

Thermal analytical investigations of ternary Mg-Al-Sr system by DSC

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The phase diagram of Mg-Al-Sr system was investigated experimentally by differential scanning calorimeter (DSC). The experimental work focused on the critical regions after reviewing the phase diagrams developed by thermodynamics and experimental results. DSC results provided information on the following thermophysical properties: onset temperature, melting enthalpy and liquidus temperatures. Invariant and univariant transformations are reported. The difficulties in performing the thermal analysis on Mg alloys are also presented. These results along with x-ray diffraction analysis will be used later to construct the entire phase diagram of Mg-Al-Sr system.

1. INTRODUCTION

Over the last few years, higher demands have been made on cast parts for automotive applications. Weight reduction of transportation vehicles is also an important issue for carmakers. The use of Mg alloys becomes significant since it offers an excellent combination of light-weight and good engineering properties [1]. The current use of magnesium alloys in more critical components such as transmission and engine parts is limited because of their restricted creep properties. In contrast to steels and many Al-alloys, the conventional Mg alloys have a relatively low resistance to creep [2].

Like pure magnesium, the Mg-Al alloys also suffer from poor creep resistance. The compound $Mg_{17}Al_{12}$ is incoherent with the α -Mg matrix, susceptible to aging and has poor metallurgical stability as temperature is increased. The precipitation of this low melting point second phase from supersaturated α -Mg contributes to grain boundary migration and creep deformation [3]. Thus the presence of this phase should be avoided in higher temperature applications.

Magnesium faces a challenge in meeting the performance of the components which operate at elevated temperature. Developments in recent years have led to the discovery of certain alloys containing rare-earth elements and calcium. However, many of these suffer from inferior die-

castability (Mg-Al-Ca) or have disadvantages in terms of marginal performance improvements (AS, Mg-Al-Ca-RE) and high material cost (AE, Mg-Al-Ca-RE) [4].

The most promising alloy system of recent development is based on Mg-Al-Sr system. It exhibits excellent mechanical properties, good corrosion resistance and excellent castability [5]. Figure 1 shows a comparison between creep deformation of different die-cast Mg-alloys. It can be seen from this figure that Mg alloy with Sr addition outperformed the other alloy systems in terms of creep resistance. Microstructure of the Mg-Al-Sr based alloys show type A and type B intermetallic phases. Type A is coupled with eutectic phase, which is Al_4Sr , while type B is bulky and designated as $Al_{13}Mg_{13}Sr$. The bulky phase has contribution to very high compressive creep resistance [4,6].

Moreover, tensile and yield strength of the alloys at 150°C found to be superior to AE42. The corrosion resistance of Mg-Al-Sr alloys is similar to AZ91D and better than AE42, which indicates that strontium does not show any adverse effect on corrosion properties [6].

Development of a reliable thermodynamic database for multicomponent alloy-systems requires a combination of experiments and computational thermochemistry. The importance

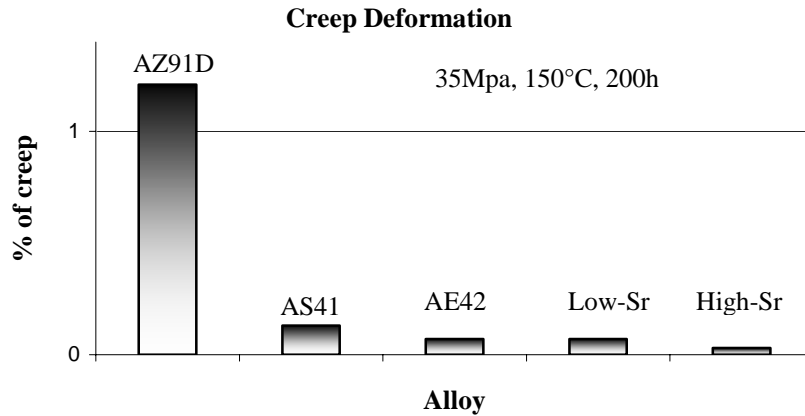


Figure 1: Comparison of creep deformation of die-cast Mg-alloys [5].

of phase diagram is immense in all aspects of material development. Due to interaction between the components, the Mg-Al-Sr phase diagram is very complicated and the phase diagram of this system is scarcely known. Within the ternary Mg-Al-Sr systems, there is a huge amount of possibilities to select alloy compositions. Therefore phase diagram calculations are needed in order to assist in selecting promising alloys.

To date little effort has been made to construct the phase relationships of Mg-Al-Sr system. Only one group published the experimental work on the phase equilibria of Mg-Al-Sr system [7]. However, Pelton *et al.* [8] presented critical evaluation and the only thermodynamic calculation of this system. Their calculated phase diagram exhibits substantial disagreement with the experimental data. This demands new experimental investigation for the verification and reassessment of this highly potential system.

Makhmudov *et al.* [9] used the methods of differential thermal analysis, microstructural and X-ray spectrum analysis and microhardness measurement for constructing the liquidus surface of the Mg-Al corners. In another work Makhmudov *et al.* [10] determined the 400°C isothermal section by examining over 200 alloys.

Whereas, Pelton *et al.* [8] calculated the ternary diagram without taking into account the formation of ternary solid solutions or compounds. They used the modified quasi-chemical model to estimate the thermodynamic

properties of the ternary liquid from the optimized binary parameters with no additional ternary terms.

A detailed experimental investigation on Mg-Al-Sr system has been conducted. The most popular thermal analysis technique is DSC, which measures endothermic and exothermic processes in materials as a function of temperature. In this paper, the results of DSC measurements on Mg-Al-Sr system are described. The thermophysical properties such as onset temperature and melting enthalpy were determined.

2. EXPERIMENTAL PROCEDURE

Thermal investigation of the Mg-Al-Sr system was performed using Setaram Setsys DSC-1200 instrument. The experimental conditions used for the analysis are presented in Table 1. In thermal analysis by DSC, selection of crucibles, the dimensions of the sample as well as the heating and cooling rates are important.

Mg-samples are highly reactive with platinum and also affect the internal alumina crucibles. In addition, the highly reactive Mg-alloys oxidize easily in solid state. Melting range, starting below 600°C, is usually accompanied with a noticeable mass loss [11].

Table 1: Experimental conditions for the determination of thermophysical properties

Item	Conditions
Heating rate	5°C/min
Cooling rate	5°C/min
Temperature range	25-800°C
Atmosphere	Flowing argon
Weight of sample	40~50 mg

To prevent chemical reactions with Mg vapors, graphite crucibles are used. In addition, sample masses are reduced and the crucibles are covered by graphite lid. All the tests were carried out in a flowing argon atmosphere. To avoid oxidation, multiple evacuating followed by rinses with argon was done.

Thirty samples were chosen by critical assessment of the experimental and thermodynamic datasets that are available in the literature. Because of the interest in the Mg alloys, special attention was directed to Mg-rich

corner, as can be seen in Figure 2. However, in this paper, only five samples (shown with solid circles in Figure 2) are discussed.

The alloys were of high purity with the nominal compositions given in Table 2. In preparing the alloys, magnesium of 99.8 wt%, aluminum of 99.9 wt.% and strontium of 99.0 wt.% were used. The charge was melted in a graphite crucible in an induction melting furnace under argon with 1% SF₆ to protect the melt from oxidation.

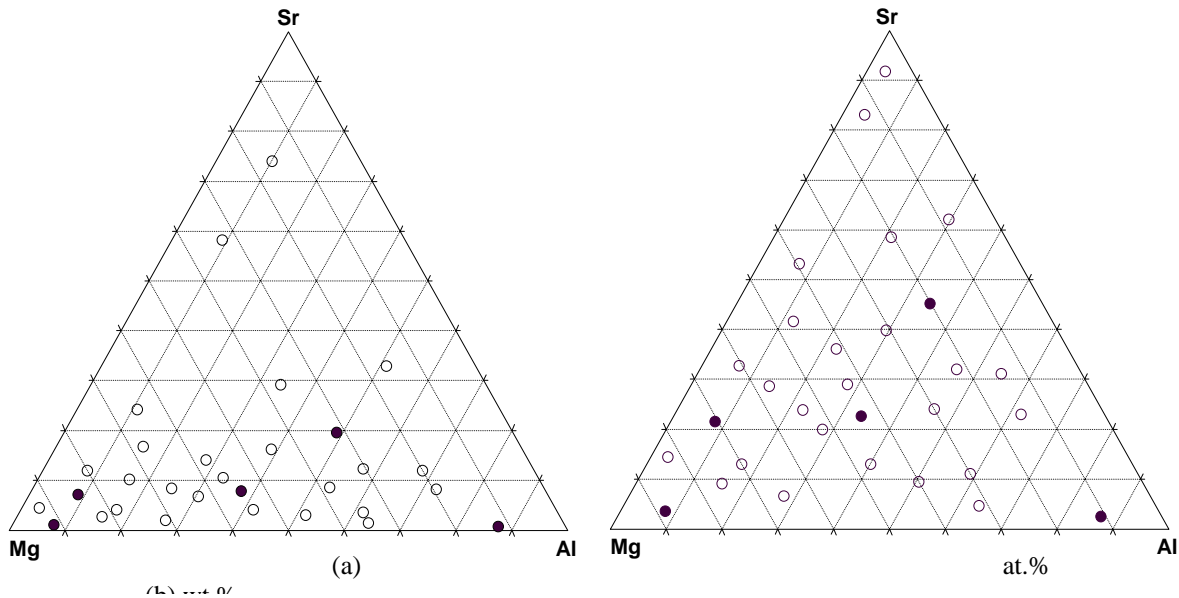


Figure 2: Mg-Al-Sr phase diagram with the investigated compositions (a) atomic % and (b) weight %.

Table 2: Nominal composition of the studied alloys.

Alloy	Wt.% of Sr	Wt.% of Mg	Wt.% of Al
Sample 1	2.6	10.7	86.7
Sample 2	21.5	70.5	8.0
Sample 3	22.6	43.8	33.6
Sample 4	3.5	88.5	8.0
Sample 5	45.2	20.2	34.6

Temperature calibration of the DSC equipment was done using standard samples of Al since its melting point is close to Mg-alloys. The samples were cut and mechanically polished to remove any possible contaminated surface layers. After that it was cleaned with acetone and placed in a graphite crucible and covered with a lid. DSC's furnace was evacuated and purged with argon three times before heating started. Samples were heated and cooled under flowing argon with the experimental conditions mentioned above. The reproducibility of every measurement was confirmed by collecting the data during three heating and cooling cycles. The estimated error of measurements between the repetitive heating is $\pm 1^\circ\text{C}$ or less. Furthermore, difference between heating and cooling peaks was in most cases lower than 15°C .

Endotherms were detected during heating while exotherms were observed during cooling. Temperatures along with enthalpy corresponding to various thermal events were obtained from the analysis of the DSC curves during heating runs.

3. RESULTS AND DISCUSSIONS

Figure 3 shows a typical DSC curve for pure Mg. It shows a sharp melting at 656°C , which is close to the melting point of magnesium (650°C). In this analysis, traces of Mg stuck to the crucible, and were removed mechanically. The shape of the DSC curve is the result of change in the heat capacity of the system. The enthalpy of transformation can be calculated from the DSC curve by:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (1)$$

Figure 4 shows the DSC spectrum of sample 1 with integration of the phase transformation peaks. It shows two predominant endothermic peaks when the sample is heated; one at 455°C and another at 572°C . The enthalpy of melting for this sample was registered as 352.99 J/g . Noticeable mass loss was observed for this sample. Moreover, no sticking of the alloy in the crucible was observed during the experiment.

All typical values for the melting enthalpy, onset temperature, peak temperature and liquidus temperature were registered.

The onset temperature during cooling was about 10°C below the onset temperatures observed in the heating process. When constructing the phase diagram these discrepancies will be neglected. The onset temperature and enthalpy for all the transitions of this sample were acquired without the subtraction of the baseline. Onset temperatures for the melting were obtained from the points of intersection of extrapolated baseline and the line of maximum slope such as for peak 1 the onset point is 455°C . The highest temperature at which the DSC signal returned to the baseline corresponds to the liquidus temperature, which is 640°C . The second peak is much bigger than the first one; this suggests two thermal events may occur in this temperature range. Hence, phase transformation preceded the melting of this sample.

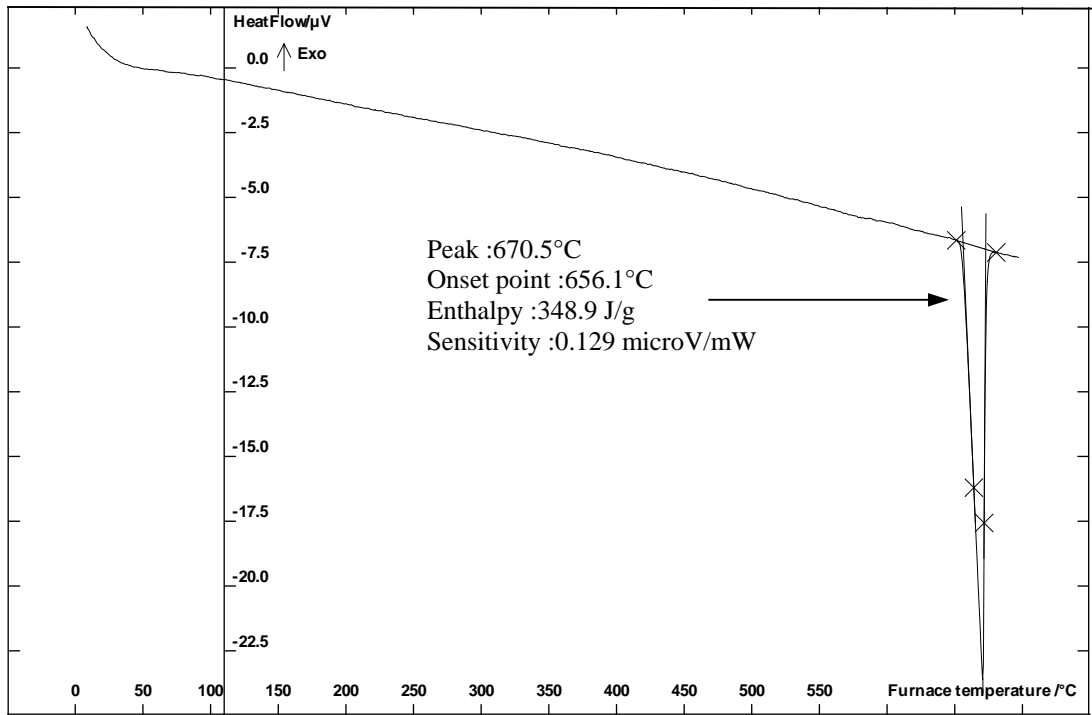


Figure 3: Typical DSC curve for pure Mg

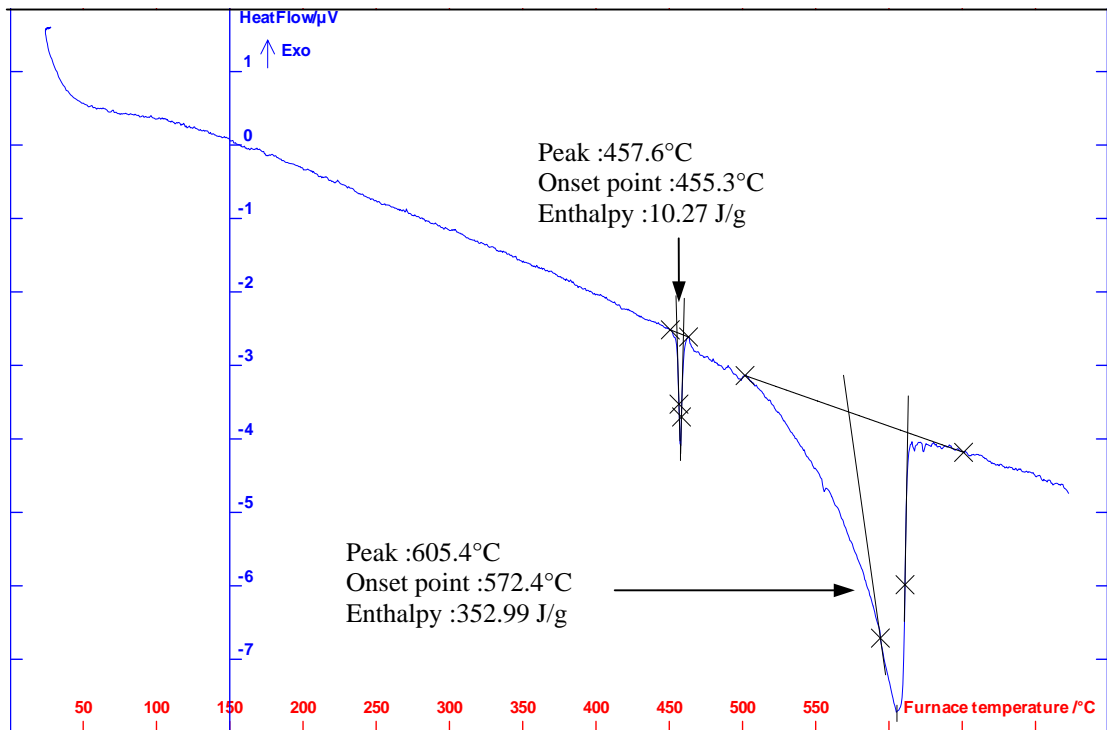


Figure 4: DSC curve of sample 1 with integration of phase change peaks.

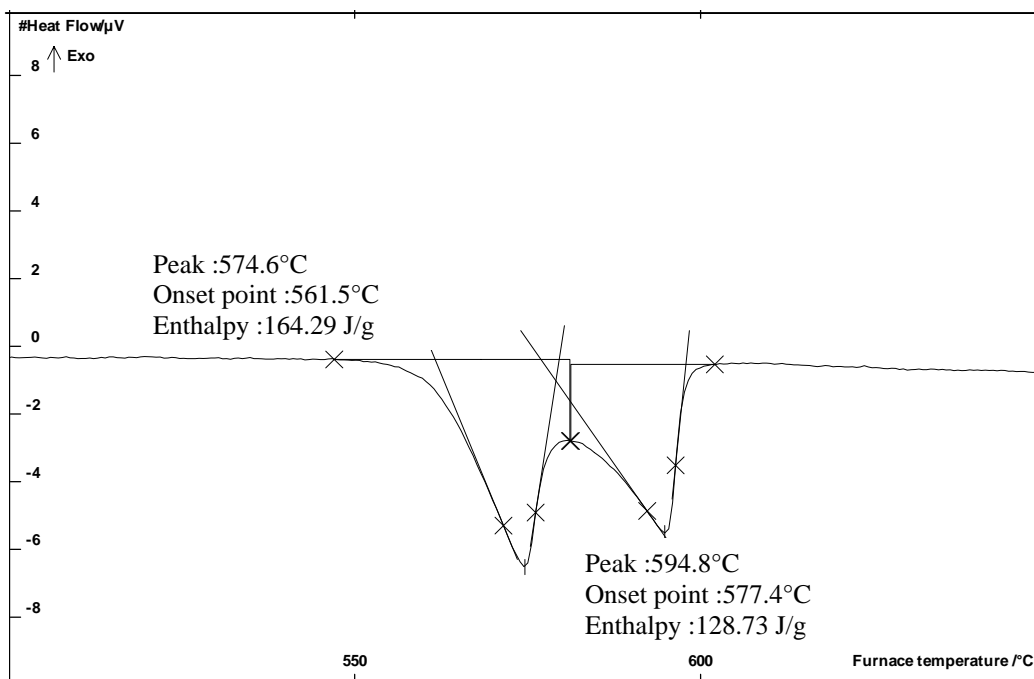


Figure 5: DSC curve of sample 2 with integration of phase change peaks.

DSC spectrum of sample 2 is shown in Figure 5. It can be seen that this sample encountered two predominant endothermic peaks, one at 561°C and 577°C, respectively. It was observed that the onset temperatures during cooling were about 10°C below the onset temperatures during heating.

Sample 2 undergoes a phase transition just prior to melting. The onset temperature and enthalpy were calculated after the subtraction of the baseline for this sample. The total values before and after the subtraction were similar. However the temperature between the overlapping peaks was found different. Figure 6 shows the DSC curves before and after the baseline subtraction.

The DSC spectra obtained in this terminal region (70 wt% Mg) show a peak without tailing. Furthermore, noticeable mass loss was also observed with no trace of the alloy on the crucible's wall.

Figure 7 shows the DSC curves obtained during heating of sample 3. This figure shows two endothermic peaks, however the DSC curve obtained during cooling and shown in Figure 8 shows three peaks. This result was observed in the three heating and cooling cycles of this sample. Difference in onset temperature between heating and cooling was found 2°C for the last peak. The enthalpy and onset temperatures were found without baseline subtraction and by using linear plot.

Figure 9 shows the DSC spectrum of Sample 4. It exhibits two endothermic peaks that overlap with each other. The overlapping peaks are resolved by horizontal plot after baseline subtractions. The onset temperatures for these two peaks are 526°C and 570°C, respectively. The enthalpy of melting is registered as 249.4 J/g. Difference in heating and cooling for the 1st peak is 1°C whereas for the second peak is 14°C.

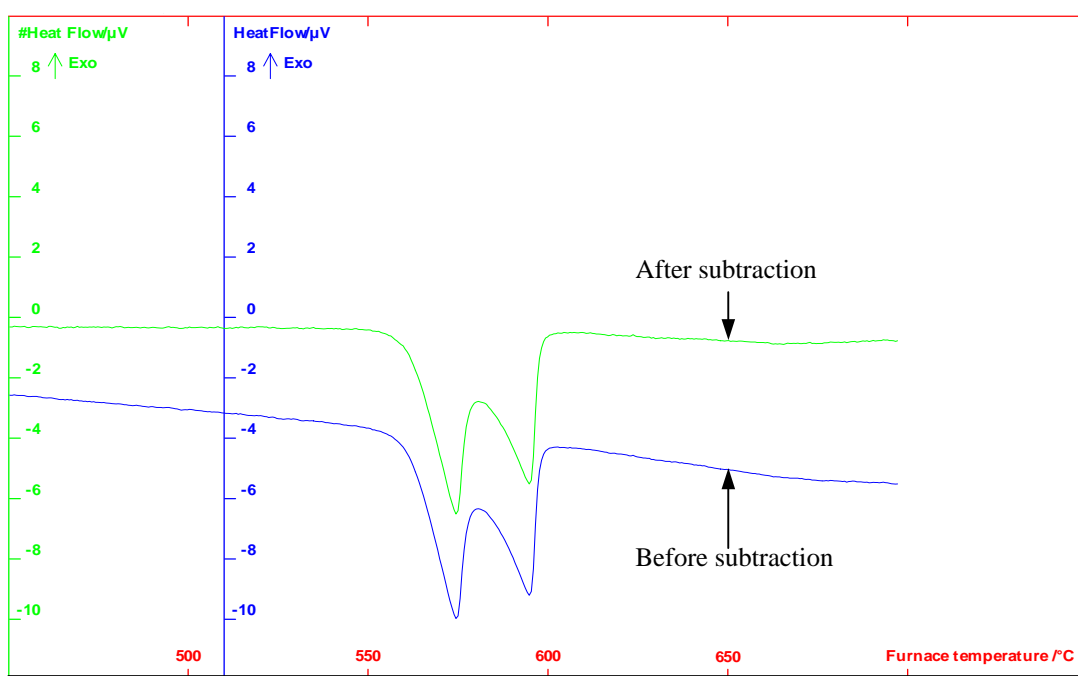


Figure 6: DSC curve of sample 2 before and after the baseline subtraction.

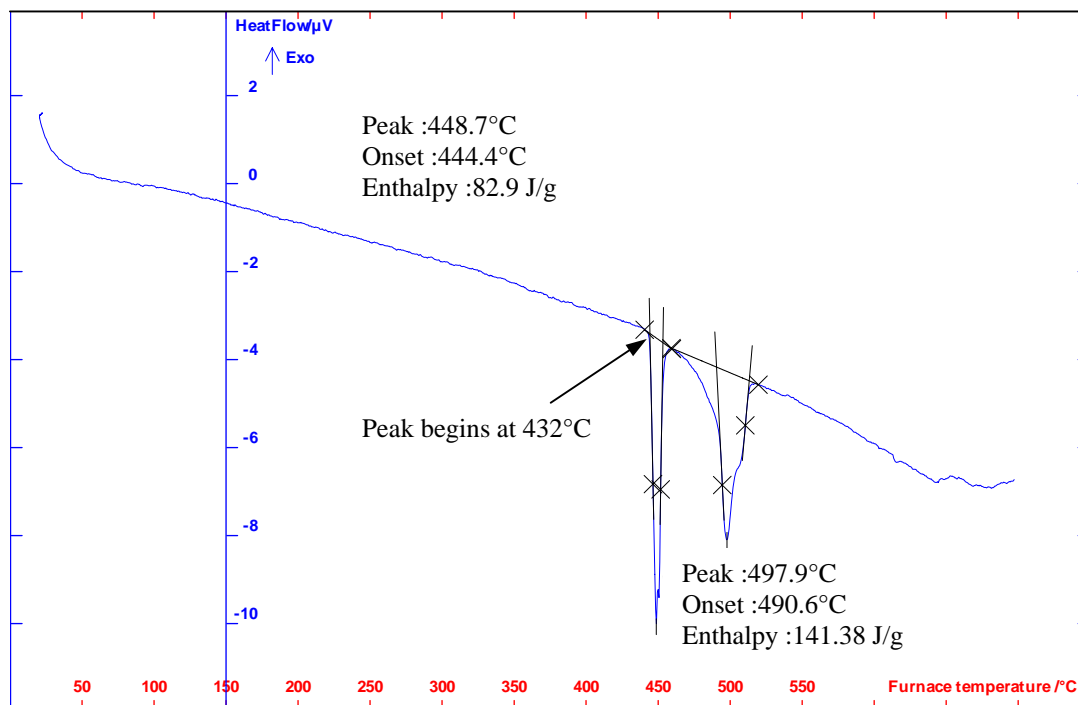


Figure 7: DSC curve of sample 3 during heating

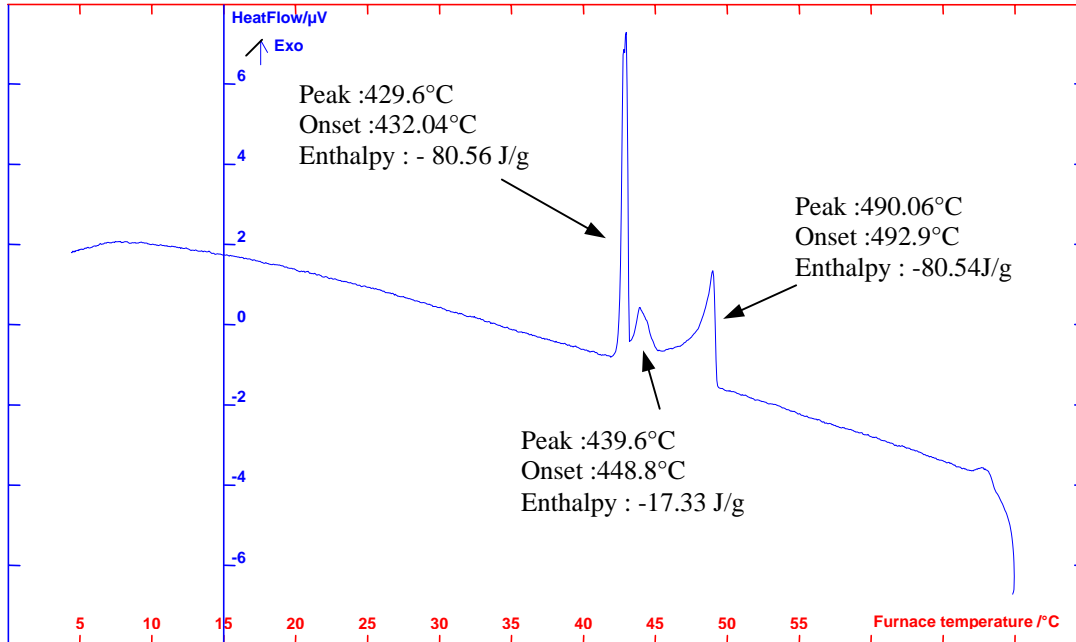


Figure 8: DSC curve of sample3 during cooling.

The DSC curve obtained for sample 4 shows that the endothermic peak at 570°C is followed by a broad tail that ends at 675°C. The absence of a single endothermic peak without any tail indicates that the sample does not melt congruently but undergoes a peritectic decomposition at 570°C.

The 1st peak is sharp and high and resembles a δ function. So it denotes the peak of eutectic melting. The second peak is non-isothermal transition (univariant) as it exhibits a peak, which is lower and broader.

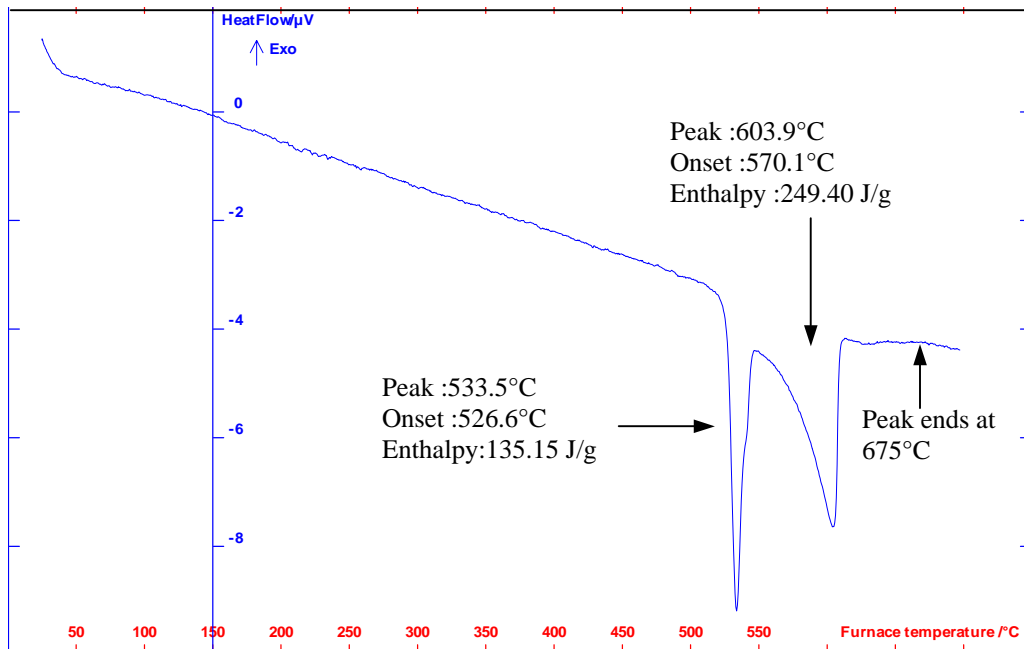


Figure 9: DSC curve of sample 4 during heating.

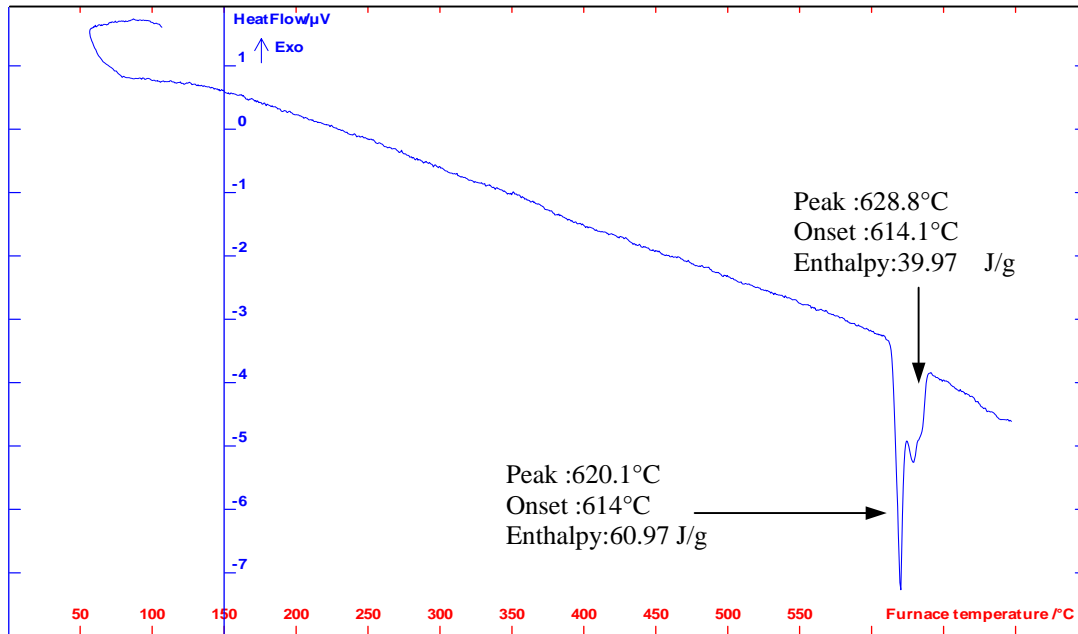


Figure 10: DSC curve of sample 5 during heating.

Figure 10 shows the DSC spectrum of sample 5. Upon heating two overlapping endothermic peaks were observed. The onset point of the 1st peak is 614°C. The peak temperature of the shoulder type peak is 628.8°C. During cooling of this sample only one exothermic sharp peak was observed. This sample is very close to eutectic composition because there are no shoulders or

any other heat effects observed after the first exotherm. This peak resembles a peak of the invariant transition since it is sharp and high and heat capacity of a system is generally infinite at this point.

Table 3 summarizes the parameters of melting for the five Mg-Al-Sr samples. Sample 3 has the

Table 3: Parameters of melting for the five samples.

Sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Onset Temp. °C (Peak 1)	457	561	444	526	614
Enthalpy J/g (Peak 1)	10.27	164	82.9	135	60
Onset Temp. °C (Peak 2)	572	577	490	570	614
Enthalpy of melting J/g	352.99	128	141	249	39
Liquidus Temp. °C	640	610	525	675	650

lowest melting point among all the samples, whereas sample 5 gives highest melting point. The composition of sample 5 is very close to one of the sample investigated by Makhmudov *et al.* [10] using DTA. The reaction temperature reported was 647°C whereas it is 614°C in this study.

4. CONCLUSIONS

- (1) Differential scanning calorimeter has permitted real time measurement of the phase changes involved in the Mg-Al-Sr system. The temperature ranges for the phase changes have been determined. Enthalpy of melting and enthalpy of compound formation were also obtained.
- (2) Thermal analysis of Mg alloys is difficult. Mg samples are highly reactive. Graphite crucible covered with a lid was used in order to prevent the chemical reaction with Mg vapor.
- (3) Invariant and univariant transformations in the studied samples were distinguished.
- (4) Among thirty samples, five samples were reported in this study. These results along with x-ray diffraction and thermodynamic modeling will be used later to construct a reassessed phase diagram.

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