

MICROSTRUCTURAL CHARACTERISATION OF SOME Al-Mg-Li-Si ALLOYS

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ABSTRACT: Detailed microstructural characterisations of as-cast and homogenised Al-Mg-Li-Si alloys have been carried out using light microscopy (LM), scanning electron microscopy (SEM), quantitative x-ray energy dispersive spectrometry (X-EDS) and x-ray diffractometry (XRD). The compound Mg_2Si was identified in all the as-cast alloys investigated. The Al_2MgLi phase was present in those alloys with Mg content greater than 3 wt.%, whilst at lower Mg content (2 wt.%) the ternary compound $AlLiSi$ was formed. A binary iron-rich phase (AlFe-type) was also detected in all the as-cast alloys. After homogenisation the Al_2MgLi phase was completely dissolved, whilst the Mg_2Si and $AlLiSi$ compounds remained undissolved in the α -matrix. The reduced solubility of the Mg_2Si was related to presence of excess Mg over that required to form Mg_2Si . A reduction in Mg concentration and the lattice parameter of the Mg_2Si compound was observed after homogenisation, associated with Li incorporation into the lattice of Mg_2Si .

Keywords: Al-Li based alloys, as-cast, homogenisation, microstructure, phases.

1. INTRODUCTION

The majority of current generation Al-Li based alloys contain significant quantities of copper although alloys based on the Al-Li-Mg system have also been developed. The presence of copper is detrimental to the attainment of low density. The work reported here is part of a study to determine if copper free, conventionally processed wrought alloys could be produced based on the Al-Li-Mg-Si system. A series of Al-Li-Mg-Si alloys with a concentration of Li between 2 to 3.15 wt.%, and containing varying amounts of Mg and Si were produced using conventional melting/casting methods. The aim of this research is to study the microstructures of these alloys in the as-cast and homogenised conditions, with emphasis on the chemical characterisation of alloy phases.

2. EXPERIMENTAL

The compositions of the alloys investigated are shown in table 1. Alloys were prepared in a graphite crucible and under an inert argon atmosphere, using a medium frequency vacuum induction melting furnace. The molten alloys were poured into a cylindrical mild-steel mould. Alloys designated A, D and E were cast in the Department of Materials, Imperial College. The rest of the alloys were produced by Comalco, Research & Technology.

Samples taken from the as-cast materials underwent homogenisation trials to aid in selecting the best homogenisation conditions for each alloy. The final homogenisation parameters are shown in table 3.

Chemical etching of prepared sample-surfaces was carried out by immersion in Keller's reagent. Light microscopy was carried out using a Nikon Epiphot reflected light microscope. SEM was carried out in a JEOL-T200, operating at 25 kV. Chemical characterisation of alloy phases was carried out on bulk samples in a JEOL JSM35-CF SEM fitted with LINK 860 fully quantitative x-ray energy dispersive micro-analytical system, operating at 20 kV. X-ray diffraction was carried out using $CuK\alpha$ radiation.

Table 1: Chemical composition of the alloys investigated

Alloy Code	Actual Composition, wt. %					
	Li	Mg	Si	Fe	Others total*	Al
A	2.8	3.97	0.08	0.17	<0.05	Bal
A2	3.15	4.35	0.05	0.02	<0.03	"
B	3.05	3.67	0.10	0.03	<0.03	"
C	3.06	3.77	0.48	0.07	<0.03	"
D	2.8	4.01	1.12	0.17	<0.04	"
D2	3.10	4.27	1.06	0.03	<0.03	"
E	2.0	2.04	0.96	0.18	<0.07	"

*Cu + Zn + Ni + Mn

3. RESULTS AND DISCUSSION

3.1. AS-CAST ALLOYS

All the alloys revealed a cored dendritic microstructure in which the grain boundaries were delineated by a network of coarse second phase constituents [Fig. 1 (a) and (b)]. Microstructural investigation of the as-cast alloys revealed the presence of four distinct constituent phases. For convenience, they were designated as P1, P2, P3, and P4. Table 2 shows the X-EDS bulk analytical results performed on each of the phases observed in the as-cast alloys. Since Li is not detected using X-EDS, those phases which give rise to less than a 100 % in their total composition were assumed to contain Li as the complement element to add to 100 %. According to these results and XRD analysis carried out on the as-cast alloys, the P1 phase was identified as Al_2MgLi , the P2 phase as Mg_2Si , the P3 probably corresponds to the binary Al_3Fe phase and the P4 phase as $AlLiSi$ (Table 3). The total volume fractions of the constituent particles, measured using the point-count method, together with the incipient melting point of the as-cast alloys are also summarised in table 3. These results indicate that a large portion of the solute content of the alloys is preferentially forming intermetallic compounds rather than dissolving in the α -matrix. A significant contribution to the volume fraction of the alloy is likely to come from the content of iron present in the alloy as impurity, especially in alloys A, D and E which have the highest concentration of iron (Table 1).

Table 2: Elemental compositions of the phases present in as-cast and homogenised alloys as determined by X-EDS in the SEM (representative alloys).

Average Composition in wt. %											
Alloy Code	Phase Type	As-Cast					Homogenised				
		Al	Mg	Si	Fe	Li (by difference)	Al	Mg	Si	Fe	Li (by difference)
A2	α -Matrix	96.4	3.6	NEG.*	-	-	95.8	4.0	NEG.*	-	-
	P1	80.3	15.7	-	-	4	-	-	-	-	
	P2	≈ 0.8	62.7	36.5	-	-	≈ 1.1	49.1	49.8	-	
	P3	68.1	-	-	31.9	-	62.9	NEG*	-	37.1	
B	α -Matrix	97.1	2.9	NEG.*	-	-	96.5	3.5	NEG.*	-	-
	P1	82.0	13.9	-	-	4.1	-	-	-	-	
	P2	≈ 0.7	63.2	36.3	-	-	≈ 1.0	49.5	49.5	-	
	P3	62.6	-	-	37.4	-	62.2	NEG*	-	37.5	
C	α -Matrix	97.0	3.0	NEG.*	-	-	96.5	3.5	NEG.*	-	-
	P1	82.1	13.5	-	-	4.4	-	-	-	-	
	P2	NEG.*	63.3	36.7	-	-	≈ 0.5	49.7	49.8	-	
	P3	60.0	-	-	40.0	-	66.3	NEG*	-	33.7	
D2	α -Matrix	97.3	2.7	NEG.*	-	-	96.6	3.4	NEG.*	-	-
	P1	85.1	11.5	-	-	3.4	-	-	-	-	
	P2	NEG.*	63.2	36.8	-	-	NEG.*	50.2	49.8	-	
	P3	68.1	-	-	31.9	-	68.6	NEG*	-	31.4	
E	α -Matrix	99.1	≈ 0.9	NEG.*	-	-	98.8	≈ 1.2	NEG.*	-	-
	P4	59.9	≈ 0.6	36.5	-	3	53.2	≈ 1.0	42.8	-	3
	P2	74.5	15.6	9.9	-	-	75.5	13.0	11.5	-	-
	P3	89.9	≈ 1.0	≈ 0.9	8.2	-	79.2	≈ 0.8	≈ 0.8	19.2	-

*NEG.: Negligible

The P1 phase (Al_2MgLi) was observed in all the as-cast alloys, except alloy E, which had the lowest Mg content (2 wt.%). This phase tarnished or oxidised upon extended exposure to the atmosphere, which is an indication of the presence of reactive elements, such as Li, in that phase. The P1 phase was predominant in alloys with low concentration of Si (alloys A, A2 and B) [Fig. 1 (c)], but as the amount of Si was increased (alloys C, D and D2) the P2 phase (Mg_2Si) became predominant in the microstructure. In alloy E, P4 ($AlLiSi$) was the predominant phase in the microstructure [Fig. 1 (b)]. The Al_2MgLi compound is typical of the Al-Li-Mg alloy system and had been previously identified in such alloys in the as-cast condition [6].

The P2 phase (Mg_2Si) is the expected constituent in all the investigated alloys. Drits *et al.* [1] found that the addition of as little as 0.05 wt.% Si to the ternary (Al + 5 wt.% Mg + Li) alloys is sufficient to cause Mg_2Si

to precipitate. This Mg_2Si compound is formed by combining Mg and Si in the weight ratio of 1.73: 1. The elemental composition of the P2 phase determined by bulk X-EDS analysis gave a Mg:Si ratio very close to that of Mg_2Si (Table 2). In addition, XRD analyses unequivocally confirmed the P2 phase as the Mg_2Si compound, as can be seen in table 4 for a selected alloy D2. However, the P2 phase was observed to be brittle and cracked on casting [Fig. 1 (d)]. Normally in cast Al-Mg-Si alloys, the Mg_2Si phase is free from cracks [7]. Therefore, Mg_2Si seems to be modified in some way due to the presence of Li. However, unnormalised analysis always gave a total composition of nearly 100%, indicating that Li is not present in the P2 phase.

The iron-rich particles (P3 phase) were present in all the alloys examined, distributed irregularly mainly at grain boundaries as shown in fig. 1(c). Since iron has a limited solid solubility in Al, virtually all the wt.% Fe in the investigated alloys is expected to form intermetallic compounds. Bulk X-EDS results suggest that the P3 phase is based on Al_3Fe (Table 2), which is normally present at low ($\sim 1^\circ C s^{-1}$) or intermediate cooling rates ($\sim 3^\circ C s^{-1}$) in DC-casting. The metastable Al_6Fe or Al_3Fe are usually found under conditions of high solidification rate

($\sim 10^\circ C s^{-1}$), [8], a condition which is not achieved in mould-cast alloys. Iron-rich phases can tie up some solute for their formation. The binary Al_3Fe -type phases, for example, may dissolve as much as 3 wt.% Si [3].

The $AlLiSi$ phase was only observed in alloy E [Fig. 1(b)], where it was seen as particles mainly delineating the grain boundaries. They were of irregular shape and were observed in greater amount than the P2. X-EDS analysis showed this compound to contain some Mg (Table 2). Similar results were obtained for the homogenised alloys. Since the size of these particles was relatively small (3-5 μm in width), the presence of Mg was probably due to matrix contribution to the analysis. No significant difference in the lattice parameter was found for P4 phase in comparison with the standard value for the $AlLiSi$ phase. However, Huang *et al.* [2] have reported the presence of some Mg dissolved in $AlLiSi$ precipitates in alloy 6061-0.72 wt.% Li.

The α -matrix was also evaluated by X-EDS analysis (Table 2). The total elemental composition always approaches 100 %, so analyses were normalised without considering the presence of Li in the α -matrix. Mg was always

Table 3: Summary of Results

Alloy Code	AS-CAST			HOMOGENISED		
	2 nd phase chemistry	Vol. % ⁽¹⁾	M.P. ⁽²⁾ (°C)	Homog. ⁽³⁾	Undissolved ⁽⁴⁾	Vol. % ⁽¹⁾
A	$Al_2MgLi + Mg_2Si + Al_3Fe$	4	548.3	24 h at 490 °C + 48 h at 510 °C	$Mg_2Si^* + Al_3Fe$	3
A2	"	9	530.4		"	2
B	"	10	545.2	24 h at 510 °C + 48 h at 530 °C	"	1.5
C	"	10	550.6		"	3.5
D	"	7	564.1	36 h at 540 °C	"	4.5
D2	"	10	554.3		"	5
E	$Mg_2Si + AlLiSi + Al_3Fe$	11	585.5	24 h at 560 °C	$Mg_2Si + AlLiSi + Al_3Fe$	5

*Li may be incorporated into this compound: $(Mg,Li)_2Si$.

(1) Total volume % 2nd phases. (2) Incipient melting point. (3) Homogenisation parameters. (4) Undissolved phases.

Table 4: Selected X-ray diffraction data for the P2 phase in the as-cast and homogenised conditions. Data from the JCPDS [10] files for the Mg_2Si phase is included for comparison.

X-ray diffraction data from present work				Data from the JCPDS file for Mg_2Si : F.C.C		
AS-CAST Alloy D2		HOMOGENISED Alloy D2		a = 0.6351 nm		
d-spacings (nm)	I* (%)	d-spacings (nm)	I* (%)	d-spacings (nm)	I* (%)	(hkl)
0.3667	40.5	0.3644	4.8	0.3668	41	111
0.2247	60.8	0.2235	8.3	0.2246	100	220
0.1914	25.5	0.1903	1.8	0.1915	15	311
-	-	-	-	0.1834	2	222
0.1589	3.4	0.1579	0.8	0.1588	13	400
0.1456	10.5	-	-	0.1457	6	331
0.1297	11.1	0.1290	2.1	0.1296	21	422
0.1222	13.7	-	-	0.1222	4	511
0.1123	5.5	-	-	0.1123	4	440
0.1074	1.5	-	-	0.1074	2	531

*Relative Intensity

present in solution in the α -matrix and the content of Si in solution was negligible. A small content of Si ($\ll 0.5$ wt.%), not detected by X-EDS analysis, could be dissolved in the α -matrix, but these results suggest that most of the Si combines preferentially with Mg to yield Mg_2Si particles, and also with Al and Li in the case of alloy E, to form $AlLiSi$ compounds. A slight increase (0.17-0.57 %) in the parameter 'a' calculated for the α -matrix compared to that reported for aluminium (0.4050 nm) was observed. This is associated with the incorporation of Mg in solution, which has the effect of expanding the Al lattice and also reduces the solubility of Li in the solid solution [4].

It seems that Si and Li in these investigated alloys mostly precipitated as intermetallic compounds during casting. Some Mg dissolved in the α -matrix, while the rest precipitated as Mg_2Si or Al_2MgLi . At low Mg content, as in the case of alloy E, the formation of the $AlLiSi$ compound is facilitated by suppressing the precipitation of Al_2MgLi .

3.2. HOMOGENISED ALLOYS

The results of the bulk X-EDS analyses performed on each of the phases which remained undissolved after homogenisation are shown in table 2. Table 3 shows the undissolved phase chemistry and the total volume fraction of phases measured after the final homogenisation treatment. The P1 phase (Al_2MgLi) was the only constituent which completely dissolved after homogenisation [Fig. 1 (e)]. The P2 phase proved to be insoluble in these experimental alloys [Fig. 1 (e)], except in alloy E where Mg_2Si was almost dissolved. The P4 phase ($AlLiSi$) was significantly spheroidised during the homogenisation treatment but remained undissolved in the α -matrix which may indicate that the solute content of alloy E exceeds the combined solid solubility of Mg, Li and Si in Al [Fig. 1 (f)]. There was an enrichment in the concentration of Mg in the α -matrix after homogenisation (Table 2), which is associated with the dissolution of the P1 phase and partial dissolution of the P2 phase in alloy E. The homogenisation treatment did not appreciably affect the morphology of the P3 phase and the phase remained essentially Al_3Fe -type (Table 2). This is an indication that the P3 phase is in an equilibrium condition.

It is well known that Mg_2Si has appreciable solubility in Al. However, its solubility falls off very sharply in the presence of an excess of Mg over that required to form Mg_2Si . The maximum equilibrium solid solubility of the Mg_2Si compound at 427 °C, for instance, is 0.64 wt.% without excess Mg. However, this solubility is considerably reduced to 0.03 wt.% in the presence of an excess of 2 wt.% Mg [9]. If it is assumed that all Si present in the investigated alloys converted to Mg_2Si , the excess of Mg in alloy E would be 0.4 wt.% which corresponds to a solid solubility in Al greater than 0.32 wt.% at 427 °C [9]. This may explain the partial dissolution of the Mg_2Si compound in this alloy. Meanwhile, in the rest of the alloys, the amount of Mg in excess of that required to form Mg_2Si would be in the range 4 wt.% (Alloy A2) to 2 wt.% (Alloy D), which corresponds to a very limited solubility in Al (<0.03 wt.%) [9]. This solid solubility limit would make Mg_2Si particles virtually insoluble in these investigated alloys.

The P2 phase was found to be compositionally affected by prolonged homogenisation treatment. In general, the content of Si had increased, accompanied by Mg depletion which gave a Mg:Si ratio of 1 or close to 1. However, the unetched and etched appearances of these P2 particles were found to be essentially identical to those of the as-cast alloys. Bulk X-EDS analyses were repeated for the homogenised alloys, but this time two samples of the same alloy, one in the as-cast condition and the other after homogenisation, were placed in the same holder and analysed side by side under the same conditions. The Mg:Si ratio for the as-cast alloy always showed a value around 1.72, whilst the value for the homogenised alloy approximated to 1, indicating that the difference in composition was due neither an error in sample preparation nor to some instrument variation. The total elemental composition was around 100% suggesting that Li may not be present. However, this is not conclusive evidence that Li is not dissolved in the Mg_2Si since this method of estimating Li by difference (100 - total wt.%) is rather qualitative. The presence of a small amount of Li in solution, such as 1 wt.%, or even 2 wt.%, would be very difficult to estimate by difference since the accuracy of an X-EDS analysis as determined by correction is ± 2 wt.% typically [5]. Therefore, this method may only be applied for a phase with a high concentration of Li, such as Al_2MgLi .

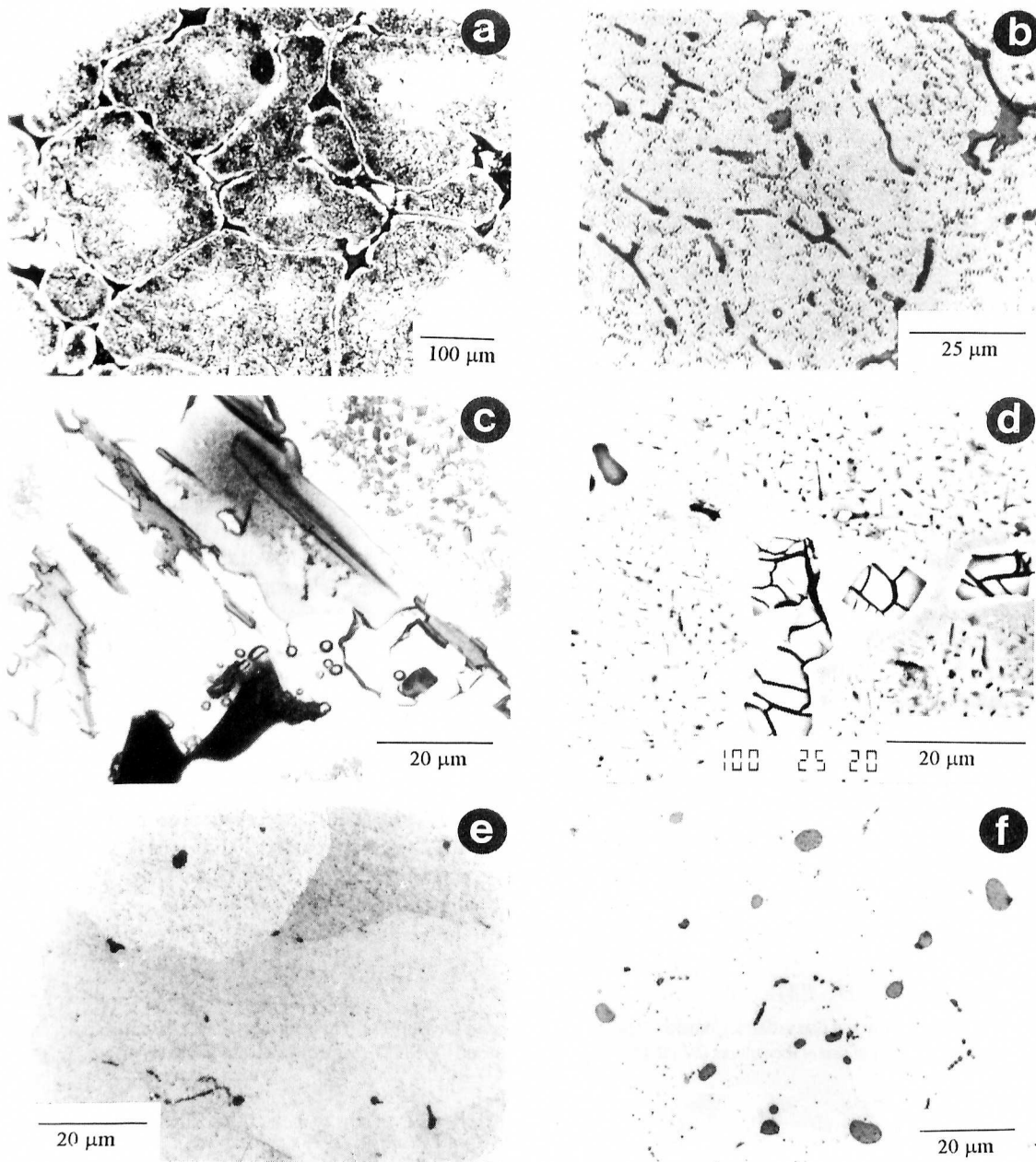


Figure 1: Typical microstructure of the alloys investigated. (Etched: Keller's reagent)

- (a) As-cast alloy B. The grey particles are the Al₂MgLi phase and the dark ones are the Mg₂Si phase. LM.
- (b) As-cast alloy E. The dark particles are the Mg₂Si phase and the grey ones are the AlLiSi phase. LM.
- (c) As-cast alloy B showing large masses of the Al₂MgLi phase (Light), needle-like Al₃Fe particles and a coarse Mg₂Si particle (dark). Precipitate free zones are observed adjacent to these particles. LM
- (d) Backscattered electron image of as-cast alloy D2 showing details of the Mg₂Si phase. Slightly etched.
- (e) Alloy B Homogenised at 510 °C for 24 h + 530 °C for 48 h. The dark particles are undissolved Mg₂Si. LM.
- (f) Alloy E homogenised for 24 h at 560 °C. The rounded grey particles are AlLiSi, the small dark particles are Mg₂Si and the thin blade-like particles (Light grey) are Al₃Fe. LM.

XRD work on these homogenised alloys showed diffraction lines which were attributed to the Mg_2Si phase as shown in table 4 for alloy D2. However, calculation of the lattice parameter 'a' from the d-spacings shows a significant difference from the standard 'a' value for the Mg_2Si phase. The lattice parameter 'a' calculated was in the range of 0.6308 - 0.6316 nm, being the maximum error in this calculation ± 0.0007 nm. This represents a contraction in the Mg_2Si lattice of about 0.55 - 0.68 % from a value for Mg_2Si of 'a' = 0.6351 nm. These results suggest that Li may have been incorporated into the lattice of Mg_2Si , substituting for some of the Mg atoms. This is consistent with the reduction in Mg concentration in the compound as well as the contraction of the Mg_2Si lattice. Li atoms are approximately 5 % smaller in size than Mg atoms and hence can reduce the lattice parameter of this compound. The magnitude of this change depends on the number of lattice positions these Li atoms occupy. The resulting compound may be considered to have an empirical formula as $(Mg, Li)_2Si$. However, further work is necessary to confirm the presence of Li in the Mg_2Si compound. This could be done by using Secondary Ion Mass Spectroscopy or by extracting the particles and using chemical analyses. No prior reference to incorporation of Li in this phase has been found in the literature.

4. SUMMARY

The Mg_2Si phase was identified in all the as-cast alloys and was characterised by the presence of cracks on its surface. An iron-rich phase was also detected in all the alloys studied and it is thought to be the equilibrium phase Al_3Fe . The ternary compound Al_2MgLi was confirmed to be present in those alloys with Mg content greater than 3 wt.%; that is, in all the as-cast alloys apart from alloy E. The $AlLiSi$ phase was identified only in alloy E, where it was present as the major second phase constituent. Homogenisation treatments, up to 72 h for some alloys, at relatively high temperature were used to completely dissolve the Al_2MgLi compound. However, the Mg_2Si phase only partially dissolved in alloy E and in the rest of the alloys it remained undissolved due to the presence of Mg in excess of that required to form Mg_2Si . The $AlLiSi$ phase also remained undissolved in the α -matrix but significantly spheroidised during the homogenisation treatment. The morphology and composition of the coarse Fe-rich phase remained practically unchanged after homogenisation treatment. It was difficult to establish the right balance between Mg, Li and Si to avoid, on the one hand, undissolved Mg_2Si and, on the other hand, the formation of the ternary compound $AlLiSi$. Lattice parameter measurements of the Mg_2Si in the homogenised condition showed a reduction in the value 'a' in the range 0.55 - 0.68%, smaller than the standard value reported for the Mg_2Si compound (0.6351 nm), which is an indication of Li incorporation into Mg_2Si . The resulting compound may be identified as $(Mg, Li)_2Si$. The incorporation of Li in the Mg_2Si phase is not reported in the literature.

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