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New Phases in the Mg-Al-Sr System

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Abstract. This work presents experimental investigation of 14 different alloys with differential scanning calorimetery (DSC), scanning electron microscopy/energy dispersive spectrometer (SEM/EDS) analysis, quantitative electron probe micro-analysis (EPMA) and X-ray diffraction (XRD) techniques to identify the phases in the Mg-Al-Sr system and to determine their compositions. DSC has permitted real time measurement of the phase changes involved in these systems. The temperature ranges for the phase transformations and enthalpy of melting and enthalpy of formation of the compounds are reported. Comparison between these results and the thermodynamic findings has been discussed. The microstructure of the Mg-Al-Sr-based alloys is primarily dominated by (Mg) and (Al_4Sr). The plate-like structure has been identified as Al_4Sr. A new ternary intermetallic with chemical composition of 69.9 ± 1.5 at.% magnesium, 19.3 ± 2.0 at.% aluminum and 8.7 ± 0.6 at.% strontium has been identified in three different alloys. This phase was characterized as a large precipitate. Three ternary solid solutions have been observed. The solubility ranges of Al in $Mg_{38}Sr_9$ and $Mg_{17}Sr_2$ are 12.5 and 8.5 at.%, respectively, whereas the solubility of Mg in Al_4Sr compound is found to be 23 at.% in the investigated samples. Further, Mg was found to dissolve 11.4 at.% Al at room temperature.

Introduction

Magnesium-based alloys are particularly attractive for transportation applications for weight reduction and higher fuel efficiency [1]. However, magnesium alloys face a challenge at higher temperature application because of their restricted creep properties. In recent years, Mg-Al-Sr alloy system has emerged as potential for heat-resistant Mg-alloys [2].

Within the ternary Mg-Al-Sr system, there is a huge amount of possibilities to select alloy compositions. The phase relations and phase stability under given conditions can be better understood using equilibrium diagrams. To date, little effort has been made to construct the phase relationships of Mg-Al-Sr system. The published experimental works on the phase equilibria of Mg-Al-Sr system are self-contradictory. The experimental work on the phase equilibria of the Mg-Al-Sr system primarily originated by Makhmudov and coworkers [3-5]. However, inconsistency was noticed between their works, which were published from 1980 to 1982. The 400°C isothermal section shows a triangulation involving (Mg), $Mg_{17}Sr_2$ and the γ phase. But it seems unlikely, as the thermodynamic stabilities of these compounds are low as compared to Al_4Sr and Al_2Sr at this temperature. The solubility limits for the binary compounds determined by Makhmudov *et al.* [5] do not agree with the 400°C isothermal section given by Makhmudov *et al.* [4] in 1981. Baril *et al.* [6] recently investigated four samples of Mg-Al-Sr system experimentally in the Mg-rich region and tentatively designated a ternary phase as $Al_3Mg_{13}Sr$. The stoichiometry is not yet clearly identified and the chemical composition is not compatible with the ternary compound Al_6MgSr_{10} reported by Makhmudov *et al.* [4]. Chartrand and Pelton [7] critically reviewed and calculated the thermodynamic properties of the Mg-Al-Sr ternary and related binary sub-systems. No ternary terms were added to the thermodynamic model due to the uncertainties related to the existence, stability, homogeneity range and the melting and decomposition

temperature of the ternary compounds. The calculated phase diagram exhibited substantial disagreement with the experimental data. The extended solubilities between solid phases were not considered in the thermodynamics assessment. A considerable discrepancy among the published results and very few experimental data demands new investigation for this system and hence a detailed investigation by DSC, XRD, SEM/EDS and EPMA analysis was carried out.

Experimental

Fourteen samples as shown in Table 1 were chosen by critical assessment of the experimental and thermodynamic datasets that are available in the literature. Special attention was focused on the Mg-rich corner because of the interest in the Mg alloys. Since Al_4Sr gives the thermodynamic stability to Mg-Al-Sr-based alloys, samples containing this phase were also chosen. Mg-Al-Sr ternary diagram with the investigated compositions in weight percentage are given in Fig. 1. Mg-Al-Sr alloys were prepared by melting stoichiometric amounts of the constituent elements in an induction-melting furnace under argon with 1%SF6 to protect the melt from oxidation. In preparing the alloys, Mg of 99.8 wt.%, Al of 99.9 wt.% and Sr of 99 wt.% were used. The actual chemical composition was measured quantitatively by ICP atomic emission spectrometry. The loss in total mass was below 2% for most of the samples.

Thermal investigation of the systems was performed using a Setaram Setsys DSC-1200 instrument. The DSC measurements were carried out with heating and cooling rates of 5°C/min from 25°C to 700°C. Slower heating rates were tried and were not found to reveal any other thermal arrests. The reproducibility of every measurement was confirmed by collecting the data during three heating and cooling cycles. More details on the interpretation of the DSC experiments were reported in our previous works [8]. Phase identification was carried out by X-ray diffraction (XRD) with a Philips diffractometer (Cu$K\alpha$ radiation) equipped with a PW 1050/25 focusing gonimometer with steps 0.02° of 2θ diffraction angle and 1s exposure time. All the samples were investigated in the powder form in the as-cast condition at room temperature. PowderCell 2.3 [9] was used to calculate the diffraction patterns for different phases and to identify their peaks. SEM/EDS and EPMA were employed to examine the phase compositions for 14 alloys. Chemical compositions of the phase were measured using a CAMECA SX51 EPMA by which the analyses were carried out on three locations for each phase and average was used for the present analysis. Heat treatment does not suggest any instability in the phases in this system after the samples were exposed to heating and cooling from 25°C to 700°C.

Results & Discussion

DSC spectra of sample 1(3.3 wt.% Sr, 87.3 wt.% Mg and 9.4 wt.% Al) with heating and cooling runs are shown in Fig. 2(a). The onset temperature, peak temperature, melting temperature and the melting enthalpy were registered. During heating of this sample, two thermal arrests, corresponding to the invariant reaction at 527°C and the univariant reaction at 605°C are observed. For this sample, the liquidus temperature is observed during cooling which is 609°C. The experimental results were compared with the thermodynamic calculations to confirm the transformation temperature along with the associated reaction. For this purpose, the vertical section and phase assemblage diagrams as shown in Fig. 2(b) and 2 (c) were calculated using FactSage [18] and the database developed by Chartrand and Pelton [11]. DSC signals from the cooling curve were also indicated on Fig. 2(b). It can be observed that the liquidus temperature matched well with the experimental values; however, the transformation temperature predicted by the thermodynamic modeling at 222°C was not observed in the DSC signals. The proportion of each phase at any temperature of interest can easily be interpreted from Fig. 2(c). For instance, at 25°C, 100 g of the overall material consists of 7.5g of Al_4Sr, 7.5g of γ and 85g of (Mg). Moreover, Fig. 2(c) shows that while cooling this sample from the melt, (Mg) solidifies first, followed by Al_4Sr and then γ.

Table 1 Samples in different phase fields

Group	Sample Nos.	Predicted phases [7]
#1	1, 2,3,4,5,6,7	(Mg)+Al_4Sr+γ
#2	8,9	(Mg)+Al_2Sr+Al_4Sr
#3	10,11	Al_4Sr+γ+β
#4	12	(Al)+Al_4Sr+β
#5	13,14	(Mg)+Al_2Sr+$Mg_{17}Sr_2$

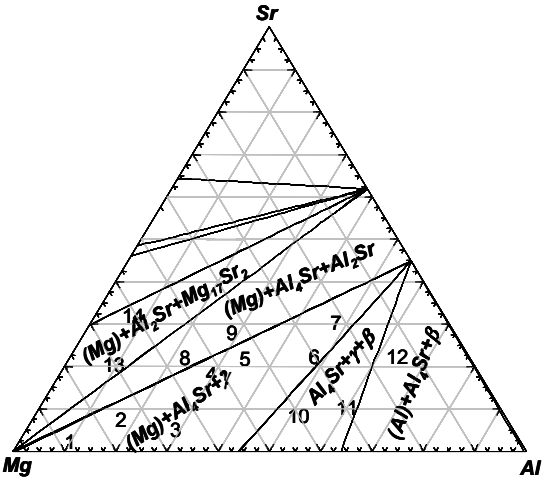
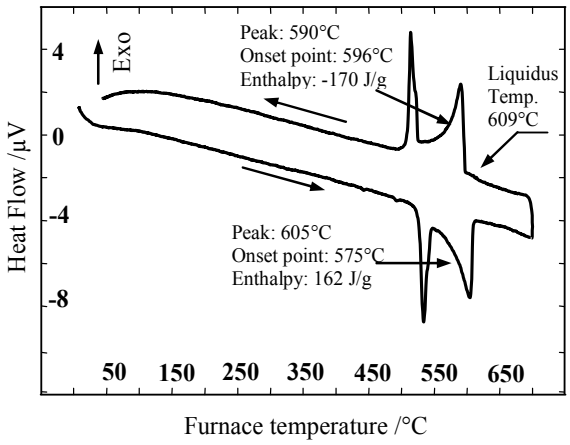


Fig. 1. Mg-Al-Sr ternary isothermal section at 25°C showing investigated compositions in wt.%.

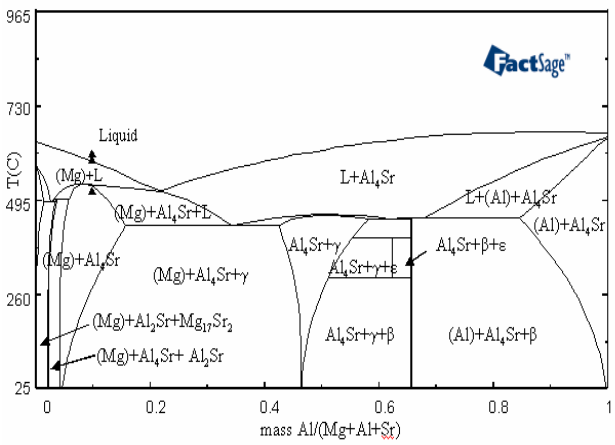
Figures 2 (d) to 2 (g) show the XRD pattern, SEM image, EDS analysis at spot A and EPMA analysis of sample 1, respectively. SEM/EDS analysis indicates that: (i) the matrix region (A) of this composition contained Mg and small amount of Al; (ii) the grain boundary region (B) contained Mg as well as Al and Sr. It can be seen from Figs. 2(d) and 2(g) that two phases (Mg) and (Al_4Sr) were identified positively in the XRD pattern and by EPMA analysis. Since the major diffraction peaks of (Mg) and $Mg_{17}Al_{12}$ (γ) at 36.601° and 36.191° overlap in addition to the very small volume fraction of γ that is present in this alloy, it was very difficult to identify γ positively in XRD pattern. Table-2 summarizes the phases at room temperature identified by the EPMA and XRD analyses. Al_4Sr phase formed during eutectic solidification process is located in the grain boundary region of the Mg and appears to be lamellae. Large ternary solubilities were observed in this alloy. Quantitative EPMA analysis as shown in Fig. 2(g) shows that Mg dissolves 4.8 at.% Al, whilst the Al_4Sr dissolves 23.2 at.% Mg. A very good agreement between the SEM/EDS, XRD and EPMA analysis was observed in terms of phase identification.

Two types of secondary phases were observed in sample 2 (8.7/76.1/15.2 Sr/Mg/Al wt.%) as shown in Fig. 3. The large bright precipitate is identified with chemical composition of 71.4 at.% Mg, 9.3 at.% Sr and 19.3 at.% Al by EPMA analysis. This phase composition is not consistent with either Baril *et al.* [10] or Makhmudov and coworker's [4] reported ternary compounds. However, the stoichiometry of these phases was not clearly identified. Sample 3 was reported as a ternary eutectic by Makhmudov *et al.* [5]. DSC spectra and the thermodynamic calculation show that this sample is not eutectic [8]. The thermodynamic calculation could not also accurately predict all the transformations that have been measured by the DSC. A new phase tentatively designated as τ_1 was identified by XRD analysis in samples 6 and 7 [8]. It may be a new ternary compound or a ternary solid solution. However, EPMA analysis concluded that the tentative phase τ_1 is substitutional solid solution of Al_4Sr that dissolves 4.93 at.% Mg in this sample.

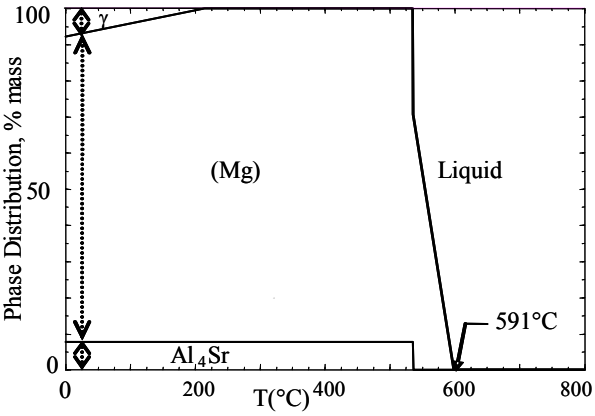
Two samples, as shown in Fig. 1, were studied in (Mg)+Al_4Sr+Al_2Sr phase field. It is noteworthy that in our XRD analysis as reported in Table-2, an existence of a new phase τ_2 has been suggested as there were some distinct peaks that are not associated with any of the known phases in the Mg-Al-Sr system appeared in the XRD pattern of samples 8 and 9 [8]. In the present EPMA analysis for sample 8, the light grey precipitate is identified with chemical composition of 69.9 at.% Mg, 8.7 at.% Sr and 21.3 at.% Al while in sample 9, this phase was identified with chemical composition of 70.6 at.% Mg, 9.2 at.% Sr and 20.2 at.% Al.. This new ternary intermetallic has been named τ_2. It is obvious from the above discussions that one ternary intermetallic formed in the studied alloys. This will definitely alter the current understanding of the Mg-Al-Sr phase diagram.



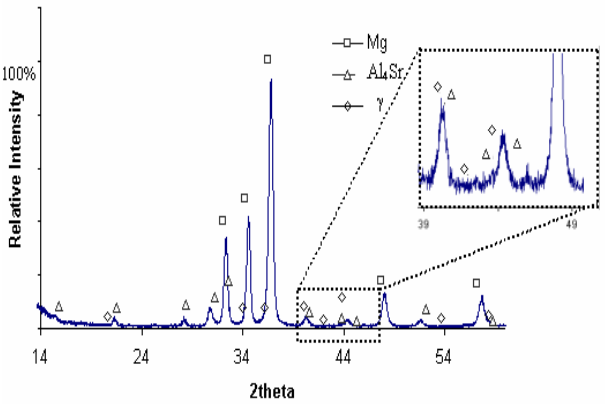
2(a)



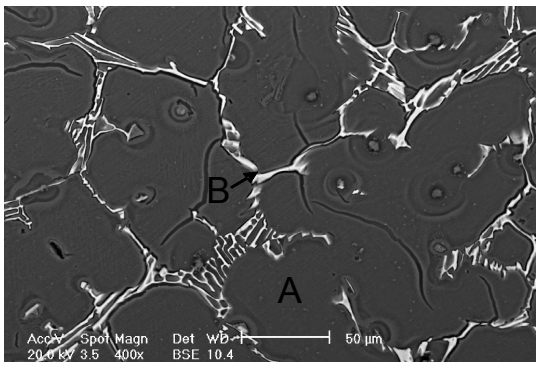
2(b)



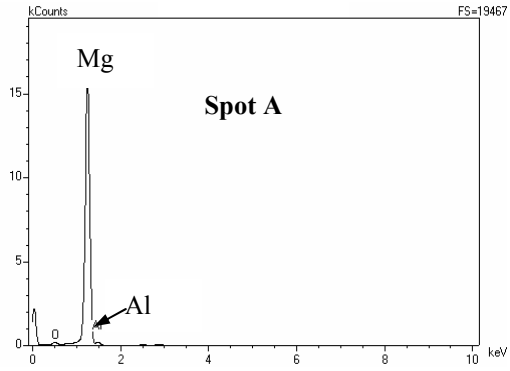
2(c)



2(d)



2(e)



2(f)

Location	at.% Mg	at.% Al	at.% Sr
A	95.18	4.81	0.01
B	23.23	58.23	18.54

2(g)

Fig. 2: (a) DSC spectra; (b) Calculated vertical section at constant 3.32 wt.% Sr; (c) Phase assemblage diagram; (d) XRD pattern; (e) SEM image; (f) EDS spectrum and (g) EPMA analysis.

Two alloys in Al_4Sr+γ+β phase field, as shown in Fig. 1, have been investigated. The DSC spectra showed that the invariant reaction for samples 10 and 11 occurred at similar temperatures; 459°C, and 453°C respectively [8]. The enthalpy of invariant reaction for samples 10 and 11 were registered as 316.67 J/g and 390 J/g respectively. XRD analysis of sample 11 as reported in Table-2 identified three phases: (Al_4Sr), γ and β while EPMA analysis shows the existence of two phases (Al_4Sr) and β which is supported by SEM/EDS analysis.

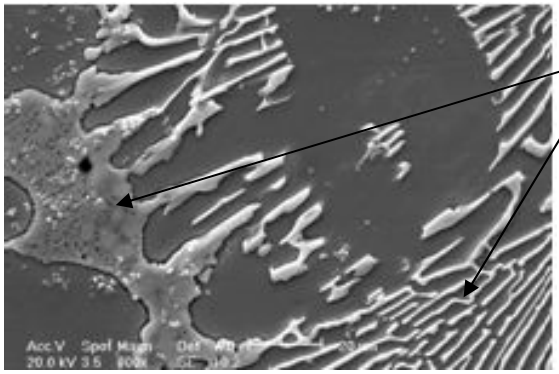


Fig. 3: SEM image of sample 2.

Table 2: Composition and room temperature phase content of the investigated samples

Composition				Identified phases		Solubilities [at.%] (EPMA)
No.	[wt.%]					
	Sr	Mg	Al	EPMA and SEM/EDX	XRD	
1	3.3	87.3	9.4	(Mg) and Al_4Sr	(Mg) and (Al_4Sr)	• 4.8 at.% Al in Mg • 23.2 at.% Mg in Al_4Sr
2	8.7	76.1	15.2	(Mg) andAl_4Sr	(Mg) and (Al_4Sr)	• 7.4 at.% Al in Mg
3	6.9	65.5	27.6	(Mg), Al_4Sr and γ	(Mg), (Al_4Sr) and γ	• 11.4 at.% Al in Mg • 7.9 at.% Mg in Al_4Sr
4	22.5	48.6	28.9	(Mg), Al_4Sr and γ	(Mg), (Al_4Sr) and γ	• 10.8 at.% Mg in Al_4Sr
5	22.5	43.8	33.7	(Mg), Al_4Sr and γ	(Mg), (Al_4Sr) and γ	• 10. 6 at.% Al in Mg • 9.2 at.% Mg in Al_4Sr
6	24.0	30.0	46.0	Al_4Sr and γ	(Al_4Sr), γ and τ_1	• 4.9 at.% Mg in Al_4Sr
7	32.0	22.0	46.0	Al_4Sr and γ	(Al_4Sr), γ and τ_1	• 5.1 at.% Mg in Al_4Sr
8	22.8	54.4	22.8	(Mg) and Al_4Sr	(Mg), (Al_4Sr) and τ_2	• 11.2 at.% Al in Mg • 14.1 at.% Mg in Al_4Sr
9	27.8	42.9	29.8	(Mg) and Al_4Sr	(Mg), (Al_4Sr) and τ_2	• 11 at.% Al in Mg • 12.5 at.% Mg in Al_4Sr
10	9.5	40.0	50.5	Al_4Sr and β	(Al_4Sr), γ and β	• 4 at.% Mg in Al_4Sr
11	11.0	30.0	59.0	Al_4Sr and β	(Al_4Sr), γ and β	• 2.1 at.% Mg in Al_4Sr
12	23	15	62	Al_4Sr and β	(Al), (Al_4Sr) and β	• 1.7 at.% Mg in Al_4Sr
13	19.9	72	8.1	(Mg) and $Mg_{17}Sr_2$	(Mg), Al_2Sr and $Mg_{17}Sr_2$	• 5 at.% Al in Mg • 8.5 at.% Al in $Mg_{17}Sr_2$
14	32.7	60.5	6.8	$Mg_{17}Sr_2$ and $Mg_{38}Sr_9$	(Mg), τ_4 and $Mg_{17}Sr_2$	• 6.43 at.% Al in $Mg_{17}Sr_2$ • 12.51 at.% Al in $Mg_{38}Sr_9$

The liquidus temperature and the number of transformations of sample 12 did not show good agreement with the thermodynamic predictions. (Al_4Sr) and β were identified positively by EPMA and XRD results. Quantitative EPMA analysis shows that β phase does not show any solubility of Sr.

In composition 13(19.90/72/8.1 Sr/Mg/Al wt.%) XRD and EPMA analyses, identified both (Mg) and ($Mg_{17}Sr_2$), as reported in Table-2; however only XRD showed the existence of Al_2Sr. Sample 14(32.74/60.55/ 6.71Sr/Mg/Al wt.%) has been identified positively with only two phases by XRD: (Mg) and ($Mg_{17}Sr_2$); whereas EPMA analysis identified $Mg_{17}Sr_2$ and $Mg_{38}Sr_9$ dissolving 12.5 at.% Al. This suggests that the extent of the $Mg_{38}Sr_9$ phase field in ternary Mg-Al-Sr system is predicted narrower in the calculated phase diagrams reported in the reference [7] and thus the system needs to be re-optimized. In sample 14, the DSC signal shows only one peak; hence this composition is at or very close to the ternary eutectic point. From the phase assemblage diagram, although all the three phases did not precipitate at the same temperature, this diagram shows that sample 14 is indeed close to a eutectic composition and thus matches with the DSC result [8].

Conclusions

A comprehensive study using DSC, XRD, SEM/EDS and EPMA analysis on the ternary equilibria in the Mg-Al-Sr system was conducted. (Al_4Sr) and (Mg) were found to be the dominating phases in the investigated alloys. In the present investigation, a new ternary intermetallic and three ternary solid solutions have been reported. Al_4Sr dissolved 23 at.% Mg which is very close to Makhmudov and coworker's [3-5] observation. A considerable discrepancy in the solid phase transformation temperature was observed which suggests that the Mg-Al-Sr system should be remodeled in light of the new experimental findings.

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