Mg-Zn-{Y, Ce} Alloys: Thermodynamic Modeling and Mechanical Properties

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Magnesium alloys are a strong candidate for various applications in automobile and aerospace industries due to their low density and specific strength. Micro-alloying magnesium with zinc, yttrium, and cerium enhances mechanical properties of magnesium through grain refinement and precipitation hardening.

Keywords: thermodynamic modeling; magnesium; phase diagram; liquidus projection

1. Introduction

Micro-alloying magnesium with RE such as zinc and yttrium resulted in promising mechanical properties $\frac{[1][2][3][4][5][6][7][8][9]}{[1][2][3][4][5][6][7]}$. Furthermore, the addition of RE elements to Mg-Zn promote activation of prismatic slip and increase the stacking fault energy, therefore weakening the texture of magnesium alloys $\frac{[3][10][11][12][13][4][5][14][15][16][17]}{[13][4][5][14][15][16][17]}$. Micro-alloying magnesium with zinc increases its fluidity in casting $\frac{[18]}{[20][21]}$, whereas yttrium addition has a remarkable effect on aging precipitation and high solid solution strengthening $\frac{[19][20][21]}{[20][21]}$. Moreover, cerium tends to precipitate a thermally high stable compound (Mg₂Ce) in magnesium rich region, which improve microstructure stability at elevated temperatures. Diluting zinc in Mg-Ce alloy significantly improves stretch formability by modifying the basal plane texture through solid solution hardening mechanism $\frac{[22][23][24][25][26]}{[25][26]}$. Moreover, the highest zinc in Mg-Ce alloy improves yield strength and ultimate tensile strength through precipitation of intermetallic compounds. Whereas the ratio of Ce/Zn increases, grain refinements and loss of formability occurs $\frac{[27][22][23][24][25][26][28][29][30]}{[25][26][28][29][30]}$. Mg-Zn-Y alloys display promising mechanical properties because of precipitates of thermally stable ternary compounds (W-Mg₃Y solid solution, I-Mg₃YZn₆, and LPSO-phase Mg₁₂ZnY) as well as high solubility of yttrium in magnesium.

To better understand phase stability, phase relation, and the effect of precipitation on age hardening, knowledge of binary and ternary phase diagrams is essential. Additionally, accurate prediction of phase diagram plays an important role in materials development and alloy design. Phase diagram is a tool used to predict the equilibrium phase(s) and phase(s) percentage at certain temperatures for specified alloys and simulate the phase consistency and solidification process of individual alloys. Moreover, the percentage of the predicted phase(s) that exist in the microstructure can be calculated.

2. Zinc-Yttrium Phase Diagram

In the work of $\frac{[31][32]}{1}$, tantalum containers were unsuccessful because of the penetration of Y-Zn liquid at high zinc contents. Mason and Chiotti $\frac{[32]}{2}$ reported three intermetallic compounds that melt congruently: YZn, YZn₂, and Y₂Zn₁₇ (YZn_{8.5}) at 1105, 1080, and 890 °C, respectively. Thermodynamic modeling of Y-Zn binary phase diagram in the work of $\frac{[33][34][35]}{2}$ presented a polymorphic transformation in the YZn₂ at 750 °C, which is in accord with $\frac{[32][36]}{2}$. Mason and Chiotti $\frac{[32]}{2}$ found five intermetallic compounds that decompose peritectically: YZn₃, Y₃Zn₁₁ (YZn_{3.67}), Y₁₃Zn₅₈ (YZn_{4.46}), YZn₆, and YZn₁₂ at 905, 896, 882, 872, and 685 °C, respectively. Mason and Chiotti $\frac{[32]}{2}$ determined the thermodynamic properties of the intermetallic compounds using dewpoint method. The large number of intermetallic compounds found in the RE-Zn system was similar and related to RE-coordination number $\frac{[37]}{2}$. Crystal structure data of Y-Zn compounds were determined by $\frac{[37][38][39][40]}{2}$. Gibbs energy of formation of the intermediate compounds in the Y-Zn system was investigated by $\frac{[41][42][43][44][45]}{2}$. The most accurate description of Y-Zn binary phase diagram was established by Zhu and Pelton $\frac{[46]}{2}$ presented some amendment to the work of Spencer et al. $\frac{[35]}{2}$. The calculated enthalpy and Gibbs energies of formation of the intermetallic compound presented in the work of $\frac{[35]}{2}$ are in good agreement with the experimental data of $\frac{[32][41][42][45]}{2}$.

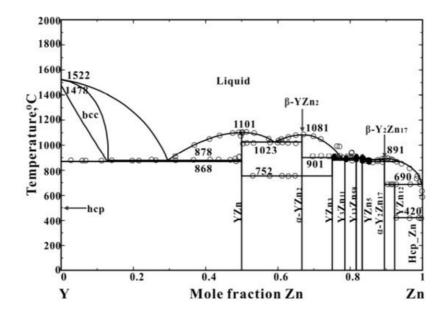


Figure 1. Yttrium-zinc phase diagram [46].

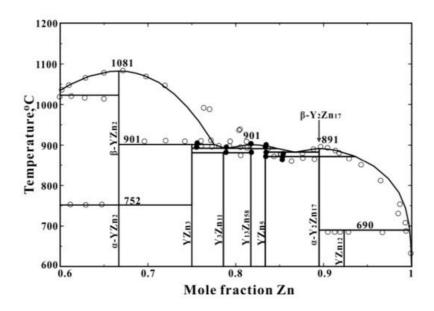


Figure 2. Yttrium–zinc phase diagram in Zn-rich region [46].

3. Mg-Zn, Mg-Y, and Mg-Ce Phase Diagrams

Liquid phase in the work of [18] was optimized using the modified quasi-chemical model (MQM). This model has been used to describe the liquid phase as this is the only scientific model that accounts for the presence of short-range ordering. Therefore, the reported phase diagrams in the work of [18] adequately describe thermodynamic properties of these systems. Islam et al. [18] critically reviewed and assessed thermodynamic data and phase diagrams of Mg-Zn, Mg-Y, and Mg-Ce systems. **Figure 3**, **Figure 4** and **Figure 5** presented the most accurate calculated binary phase diagrams for these systems [18]. It is worth mentioning that the liquid phase was optimized using a modified quasi-chemical model to accurately describe short range ordering in the liquid.

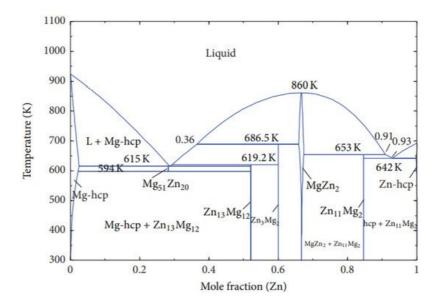


Figure 3. Mg-Zn phase diagram [47].

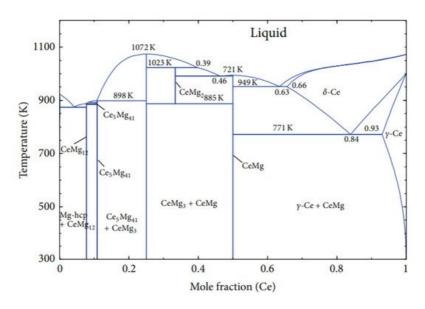


Figure 4. Mg-Ce phase diagram [18].

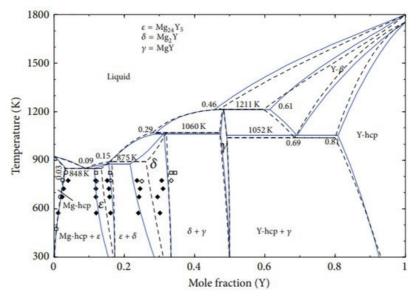


Figure 5. Mg-Y phase diagram solid lines $\frac{[34]}{}$ in comparison to $\frac{[48]}{}$ showed in dotted line $\frac{[18]}{}$.

4. Magnesium-Zinc-Yttrium Ternary Phase Diagram

Liquidus projections of the ternary Mg-Zn-Y phase diagram reported by Gröbner et al. [49] and Zhu and Pelton [50] are shown in **Figure 6**a,b, respectively.

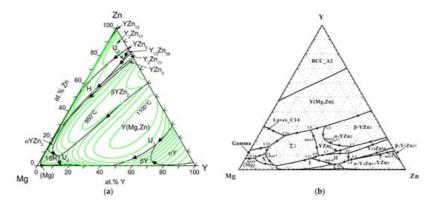


Figure 6. Liquidus projections of the ternary Mg-Zn-Y phase diagram; (a) Gröbner et al. [49] and (b) Zhu and Pelton [50].

5. Mechanical Properties of Mg-Zn-{Ce, Y} Alloys

Alloying Mg-Zn with rare earth elements is promising in modifying magnesium texture. Among rare-earth element, many researchers reported that micro-alloying Mg-Zn with yttrium or cerium exhibited a comparable ductility and formability with commercial magnesium alloys. **Table 1** and **Table 2** summarize the mechanical properties of the published alloys in Mg-Zn-Y [51][52][53][54] and Mg-Zn-Ce [55][27][22][26][53][54][56], respectively.

Table 1. Mechanical properties of Mg-Zn-Y alloys.

Nominal Composition (wt.%)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Ductility	Process Conditions
Mg-2Zn+0.4Y	160	240	30%	Samples were cast at 690 °C and then extruded at 310 °C $^{[51]}$
Mg-14.4Zn-3.3Y	365 ± 3.5	380	8%	Samples were cast and solutionized at 480 °C for 24 h followed by extrusion at 430 °C, then aged at 150 °C $^{[52]}$
Mg-14.4Zn-3.3Y	171	320	12	Samples were cast and solutionized at 480 °C for 24 h followed by extrusion at 430 °C [52]
Mg-1.5Zn-0.2Y	135	238	17%	The ingots were homogenized at 450 °C for 12 h, then rolled at 400 °C, and after that sheet annealed at 350 °C for 1 h $^{[53]}$
Mg-6.0Zn-1.0Y	268.3		12.9%	Alloys were solutionized at 480 °C and then extruded at 390 °C $^{[\underline{54}]}$
Mg-6.0Zn-1.0Y	288.7		17.3%	Alloys were solutionized at 480 °C and then extruded at 390 °C and aged at 150 °C for 48h ^[54]
Mg-3.0Zn-0.5Y	262	18.3%		Alloys were solutionized at 480 °C and then extruded at 350 °C $^{\circ}$ C $^{\circ}$ C

Table 2. Mechanical properties of Mg-Zn-Ce alloys.

Nominal Composition (wt.%)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Ductility	Process Conditions
Mg-2Zn+0.4Ce	190	255	18%	Samples were cast at 690 °C and then extruded at 310 °C $^{[55]}$
Mg-2Zn-0.2Ce (ZE20)	69	170	31%	
Mg-5Zn-0.2Ce (ZE50)	135	247	15%	Samples were cast at 700 °C and then extruded at 400 °C [55]
Mg-8Zn-0.2Ce (ZE80)	136	289	16%	
Mg-1.5Zn-0.2Ce	140	240	19%	The ingots were homogenized at 450 °C for 12h, then rolled at 400 °C and after that sheet annealed at 350° C for 1 h $^{[53]}$
Mg-6Zn-0.2Ce	225	270	30%	Alloys were cast at 750 °C and homogenized at 350 °C for 12 h. After extrusion, alloys aged at 175 °C from 0.5 to 80 h $^{[54]}$

Nominal Composition (wt.%)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Ductility	Process Conditions	
Mg-2%Zn- 0.5%Ce (ZE20)	199.2	~245	6%	Samples were prepared by continuous casting, then homogenized at 823 K for 8 h. Sheets were rolled by conventional rolling at 673 K ^[56]	
Mg-2%Zn- 0.5%Ce (ZE20)	125	~235	13.8%	Samples were prepared by continuous casting, then homogenized at 823 K for 8 h. Sheets were rolled by conventional rolling at 673 K. Sheets were annealed at 673 K ^[56]	
Mg-2%Zn- 0.5%Ce (ZE20)	~170	~240	28.23	Samples were prepared by continuous casting, then homogenized at 823 K for 8 h. Sheets were rolled by packed rolling at 673 K. Sheets were annealed at 673 K	
Mg-2%Zn- 0.5%Ce (ZE20)	~165	~236	33.4%	Samples were prepared by continuous casting, then homogenized at 823 K for 8 h. Sheets were rolled by packed rolling at 723 K. Sheets were annealed at 723 K	
Mg-0.5Zn-0.2Ce	133	213	25%		
Mg-1.0Zn-0.2Ce	110	202	23%	0	
Mg-1.5Zn-0.2Ce	116	206	29%	Samples were heated at 723 K for 20 min and sheets were rolled by unidirectional rolling at 353 K. Then, sheets were annealed at 623 K for 90 min [22]	
Mg-2.0Zn-0.2Ce	118	222	25%	623 K 101 90 IIIIII —	
Mg-2.5Zn-0.2Ce	131	228	16%		
Mg-1.5Zn-0.2Ce	153	231	26%	Samples were extruded at 703 K and then annealed at 623K for 90 min $^{\left[26\right] }$	
Mg-1.5Zn-0.2Ce	194	248	20%	Samples were extruded at 573K and then annealed at 623K for 90 min $^{\left[26\right] }$	
Mg-1.0Zn-1.0Ce	95	191	22%		
Mg-2.0Zn-1.0Ce	101	197	26.2%	Samples were annealed at 350 °C and then annealed at 450 °C	
Mg-4Zn-1.0Ce	109	220	18%	for 1 h ^[27]	
Mg-1.0Zn-0.5Ce	95	191	30%		

The addition of yttrium to Mg-Zn alloys enhances the formation of magnesium solid solution in ternary systems due to high solid solubility of yttrium in magnesium. Meanwhile, precipitation of nano-scale ternary phases as a result enhances mechanical properties.

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