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TECHNICAL PAPER

Thermodynamic Designing of Heat Treatable Mg–Zn–X (X = Sn, Y) Alloy Suitable for Semi-solid Processing

K. R. Ravi[1]

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Abstract Current work outlines the thermodynamic prediction of Mg–Zn–X (X = Sn, Y) alloys amenable for both semi-solid metal (SSM) processing and age hardening treatment. Semi-solid processing capability of Mg–Zn–X (X = Sn, Y) alloy has been evaluated by measuring the metallurgical parameters such as 'solidification interval', 'temperature liquid fraction sensitivity' and 'highest knee point' from non-equilibrium Scheil solidification curve. According to thermodynamic prediction, binary Mg–Zn and ternary Mg–Zn–Sn alloys are suitable for heat treatment; however, wide solidification intervals in these systems restrict their SSM processing ability. Formation of binary Zn_2Y and ternary W-$Mg_3Zn_2Y_3$ intermetallic phases in Mg–Zn–Y alloy has been predicted to improve their SSM processing potential and at the same time Mg–Zn–Y alloy is found to be suitable for heat treatment process.

Keywords Semi-solid processing · Heat-treatment · Mg alloys · Thermodynamic calculation

1 Introduction

Semisolid metal processing has become an important industry forming process. It combines the advantages of casting and metal forming processes, and thus facilitate in forming near net-shape components with improved mechanical properties [1]. Currently, semi-solid metal (SSM) processing for magnesium alloys is constrained to a few commercial Mg–Al–Zn alloys, such as AZ91, AM50 and AM60 [2, 3]. Although Mg–Al–Zn alloys offer a good combination of castability and mechanical properties at room temperature, they are not suitable for use at temperatures above 120 °C due to their poor creep resistance [4]. Therefore, it is desired to develop new magnesium alloys suitable for SSM processing, especially those with higher performance at elevated temperatures.

Rare earth and or Sn added Mg–Zn alloys have been extensively studied by several authors because of their superior mechanical properties at elevated temperature over conventional AZ series alloys [5–7]. However, these types of Mg alloys suffers from low ductility due to porosity and segregation of large fraction of eutectic phase along the grain boundaries [8]. Semi-solid processing has the potential in refining the eutectic phase as well as decreasing the porosity in castings; hence it is expected to improve the ductility of these materials. Moreover, if semi-solid formed alloy is amenable to heat treatment, it can derive additional strengthening from precipitation hardening process. According to author's knowledge, so far no work has been reported on semi-solid processing of heat treatable Mg–Zn–X (X = Sn, Y) alloys, either experimentally or theoretically. Hence, in the present study, Mg–Zn–X (X = Sn, Y) alloys suitable for both semi-solid processing and age hardening treatment are predicted using thermodynamic calculation (CALPHAD approach).

1.1 Semi Solid Processing Criteria

1.1.1 Solidification Interval

Studies on light alloys suggest that the minimum of 30 °C solidification interval is necessary for successful SSM processing [9]; hence it is identified as the lower limit for

✉ K. R. Ravi
krravi.psgias@gmail.com

[1] PSG Institute of Advanced Studies, Coimbatore 641 004, Tamil Nadu, India

SSM processing. During semi-solid process, the leftover liquid metal after slurry preparation solidifies similar to conventional casting. In such a process, wide solidification interval of an alloy may result in 'hot tearing'. Therefore, an ideal alloy for SSM processing should have a temperature interval that just suffices for subsequent mould filling. Among the Mg alloys, AZ91 alloy is successfully utilized for semi-solid processing with-out significant hot tearing issues and it has the solidification range of ~196 °C. Hence, upper limit for solidification interval is set as 196 °C for successful SSM processing.

1.1.2 Temperature Sensitivity of Liquid Fraction (df_L/dT)

Studies on Al and Mg alloys suggest that to achieve repeatable and controllable SSM processing, the 'temperature liquid fraction sensitivity' (df_L/dT) should be ≤ 0.03 [9]. However, there is no consensus among the researchers about the optimum range of liquid fraction that is suitable for SSM process. Since, non-dendritic slurry preparation for most magnesium alloys is carried out in the liquid fraction range of 0.6–0.8 [10], the author has chosen the midpoint 0.7 as the measuring point of 'temperature fraction liquid sensitivity', (df_L/dT).

1.1.3 Knee Point Criteria

According to Liu et al. [9] and Liang et al. [11], 'highest knee point' for successful SSM processing should exist between 0.3 to 0.5 liquid fractions. Interestingly, AZ91 is one of the widely accepted magnesium alloys for semi-solid processing and it has 'highest knee point' at 0.17. Accordingly, the 'highest knee point' for semi-solid processing has been revised to 0.17–0.5 liquid fractions.

1.2 Heat Treatment Criteria

Single phase region of α-Mg (hcp) is required to permit solution treatment at high temperature. The solubility of solute should decrease with decreasing temperature. Precipitation of intermetallics at elevated temperatures is necessary for precipitation hardening.

2 Results and Discussion

2.1 Binary Mg–Zn Alloys

Binary Mg–Zn alloys (up to 6 wt% of Zn) are well known to have heat treatment capability. In order to analyze their SSM processing capability, both equilibrium and Scheil models are used to obtain fraction of liquid vs temperature curve for various Mg–Zn alloys and it is shown in Fig. 1.

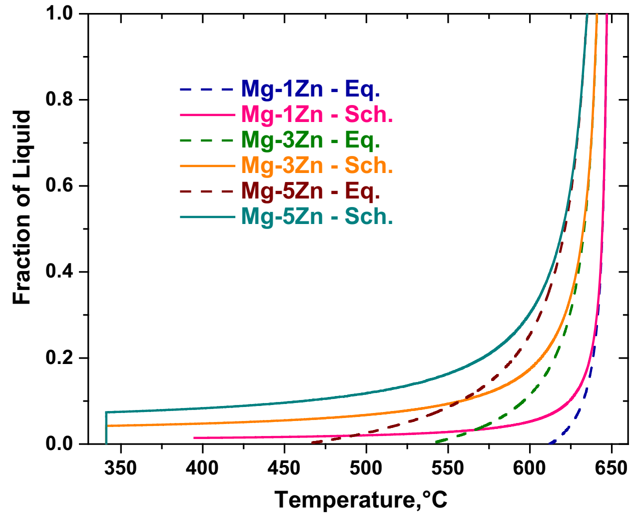

Fig. 1 Equilibrium and non equilibrium Scheil solidification curve of binary Mg–Zn alloys

The equilibrium model assumes that equilibrium diffusion of solute occurs in both liquid and solid phase during solidification, while Scheil solidification model assumes complete mixing of solute in the liquid phase and no diffusion in the solid phase. For all Zn content, a remarkable difference can be observed between equilibrium and Scheil solidification curves (Fig. 1). It puts forward a question that which solidification path should be used for SSM processing alloy design.

Solidification of alloys during semi-solid processing occurs in two distinct stages (i) the primary solidification during non-dendritic slurry preparation, wherein solidification of alloys occurs by equilibrium process and (ii) the secondary solidification in the shot sleeve or in die cavity at a high cooling rate, which is close to non-equilibrium Scheil solidification path. Among the SSM processing criteria used in the present study, the 'solidification interval' and 'highest knee point' affect the secondary solidification process where non-equilibrium Scheil solidification process is active. On the other hand, 'temperature liquid fraction sensitivity' plays a significant role in non-dendritic slurry preparation. Interestingly, in all binary Mg–Zn alloy system studied, when liquid fraction is more than 0.5, both Scheil and equilibrium solidification curve closely matches with each other (Fig. 1). It suggests that Scheil solidification curve can provide sufficient information about all the three semi-solid processing criteria used in the present investigation. Hence, further evaluation on SSM processing criteria has been done with the aid of Scheil solidification curve.

Figure 2 presents the solidification parameters estimated from Scheil solidification curve of Mg–Zn alloy. It can be seen that the solidification interval of Mg–Zn alloy is large and it is not significantly altered by Zn addition. For the

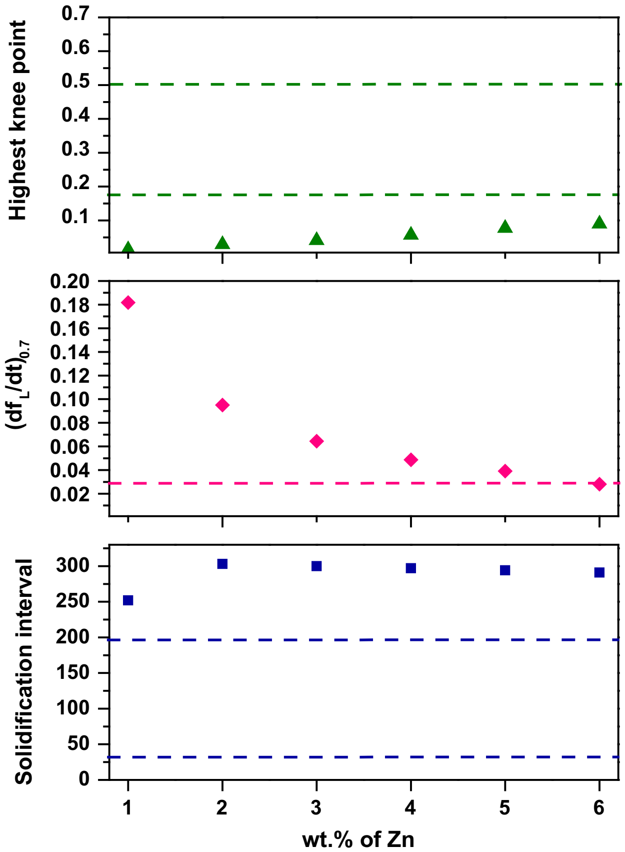

Fig. 2 Evaluation of thermodynamically calculated solidification parameters for binary Mg–Zn alloy

entire Mg–Zn alloy studied in this work, solidification interval is higher than the upper limit of 196 °C. Similarly, none of the Mg–Zn alloy satisfies both 'highest knee point' and 'temperature sensitivity of liquid fraction' criteria. It suggests that binary heat treatable Mg–Zn alloys are not suitable for SSM processing.

2.2 Ternary Mg–Zn–Sn alloys

An iso-thermal section of Mg–Zn–Sn alloy system at 400 °C has been calculated, and the Mg-rich corner is presented in Fig. 3. According to this isothermal section, a single phase HCP solid solution, α-Mg, is stable up to ~6 wt% of Zn and ~7 wt% of Sn. Phase fraction as a function of temperature has been calculated for Mg–4Zn–5.5Sn alloy (composition is in the edge of single-phase region) and is shown in Fig. 4. According to Fig. 4, Mg_2Sn and $MgZn_2$ phases dissolve at 418 and 250 °C, respectively and single phase α-Mg solid solution exist in the temperature range of 418–454 °C. Therefore, the two requirements for a heat-treatable alloy, i.e., the existence of a single phase region and the precipitation of intermetallic compounds, are met by the Mg–4Zn–5.5Sn alloy.

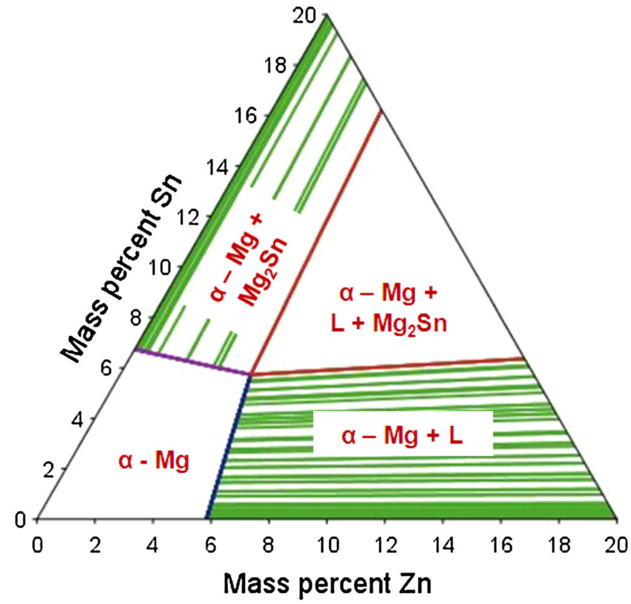

Fig. 3 Isothermal section of Mg–Zn–Sn phase diagram at 400 °C

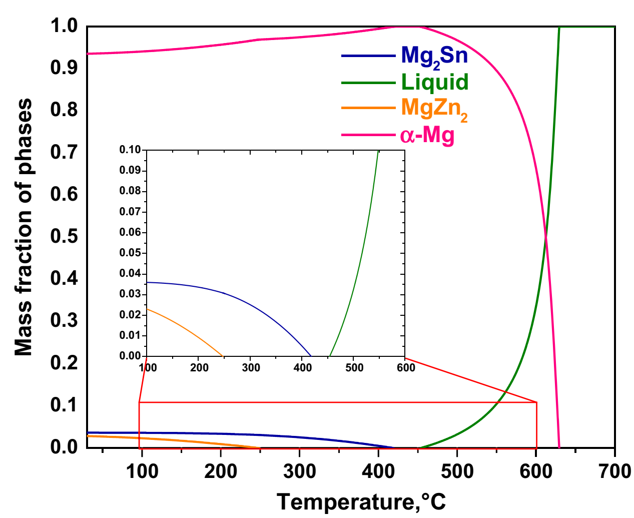

Fig. 4 Equilibrium phase fraction as a function of temperature for Mg–4Zn–5.5Sn alloy

Within the single phase solid solution range, at every 1 wt% interval of Zn (up to 5 wt%) and Sn (up to 6 wt%), 30 Mg–Zn–Sn alloys are selected and their SSM processing capacity has been analyzed, the results are summarized in Table 1. It can be seen that except Mg–4Zn–xSn and Mg–5Zn–xSn alloys, all the other alloy system studied in this work meet none of the SSM processing criteria. Mg–5Zn–4Sn, Mg–5Zn–5Sn and Mg–5Zn–6Sn alloys satisfy both 'highest knee point' and 'temperature liquid fraction sensitivity' criteria. Solidification intervals in all the Mg–Zn–Sn ternary alloys studied in this work are well above the specified limit of 196 °C. It can be inferred that during solidification of Mg–Zn–Sn alloys, Sn addition to Mg–Zn

Table 1 Identification of heat treatable ternary Mg–Zn–Sn alloy suitable for semi-solid processing based on thermodynamic calculations

	Sn-1	Sn-2	Sn-3	Sn-4	Sn-5	Sn-6
Zn-1	N	N	N	N	N	N
Zn-2	N	N	N	N	N	N
Zn-3	N	N	N	N	N	N
Zn-4	N	N	N	⬟	⬟	⬟
Zn-5	N	⬟	⬟	⬟ ▲	⬟ ▲	⬟ ▲

N—Alloys satisfying none of the SSM processing criteria

Alloys satisfying ⬟ Temperature liquid fraction sensitivity ▲ Highest knee point criteria

does not increase the eutectic, $MgZn_2$, phase formation temperature rather it decreases; as a result solidification interval for Mg–Zn–Sn alloy is very large. Even though the Mg–Zn–Sn alloys are amenable to heat treatment process, extremely large solidification interval restricts their SSM processing potential.

2.3 Ternary Mg–Zn–Y alloys

The addition of third element can decrease the large solidification interval of Mg–Zn alloy if it forms a high temperature ternary intermetallic phase instead of low-temperature eutectic $MgZn_2$ phase. Since, Yttrium has the potential to form high-temperature ternary intermetallic phases such as W-$Mg_3Y_2Zn_3$ and X-$Mg_{12}YZn$ in Mg–Zn–Y alloys [6, 7], Ytrrium has been identified as a third element to improve the SSM processing ability of Mg–Zn–X alloys. For this purpose, in Mg–Zn–Y alloy, up to 5 wt% of Zn and 5 wt% of Y, at each 1 wt% interval, 25 alloy systems are selected and their SSM processing and heat treatment suitability have been analyzed.

Scheil solidification curve of Mg–3Zn–xY alloy is shown in Fig. 5. Barring a small bent at ~590 °C which represents the L + α-Mg → L + α-Mg + Zn_2Y phase transformation, solidification behavior of Mg–3Zn–1Y alloy is very similar to Mg–3Zn alloy. When 2 wt% of Y is added to Mg–3Zn alloy, a ternary intermetallic W-$Mg_3Y_2Zn_3$ phase formation occurs at ~580 °C along the Zn_2Y phase formation. Interestingly, formation of ternary W-$Mg_3Y_2Zn_3$ phase, completely suppresses the formation of low-temperature eutectic, $MgZn_2$, phase. This process has resulted significant decrease in solidification interval of Mg–3Zn–2Y alloy up to 110 °C. With increasing addition of Y to Mg–Zn alloy, further decrease in solidification interval has been observed along with the formation of an additional ternary intermetallic X-$Mg_{12}YZn$ phase.

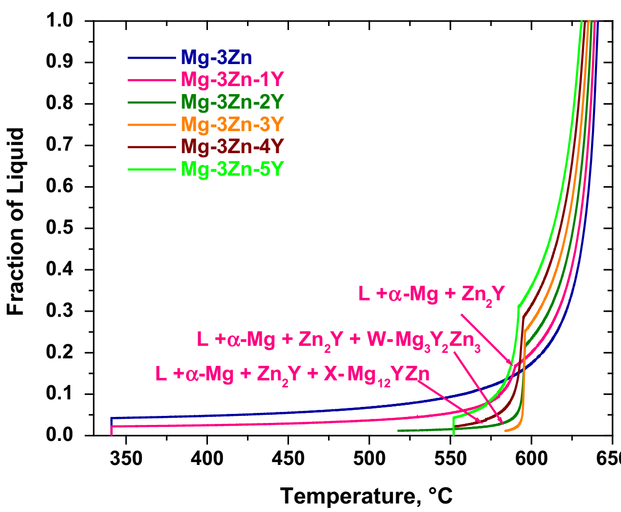

Fig. 5 Non equilibrium Scheil solidification curve of ternary Mg–3Zn–xY alloy

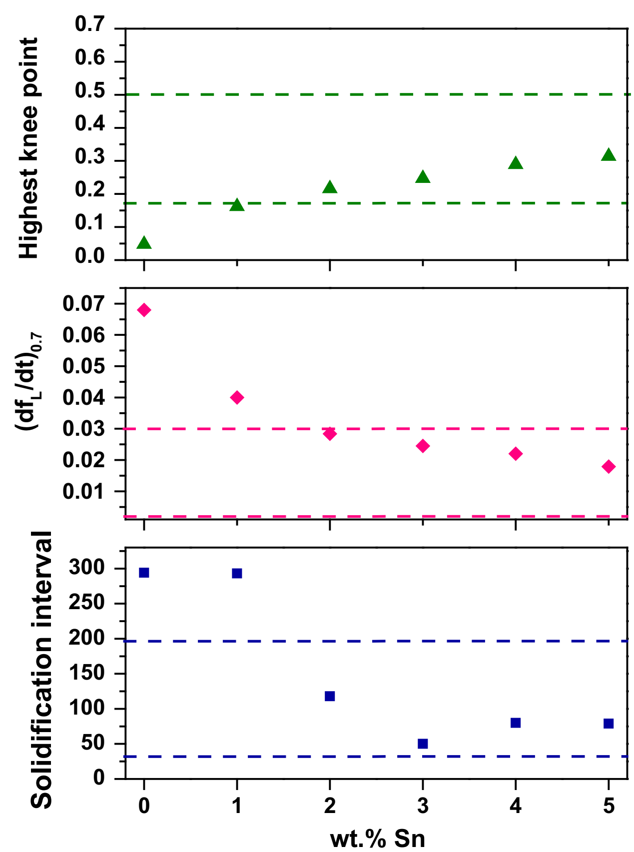

Fig. 6 Evaluation of thermodynamically calculated solidification parameters for Mg–3Zn–xY alloy

Figure 6 describes the role of Y on SSM processing capability of Mg–3Zn alloys. It is evident that the solidification interval of Mg–3Zn alloy can be brought inside the ideal values specified for semi-solid processing by adding minimum of 2 wt% Y. At the same time, a bent created by the Y addition to Mg–Zn alloy i.e. Zn_2Y formation, increases the 'highest knee point' beyond the threshold value of 0.17, which also favors the SSM processing. Moreover, the value of 'temperature liquid fraction sensitivity' found to decrease with the increase in Y addition to Mg–Zn alloy. In a nutshell, when Y addition to Mg–3Zn alloy is equal to or higher than 2 wt%, Mg–3Zn–xY alloy meet all the three criteria specified for SSM processing.

Similar analysis has been done for other Mg–Zn–Y alloys selected in this study; the outcome is presented in Fig. 7. Though, low Zn containing Mg–Zn–Y alloys (Mg–1Zn–xY and Mg–2Zn–xY) have smaller solidification interval, the 'temperature liquid fraction sensitivity' value for these alloys are higher than that of ideal value, 0.03, which constrict their SSM processing ability. On the other hand, in high Zn containing Mg–Zn–Y alloys (Mg–4Zn–xY and Mg–5Zn–xY), at lower addition level of Y, the amount of Y is not sufficient to suppress the formation of low temperature eutectic, $MgZn_2$, phase. As a result, solidification interval for these alloys is wide and hence these alloys are not suitable for SSM processing. Out of 25 Mg–Zn–Y alloys studied in this work, 13 alloys have satisfied all the three SSM processing criteria mentioned in the Sect. 1.1.

In order to check whether the SSM processable alloys are suitable for age hardening treatment, vertical section of Mg–3Zn–xY alloy has been generated (Fig. 8). According to Fig. 8, Mg–3Zn–xY alloys do not have a single phase

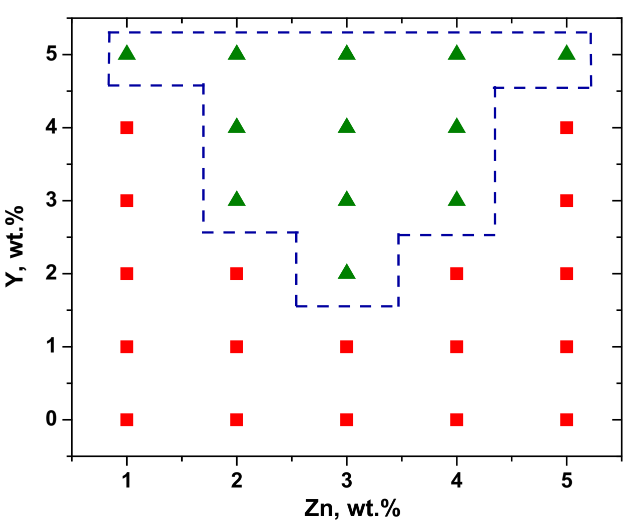

Fig. 7 Identification of Mg–Zn–Y alloys suitable for semi-solid processing based on thermodynamic calculations. Alloy system marked (*filled triangle*) satisfying and (*filled square*) not satisfying SSM processing criteria

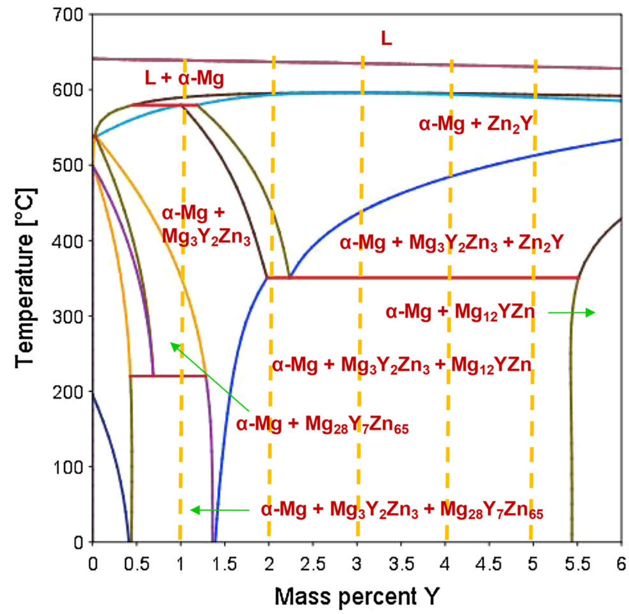

Fig. 8 Vertical section of Mg–3Zn–xY alloy phase diagram

region of α-Mg to facilitate the solutionizing treatment at high temperature. However, studies on Mg–3.0Zn–0.5Y (at.%) alloy suggest that the yield strength can be significantly improved by age hardening treatment [7, 12]. Interestingly, this alloy also does not have single phase region of α-Mg at solutionizing temperature of 400 °C. At this temperature along with α-Mg solid solution, I-Mg_3YZn_6 phase also exist. During solution treatment, the ternary intermetallic Z-$Mg_{28}Y_7Zn_6$ phase dissolves in α-Mg solid solution. Subsequent quenching and ageing treatment assist in re-precipitation of fine Z-$Mg_{28}Y_7Zn_6$ phase which improves the yield strength of Mg–3.0Zn–0.5Y (at.%) alloy.

To assess the possibility of utilizing similar heat treatment approach in SSM processable Mg–Zn–Y alloy, property diagram of Mg–3Zn–2Y and Mg–3Zn–5Y alloy has been generated and it is shown in Fig. 9. In Mg–3Zn–2Y alloy, 1.9 wt% of W-$Mg_3Y_2Zn_3$ phase and 2.8 wt% of X-$Mg_{12}YZn$ phase dissolves in α-Mg solid solution at 450 and 355 °C, respectively. Similarly, in Mg–3Zn–2Y alloy, 17.8 wt% of X-$Mg_{12}YZn$ phase and 0.1 wt% of W-$Mg_3Y_2Zn_3$ phase dissolves in α-Mg solid solution at 515 and 350 °C, respectively. In both the alloy, approximately 1 wt% of undissolved Zn_2Y phase can be seen along with α-Mg solid solution. Dissolution of significant amount of room temperature ternary intermetallic phases at high temperature and very low fraction of undissolved phase in α-Mg suggest that significant strengthening in these alloys can be achieved through age hardening treatment. However, heat treatment suitability of Mg–Zn–Y alloy can be verified only through appropriate experiments.

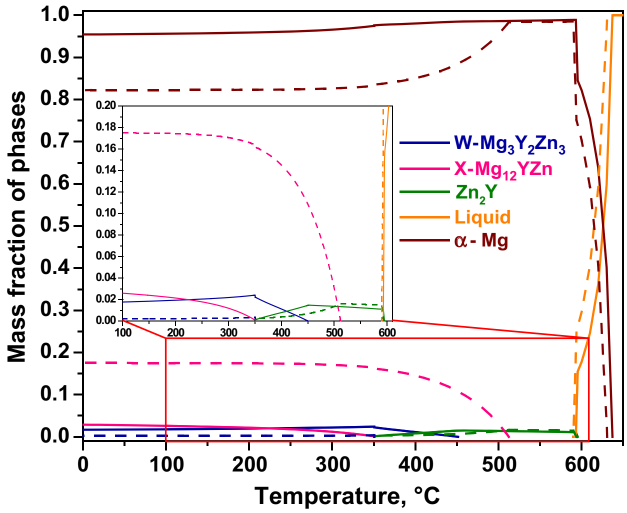

Fig. 9 Equilibrium phase fraction as a function of temperature in Mg–3Zn–2Y and Mg–3Zn–5Y alloys. (___) and (---) represents Mg–3Zn–2Y and Mg–3Zn–5Y alloy respectively

3 Conclusions

In this work, semi-solid processing and heat treatment viability of binary Mg–Zn and ternary Mg–Zn–Sn and Mg–Zn–Y alloys system have been successfully evaluated based on thermodynamic analysis. Presence of low temperature eutectic, $MgZn_2$, and associated wide solidification interval restrict the SSM processing capability of binary Mg–Zn and ternary Mg–Zn–Sn alloys, nevertheless these alloys have excellent age hardening ability. Y addition to Mg–Zn reduces the solidification interval and 'temperature sensitivity of liquid fraction' and increases the 'highest knee point'; as a result it improves the SSM processing potential of Mg–Zn–Y alloys. In a nutshell, among the alloy systems studied in this work, few alloys within the family of Mg–Zn–Y system have been identified as suitable for both SSM processing and age hardening treatment.

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