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Thermodynamic modelling and *in-situ* neutron diffraction investigation of the (Nd + Mg + Zn) system

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ABSTRACT

All available phase diagram data for the (Nd + Mg + Zn) system were critically assessed. *In-situ* neutron diffraction (ND) experiments were performed on selected samples to identify phases and transition temperatures. A critical thermodynamic evaluation and optimization of the (Nd + Mg + Zn) system was carried out and model parameters for the thermodynamic properties of all phases were obtained. The phase transformation behaviour of selected samples was well resolved from the ND experiments and experimental values were used to refine the thermodynamic model parameters.

1. Introduction

Magnesium being the lightest structural metal, Mg-based alloys have many applications. Zinc is one of the most commonly used alloying elements in Mg (AZ series), and the rare earth (RE) metals have been shown to improve creep resistance [1,2] and sheet formability (by reducing texture [3–6]).

Information on phase behaviour is essential for the design of new (RE + Mg + Zn) alloys. However, few studies of the phase diagrams and thermodynamic properties of these systems have been made. The present study was thus undertaken to better define the phase diagrams of the (RE + Mg + Zn) ternary systems through the technique of critical thermodynamic assessment and optimization coupled with limited experimentation.

Thermodynamic evaluations and optimizations have already been reported for the binary (Mg + Zn) system [7], all binary (Mg + RE) systems [8–11] and all binary (RE + Zn) systems (including (Sc + Zn) and (Y + Zn)) [12,13]. The liquid phase of the (Mg + Zn) system has been re-modelled with the Modified Quasichemical Model (MQM) as will be discussed in Section 4. An evaluation, optimization and experimental phase diagram study of the (Ce + Mg + Zn) system has been reported previously [14]. In the present article we report on our evaluation, optimization and experimental phase diagram study of the (Nd + Mg + Zn) system. In subsequent articles we shall report on our evaluations and optimizations of other ternary (RE + Mg + Zn) systems [15,16]. As expected, all (RE + Mg + Zn) systems are very similar. The present work on the (Nd + Mg + Zn) system was greatly aided by our simultaneous assessments of all the other (RE + Mg + Zn) systems.

2. Phase equilibrium and thermodynamic data

The (Nd + Mg + Zn) system has been investigated by several research groups, who used different designations for the ternary phases. Phases with ternary phase fields considered in the present optimization are summarized in table 1. The nomenclature employed in our previous report on the (Ce + Mg + Zn) system [14] is used again here. Consequently, τ2, τ3, τ4, τ5 and τ7 are found in the (Nd + Mg + Zn) system while τ1 and τ6 are not. These two phases may be stable in the (Nd + Mg + Zn) system given that Ce and Nd have very similar properties. However, the existence of τ1 is in doubt and no detailed experimental investigation has been made in the composition range where τ6 might be found. Furthermore, neither τ1 nor τ6 has been reported in any (RE + Mg + Zn) system other than (Ce + Mg + Zn) [14]. Hence, they are not assumed in the (Nd + Mg + Zn) system. All phases shown in table 1 (except $Nd(Mg,Zn)_{12}$ which is not stable at 300 °C according to our calculations) can also be seen in the calculated isothermal section at 300 °C shown in figure 1.

The ternary compounds τ2, τ4, τ5 and τ7 are assumed to have the same stoichiometries as the corresponding phases in the (Ce + Mg + Zn) system [14] since the latter have been well studied.

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TABLE 1
Phases with ternary phase fields in the (Nd + Mg + Zn) system.

Phase name	Prototype-Pearson symbol-space group	Thermodynamic model	
Nd(Mg,Zn)	CsCl-cP2-$Pm\bar{3}m$ [19–21]	(Nd,Mg)(Mg,Zn)	NdMg and NdZn form continuous solution [17,19]
$NdMg_3$	BiF_3-cF16-$Fm\bar{3}m$ [19]	(Nd,Mg)(Mg,Zn)$_3$	Reported Zn solubility 40 at.% at 297 °C [19] Reported Zn solubility 50 at.% at 320 °C [17] Reported Zn solubility 30 at.% at 300 °C [18]
Nd(Mg,Zn)$_{12}$	$Mn_{12}Th$-tI26-I4/mmm [19]	Nd(Mg,Zn)$_{12}$	Reported as $NdMg_6Zn_3$ in reference [19], as Nd(Mg,Zn)$_{11.5}$ in reference [22] with Zn content 26.9 to 41.3 at.% Reported as *T*-Nd(Mg,Zn)$_{12}$ and τ1 in reference [17] and *T* in reference [18]
[a]τ1	[b]$Al_{11}La_3$-oI28-Immm		
τ2	Unknown	$Nd_2Mg_{53}Zn_{45}$	Assumed stoichiometric in present study. Reported as τ4 in reference [18]
τ3	$MnCu_2Al$-cF16-$Fm\bar{3}m$ [19,23]	NdMg(Mg,Zn)$_2$	Reported as X in references [24–28] Reported as B ($Nd_3Mg_8Zn_{11}$) in reference [19] Reported as τ3 in reference [18] and *T'* in reference [17]
τ4	[b]$TbCu_7$-hP8-P6/mmm	$Nd_2Mg_5Zn_9$	Assumed stoichiometric in present study Reported as τ2 in reference [17], τ1 in reference [18] Reported as D ($Nd_2Mg_7Zn_{11}$) in reference [19]
τ5	[b]$Ce_3Mg_{13}Zn_{30}$-hP92-P6$_3$/mmc	$Nd_3Mg_{13}Zn_{30}$	Assumed stoichiometric in present study Reported as C ($NdMg_7Zn_{12}$) in reference [19], τ5 in reference [18]
[a]τ6	Unknown		
τ7	[b]$Ce_{20}Mg_{19}Zn_{81}$-cF480-$F\bar{4}3m$	$Nd_{20}Mg_{19}Zn_{81}$	Assumed stoichiometric in present study Reported as τ6 in reference [18]

Elements within brackets substitute on the same sublattice.
[a] Possible stable phase not considered in the present work. τ1 was modelled as $Ce_3Zn_9(Mg,Zn)_2$ and τ6 was modelled as $Ce_6Mg_{11}Zn_{83}$ in the (Ce + Mg + Zn) system. Please refer to reference [14] for details.
[b] Crystal structure of these phases are proposed based on crystallographic information from similar phases in the (Ce + Mg + Zn) system [14].

As mentioned previously [14], limited ternary homogeneity ranges were reported for τ4, τ5 and τ7 in the (Ce + Mg + Zn) system. For lack of evidence to the contrary, these phases are all assumed to be stoichiometric compounds in the (Nd + Mg + Zn) system.

The phase Nd(Mg,Zn) in table 1 is a solid solution of NdMg and NdZn. The phase $NdMg_3$ is a solution with limited solubility of Zn. $NdMg_{12}$ and $NdZn_{12}$ (both of the $Mn_{12}Th$ structural prototype) are metastable in their respective binary systems; however, their solution has been reported to be stable in the ternary composition region according to several investigators as summarized in table 1. Although some limited solubility of Mg in $NdZn_2$, $NdZn_3$, Nd_3Zn_{11}, $Nd_{13}Zn_{58}$, α-Nd_2Zn_{17} and Nd_3Zn_{22} and of Zn in Nd_5Mg_{41} has been reported [17,18], as will be discussed later in this section, it is likely that the samples were not at equilibrium; hence, we have assumed that these and all other binary phases do not extend into the ternary system. The prototypes, Pearson symbols and space groups of all binary phases were given previously [7,8,12].

Using thermal, micro-structural and micro-hardness analysis, Drits *et al.* [24] investigated the (Nd + Mg + Zn) system in the Mg-rich region. Five isopleths were investigated but only the three shown in figure 2 were reported. Three ternary compounds (X, Y and Z) were proposed but their compositions were not given. Four invariant reactions were also reported:

$$L \longleftrightarrow (Mg) + Nd_5Mg_{41} + X \text{ at } 520 \pm 3\ ^\circ C, \quad (1)$$

$$L + X \longleftrightarrow (Mg) + Y \text{ at } 473 \pm 3\ ^\circ C, \quad (2)$$

$$L + Y \longleftrightarrow (Mg) + Z \text{ at } 440 \pm 3\ ^\circ C, \quad (3)$$

$$L \longleftrightarrow (Mg) + Mg_{51}Zn_{20} + Z \text{ at } 336 \pm 3\ ^\circ C. \quad (4)$$

Three partial isothermal sections (200, 250 and 300 °C) in the Mg-rich region were established by the same group using micro-structural analysis [25]. However, the compositions and crystal structures of the three ternary compounds were still not resolved. Four partial isothermal sections (200, 300, 400 and 500 °C) in the Mg-rich region, as well as the compositions of the three ternary compounds, were later proposed by the same group [27,28]. The three ternary compounds were proposed as $MgNd_4Zn_5$, $Mg_6Nd_2Zn_7$ and $Mg_2Nd_2Zn_9$ according to X-ray spectral analysis. However, the compositions were determined from samples containing yttrium, thereby casting doubt on the results. None of these isothermal sections have been considered in the present study because only very limited composition ranges were examined.

The (Nd + Mg + Zn) system was later investigated by Kinzhibalo *et al.* [19] over the entire composition range by X-ray diffraction (XRD). An isothermal section at 297 °C was established and four ternary compounds were reported: $NdMg_6Zn_3$, $Nd_3Mg_8Zn_{11}$, $Nd_2Mg_7Zn_{11}$ and $NdMg_7Zn_{12}$. $Nd_3Mg_8Zn_{11}$ was reported to have

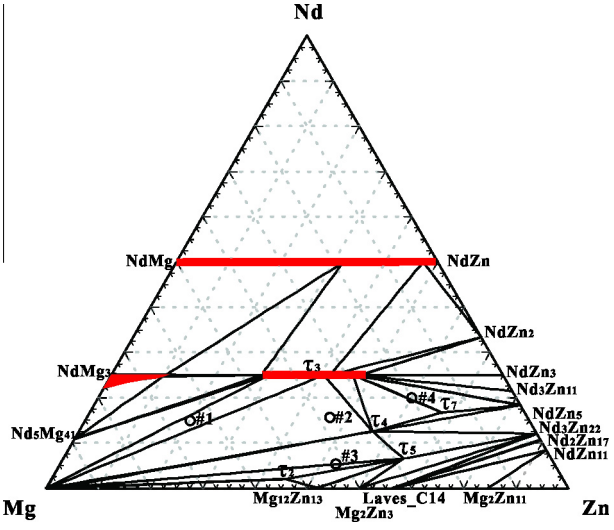

FIGURE 1. Calculated optimised isothermal section of the (Nd + Mg + Zn) system at 300 °C showing the compositions of the four samples in the present ND experiments (mole fraction). The ternary compounds τ2, τ4, τ5 and τ7 are assumed to have the same.