Cerium – Magnesium – Zinc

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Introduction

The system was first studied in the region between 0 and 80 mass% Mg by [46Kor]. Starting materials were Mg (purity 99.8 to 99.9 %), Zn of undefined purity, and Ce (purity 96 %). The alloys were fused in alumina crucibles under a protective flux of KCl-LiCl. Ce was introduced as a Ce-Mg prealloy containing 21 to 22 % Ce. Thermal analysis was used to construct six vertical sections with a constant mass ratio Zn:Ce of 1:5, 1:2, 1:1, 2:1, 4.5:1 and 10:1, and to draw a liquidus surface of the Mg corner. Samples were annealed at 335°C for 240 h, at 300°C for 360 h, and at 200°C for 480 h. Some samples were allowed to cool "slowly" [46Kor] in the furnace. The annealed samples"" were water quenched, and subsequently etched with 2 % alcoholic nitric acid. From the microstructure of the etched samples, the combined solubility of Zn and Ce in Mg was determined.
Subsequent reports [77Mel, 78Mel, 83Mel, 89Dri] studied the phase relations in the Ce-Mg-Zn ternary system in the region Mg-$MgZn_2$-CeMg-CeZn. The alloys used in the experiments were prepared by fusing the elements in crucibles ([89Dri] states alumina crucibles) under a protective layer of VI2 flux. The starting materials were metal ingots of purity better than 99.5 mass% [77Mel, 78Mel, 89Dri]. Phase triangulation in the region Mg-$MgZn_2$-CeMg-CeZn has been evaluated by means of X-ray powder diffraction [78Mel] from 150 alloys annealed at 300°C for 240 h and quenched into water. Four ternary compounds were observed, τ_1 to τ_4, the crystal structures of τ_1 and τ_3 being unknown. [89Dri] constructed two polythermal sections in the Mg rich corner at 24 mass% Zn and 34 mass% Zn, both ranging from 0 to 20 mass% Ce. Methods used were DTA (cooling rates 2 to 5 K/min), EMPA, SEM and X-ray powder diffraction. Microstructure was investigated after mechanical polishing, applying a solution of 30 % H_3PO_4 in alcohol as etchant.

[80Zak], in his review, plotted, based on [46Kor], the curves of the combined solubility of Zn and Ce in (Mg).

Binary Systems

The accepted Mg-Zn binary system has been calculated on the basis of a critical assessment [92Aga]. The Ce-Mg and Ce-Zn binary systems have been accepted from [Mas2]. The crystallographic data relevant to the binary boundary systems are listed in Table 1.

Solid Phases

Four ternary compounds τ_1, τ_2 , τ_3, and τ_4 have been observed, of which τ_2 and τ_4 exhibit extended solid solution ranges at constant Ce contents [78Mel]. The lattice parameters of the solid solution ranges are given in Table 1. [89Dri] assumed that τ_2 derives from the isostructural binary compound $CeMg_{10.3}$.

Invariant Equilibria

[46Kor] found a ternary eutectic at 341 to 343°C with a composition corresponding to 50 mass% Mg, 47.5 mass% Zn, and 2.5 mass% Ce. On the basis of the two experimentally established isothermal reactions $L + \tau_2 \rightleftharpoons (Mg) + \tau_1$ at 349±1°C and $L \rightleftharpoons (Mg) + \tau_1 + Mg_{51}Zn_{20}$ at 341±1°C [89Dri], and the eutectoid ternary decomposition of $Mg_{51}Zn_{20}$ mentioned by [89Dri], a partial reaction scheme has been derived of the region close to the binary phases MgZn and $Mg_{51}Zn_{20}$ (Fig. 1). The reaction scheme requires a further transition reaction rather close to the ternary eutectic at 340°C. No experimental details are hitherto available regarding the sequence of the two reactions, which is due to the extremely close region of their appearence. Therefore, these two reactions were integrated into a degenerate rection $D_{1,2}$ at ~340°C slightly below the binary formation temperature of $Mg_{51}Zn_{20}$.

Liquidus Surface

A projection of the liquidus surface of the region between 0 and 80 mass% Mg showing the ternary eutectic E_1 has been given by [46Kor]. It is not reproduced here for two reasons: Firstly, the Ce used was of inadequate purity. Secondly, the location of the eutectic trough starting at the Ce-Mg binary and joining E_1 is only approximate according to [46Kor].

Isothermal Sections

[46Kor] gave a projection of the solubility isotherms for Mg-rich samples annealed at 335°C, 300°C, and 200°C, and for samples allowed to cool "slowly" to 20°C. Because of the low purity of Ce [46Kor] used, the values of the maximum combined solubilities of (Ce + Zn) in Mg (e.g., 4.9 mass% at 335°C) have to be considered only approximate. Nonetheless, it is evident that the combined solubility rapidly increases with increasing Zn content.

A partial isothermal section at 300°C has been evaluated by [78Mel] for the region Mg-$MgZn_2$-CeMg-CeZn (see Fig. 2). The tie line between τ_1 and $Mg_{51}Zn_{20}$ given by [78Mel] has been omitted because $Mg_{51}Zn_{20}$ is not stable at 300°C [92Aga]. Phase equilibria in this section are characterized by the existence of extended binary and ternary solid solutions, each at a constant Ce content.

Miscellaneous

Two vertical sections from Mg to 80 mass% $Ce_{10}Zn$ and from Mg to 80 mass% CeZn are given by [46Kor]. Although they were found to approximately comply with later data, they are not reproduced here due to the low purity Ce [46Kor] used. Two vertical sections have also been established by [89Dri] at 24 mass% Zn and 34 mass% Zn, both ranging from 0 to 20 mass% Ce. Both sections are reproduced in Figs. 3 and 4, repectively, with small changes to comply with the exact location of the Ce-poor boundary of the (Mg) + τ_2 two phase field in the isothermal section at 300°C established by [78Mel]. Details concerning the area near to the Mg-Zn binary system are schematically shown in Fig. 5.

Ageing, hardness, and corrosion behaviour of alloys were studied by [46Kor].

Further investigations in this system should focus on structure determination of the ternary compounds τ_1 and τ_3, and on experimental investigation of the unknown regions of the phase diagram.

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Table 1: Solid Phases

Phase/ TemperatureRange(°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
Mg	*hP*2	*a* = 320.94	[Mas2]
< 650	Mg	*c* = 521.07	
		a = 320.99	[V-C2]
		c = 521.08	
		a = 319.57	at 2.8 at.% Zn [V-C2]
		c = 518.82	linear dependency
Ce_5Mg_{41}	*tI*92	*a* = 1478	[Mas2, V-C2]
< 635	Ce_5Mg_{41}	*c* = 1043	
$CeMg_{10.3}$	*hP*38	*a* = 1033	[Mas2, V-C2]
621-611	Th_2Ni_{17}	*c* = 1025	
$CeMg_{12}$ (ß)	*oI*338		Pseudotetragonal long-range order
< 616	$CeMg_{12}$ (ß)	*a* = 1033	variant of $CeMg_{12}$ [65Woo]
		b = 1033	at 7.69 at.% Ce [65Woo]
		c = 7750	
		a = 1032.1	at 8.85 at.% Ce [79Dar]
		b = 1032.1	
		c = 7701	
		a = 1032.4	at 8.33 at.% Ce [79Dar]
		b = 1032.4	
		c = 7723	
		a = 1033.7	at 7.69 at.% Ce [79Dar]
		b = 1033.7	
		c = 7737	
		a = 1032.0	at 7.14 at.% Ce [79Dar]
		b = 1032.0	
		c = 7724	

Phase/ TemperatureRange(°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
$Mg_{51}Zn_{20}$ 325-341	*oI*158 $Mg_{51}Zn_{20}$	*a* = 1408.3 *b* = 1448.6 *c* = 1402.5	[V-C2] Composition $Mg_{0.718}Zn_{0.282}$ [92Aga]; labelled "Mg_7Zn_3" in [Mas2]
MgZn < 347	*oP*48 MgZn	*a* = 923 *b* = 533 *c* = 1760	Composition $Mg_{0.48}Zn_{0.52}$ [92Aga] [Mas2, 59Ray]
Mg_2Zn_3 < 416	*mC*110 Mg_4Zn_7	*a* = 2596 *b* = 524 *c* = 2678 *β* = 148.6°	[V-C2], labelled Mg_4Zn_7 Composition $Mg_{0.40}Zn_{0.60}$ [92Aga]
$MgZn_2$ < 587	*hP*12 $MgZn_2$	*a* = 522.3 *c* = 856.6	[92Aga, V-C2]
$CeMg_{1-x}Zn_x$ CeMg < 711 CeZn < 825	*cP*2 CsCl 	 *a* = 390.8 *c* = 390 *a* = 370.4 *c* = 371.3	0 ≤ x ≤ 1 at 300°C [78Mel] linear dependency, scaled from diagram [Mas2] [V-C2], at 25°C [78Mel], quenched from 300°C [Mas2] [V-C2] [78Mel]
$Ce(Mg_{1-x}Zn_x)_{12}$ (α)	*tI*26 $ThMn_{12}$		0 ≤ x ≤ 0.08 at 300°C [78Mel]
$CeMg_{12}$ (α) < 616		*a* = 1033 *c* = 596	[Mas2] [V-C2]
$CeMg_{12}$ (ß)			see above description
$Ce(Mg_{1-x}Zn_x)_3$ $CeMg_3$ < 798	*cF*16 BiF_3 	 *a* = 744.3 *a* = 742.8 *a* = 707.6	[Mas2] 0 ≤ x ≤ 0.39 at 300°C [78Mel], linear dependence at x = 0, at 300°C [V-C2] at x = 0, quenched from 300°C [78Mel] at x = 0.39, quenched from 300°C [78Mel]
* τ_1, $CeMg_7Zn_{12}$	*h*** ?	*a* = 1471.0 *c* = 880.0	[78Mel, 89Dri, 86Kin]
* τ_3, $CeMg_3Zn_5$	? ?	?	[78Mel]
* τ_4, $Ce(Mg,Zn)_3$	*cF*16 Li_2AgMg or $MnCu_2Al$	 *a* = 706.4(4) *a* = 701.1 *a* = 708.9	from 35 to 45 at.% Zn at 300°C [78Mel] for $CeMg_{1.5}Zn_{1.5}$ [77Mel, 78Mel] for $CeMg_{1.2}Zn_{1.8}$ [78Mel] for $CeMg_{1.6}Zn_{1.4}$ [78Mel]

Phase/ TemperatureRange(°C)	Pearson Symbol/ Prototype	Lattice Parameters (pm)	Comments
* τ_2, $Ce(Mg,Zn)_{10.1}$	*hP*38 Th_2Ni_{17}		from 9.1 to 45.5 at.% Zn at 300°C; possibly related to $CeMg_{10.3}$ [89Dri] labelled $Ce(Mg,Zn)_9$ by [78Mel]
		a = 1010 *c* = 997	at $Ce(Mg_{0.9}Zn_{0.1})_{10.1}$ [89Dri]
		a = 960 *c* = 947	at $Ce(Mg_{0.5}Zn_{0.5})_{10.1}$ [89Dri]

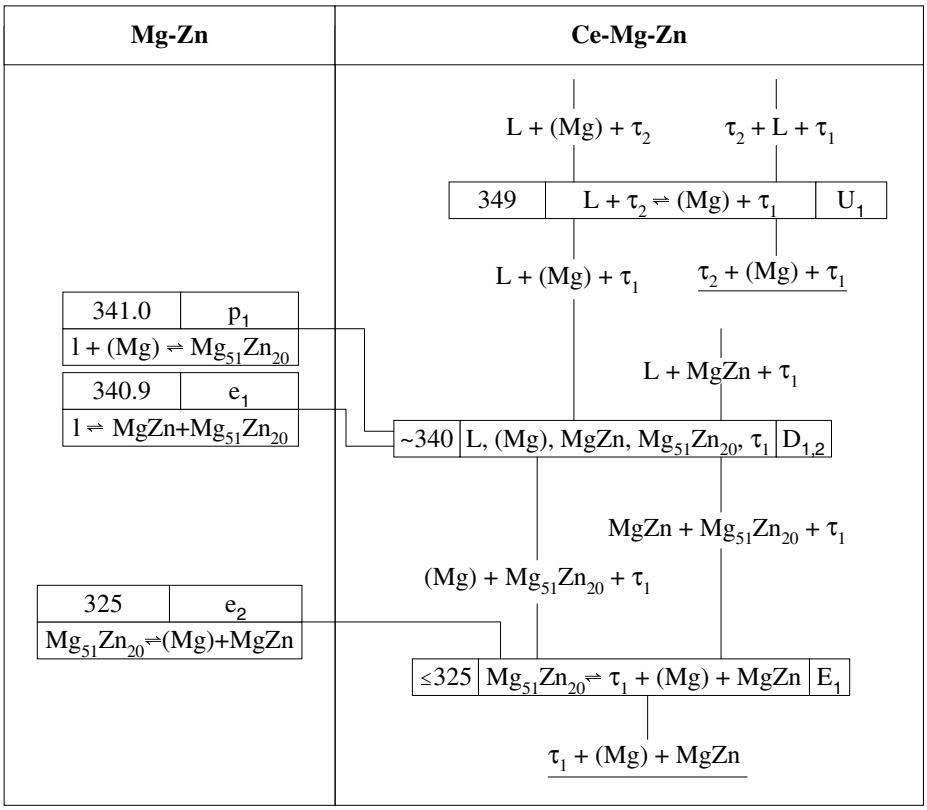

Figure 1: Reaction scheme

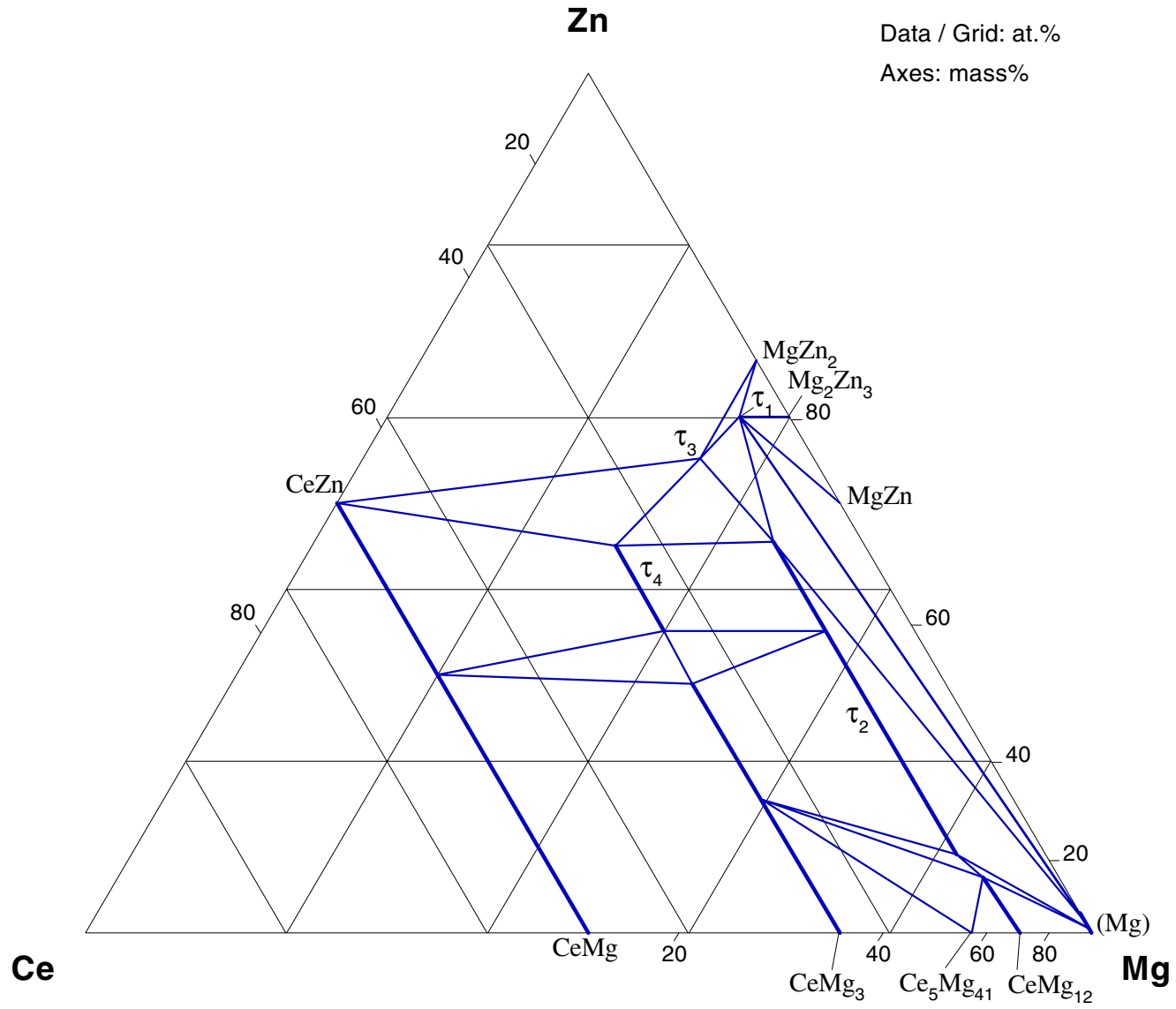

Figure 2: Partial isothermal section at 300°C

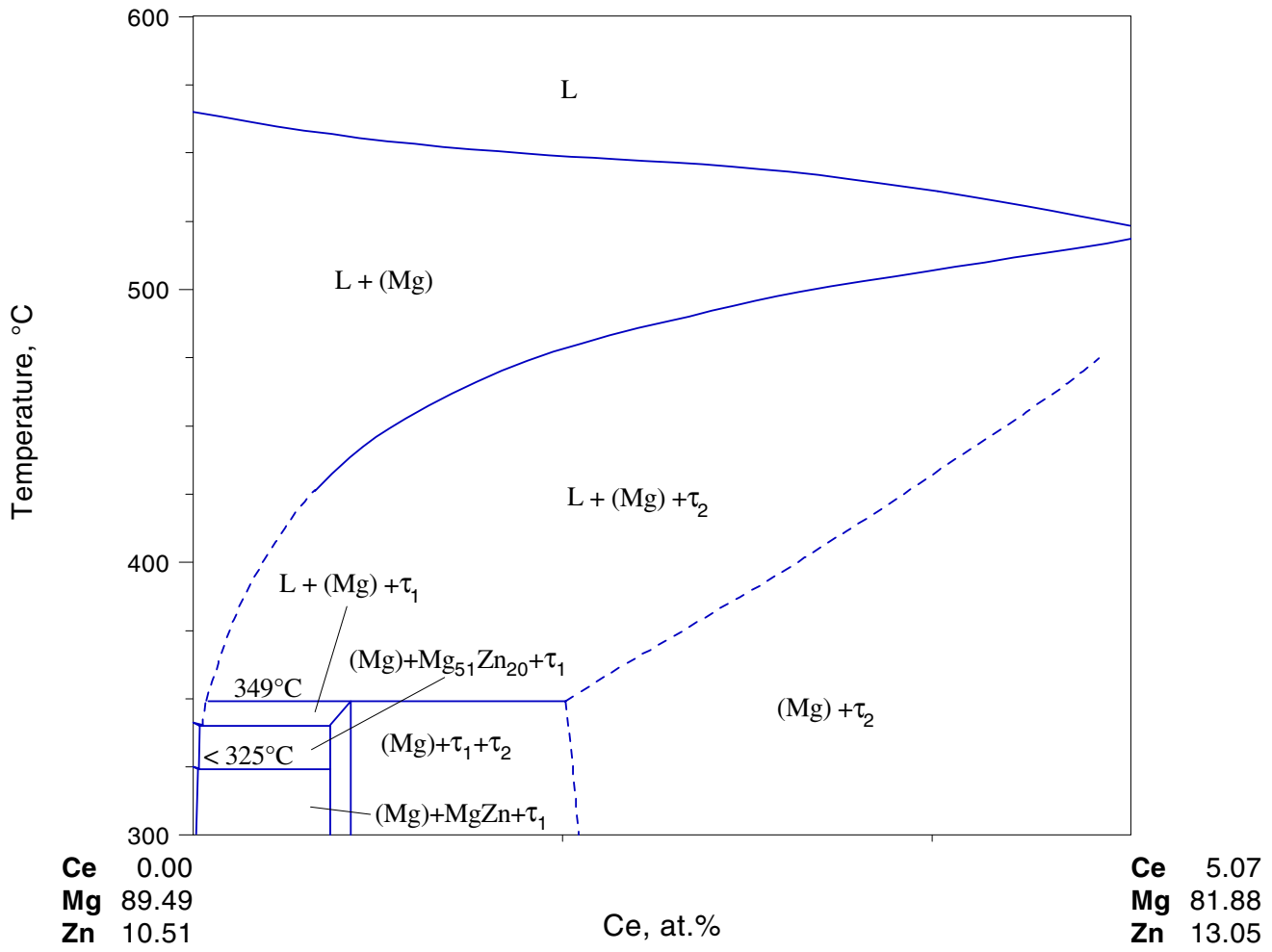

Figure 3: Vertical section at 24 mass% Zn

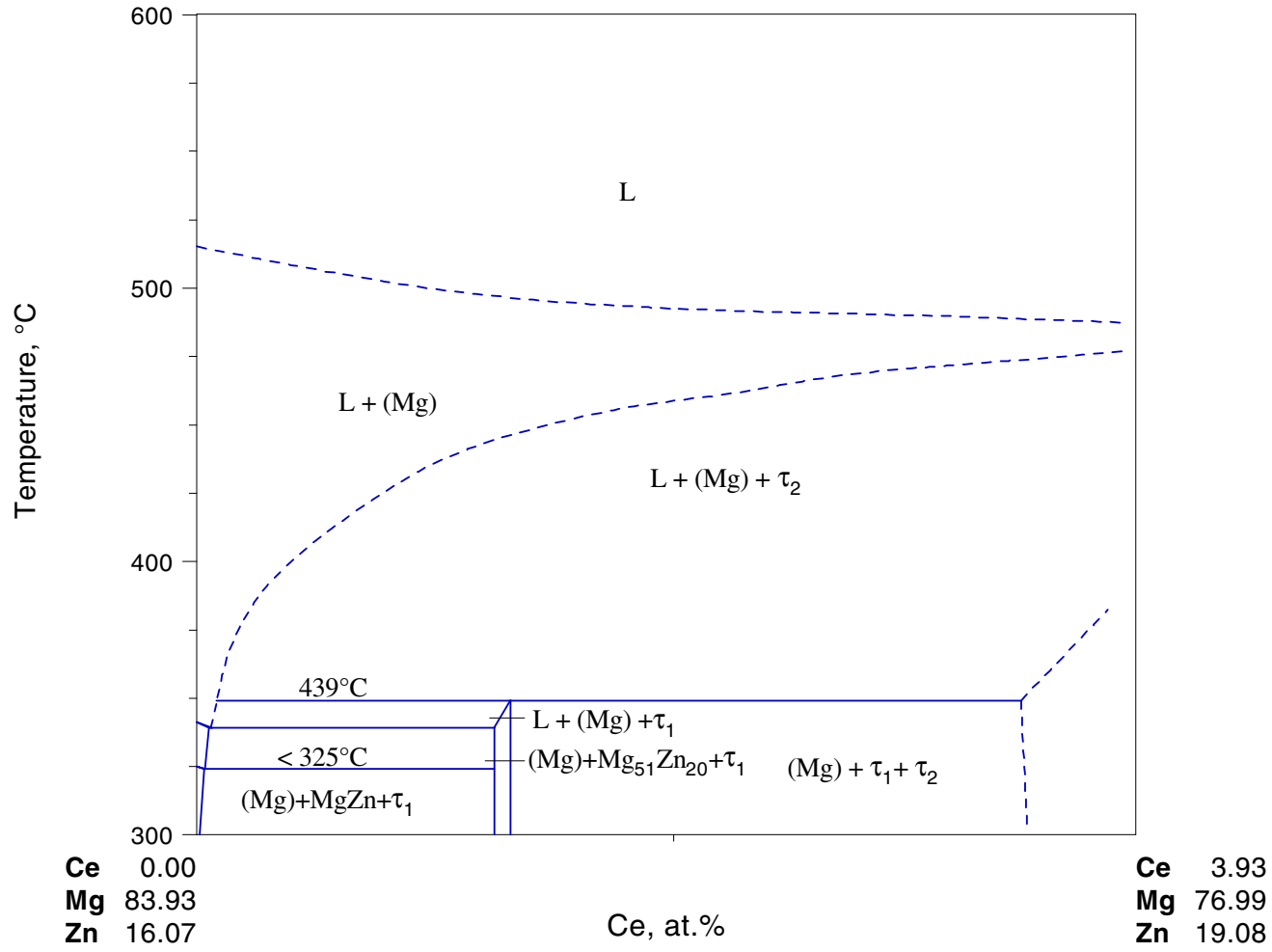

Figure 4: Vertical section at 34 mass% Zn

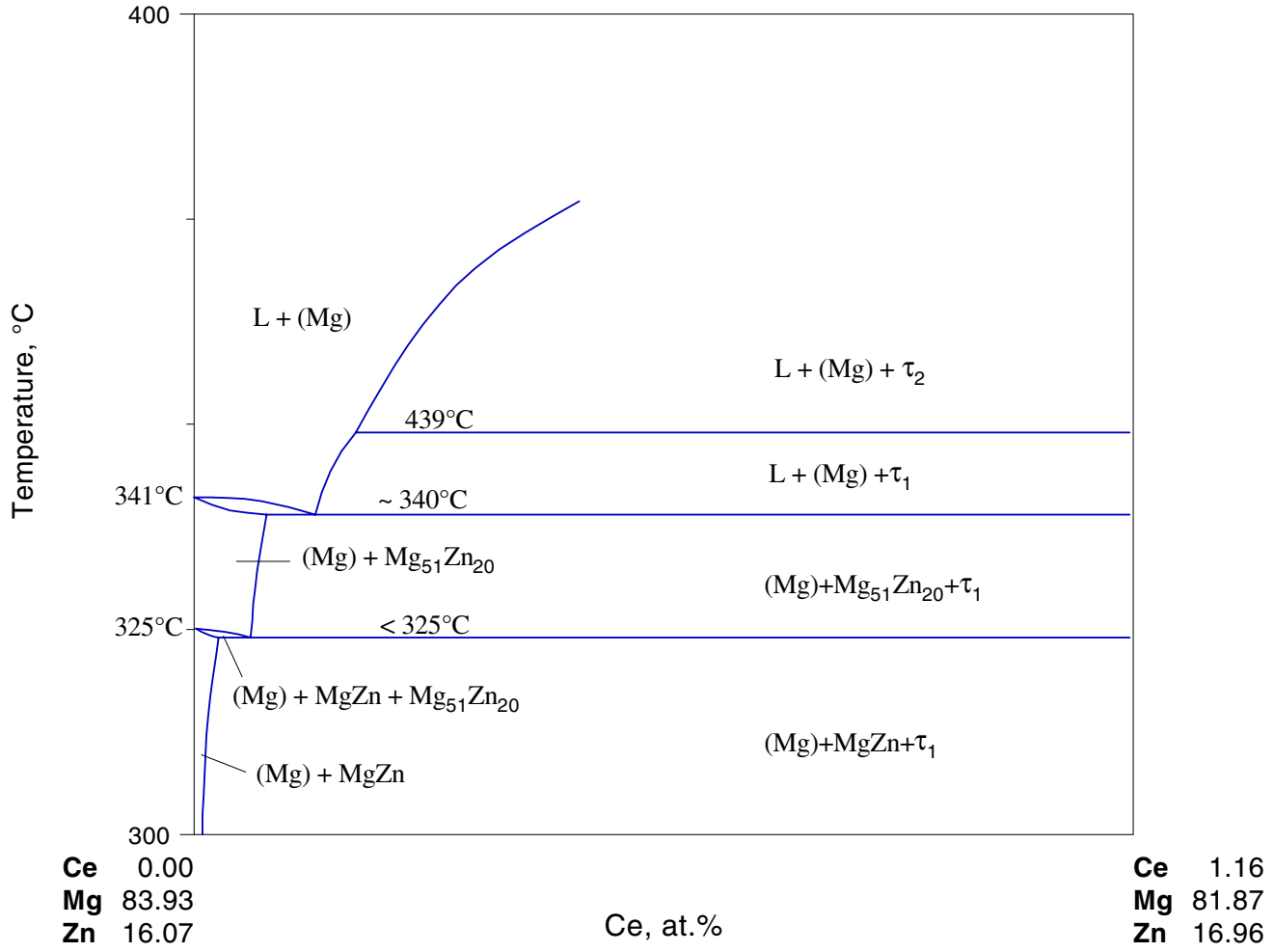

Figure 5: Schematic vertical section of the Ce - Mg - Zn phase diagram