THE Mg-Mn-Nd SYSTEM: EXPERIMENTAL INVESTIGATION COUPLED WITH THERMODYNAMIC MODELING

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Abstract

The Mg-Mn-Nd phase diagram was experimentally investigated using differential scanning calorimetry (DSC) to verify the phase transformation temperatures and X-ray diffraction (XRD) for phase identification. The system was thermodynamically modeled using the CALPHAD approach. The Quasi-chemical model (QCM) was used to describe the liquid phase of each constituent binary. The intermediate solid solubilities were modeled by the compound energy formalism (CEF), and the terminal solution phases were modeled as substitutional solutions using the random mixing model. XRD results were used to describe the phase relationships for the annealed samples at 450°C. The preliminary calculations of the isothermal section at 450°C were found to be in general agreement with experimental results. Two different vertical sections were calculated and compared with the experimental results obtained by DSC.

Introduction

Magnesium and its alloys have an increasingly important role in structural automotive parts and electronic consumable products where weight saving is important. Magnesium alloys containing manganese and neodymium exhibit very good mechanical properties at elevated temperatures [1]. Magnesium is alloyed with rare earth elements to overcome the poor mechanical performance at elevated temperature [2]. This is attributed to the formation of the fine Mg_xNd_y intermetallic stable compounds at the grain boundaries [3]. Besides, addition of Mn increases the corrosion resistance and the creep behavior of Mg alloys [4]. Therefore, it is necessary to understand the phase equilibria in the Mg-Mn-Nd ternary phase diagram to allow for better alloy design and development.

The available information on the constituent binary systems was used to extrapolate the thermodynamic description of the Mg-Mn-Nd ternary system. The Mg-Mn system model is taken from Asgar-Khan and Medraj [5] who used the modified quasi-chemical model (MQC) to describe the liquid phase. Although Kang et al. [6] also modeled the system using MQC, their model is not adopted in the present work, because their estimated value of the critical temperature of the liquid miscibility gap is much lower than the value calculated by Gröbner et al. [7]. Asgar-Khan and Medraj [5] model, however, showed good compliance with the experimental results of Gröbner et al. [7]. Asgar-Khan and Medraj [5] model, however, showed good compliance with the experimental results of Gröbner et al. [7].

The liquid phase of the Mg-Nd system was remodelled in this work. The $Mg_{41}Nd_5$, Mg_3Nd, and Mg_2Nd phases are treated as stoichiometric compounds [8, 9]. The HCP(Mg), dHCP(α-Nd), and BCC-A2 solution phases were described with a substitutional solution model. The Mn-Nd system was investigated experimentally in this work and found to be different from what was earlier reported. The experiments proved the existence of two solubility ranges of Mn in HCP (α-Nd) and BCC (β-Nd). Hence, this system was remodeled during this work.

Very limited experimental work on the Mg-Mn-Nd phase diagram was available in the literature. The system was first assessed by Drits et al. [1] using thermal analysis, microscopic investigation, and electrical resistivity measurements. The study was limited to the Mg-rich corner up to 4 wt%

Mn and 10 wt% Nd to determine the boundaries of the solid solution region (by rapid quenching and annealing at 570°C, 600°C, and 630°C). As a result of resistivity measurements, a peritectic reaction L+Mn ↔ α+Mg_9Nd was reported at 559.6°C. Also, two phases, Mn and Mg_9Nd, were found to be in equilibrium with the Mg-based solid solution. Since their study [1] was focused on obtaining the ranges of the Mg-based solid solution no information was reported on the phase relations or liquidus temperatures in the studied region. The results obtained by Drits et al. [1] were used later by Drits and Bochvar [10] to improve the thermal expansion properties of the Mg-Mn-Nd-Ni quaternary alloys. They concluded that, addition of Ni to the ternary alloy resulted in lower amounts of Mn and Nd in the solid solution [10]. No information on the thermodynamic description of the Mg-Mn-Nd ternary system was found in the literature. In this work, the Mg-Mn-Nd ternary diagram is modeled using CALPHAD method. CALPHAD method is based on the fact that a phase diagram is a representation of the thermodynamic properties of a system. The core idea is to extrapolate the equilibrium and thermodynamic information from binary systems to ternary and higher-order systems [11]. The Mg-Nd, Mn-Nd, and Mg-Mn constituent binaries are used to construct the Mg-Mn-Nd ternary system using the quasi-chemical model for the liquid phases, and the random solution model for the terminal solid solution phases. The intermediate solid solution BCC-B2 in the Mg-Nd binary system is modeled by the compound energy formalism (CEF).

Experimental procedure

The samples were prepared from the pure elements using an arc melting furnace with a water cooled copper crucible under argon using a non-consumable tungsten electrode. The samples were melted several times to ensure homogeneity. ICP analysis was carried out to obtain the actual global composition of the samples. Part of magnesium content was found to evaporate during melting due to alloying with comparatively high melting temperature elements (Mn= 1246°C and Nd=1025°C). The samples were wrapped in tantalum foil and encapsulated under argon-filled quartz tube then annealed at 450°C for one week then quenched in cold water. After annealing, a SETARAM-Setsys1200 differential scanning calorimeter (DSC) was used to investigate the phase transformations and melting temperature of the prepared samples using heating and cooling rates of 10K/min. The DSC cycles were repeated at least three times for each sample to ensure the reproducibility of the results. Graphite crucibles were not used because carbide formation occurred in the samples, and extra peaks in the DSC curve were detected. Therefore, alumina crucibles were used to avoid any reaction between the sample and the crucibles. The device was calibrated using a set of pure elements Zn, Al, Ag, Cu and Au. XRD analysis was performed from 20° to 120° with 0.02° step size to measure the relative amounts of the examined phases using Rietveld analysis. Eight compositions of Mg-Mn-Nd ternary alloys shown in Figure 1 were investigated.

Results and discussion

Based on the experimental data, the location of pertinent solid phases of the Mg-Mn-Nd system at 450°C is presented in the calculated isothermal section as shown in Figure 1. The samples were chosen to cover systematically the full ternary phase diagram. Table 1 shows the results of the identified phases using XRD analysis. The calculated isothermal section showed good agreement with experimental results from samples #2, #4, #5, #7, and #8. Three phases were observed in sample #1; traces of Mn, Mg_3Nd, and an unknown phase as shown in the XRD results in Figure 2. Similar peaks of the unknown phase were detected in sample #3. This indicates that a ternary compound may exist in these samples.

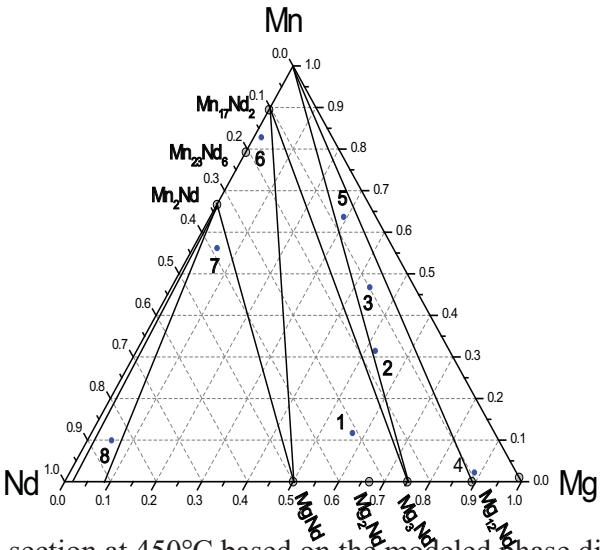

Figure 1: Isothermal section at 450°C based on the modeled phase diagram and the actual compositions of the samples

Table 1: The actual compositions of the prepared samples in at% and the XRD results of the annealed samples at 450°C

Sample #	Composition at%			Identified phases using XRD		
	Mg	Mn	Nd			
1	57.12	11.73	31.16	Mn	Mg_3Nd	Unknown
2	52.24	31.47	16.29	Mn	Mg_3Nd	
3	43.39	46.78	9.84	$Mg_{12}Nd$	Mg_3Nd	Unknown
4	88.59	2.22	9.20	$Mg_{12}Nd$	Mg_3Nd	
5	29.20	63.73	7.07	Mn	Mg_3Nd	
6	1.60	82.86	15.54	Mn	Mn_2Nd	
7	5.24	56.20	38.56	MgNd	$Mn_{23}Nd_6$	
8	5.26	9.96	84.78	MgNd	Mn_2Nd	

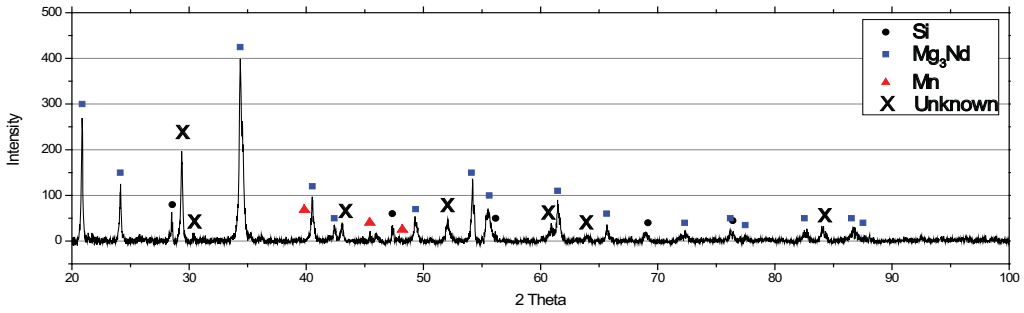

Figure 2: The XRD pattern of sample #1

The $Mn_{23}Nd_6$ and MgNd phase fields were positively identified through samples #7 and #8 respectively. The as cast pattern of sample #6 showed primary Mn precipitates; this may be due to the tendency of Mn to form very fine precipitates during solidification [12]. After annealing, Mn peaks became stronger as illustrated in Figure 3 due to the continuation of Mn precipitation during annealing. The Si peak was used as a calibration standard for the peaks position and displacement.

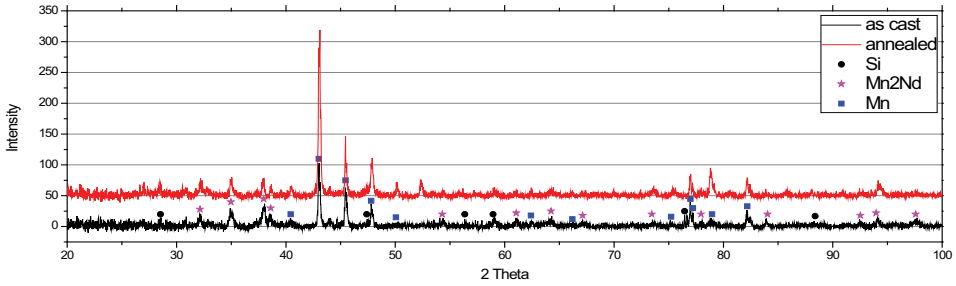

Figure 3: Comparison between the XRD patterns of the as-cast and annealed conditions of sample #6. The intensity of Mn peaks is higher in the annealed sample.

The experimental data was superimposed on the calculated vertical sections of the phase diagram and compared with the calculated phase transformations. The examples of such comparisons are presented in Figure 4

(a) (b)

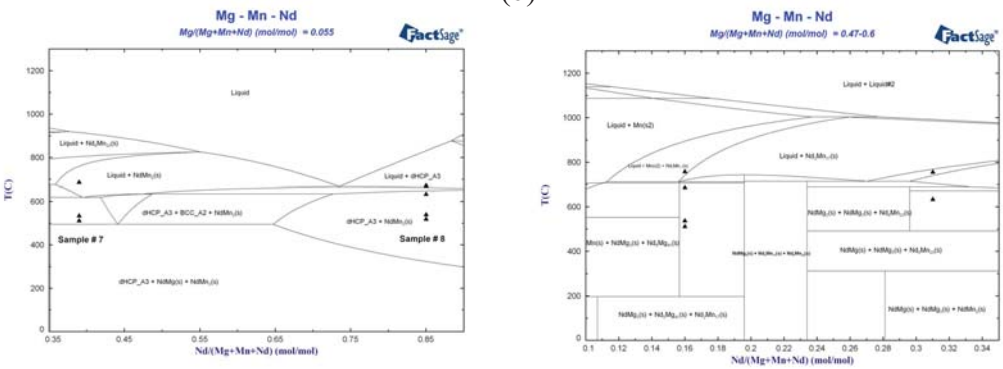

Figure 4: Two calculated vertical sections compared with the DSC experimental data

Five from the eight samples have shown good correspondence with the thermodynamic calculations. Three samples have demonstrated several signals that deviate from the calculated phase transformations as shown in Figure 4 (a). Additional EPMA and DSC study is ongoing to clarify these deviations. The presence of ternary compound may be the cause of the discrepancies.

The DSC curve of sample #2 (heating and cooling cycles) are shown in Figure 5. Three peaks were identified during heating and cooling. The difference between the onset of heating and onset of cooling for the first peak refers to super cooling [13]. The other onsets show good correspondence with each other. The phase transformations in the vertical section (Figure 4 (b)) were identified experimentally in Figure 5. However, it was difficult to identify the liquidus temperature of sample #2 due to the presence of the miscibility gap between Mg and Mn in the system.

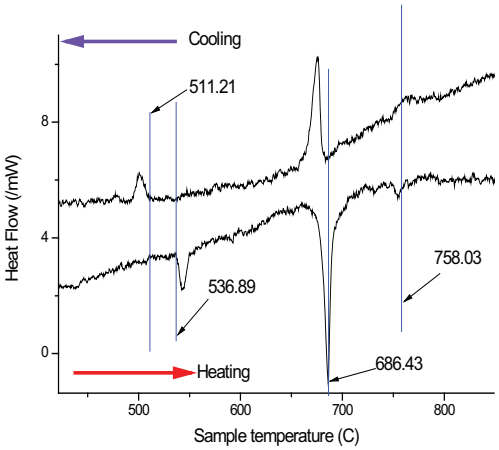

Figure 5: The DSC curve of sample #2 showing the phase transformation peaks of 10°C/min heating and cooling cycles

Conclusions

The phase relationships of the Mg-Mn-Nd system at 450°C are determined. The isothermal section at 450°C is constructed experimentally using XRD study. The ternary system is thermodynamically modeled using CALPHAD approach and the FactSage™ software package, taking into account all the experimental results. DSC results of the phase transformation temperatures were compared with two vertical sections. The thermodynamic model has shown a reasonable agreement with the experimental results. Further work on determining the phase regions, invariant points, and solid solubilities using key samples and diffusion couples experiments is underway using EPMA study.

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