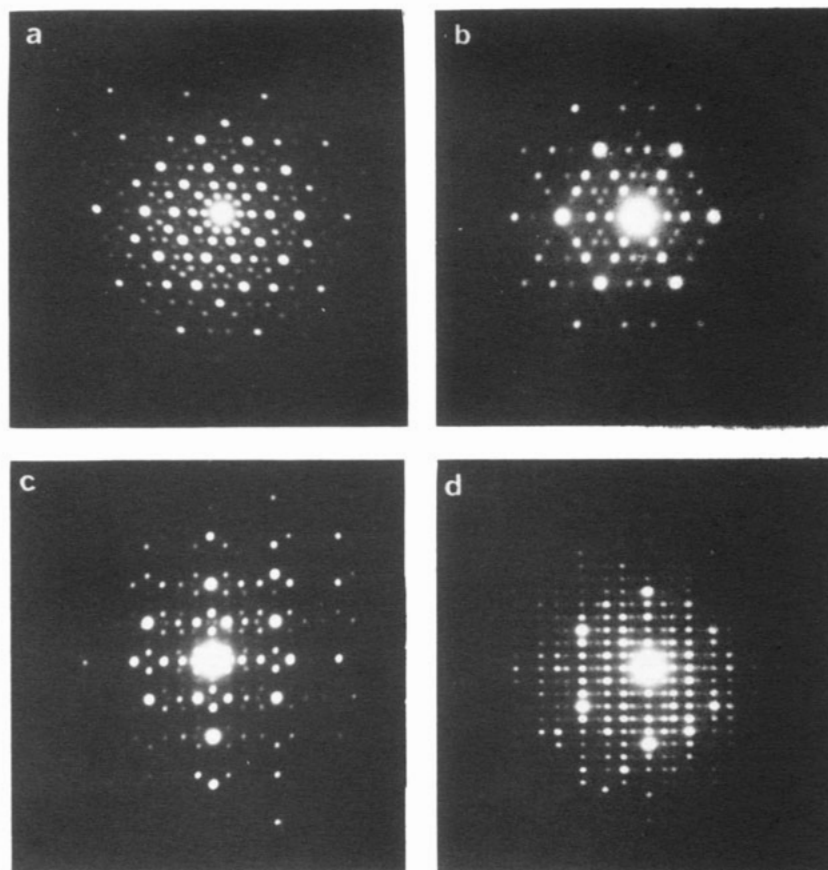
Figure 2. SAED patterns of (*a*) fivefold, (*b*) threefold and (*c*) twofold axes of the I-phase in rapidly quenched specimens a–c and (*d*) the D pattern perpendicular to the tenfold axis of the decagonal phase in specimen b.

of specimens d–f are in good agreement with $Al_{13}Fe_4$. The [010] axis pattern of this phase is shown in figure 3(*c*) and its x-ray reflections are denoted by F in figures 1(*d*)–1(*f*).

The grain size of the I-phase is about 1 μm in rapidly quenched alloys a–d when the I-phase is the main phase of the alloy, while it is much smaller (0.2 μm) in alloys e and f, when the I-phase is the minor or trace phase of the alloy. On the other hand, the crystalline phases are randomly distributed at grain boundaries of the I-phase and have smaller grain sizes than the I-phase. In alloys e and f, the grain size of the $Al_{13}Fe_4$ is about 2 μm and that of the α-AlMnFeSi phase is about 1 μm.

All the main, minor and trace phases identified in six rapidly quenched Al–Si–Mn–Fe alloys are summarised in table 1.

3.2. Study of the crystallisation process

The crystallisation process in rapidly quenched Al_6Mn has been studied by using high-temperature x-ray diffractometry. Figure 4 shows four x-ray diffraction patterns selected
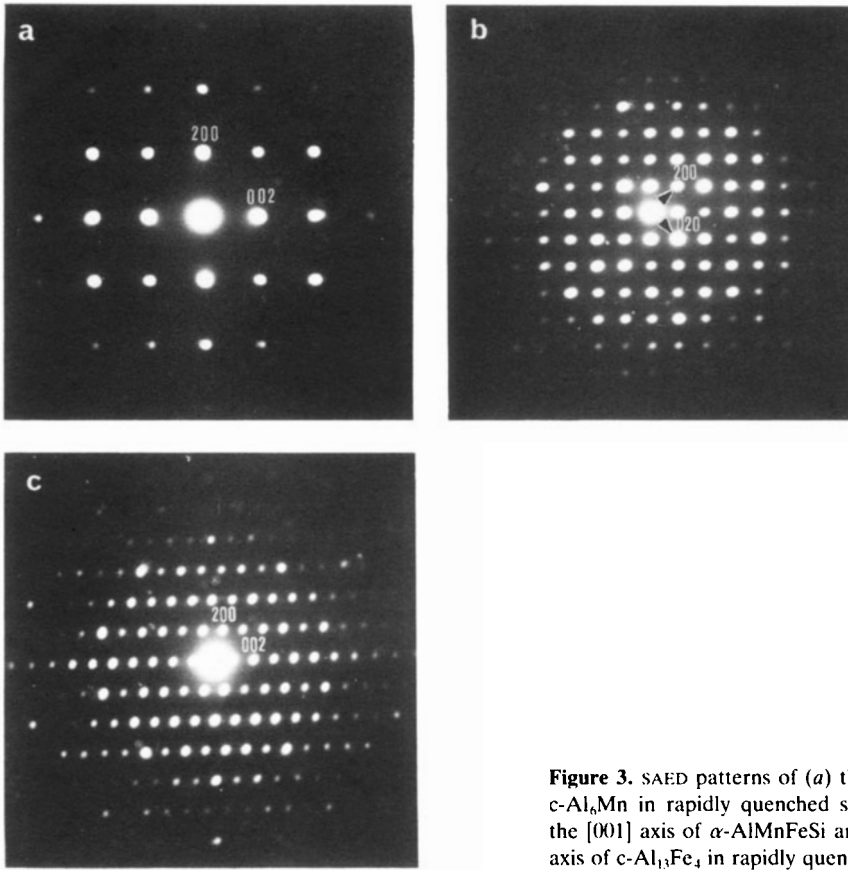
Figure 3. SAED patterns of (*a*) the [010] axis of c-Al₆Mn in rapidly quenched specimen a, (*b*) the [001] axis of α-AlMnFeSi and (*c*) the [010] axis of c-Al₁₃Fe₄ in rapidly quenched specimens d–f.
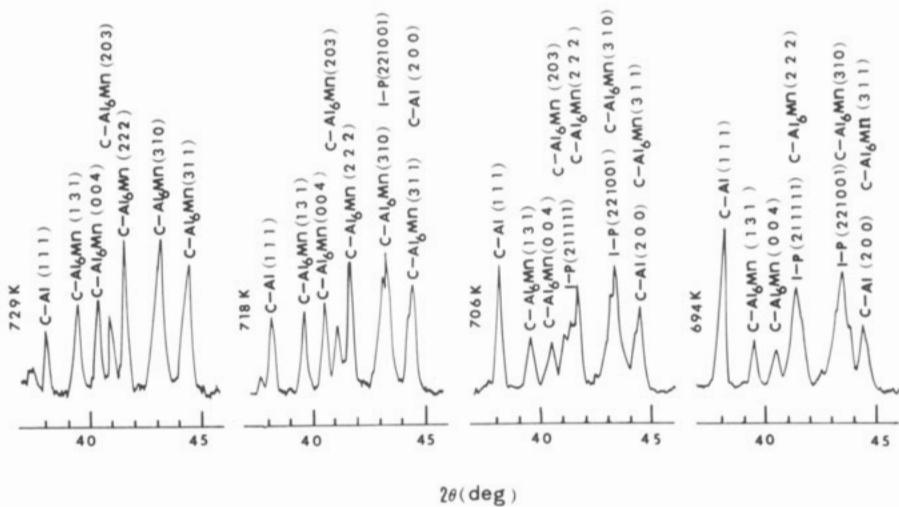

Figure 4. Selected x-ray diffraction patterns for alloy a (Al₆Mn) during heating.
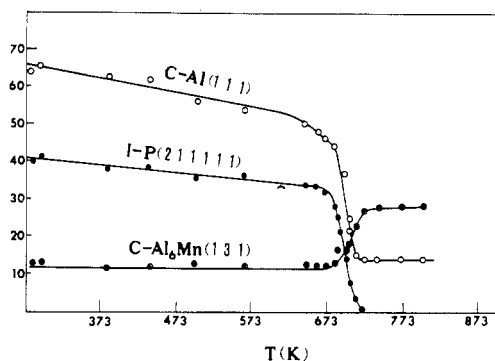
Figure 5. Diffraction intensities of I-phase (211111), c-Al$_6$Mn(131), and c-Al(111) reflections as a function of the temperature.

intensities of I(211111), c-Al$_6$Mn(131) and c-Al(111) when the temperature is raised. From room temperature to 683 K no obvious variation was observed. During the 20 min of heating from 683 to 723 K the diffraction intensities of the I-phase decreased to almost zero rather quickly. At the same time the intensities of the crystal phase c-Al$_6$Mn increased and c-Al decreased. This means that the obvious crystallisation process occurs in the temperature range 683–723 K at a heating rate of 2 K min^{-1}.

In order to obtain the temperature range of the crystallisation process of the other Al–Si–Mn–Fe alloys, the samples were annealed at temperatures of 623, 673, 723, 753, 823, 873, 923 and 953 K for 1 h. The x-ray diffraction patterns of the samples annealed at different temperatures have been obtained. By comparing the x-ray diffraction patterns of the alloys annealed at different temperatures, especially by observing the variation in the intensities of the I-phase reflections, the crystallisation temperature range of each alloy was obtained and is listed in table 1; these are 873–953 K for alloy b and 753–823 K for alloys c–f.

3.3. Phase identification of the annealed alloys

Figure 6 shows parts ($35° < 2\theta < 50°$) of the x-ray powder diffraction patterns of the annealed Al–Si–Mn–Fe alloys. Combining the x-ray patterns and SAED patterns, five crystalline phases have been identified. They are as follows.

(1) c-Al$_6$Mn which is the main phase in specimen a and minor phase in specimens b and c.

(2) c-Al, which is one of the main phases in specimen c.

(3) c-(α-AlMnFeSi) which is the main phase in specimens b–f.

(4) c-Al$_{13}$Fe$_4$ which is the trace phase in specimens d–f.

(5) c-Al$_{11}$Mn$_4$ (Murry *et al* 1987), an orthorhombic phase with space group $P\frac{2_1}{m}\frac{2_1}{m}\frac{2_1}{a}$(62), $a = 1.479$ nm, $b = 1.242$ nm and $c = 1.259$ nm. The reflection conditions of *Pnma* are $0kl (k + l = 2n)$, $hk0 (h = 2n)$, $h00 (h = 2n)$, $0k0 (k = 2n)$ and $00l (l = 2n)$. The Al$_{11}$Mn$_4$ phase was denoted as Al$_3$Mn earlier by Hofmann (1938) and by Taylor (1960). This phase has been identified in this work by the SAED technique in the annealed alloy b as one of the trace phases. Figure 7 shows its [100]-axis SAED pattern. In this pattern the reflections with $k + l = 2n + 1$, which should disappear for *Pnma*, do appear but with lower intensities. This may result from ordering during annealing.

The grain size of the Al$_6$Mn phase becomes 4–5 μm, which is much larger than in quenched alloys, and that of the α-AlMnFeSi phase becomes 2–3 μm compared with
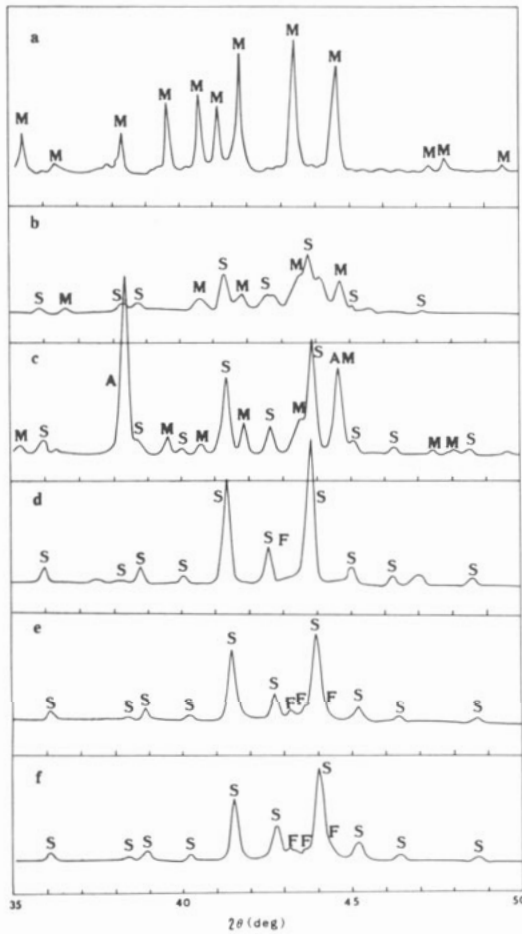
Figure 6. Parts of the powder x-ray diffraction patterns (Cu Kα) of the annealed alloys for the compositions and annealing temperatures (a) Al_6Mn, 723 K, (b) $Al_{82}Mn_{17}Fe_1$, 953 K, (c) $Al_{86}Si_4Mn_{10}$, 823 K, (d) $Al_{75}Si_7Mn_{14}Fe_4$, 823 K, (e) $Al_{78}Si_4Mn_{12}Fe_6$, 823 K, and (f) $Al_{75}Si_6Mn_{10}Fe_9$, 823 K: A, c-Al; M, c-Al_6Mn; S, α-AlMnFeSi; F, c-$Al_{13}Fe_4$.
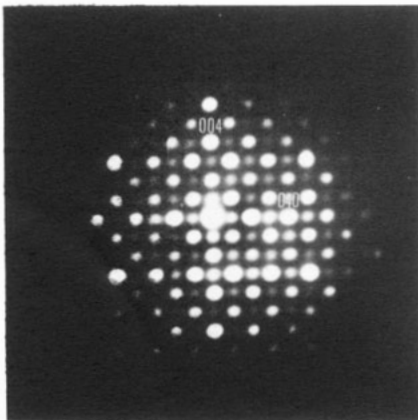

Figure 7. SAED [100] axis pattern of $Al_{11}Mn_4$, obtained from alloy b annealed at 953 K for 1 h.

the value of 1 μm in quenched alloys. The grain size of the $Al_{13}Fe_4$ phase remains about 2 μm, the same as in quenched alloys.

All the main, minor and trace stable phases identified in annealed Al–Si–Mn–Fe alloys are summarised in table 1.

Acknowledgment

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