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Intermetallic phases in Al–Mn alloys

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The intermetallic phases present in high-purity and commercial purity Al–Mn alloys (up to 2% Mn) in as-cast and heat-treated conditions were extracted electrolytically in 10% HCl in methanol solution and identified by X-ray diffraction. As iron is known to increase the coarse cast-intermetallic particles and to cause refinement of the grain size after recrystallization, different amounts of iron (up to 0.5%) were added and the resulting intermetallic phases were extracted and identified with and without heat treatment. The unidentified phase α-Al (Mn, Fe)Si, reported by Sperry and others, was recognized as corresponding for ASTM card number 6-0669 and the conditions favourable for its formation were determined. This phase may be responsible for refining the grain size after recrystallization in commercial purity alloys as compared to high-purity Al–Mn alloys and may therefore be tried as an inoculant (by adding powdered compound to liquid alloys) for grain refining.

1. Introduction

Al–Mn alloys (up to 2% Mn) with various advantages of good mechanical properties, good corrosion resistance, ease of welding and brazing suggest themselves for many engineering, chemical, transportation, building, desalination, marine and food handling applications. The size, shape and distribution of intermetallic compounds are known to affect the recrystallized grain size of Al–Mn alloys [1–12]. Because these alloys are generally used in the form of sheet, strip or foil, the problem of grain refinement assumes added importance.

It is in the context of producing fine recrystallized grains that it was planned to (i) extract and identify the nature and composition of different intermetallic phases present in as-cast and heat-treated Al–Mn alloys of high- (99.99%) and commercial (99.7%) purity, and (ii) to establish the conditions favourable for the formation of certain phases by alloy additions and/or heat treatment.

The presence of intermetallic phases in Al–1.25% Mn alloys (3S) was studied by Sperry [13] in connection with grain refinement. He ascribed the formation of an unidentified phase α-Al (Mn, Fe)Si to slow rates of cooling, according to the solidification reactions:

$$\text{liquid} + \text{Al}_6\,(\text{Mn, Fe}) \rightarrow \alpha\text{-Al (Mn, Fe)Si} + \text{Al solid solution (peritectic)}$$

$$\text{liquid} \rightarrow \alpha\text{-Al (Mn, Fe)Si} + \text{Al solid solution (eutectic)}$$

Silicon present in the solid solution (as an impurity) reacts with eutectic Al_6 (Mn, Fe) to form α-Al (Mn, Fe)Si, thereby reducing the manganese content of the matrix. The latter grows in size as it replaces the former. It restrains normal grain growth by blocking the movement of grain boundaries, thereby refining the recrystallized grains in commercial aluminium as compared to high-purity aluminium [14].

It should be noted at this juncture that most phases in the Al–Mn–Si system form by peritectic reactions and are not easily nucleated when they crystallize from the liquid state. The exact location of phase boundaries is tentative. Many variations have been used regarding the terminology and crystallographic data adopted for various intermetallic phases in the ternary Al–Mn–Si system, especially regarding the α-AlMnSi phase: it has been designated α-MnSi by Phillips [15], C-AlMnSi by Phragmen with a cubic structure [16], α-AlMnSi with a cubic structure (a_0 = 1.2670 nm) and composition $\text{Mn}_{12}\text{Si}_7\text{Al}_5$ by Robinson [17]. Armand [18, 19] investigated the region corresponding to α-phase and found that it comprised of four phases. Munson [20] has ascribed a simple cubic structure to α-AlMnSi but very nearly bcc, i.e. α-($\text{Al}_{12}\text{Mn}_3\text{Si}$); it becomes bcc α-Al(Fe, Mn)Si, i.e. α-Al_{12}(Mn, Fe)$_3$Si, as the iron content increases. Mondolfo and co-workers [21–24] have ascribed composition of $\text{Al}_{15}\text{Mn}_3\text{Si}$ to α-AlMnSi phase in which up to 90% Mn can be replaced by iron. Watanable [25] has shown the thermal transition from Al_6(Fe, Mn) produced on casting changing to Al_{12}(Mn, Fe)$_3$Si on annealing Al–Mn–Fe–Si alloys.

The intermetallic phases are known to be affected by the presence of iron as an impurity or as an alloy addition. Iron reduces the equilibrium solid solubility of 1.9% Mn in aluminium to 0.3 to 0.4% Mn and accelerates the decomposition of supersaturated solid solution. According to Varivoda *et al.* [26] and Moisan *et al.* [27], iron refines the grain size of Al–Mn alloys and it is effective in accelerating precipitation in the presence of silicon [28]. Silicon content above the impurity level in Al–Mn alloys has been found to be of no advantage [29]. Silicon addition has been reported to greatly accelerate the decomposition in supersaturated solid solution with the precipitation of α-Al_{12}MnSi phase prior to recrystallization. The dense particle dispersion (interparticle spacing 0.8 to 1.5 μm) effectively pins the subgrain boundaries of the

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TABLE I Composition of Al–Mn alloys

Serial no.	Alloy designation		Mn (wt %)	Fe (wt %)	Si (wt %)
	High-purity Al (99.99%)	Commercial Al (99.7%)			
1.	K	–	1.5	–	–
2.	–	N	0.9	0.31	0.25
3.	P	–	1.3	0.50	0.07
4.	Q	–	1.7	0.40	trace
5.	R	–	1.8	0.30	0.06

recovered material and formation of viable recrystallization nuclei is prevented, giving rise to coarse final grain size [30]. To achieve accelerated recrystallization and uniform fine grain size, dispersed particles should be greater than 0.5 μm in size and interparticle spacing should be approximately 4 μm [8–13].

2. Experimental details

2.1. Preparation of alloys

A master alloy with high-purity aluminium (99.99%) and electrolytic manganese (99.80%) was prepared in an electron-beam melting furnace and was later diluted in a resistance furnace to give alloy K (1.5% Mn). With a view to determining the effect of impurities present in commercial grade aluminium (such as iron and silicon) on the precipitation of intermetallic phases, commercial aluminium (99.7% pure) was alloyed with electrolytic manganese in EBM and diluted to produce alloy N (0.9% Mn). Next, varying amounts of iron (0.3%, 0.4% and 0.5%) were added to high-purity Al–Mn alloys to establish the effect of iron in chill-cast alloys P, Q and R, Table I.

2.2. Controlled solidification of alloys

Samples (1 cm thick) were cut from all alloys, ground and polished on silicon carbide papers. The technique of anodic oxidation etching has been developed by the author to distinctly reveal the cast, homogenized, aged and recrystallized structures of aluminium and Al–Cu alloys [31], Al–Mn and Al–Mg alloys [32]. Anodic etching in case of Al–Mn alloys was performed at 60 to 70° C for 5 min and a constant current density of 15 A dm^{-2} using the following electrolytes: 40 ml H_2SO_4; 6 ml H_3PO_4; 1 ml HNO_3; 88 ml distilled water.

The chill castings were found to show a variation in cell sizes across the section. Small parts (20 g) of such castings were removed, remelted and cast under isothermal conditions by dropping the molten alloy directly into a salt bath maintained at specified temperatures. The alloy K was poured from 740° C directly into a salt bath maintained at temperatures of 580, 550, 500, 450, 400 and 340° C, respectively (alloys K_a to K_f).

The alloy N was poured from 700° C into a salt bath maintained at temperatures of 600, 530, 500, 450, 400 and 350° C, respectively (N_a to N_f). The alloy N was also poured from 800° C and solidified at temperatures of 600, 550, 500, 450, 400 and 350° C, respectively (N_I to N_{VI}).

2.3. Effect of heat treatment

In order to study the effect of heat treatment, the chill-cast alloys, N, Q and R were heated at 450° C for 5 h (N_H, P_H, R_{1H}). The conventional prolonged heat treatment was done on a sample of alloy R which was heated at 610° C for 7 h followed by heating at 540° C for 24 h (R_{2H}).

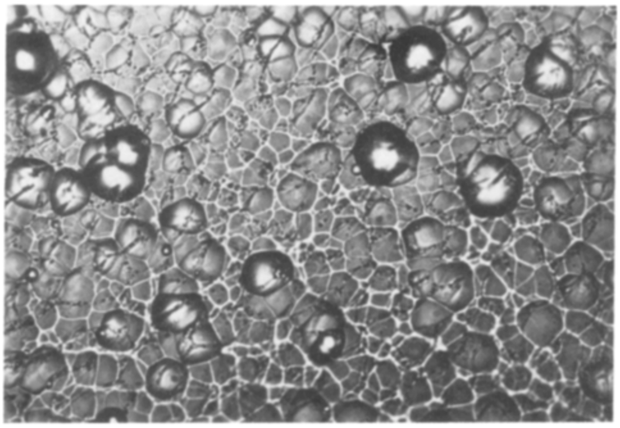

Figure 1 The anodically etched microstructure of alloy P (Al–1.3% Mn–0.5% Fe) in the chill-cast condition [33] × 500.

2.4. Extraction and identification of intermetallic phases

Representative samples were cut from alloys K_a to K_f, N_a to N_f, N_I to N_{VI}, N_H, P, P_H, R, R_{1H}, R_{2H} and used for extraction of intermetallic phases. A 10% hydrochloric acid solution in methanol was prepared and electrolysis was done using the sample as anode for 2 h or more. This solution was found to selectively remove aluminium alloy matrix by anodic dissolution leaving intermetallic phases as insoluble residues. The solution was centrifuged and the residue was washed several times with alcohol to remove traces of acid. The residue was then dried and identified by X-ray diffraction using the Debye–Scherrer technique and Cu$K\alpha$ radiation. The representative results of X-ray diffraction analysis are given in Tables II to VIII. The d-values were compared for the presence of various phases with those given in standard ASTM cards.

3. Observations

The following observations were made.

(i) In alloys K and N (chill cast) no intermetallic phases were detected.

(ii) The alloy K poured from 740° C and solidified under controlled conditions at 580, 500, 450, 400 and 340° C (K_a, K_c, K_d, K_e, K_f) showed no intermetallic phase on diffraction. The alloy solidified at 550° C (K_b), however, showed the presence of Al_6Mn phase.

(iii) Controlled solidification of alloy N showed that the formation of three intermetallic phases Al_6Mn, α-AlMnSi (ASTM card no. 6-0669) and $AlMn_{8.4}$ (ASTM card no. 3-1177) took place at solidification temperatures of 550 and 500° C when poured from 800° C and at solidification temperatures of 600, 500, 450 and 400° C when poured from 700° C (representative Tables II to IV). The results were reasonably consistent.

(iv) Iron-bearing alloy P (0.5% Fe) in the chill-cast condition was found to contain Al_6Mn, α-AlMnSi, $AlMn_{8.4}$ and Al_9Mn_3Si phases (Table V).

TABLE II The observed *d*-values for alloy N_{II} (Al–0.9% Mn) poured from 800° C and solidified at 550° C

Line	Observed values, sample N_{II}		Standard *d*-lines for various phases from ASTM cards					
	d (nm)	I/I_0 (visual)	Al_6Mn		$Mn_{12}Si_7Al_5$		$AlMn_{8.4}$	
			d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
1.	0.3210	5	0.3246	10	–	–	–	–
2.	0.2827	5	–	–	0.2838	30		–
3.	0.2583	5	0.2621	20	–	–	–	–
4.	*0.2306*	100	*0.2269*	50	0.2315	50	–	–
5.	0.2228	10	0.2217	20	0.2246	10	–	–
	–	–	–	–	*0.2176*	90	–	–
6.	0.2134	10	*0.2153*	50	0.2115	60	*0.212*	80
	–	–	*0.2081*	100	*0.2057*	100	–	–
7.	*0.1992*	80	*0.2027*	50	0.2006	40	*0.201*	80
8.	0.1872	5	0.1892	30	0.1869	50	–	–
9.	0.1788	40	–	–	0.1759	20	0.176	40
10.	0.1502	2	–	–	0.1515	60	0.150	70
11.	0.1452	5	0.1439	4	0.1473	30	–	–
12.	*0.1423*	80	0.1429	15	–	–	0.142	70
13.	0.1297	10	–	–	0.1308	10	–	–
14.	0.1272	20	–	–	*0.1267*	70	0.127	50
	–	–	–	–	–	–	*0.125*	100
15.	*0.1221*	90	–	–	*0.1208*	90	*0.118*	100
16.	0.1167	30	–	–	–	–	0.116	70

Note: The strongest lines are in italics, and all the strongest lines from the ASTM cards are quoted in each case.

(v) The microstructures (anodically oxidized) of alloy P in the chill-cast condition showed the precipitate concentrated in primary aluminium dendrites (Fig. 1) [32].

(vi) Iron-bearing alloy Q (0.4% Fe) contained α-AlMnSi, $AlMn_{8.4}$ and Fe_2Al_5 phases in the chill-cast condition (Table VI).

(vii) The alloy R (0.3% Fe) contained only $AlMn_{8.4}$ in the chill-cast condition.

(viii) The commercial purity alloy N which contained no intermetallic phase in the chill-cast condition, on heating at 450° C for 5 h (N_H) showed the appearance of phase α-AlMnSi only (Table VII).

(ix) Heating alloy P at 450° C for 5 h (P_H) gave a diffraction pattern indicating sharper and an increased number of lines corresponding to each phase found in the chill-cast condition.

(x) The alloy R (0.3% Fe) on heating at 450° C for 5 h (R_{1H}) still showed the presence of $AlMn_{8.4}$ only.

(xi) The alloy R on heating at 610° C for 7 h followed by heating at 540° C for 22 h (R_{2H}) precipitated the phase α-AlMnSi (The Al_6Mn phase was significantly absent).

(xii) Some ambiguity arose with *d*-spacings of Al_6Mn and α-AlMnSi phases because in commercial purity alloys, iron may partially substitute manganese.

4. Results and discussion

In the present investigation, it was found that extraction of phases in Al–Mn alloys can be conveniently obtained by passing a current in a solution of 10% HCl in methanol and the extract obtained in 2 h is sufficient to identify the intermetallic phases using X-ray diffraction analysis.

TABLE III The observed *d*-values from alloy N_a (Al–0.9% Mn) poured from 700° C, solidified at 600° C

Line	Observed values, sample N_a		Standard *d*-lines from ASTM cards					
	d (nm)	I/I_0 (visual)	Al_6Mn		$Mn_{12}Si_7Al_5$		$AlMn_{8.4}$	
			d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
1.	0.3190	5	0.3246	10	–	–	–	–
2.	0.2820	5	0.2875	6	0.2838	30	0.285	60
3.	0.2470	5	0.2462	6	0.2490	50	–	–
4.	*0.2278*	100	*0.2269*	50	*0.2315*	50	–	–
5.	0.2210	20	0.2217	20	*0.2176*	90	–	–
	–	–	*0.2153*	50	–	–	–	–
6.	0.2100	20	*0.2081*	100	0.2115	60	*0.212*	80
7.	*0.2038*	100	*0.2027*	50	*0.2057*	100	*0.201*	80
8.	*0.1980*	100	–	–	0.2006	40	–	–
9.	0.1850	5	0.1834	10	0.1869	50	–	–
10.	0.1511	5	–	–	0.1515	60	0.150	70
11.	0.1456	5	–	–	0.1473	30	0.142	70
12.	*0.1418*	80	–	–	–	–	–	–
13.	0.1294	10	–	–	*0.1267*	70	0.127	50
	–	–	–	–	–	–	*0.125*	100
14.	*0.1212*	90	–	–	*0.1208*	90	0.122	70
15.	0.1170	20	–	–	–	–	*0.118*	100

TABLE IV The observed *d*-values of alloy $\mathrm{N_e}$, poured from 700° C and solidified at 400° C

Line	Sample $\mathrm{N_e}$		Standard *d*-values from ASTM cards					
	d (nm)	I/I_0 (visual)	$\mathrm{Al_6Mn}$		$\mathrm{Mn_{12}Si_7Al_5}$		$\mathrm{AlMn_{8.4}}$	
			d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
1.	0.459	20	–	–	0.450	50	–	–
2.	0.418	10	–	–	*0.402*	70	–	–
3.	*0.2280*	100	*0.2269*	50	0.2315	50	–	–
4.	0.2186	5	0.2187	20	0.2176	90	–	–
5.	0.2132	5	*0.2153*	50	*0.2115*	60	*0.212*	80
	–		*0.2081*	100	*0.2057*	100		
6.	*0.1983*	90	*0.2027*	50	0.2006	40	*0.201*	80
7.	0.1910	5	0.1912	15	–	–	*0.192*	80
8.	0.1698	10	0.1702	5	0.1665	30	0.170	80
9.	0.1415	80	–	–	–	–	0.142	70
	–	–	–	–	–	–	*0.125*	100
10.	*0.1218*	90	–	–	*0.1208*	90	0.122	70
11.	0.1167	60	–	–	–	–	*0.118*	100
							0.116	70

High-purity alloy K (1.5% Mn) shows no intermetallic phase in the chill-cast condition nor when poured from 740° C and solidified under controlled conditions at 580, 500, 450, 400 and 340° C (except that it shows $\mathrm{Al_6Mn}$ in alloys solidified at 550° C). On the other hand, commercial purity alloys N (0.9% Mn) also indicate no intermetallic phase in the chill-cast condition but on pouring from 700° C and solidifying at 600, 530, 500, 450 and 400° C they show the presence of phases $\mathrm{Al_6Mn}$, α-AlMnSi and $\mathrm{AlMn_{8.4}}$. Also, when this alloy is poured from a higher temperature of 800° C, these phases are indicated only at higher solidification temperatures of 550 and 500° C and not at lower temperatures. This points to two facts. First, the purity of the alloy is of vital importance, the commercial purity alloy favours the formation of these phases because of the impurities present (Fe, Si mainly) and second, these phases are precipitated more easily when pouring takes place from a lower temperature of 700° C.

The effect of heating commercial purity, chill-cast alloy at 450° C for 5 h is to precipitate the phase α-AlMnSi. These observations thus show that the formation of phase α-AlMnSi is favoured on solidification at higher temperatures and low pouring temperatures and suppressed in the reverse case. Another way to precipitate the phase is to heat the commercial purity alloy at 450° C for 5 h.

The effect of the addition of 0.5% iron to Al–Mn alloys is to favour the formation of phase α-AlMnSi in the chill-cast condition along with other phases such as $\mathrm{Al_6Mn}$, $\mathrm{AlMn_{8.4}}$ and $\mathrm{Al_9Mn_3Si}$. According to Mondolfo *et al.* [33], in commercial purity Al–Mn alloys, iron can substitute manganese to different extents in various intermetallic phases. Because of practically little difference between the atomic diameters of iron and manganese, the diffraction patterns will not be modified significantly. The microstructure reveals that the precipitate is concentrated in primary aluminium dendrites (Fig. 1) [32] confirming Sperry's observation of a fine precipitate (unidentified) in primary aluminium dendrites. This alloy on heating at 450° C for 5 h shows clearer and a greater number of lines compared to the as-cast diffraction pattern.

The alloy Q containing 0.4% Fe, shows phases α-AlMnSi, $\mathrm{AlMn_{8.4}}$, $\mathrm{Fe_2Al_5}$ in the as-cast condition. $\mathrm{Al_6Mn}$ is found to be absent. This is the critical

TABLE V The *d*-values of alloy P (Al–1.3 Mn–0.5 Fe–0.07 Si) in the chill-cast condition

Line	Observed values, sample P		Standard *d*-values from ASTM cards					
	d (nm)	I/I_0 (visual)	$\mathrm{Al_6Mn}$		$\mathrm{Mn_{12}Si_7Al_5}$		$\mathrm{Al_9Mn_3Si}$	
			d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
1.	0.2455	5	0.2462	6	–	–	0.2456	50
2.	*0.2291*	100	*0.2269*	50	0.2315	50	–	–
3.	0.2218	5	0.2217	20	–	–	–	–
4.	0.2142	5	*0.2153*	50	*0.2176*	90	–	–
5.	0.2102	5	*0.2081*	100	0.2115	60	*0.2088*	100
	–	–	–	–	–	–	*0.2075*	100
6.	0.2042	50	*0.2027*	50	*0.2057*	100	*0.2019*	85
7.	*0.1992*	90	–	–	0.2006	40	–	–
8.	0.1857	5	–	–	0.1869	50	0.1852	50
9.	0.1428	80	0.1429	15	–	–	–	–
10.	0.1342	5	–	–	0.1336	30	0.1347	50
11.	0.1311	5	–	–	0.1308	10	0.1319	30
12.	0.1247	5	–	–	–	–	0.1252	70
13.	*0.1216*	90	–	–	*0.1208*	90	0.1219	30
14.	0.1198	5	–	–	–	–	0.1200	20

TABLE VI The *d*-values of alloy Q (Al–1.7 Mn–0.4 Fe) in the chill-cast condition

Line	Observed values, sample Q		Standard *d*-values from ASTM cards					
	d (nm)	I/I_0 (visual)	$Mn_{12}Si_7Al_5$		$AlMn_{8.4}$		Fe_2Al_5	
			d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
1.	0.3550	5	0.3665	30	0.368	20	–	–
2.	0.3206	10	–	–	–	–	*0.320*	40
3.	0.2760	5	0.2712	10	–	–	–	–
4.	0.2472	10	0.2490	50	–	–	–	–
5.	*0.2286*	90	0.2315	50	–	–	–	–
6.	0.2214	10	*0.2176*	90	–	–	–	–
7.	0.2144	20	0.2115	60	*0.212*	80	*0.211*	100
8.	0.2038	60	*0.2057*	100	*0.201*	80	*0.205*	100
9.	*0.1981*	90	0.2006	40	–	–	–	–
10.	0.1865	5	0.1869	50	–	–	–	–
11.	0.1515	5	0.1515	60	0.150	70	0.152	10
12.	0.1455	5	0.1473	30	–	–	–	–
13.	0.1415	80	–	–	0.142	70	0.142	2
14.	0.1365	5	–	–	0.136	50	–	–
15.	0.1329	5	0.1336	30	–	–	–	–
16.	0.1308	10	0.1308	10	–	–	0.130	2
17.	0.1267	5	*0.1267*	70	0.127	50	0.127	10
18.	0.1248	5	–	–	*0.125*	100	0.124	8
19.	*0.1215*	90	*0.1208*	90	0.122	70	0.121	10
20.	0.1165	50	–	–	*0.118*	100	–	–
					0.116	70		

amount of iron found to be necessary to form phases in the chill-cast condition. In an alloy containing 0.3% Fe, long heat treatment has to be resorted to, in order to precipitate the phase α-AlMnSi at the expense of Al_6Mn which remains significantly absent (Table VIII). This shows that a decrease in the iron content from 0.5% to 0.4% facilitates the formation of α-AlMnSi phase and suppresses the formation of Al_6Mn phase in favour of the former. This is a useful piece of information because Al_6Mn, which is responsible for surface defects during rolling, can thus be eliminated in favour of α-AlMnSi.

It appears that α-AlMnSi phase with composition $Mn_{12}Si_7Al_5$ as given by ASTM card no. 6-0669 [17] is the same unidentified phase α-Al (Mn, Fe)Si which was observed by Sperry metallographically during heat treatment of 3S alloy. He held these particles responsible for refining the recrystallized grains in commercial aluminium as compared to high-purity aluminium.

It is this context, that it was felt that the phase $Mn_{12}Si_7Al_5$ may be responsible for refining the recrystallized grain of Al–Mn alloys. This phase was also observed by Hirasawa [34] on extended holding at 350° C of Al–Mg–Si–Mn alloys. The precipitate of α-$Mn_{12}Si_7Al_5$ nucleated upon the interface of the age-hardening phase Mg_2Si. Cogen *et al.* [35] recently extracted phases from alloy 6061 (containing 0.4 to 0.8 Si, 0.7 Fe, 0.15 to 0.40 Cu, 0.15 Mn, 0.8 to 1.2 Mg, 0.25 Zn) solution treated at 535° C for 2 h, aged at 300° C for 24 h. They found that this alloy contains (both in solution treated and aged conditions) the intermetallic compound $Mn_{12}Si_7Al_5$.

In view of the above work, combined with earlier observations, the intermetallic compound $Mn_{12}Si_7Al_5$ can be tried as an inoculant for 3S alloys (Al–1.25% Mn) to reduce long soaking periods for refining the grain size after recrystallization. Work is in progress by preparing the compound (65% Mn, 20% Si, 14% Al) and adding different amounts of the powder

TABLE VII The observed *d*-values of alloy N heated at 450° C for 5 h: N_H

Line	Observed values, sample N_H		Standard *d*-values from ASTM cards, $Mn_{12}Si_7Al_5$	
	d (nm)	I/I_0 (visual)	*d* (nm)	I/I_0
1.	*0.3290*	80	0.3395	30
2.	0.2461	20	0.2490	50
3.	*0.2306*	100	0.2315	50
4.	0.2146	20	*0.2176*	90
	–	–	*0.2057*	100
5.	*0.2005*	80	*0.2006*	40
6.	0.1802	20	0.1759	20
7.	0.1669	20	0.1665	30
8.	0.1532	10	0.1515	60
9.	*0.1418*	80	0.1473	30
10.	0.1339	5	0.1336	30
11.	0.1281	20	0.1267	70
12.	*0.1218*	80	*0.1208*	90

TABLE VIII The observed d-values of alloy R (Al–1.8 Mn–0.3 Fe) heated at (610°C for 7 h) followed by heating at (540°C for 24 h)

Line	Observed values, sample R_{2H}		Standard d-values from ASTM cards					
	d (nm)	I/I_0 (visual)	$Mn_{12}Si_7Al_5$		$AlMn_{8.4}$		Fe_2Al_5	
			d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
1.	0.424	5	0.450	50	–	–	–	–
2.	0.3187	5	–	–	–	–	0.320	10
3.	0.2862	5	–	–	0.285	60	–	–
4.	0.2488	5	0.2490	50	–	–	–	–
5.	*0.2310*	90	0.2315	50	–	–	–	–
6.	0.2247	20	0.2246	10	–	–	–	–
7.	0.2130	40	–	–	*0.212*	80	*0.211*	100
8.	0.2056	90	*0.2057*	100	–	–	*0.205*	100
9.	*0.1993*	100	0.2006	40	*0.201*	80	–	–
10.	0.1881	10	0.1869	50	–	–	–	–
11.	0.1516	5	0.1515	60	0.150	70	–	–
12.	0.1463	10	0.1473	30	–	–	–	–
13.	0.1425	20	–	–	0.142	70	0.142	2
14.	0.1364	5	–	–	0.136	50	0.135	2
15.	0.1307	20	0.1308	10	–	–	0.130	2
16.	0.1282	5	–	–	0.127	50	0.127	10
17.	0.1254	10	–	–	*0.125*	100	0.124	8
18.	0.1220	80	–	–	0.122	70	0.121	16
19.	0.1165	5	–	–	*0.118*	100	0.118	3
					0.116	70		

to molten 3S alloy (Al–1.25% Mn), giving encouraging results on a bench scale. Alternatively, the alloy composition can be adjusted to promote the formation of this phase on casting and homogenization, so that subsequent deformation and recrystallization will give a fine grain size.

5. Conclusions

1. Extraction of intermetallic phases in dilute Al–Mn alloys can be done electrolytically in 10% HCl solution in methanol and sufficient residue can be obtained in 2 h for identification by X-ray diffraction.

2. High-purity Al–Mn alloy (1.5% Mn) in chill-cast and controlled-cast conditions showed no intermetallic phase (except Al_6Mn phase in alloy K_b solidified at 550° C and poured from 740° C).

3. Chill casting of commercial purity 0.9% Mn alloy (N) also showed no intermetallic phase. Heating at 450° C for 5 h, however, produced the phase $Mn_{12}Si_7Al_5$.

4. Alloy N solidified under controlled conditions contained phases Al_6Mn, $Mn_{12}Si_7Al_5$, $AlMn_{8.4}$ for solidification temperatures $\geqslant 500°$ C (pouring temperature = 800° C), and $\geqslant 400°$ C (pouring temperature = 700° C). These phases, therefore, form more easily in alloys solidifed at higher temperatures and when pouring takes place from lower temperatures. The purity of the alloys is also important in the precipitation of phases.

5. The presence of a critical amount of 0.4% Fe facilitates the formation of $Mn_{12}Si_7Al_5$ phase and suppresses the formation of Al_6Mn phase in the chill-cast condition.

6. The phase $Mn_{12}Si_7Al_5$ is the unidentified phase α-Al (Mn, Fe)Si reported earlier and may be used as an inoculant to refine the grain size after recrystallization of Al–Mn alloys.

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