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Microstructure and Microanalysis Studies of Some Lanthanum-Magnesium Based Hydrogen Storage Alloys

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Abstract. Microstructures and chemical compositions of some commercial La-Mg based alloys have been investigated. The hydrogen storage alloys can be represented by the formulae La_2Mg_x, $La_2Mg_{x-1}Ni$ and $LaMg_2Ni_9$ (x=12 or 17). The determination of the microstructures and phase compositions of these alloys has been carried out using scanning electron microscopy and energy dispersive X-ray analysis.

Introduction

It is well known that the low-cost Mg-based alloys are very promising materials for hydrogen storage. Over many years, extensive research has concentrated on the study of the storage performance of several La-Mg and La-Mg-Ni-based alloys (examples in Refs. [1-5]). Recently, it has been reported that the $La_2Mg_{16}Ni$ alloy has a hydrogen storage capacity of approximately 4 wt.% at room temperature [6]. The capacity improvement has been achieved by mechanical milling the La-Mg based alloy using organic compounds as the milling medium (tetrahydrofuran, cyclohexane, benzene, ethanol) [6-10]. However, much less effort has been expended on the investigation of the microstructures of these hydrogen storage alloys. In this study, various commercial ingot alloys of compositions La_2Mg_{12}, La_2Mg_{17}, $La_2Mg_{11}Ni$, $La_2Mg_{16}Ni$ and $LaMg_2Ni_9$ have been investigated using scanning electron microscopy (SEM). The phases found in these alloys have been identified using energy dispersive X-ray analysis (EDX). The characterization of the well-known $LaNi_5$ alloy has also been included in the present work for a comparison.

Experimental

Commercial alloys in the as-cast state were studied in this investigation. Ingots were prepared in a rectangular water-cooled copper mould in batches of approximately 5 kg. The chemical analyses of the as-cast alloys are given in Table 1. For convenience of comparison, the equivalent substituted composition, in at.%, is also given. Good agreement was found between the specified composition values and those determined by analyses of the alloys. As per the supplier's specification, the alloys contained sulfur, oxygen, nitrogen (<10 ppm) and carbon as impurities (<130 ppm). Samples for microstructure studies were prepared using conventional metallographic procedures. The microstructures of the specimens were examined using a scanning electron microscope with an energy dispersive X-ray (EDX) analysis facility. Averaged data were obtained from separate measurements carried out on the different phases.

Table 1. Composition of the as-cast $LaNi_5$, La_2Mg_x, $La_2Mg_{x-1}Ni$ and $LaMg_2Ni_9$ alloys.

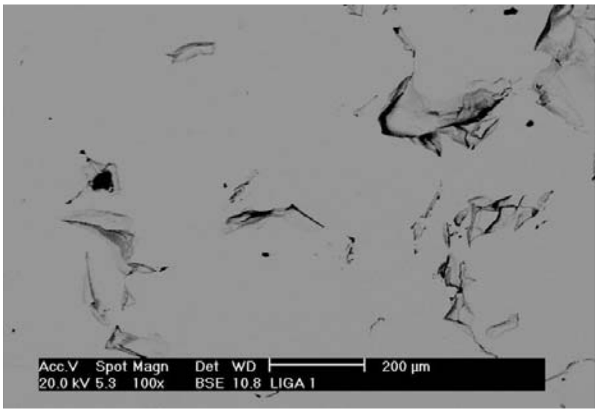
Nominal composition and Substitution composition (at.%)	x	Specified and analyzed composition (wt.%)			
		La	Mg	Ni	C*
$LaNi_5$ ($La_{16.67}Ni_{83.33}$)	-	32.13	--	67.87	--
		32.12	--	67.78	79
La_2Mg_{12} ($La_{14.29}Mg_{85.71}$)	12	48.78	51.22	--	--
		49.24	50.66	--	131
$La_2Mg_{11}Ni$ ($La_{14.29}Mg_{78.57}Ni_{7.14}$)	12	46.01	44.27	9.72	--
		46.76	43.61	9.53	103
La_2Mg_{17} ($La_{10.53}Mg_{89.47}$)	17	40.20	59.80	--	--
		40.47	59.43	--	120
$La_2Mg_{16}Ni$ ($La_{10.53}Mg_{84.21}Ni_{5.26}$)	17	38.30	53.61	8.09	--
		38.12	54.59	7.19	112
$LaMg_2Ni_9$ ($La_{8.33}Mg_{16.67}Ni_{75}$)	-	19.41	6.79	73.80	--
		19.59	6.29	74.02	40

*ppm (impurity)

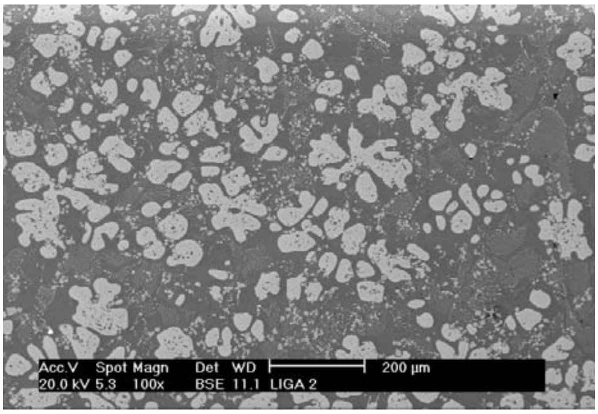
Results and Discussion

Backscattered electron images of the as-cast La-Mg based alloys are shown in Figs. 1 and 2. Due to the compositional variations, each La-Mg based alloy showed a singular grain structure. In the as-cast state, the $LaNi_5$ alloy consists of a single-phase coarse equiaxial grain structure. The remaining alloys are mainly composed of the matrix phase and other secondary phases at the grain boundaries. These alloys exhibit a more refined grain structure. The chemical composition of the phases is discussed later. In the as-cast condition, the La_2Mg_{12}, La_2Mg_{17} and $La_2Mg_{16}Ni$ alloys consist of only two phases, the matrix phase (M) and a gray phase (G). A comparison between these microstructures revealed that there has been a significant change in the grain structure with the increase in the Mg-content and with the introduction of Ni. As the Mg-content was increased in the La_2Mg_x alloys there has been a change in the shape of the phases and a preponderance of the matrix phase in the microstructure. In the La_2Mg_{17} alloy, the grain boundaries showed no sharp corners whereas in the $La_2Mg_{16}Ni$ alloy, the boundaries showed right angles. The as-cast $La_2Mg_{11}Ni$ and $LaMg_2Ni_9$ alloys consist of three phases. The former is composed of the matrix phase (M), the gray phase (G) and a dark gray (DG) phase. The latter is composed of M, G and a dark phase (D). It is worthy noting that the $La_2Mg_{11}Ni$ alloy, distinctly from the others alloys, showed no preponderance of the matrix phase over the other phases. The $LaMg_2Ni_9$ alloy, on the other hand, showed a distinct, almost columnar, grain structure.

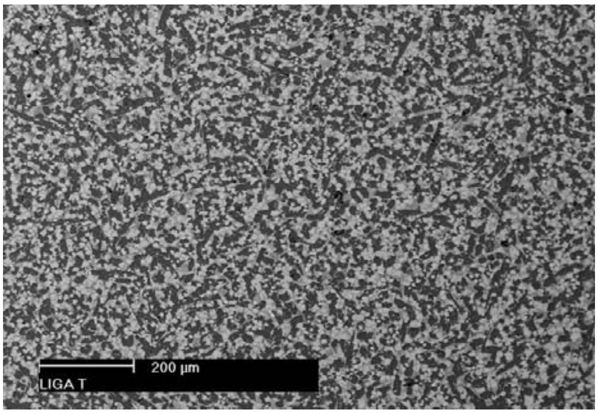
The chemical compositions of the matrix phases in the La-Mg based alloys, as determined by EDX, are presented in Table 2. The matrix phase of the $LaNi_5$ alloy revealed a Ni:La atomic ratio of about 5, indicating it to be a 1:5-type phase. The matrix phase of the La_2Mg_{12} and La_2Mg_{17} alloys showed a Mg:La atomic ratio of ~8.0. The $La_2Mg_{16}Ni$ alloy showed a (Mg+Ni):La atomic ratio of 8.0. This ratio for the $La_2Mg_{11}Ni$ alloy was 7.3. As a consequence of the alloy nominal composition, the matrix phase of the $LaMg_2Ni_9$ alloy, exhibited a distinct composition from the other alloys.



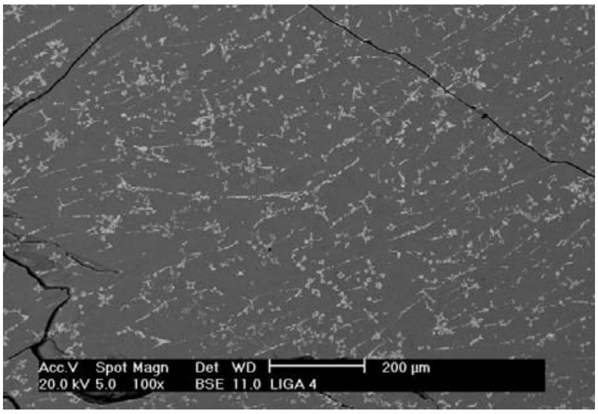
(1) $LaNi_5$



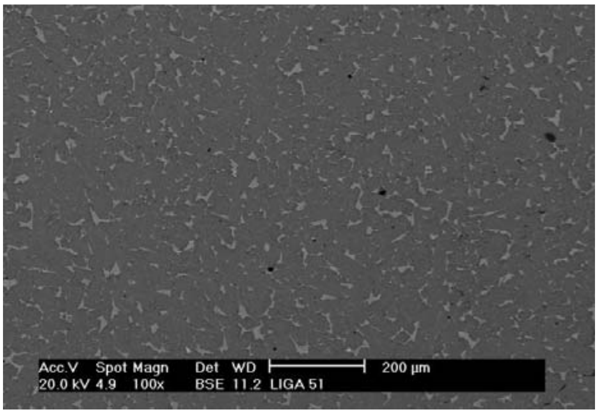
(2) La_2Mg_{12}



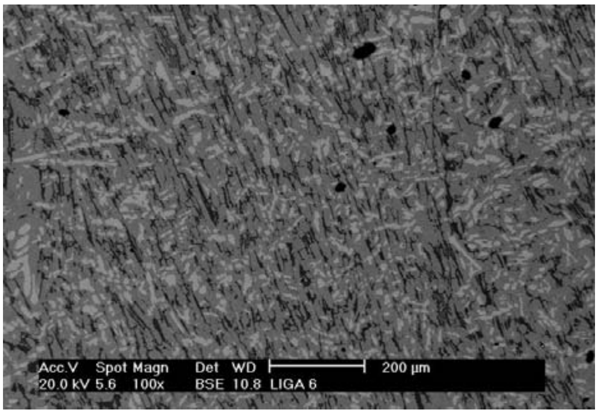
(3) $La_2Mg_{11}Ni$



(4) La_2Mg_{17}

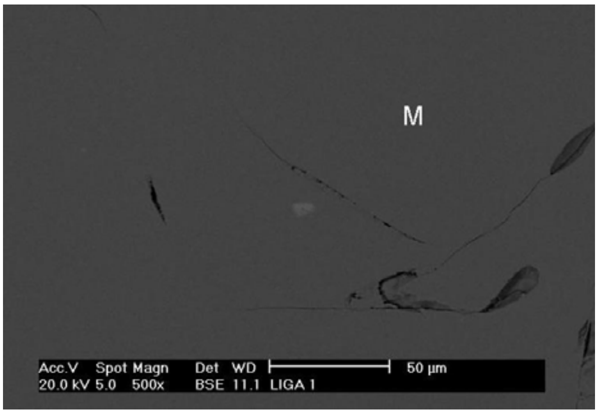


(5) $La_2Mg_{16}Ni$

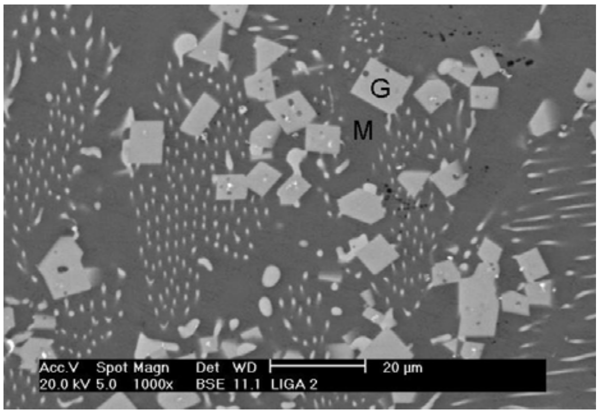


(6) $LaMg_2Ni_9$

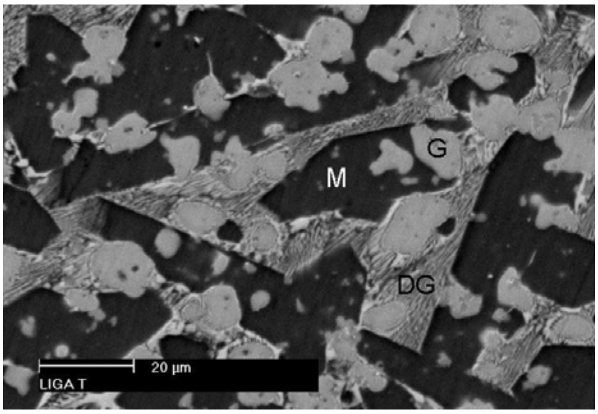
Figure 1. Backscattered electron images showing a general view of the microstructures of the La-Mg based alloys in the as-cast state.



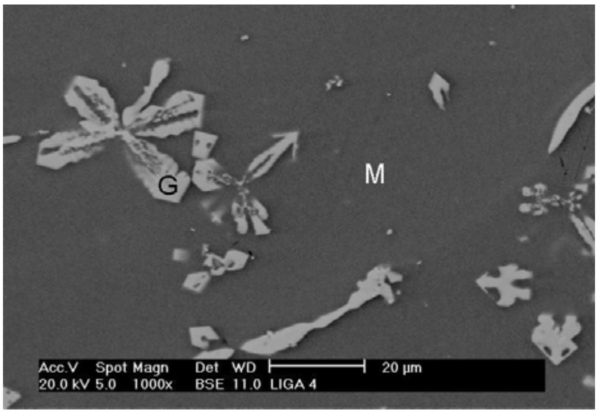
(1) $LaNi_5$



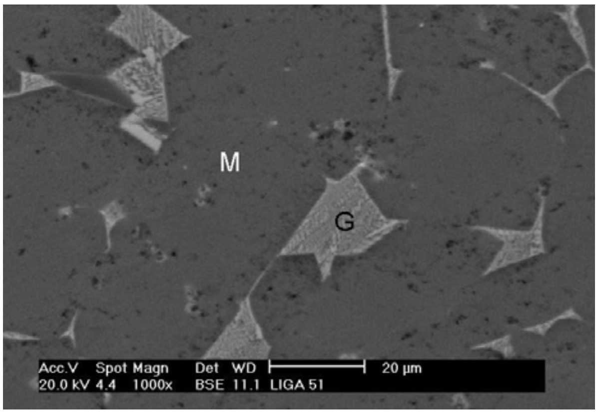
(2) La_2Mg_{12}



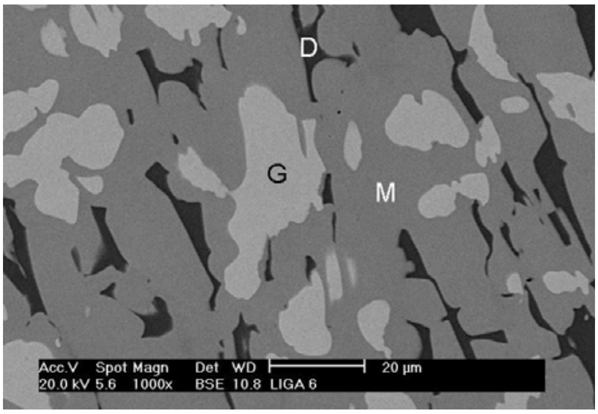
(3) $La_2Mg_{11}Ni$



(4) La_2Mg_{17}



(5) $La_2Mg_{16}Ni$



(6) $LaMg_2Ni_9$

Figure 2. Backscattered electron images of details of the La-Mg based alloys in the as-cast state.

Table 2. Composition determined by EDX at the centers of the matrix phase in the La-Mg based alloys. *N* is the number of independent measurements in the phase.

Alloy nominal composition composition [at.%]	Analyzed composition [at.%]			*N*	Phase stoichiometry		
	La	Mg	Ni		La	Mg	Ni
$LaNi_5$	16.8±0.2	-	83.2±0.2	4	1.0	-	5.0
La_2Mg_{12}	11.2±0.1	88.5±0.1	-	5	2.0	16.0	-
La_2Mg_{17}	11.3±0.1	88.7±0.1	-	3	2.0	16.0	-
$La_2Mg_{11}Ni$	12.1±0.4	84.3±0.5	3.6±0.3	7	3.0	23.0	1.0
$La_2Mg_{16}Ni$	11.0±0.1	85.6±0.2	3.4±0.1	5	3.2	25.0	1.0
$LaMg_2Ni_9$	8.7±0.3	14.3±0.2	77.0±0.4	4	1.0	2.0	9.0

The chemical compositions of the others phases found in the different alloys are presented in Table 3. Noticeably, the gray phase in the La_2Mg_{12} and La_2Mg_{17} alloys has similar composition. Again, the gray phase in the $La_2Mg_{16}Ni$ alloy and the dark gray phase in the $La_2Mg_{11}Ni$ alloy also have similar composition.

Except for the $La_2Mg_{16}Ni$ and $LaMg_2Ni_9$ alloys, the La content in the gray phase (21~24 at.%) is twice that measured for the matrix phase (11~12 at.%). The $LaMg_2Ni_9$ alloy showed a gray phase with low Mg content (~1.3 at.%) and the La content in the dark phase was below the detection limit of EDX (assumed as 1 at.%).

Table 3. Composition determined using EDX at the centers of the others phases in the as-cast La_2Mg_x, $La_2Mg_{x-1}Ni$ (x=12 or 17) and $LaMg_2Ni_9$ alloys.

Alloy nominal composition and phase detected	Analyzed composition [at.%]			*N*	Phase stoichiometry		
	La	Mg	Ni		La	Mg	Ni
La_2Mg_{12} (gray)	24.0±0.3	75.6±0.5	-	4	1.0	3.0	-
La_2Mg_{17} (gray)	23.4±1.4	76.2±1.2	-	5	1.0	3.0	-
$La_2Mg_{11}Ni$ (gray)	22.3±0.4	72.5±0.6	5.2±0.4	8	4.0	14.0	1.0
(dark gray)	13.9±1.1	67.3±0.8	18.7±0.4	5	1.0	5.0	1.0
$La_2Mg_{16}Ni$ (gray)	14.0±0.2	66.1±0.7	19.9±0.7	5	1.0	5.0	1.0
$LaMg_2Ni_9$ (gray)	16.0±0.3	1.3±0.4	82.7±0.6	4	1.0	-	5.0
(dark)	<1	28.9±0.3	70.2±0.4	3	-	1.0	2.0

Further investigations are underway to determine the hydrogenation/pulverization behavior of these alloys and the influence of the alloy microstructure and phases in this process. X-ray diffraction (XRD) analysis is also in progress in an attempt to help explain the changes in the microstructures and compositions observed in this investigation. The results will be presented and discussed in detail in a forthcoming paper.

Conclusions

Hydrogen storage alloys with composition $LaNi_5$, La_2Mg_{12}, La_2Mg_{17}, $La_2Mg_{11}Ni$, $La_2Mg_{16}Ni$ and $LaMg_2Ni_9$, investigated in this study, showed very distinct microstructures. The standard $LaNi_5$ alloy, showed a microstructure with large equiaxial grains, whereas the $LaMg_2Ni_9$ alloy showed a distinct, almost columnar grain structure. Some phases, analyzed by EDX, showed similar composition but many disparities have also been detected. These particular features of each alloy will change the hydrogen absorption/desorption behavior of these materials and this is presently being accessed.

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