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Ternary intermetallic compounds across the Mg-NiY line at 673 K

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Abstract

The phase relationship of the Mg-Ni-Y system along the Mg-NiY line has been investigated using electron probe micro analysis (EPMA) at 673 K. Three two phase regions (Mg_2Y+τ_6, Mg_2Y+ $MgNiY(\tau_3)$, MgY+$Mg_3Ni_2Y_4(\tau_1)$) and two three phase regions (Mg_2Y+$Mg_3Ni_2Y_4(\tau_1)$+ $MgNi_2Y_2(\tau_2)$ and NiY+$Mg_3Ni_2Y_4(\tau_1)$+$MgNi_2Y_2(\tau_2)$) have been identified. One new ternary compound $Mg_5NiY(\tau_5)$ was found and reported for the first time. Ternary solubility of the $Mg_{8\text{-}13}NiY(\tau_6)$ compound has been established which extends from 77.10 at.% Mg until 86.77 at.% Mg along the Mg-NiY section. Solubility of the third element in the binary compounds, NiY, Mg_2Y and MgY has also been determined.

Introduction

The Mg-Ni-Y system is an important alloy system because of its significance in the production of the nickel-metal hydride batteries (MH). Batteries are useful source of energy for spacecraft, military and defense, communication, power tools and consumer appliances because of their ability to store energy in a clean, convenient and efficient manner. Hence there is a growing need for high-specific power, high-specific energy and low-cost batteries [1].Because of the environmental concern and low capacity of the existing nickel/cadmium rechargeable batteries, reliable substitute for cadmium is required. The nickel-metal hydride battery (MH) with a hydrogen storage alloy as a negative electrode has shown a high potential in that aspect [1,2]. That is why extensive attention has been paid to the utilization of magnesium-based alloys as hydrogen storage materials owing to their high storage capacity and low density [3]. The Mg-Ni-Y system is considered to be one of the promising candidates [1]. Besides, this ternary is one of the promising Mg-based metallic glass systems [4]. Therefore, understanding the phase relationship in this system would be vital for identifying promising alloys for the above mentioned purposes.

Limited investigation has been done on the Mg-Ni-Y system. An isothermal section at 673 K of the Mg-Ni-Y system (Ni ≥ 50%) was investigated by Yao et al. [5] who confirmed the existence of two ternary compounds Mg_2Ni_9Y and $MgNi_4Y$ at 673 K. The compositions of these ternary compounds were reported earlier by Kadir et al. [6-8] and Aono et al. [9]. Combining all the available information, Mezbahul-Islam and Medraj [10] thermodynamically modeled this system. They used the modified quasichemical model [11-13] for the liquid phase in order to account for the tendency of short range ordering in the liquid. On the basis of their thermodynamic model of the system [10],

another experimental investigation on this system has been performed by the same authors [14], where they reported five new ternary compounds. But they [14] did not mention the phase relationship between these compounds. In this paper, EPMA analysis has been carried out on key alloys to establish the equilibrium phase triangulations along the Mg-NiY line of the Mg-Ni-Y system at 673 K.

Experimental Procedure

The alloys for the experiments were prepared at CANMET-MTL and Concordia University. High purity elements (Mg-99.8 wt.%, Ni-99.9 wt.%, and Y-99.9 wt.%) were used at both places. Samples 1 and 4 were prepared at CANMET where first, Cu was melted under protective argon flow and was covered by graphite pellet at 1773 K. Then Y was added and temperature was lowered to 1173 K and held until it dissolved completely. The Mg was plunged with graphite rod below 1353 K. The furnace power was lowered and the melt was stirred slowly with graphite rod and let to solidify in the crucible. Samples 2, 3 and 5 were prepared at Concordia University using the induction melting furnace under flowing argon. The metals in proper proportions were molten in a water cooled Cu crucible. During the process, the induction coil generates a magnetic field that induces eddy current in the metals that heats the samples. This is a clean and convenient way of preparing alloys. The actual global compositions of the samples were identified by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The samples were annealed at 673 K for 4 weeks. These were then characterized by light optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) using point and line scans. The error of the EPMA measurements was estimated to be ±2 at.%. This value was obtained from the comparison and statistical analysis of the compositions of selected phases from several samples.

Results and Discussion

In order to construct the isothermal section of the Mg-Ni-Y system, several samples have been prepared based on the current literature data [10,14]. The preliminary results have shown formation of the several intermetallic phases along the Mg-NiY section of the system. Therefore, this section was investigated in more details and results of this study are presented in this work.
Five ternary samples were prepared near the Mg-NiY section to determine corresponding phases and their relations with the binary intermetallics. The samples were investigated using ICP and EPMA analysis. The results are summarized in Table 1. Each composition presented in Table 1 is an average value of at least 3 EPMA measurements on different spots. The SEM images of the alloys are shown in Figure 1. Based on these results a partial isothermal section at 673 K for the Mg-Ni-Y system has been proposed in Figure 2.

Some of the binary intermetallic compounds have been found to have ternary solubility. The MgY phase has been found to have approximately 4 at.% Ni solubility. The SEM image of sample 1, in Figure 1(a), shows the coexistence of MgY with τ_1 and the eutectic structure. The ternary solubility of Mg_2Y has been detected by the EPMA measurements during the analysis of samples 2 and 3. Their microstructures are presented in Figures 1(b) and 1(c) and the phase compositions have been listed in Table 1. It shows limited solubility of Ni (approximately 1 at.%) in the Mg_2Y compound. Also, limited solubility of NiY (approximately 0.60 at.% of Mg) was found in sample 4 (see Figure 1(d)) by the EPMA measurement as listed in Table 1.

Five ternary compounds in the region of interest were determined and describe in our previous work [14]. One new ternary compound, τ_5, has been identified near the Mg-rich corner as can be seen in the SEM image of the sample 5 in Figure 1(e). The results of EPMA measurement of this sample are listed in Table 1. Based on this data, we assigned the Mg_5NiY composition for this compound. The microstructure shows that this phase is in equilibrium with τ_3 and τ_6.

Table 1: EPMA data on selected Mg-Ni-Y alloys annealed 4 weeks at 673 K

Sample no.	Actual Composition by ICP (at.%) Mg; Ni; Y	Phases	Compositions By EPMA (at.%) Mg; Ni; Y
1	39.10; 19.69; 14.21	$Mg_3Ni_2Y_4(\tau_1)$ MgY Eutectic	33.84; 21.71; 44.45 47.07; 3.99; 48.95 Not determined
2	52.86; 14.47; 32.67	$Mg_3Ni_2Y_4(\tau_1)$ Mg_2Y $MgNi_2Y_2(\tau_2)$	32.95; 24.75; 42.29 71.50; 0.71; 27.79 22.03; 37.06; 40.91
3	54.01; 15.97; 30.01	$MgNi_2Y_2(\tau_2)$ $MgNiY(\tau_3)$ $Mg_{8\text{-}13}NiY(\tau_6)$ Mg_2Y	21.76; 37.73; 40.50 35.35; 31.55; 33.09 77.10; 9.22; 13.68 73.37; 1.16; 25.47
4	29.25; 25.66; 45.09	NiY $MgNi_2Y_2(\tau_2)$ $Mg_3Ni_2Y_4(\tau_1)$	0.59; 49.11; 50.30 20.76; 37.93; 41.31 33.97; 21.91; 44.12
5	69.07; 9.45; 21.48	$Mg_{8\text{-}13}NiY(\tau_6)$ $Mg_5NiY(\tau_5)$ $MgNiY(\tau_3)$	78.67; 8.92; 12.41 70.35; 12.69; 16.96 36.48; 31.08; 32.45

The existence of τ_6 compound has been confirmed by the analysis of samples 3 and 5, as can be seen in Figures 1(c) and (e). The EPMA measurement listed in Table 1, confirmed our previous study [14] that revealed a large solubility of this compound which extends from 77.10 at.% Mg to 86.77 at.% Mg with almost equal amount of Ni and Y.

The SEM image of sample 4 in Figure 1(d) shows the equilibrium relation among τ_1, τ_2 and NiY. Therefore, a phase triangulation has been established among them as can be seen in Figure 2. The τ_1 is the dominating phase in the sample, because the actual composition of this sample is very close to the composition of this compound. The second triangulation among τ_1, τ_2 and Mg_2Y phases has been established based on the phase analysis of sample 2 (Figure 1(b)) where they are in equilibrium with each other.

A two phase region between τ_1 and MgY can be seen in the SEM image of the sample 1 in Figure 1(a). These two phases coexist with the eutectic structure. The τ_2-τ_3 phase equilibrium was detected in sample 3. As shown in Figure 1(c), the τ_3 phase always surrounds τ_2 phase. This indicates a congruent melting of the τ_2 compound. The τ_3 is a peritectic phase that is formed around τ_2 compound. We can expect that in this sample τ_2 will be transformed to τ_3 phase after a very long heat treatment process. Analyzing this sample, equilibrium between τ_3 and Mg_2Y as well as Mg_2Y and τ_6 phases can be recognized. Also, sample 5, in Figure 1(e), show the equilibrium relation between the τ_5 and τ_6 phases.

Sample 3, located near the central part of the triangle did not reach complete equilibrium even after sufficient heat treatment. Basically, it showed most of the ternary compounds existing between 20 to 80 at.% of Mg with low contrast, which makes their identification difficult. This can be seen in the SEM image in Figure 1(c), where τ_2, τ_3 and τ_6 coexist with Mg_2Y. However, by assuming local equilibrium between the contacting phases valuable information was extracted.

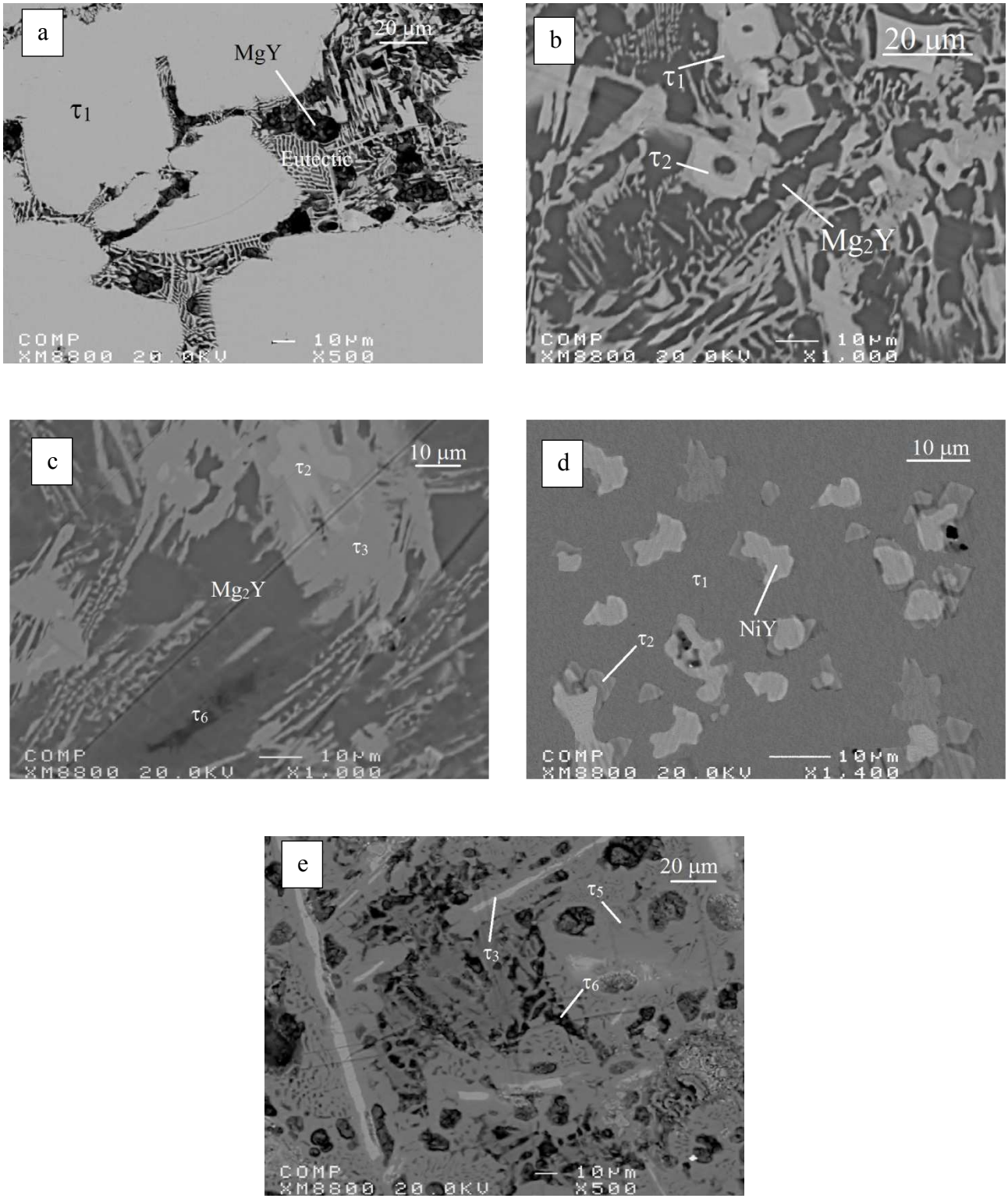

Figure: 1 SEM image of the selected Mg-Ni-Y samples: (a) Sample 1 (39.10/19.69/14.21 Mg/Ni/Y at.%); (b) Sample 2 (52.86/14.47/32.67 Mg/Ni/Y at%.); (c) Sample 3 (54.01/15.97/30.01 Mg/Ni/Y at.%); (d) Sample 4 (29.25/25.66/45.09 Mg/Ni/Y at.%); (e) Sample 5 (69.07/9.45/21.48 Mg/Ni/Y at.%) annealed for 4 weeks at 673 K.

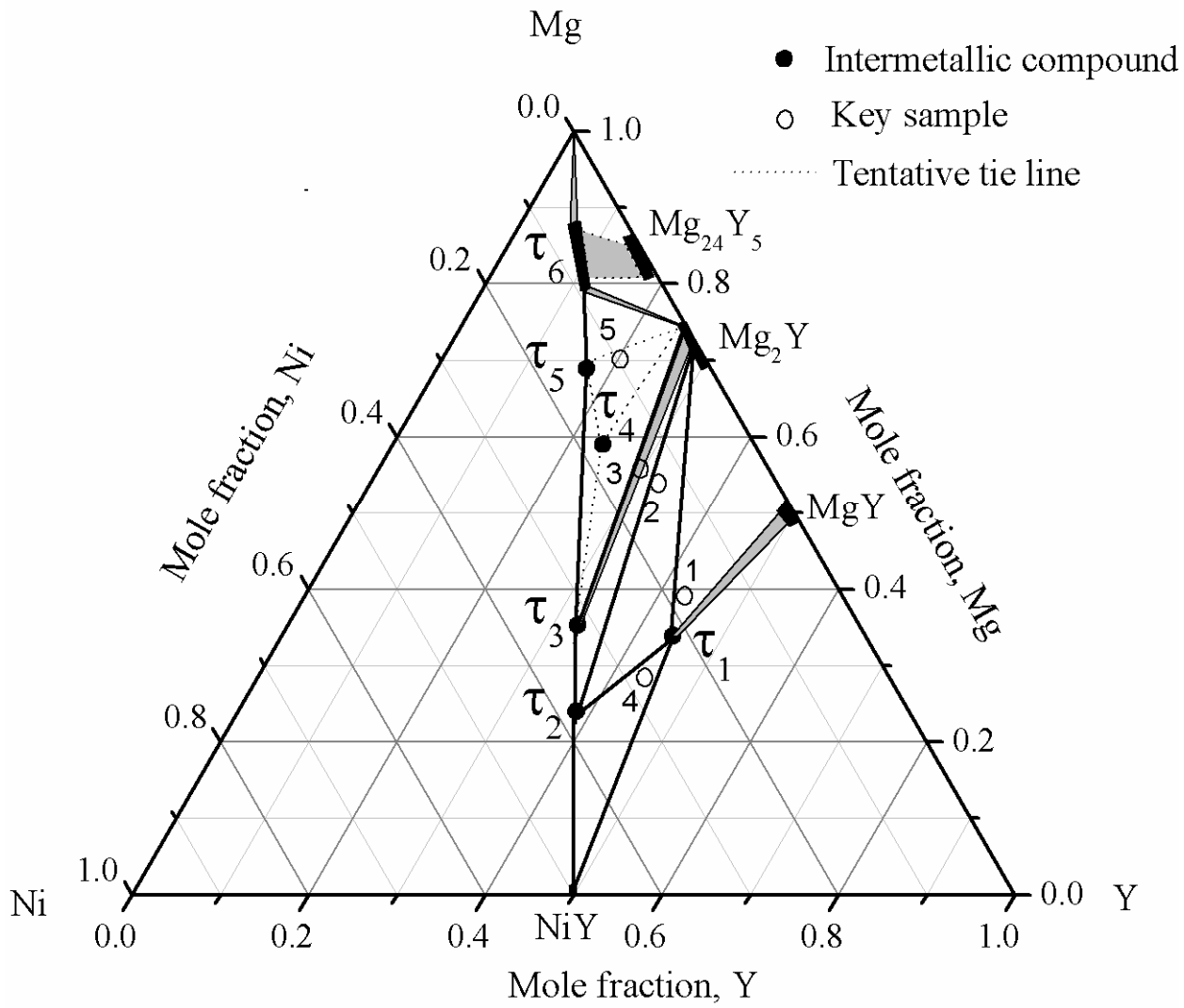

Figure 2: Phase relationships of the intermetallic compounds along the Mg-NiY line at 673 K.

By summarizing all the results, phase relationships among the compounds on the Mg-NiY line at 673 K has been proposed in Figure 2. The solid circles represent the composition of the ternary compounds. Also, positions of the samples are shown by the open circles.

The Mg-Ni-Y system showed a lot of similarities with the Mg-Cu-Y system which has ten intermetallic compounds as reported by Negri et al. [15] and studied by our group [16,17]. Using this similarity, some of the triangles have been predicted and plotted by dotted lines. These will be confirmed by further experimental work on this system in the near future.

Summary

The phase relationship in the Mg-Ni-Y system along the Mg-NiY line at 673 K has been established using EPMA study. One new ternary compound Mg_5CuY (τ_5) has been reported in this work. The existence of six ternary compounds has been confirmed using five samples. Three two phase regions (Mg_2Y + τ_6, Mg_2Y+ τ_3, MgY + τ_1) and two three phase regions (Mg_2Y + τ_1+τ_2 and NiY +τ_1+τ_2) have been identified. Ternary solubility of the τ_6 compound has been found. which extends from 77.10 at.% Mg until 86.77 at.% Mg with almost equal amount of Ni and Y. Ternary solubility of the binary compounds, NiY, Mg_2Y and MgY have also been reported. Further work on determining the crystal structures of the ternary compounds and identifying the phase relationships in other parts of the Mg-Ni-Y system is still needed. This is currently being carried out by our group and will be published in the near future.

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