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Effect of Heat Treatment on the Microstructure of Mg-4Al-Nd Alloys

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Abstract: In the present work, Mg-4Al-xNd (x = 0, 1, 4 wt.%) alloys were prepared by a stir casting method, and the effect of the addition of Neodymium (Nd) as-cast and of heat-treated microstructures was studied. The addition of 1 wt.% Nd preferentially formed the Al_2Nd phase and completely suppressed the formation of the intermetallic $Mg_{17}Al_{12}$ (γ) phase, which was initially present in the base alloy (Mg-4Al alloys). On increasing the Nd percentage from 1 to 4 wt.% in the base alloy, two intermetallic phases, Al_2Nd and $Al_{11}Nd_3$, were observed in the microstructure, as higher levels of Nd led to a peritectic reaction between Al and the Al_2Nd phase, and part of the Al_2Nd transformed into the $Al_{11}Nd_3$ phase. The hardness of the as-cast alloy increased with the Nd content. Thus, the hardness increased from 57.1 ± 4.1 Hv of Mg-4Al to 66.5 ± 2.6 Hv of Mg-4Al-4Nd. It was also found that solutionizing and isothermal aging of alloys containing Nd at 180 °C for 96 h led to the size reduction of Al- and Nd-containing intermetallics without altering their morphologies. Further, it was found that Nd does not have any effect on the aging kinetics of the alloys because all of the alloys with and without Nd attained peak hardness at 24 h of aging time.

Keywords: magnesium alloys; microstructure; Neodymium; intermetallics; Vickers micro hardness

1. Introduction

Magnesium alloys possess an attractive combination of properties such as outstanding specific strength and stiffness, high damping capacity, excellent dimensional stability, and recyclability [1]. The most widely used magnesium alloys are based on the Mg-Al system, where Al is added to improve strength and castability. In addition, Mg-Al alloys have a wide freezing range, and as a result, in the process of cooling from a liquid state to a solid state, a precipitation of γ-$Mg_{17}Al_{12}$ intermetallic phase occurs at the grain boundary and is considered to be the main strengthening phase at room temperature [2]. However, the use of Mg-Al alloys is restricted to non-critical parts due to their poor hardness and creep properties at temperatures beyond 120 °C [3–5]. This is attributed to the discontinuous grain boundary precipitation of a low melting point γ phase from the supersaturated solid solution of α-Mg along with the coarsening of γ in the interdendritic eutectic region at elevated temperatures [6]. In order to circumvent the deleterious effect of the γ phase, several alloying elements such as Ca, Sr and rare earth elements that are preferentially reactive to Al over Mg have been added to Mg-Al alloys [7–9].

Commonly, rare earth elements in Mg-Al alloys suppress the formation of the $Mg_{17}Al_{12}$ phase during solidification due to the preferential reaction of Al and rare earth (RE) to form Al-RE intermetallic phases. The addition of rare earth elements to an Mg-4Al alloy leads to formation of Al_2RE and $Al_{11}RE_3$ phases. However, the thermodynamic stability of the Al_2RE phase is higher than that of the $Al_{11}RE_3$ phase. At temperatures above 150 °C, the $Al_{11}RE_3$ phase decomposes to form Al_2RE and Al. This Al comes back into the solid-solution after phase transformation and forms a γ phase, as a result of which the properties deteriorate at elevated temperatures [5,10]. Hence, there is a need for an alternative element that could augment the properties of Mg-4Al at higher temperatures. For this, Neodymium (Nd) could be an effective strengthening element in Mg for elevated temperature applications [11,12]. Nd forms more stable intermetallics with Al and thus restricts the γ phase formation. However, limited work has been reported on the effect of Nd in Mg-Al alloys [12–15]. Zheng et al. [15] studied the effect of aging time on Vickers hardness of Mg-4Al-4Nd-0.5Zn-0.3Mn alloy and reported that the morphologies of the Al_2Nd and $Al_{11}Nd_3$ phases change from large polyhedral and long rod-like to granular and short rod-like precipitates, respectively, at T6 conditions. This refinement of precipitates after heat treatment improves the hardness and yield strength of the alloy both at room temperature and at elevated temperatures. Reports indicate that T6 heat treatment offers several advantages in Mg-Al alloys such as improved ductility, strength, hardness, and resistance to dynamic loads [11,16]. Therefore, the present work aims to study the effect of Nd on the microstructure and mechanical properties of Mg-4Al alloy in cast as well as under heat-treated conditions.

2. Materials and Methods

In this study, Mg-4Al-xNd (x = 0, 1, 4 wt.%) alloys were prepared by the stir casting method in a protective atmosphere of SF_6 (1%, v/v) and N_2 (Bal.) at a temperature of 720 °C. In order to ensure homogeneous mixing, the melt was stirred with the help of a mild steel mechanical stirrer at a speed of 25 rpm for 5 min. Nd addition to the abovementioned alloy was achieved by using a Al-12Nd master alloy, which was prepared separately by melting commercially pure Al and Nd in a graphite crucible using an electric resistance furnace at a temperature of 750 °C, and was then held for 45 min for the complete dissolution of Nd, after which the melt was poured into a steel mold. For the Mg-4Al-xNd (x = 0, 1, 4 wt.%) alloy preparation, commercially pure Mg and Al were melted in a graphite crucible using an induction furnace. Thereafter, the requisite amount of Al-12Nd master alloy was added to the melt at 720 °C and held for 10 min with continuous stirring. The melt was then poured by bottom pouring arrangements into a preheated (200 °C) mild steel mold with a diameter of 7 cm and a height of 10 cm. Cast samples were sectioned from the middle of the ingot and prepared as per standard metallographic techniques. The samples were etched in a freshly prepared etchant (100 mL ethanol, 20 mL distilled water, 6 mL acetic acid and 12 g picric acid). A field emission scanning electron microscope (FESEM) (Carl Zeiss, Merlin, Germany) equipped with an energy dispersive X-ray spectrometer (EDS) was employed for microstructural characterization. The phase analysis of the alloys were conducted by the X-ray diffraction method (XRD) (Bruker, Model: D8 Discover, Canton, MA, USA) using a Siemens diffractometer operating at 40 kV and 40 mA with Cu Kα radiation (λ = 1.54 Å). The image analysis was carried out using Image J software (Version: k 1.45).

The as-cast Mg-4Al-xNd (x = 0, 1, 4 wt.%) alloys were solution treated at 400 ± 1 °C for 8 h to obtain a homogeneous solid solution, and were subsequently quenched in water at room temperature. The alloys were then artificially aged in an air circulated muffle furnace (KANTHAL, Sandvik Group, Sweden) at 180 ± 1 °C [16,17] up to 96 h in the interval of 24 h followed by air cooling. Vickers micro hardness tests were carried out to investigate the aging behavior of the alloys. Hardness measurements were carried out using a Micro Hardness Tester (Model: LM-247; Make: LECO, Saint Joseph, MI, USA) at a load of 10 gf with a dwell time of 13 s. All hardness values of as-cast and heat-treated alloys are expressed as an average of at least 10 symmetrical indentations.

3. Results

3.1. Phase Analysis and Microstructure

Figure 1 shows the X-ray diffraction pattern of Mg-4Al, Mg-4Al-1Nd and Mg-4Al-4Nd cast alloys. Mg-4Al alloy is characterized by α-Mg and γ ($Mg_{17}Al_{12}$) peaks. The addition of 1 wt.% Nd to Mg-4Al alloy resulted in the complete suppression of the γ phase, and peaks of α-Mg and Al_2Nd phases were observed. When the Nd content was increased in the alloy to 4 wt.%, peaks of new intermetallics $Al_{11}Nd_3$ along with the existing α-Mg and Al_2Nd peaks were seen in the pattern. Zou et al. also reported Al_2Nd and $Al_{11}Nd_3$ intermetallics phases in ZA52 alloy after the addition of Nd [18]. The formation of intermetallics could be explained by noting electronegativity of the elements, as it is known that the probability of compound formation between two elements depends on the difference in electronegativity. The values of electronegativity for Mg, Al and Nd are 1.31, 1.61 and 1.14, respectively. Here, it is clear that Nd and Al have a higher electronegativity difference compared to that of Mg-Nd and Mg-Al, hence it led to the formation of Al-Nd intermetallics [19,20]. In the solidification sequence, the Al-Nd phases formed prior to the γ phase because the intermetallics of Al and Nd formed at a much higher temperature compared to the γ phase [13,18]. Al_2Nd is a proeutectic phase while $Al_{11}Nd_3$ is the result of the peritectic reaction between Al_2Nd particles and liquid Al, because high Nd content promotes the rate of the peritectic reaction.

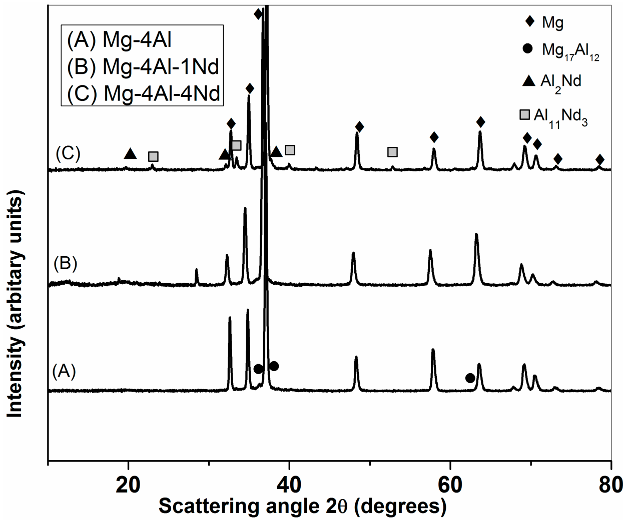

Figure 1. XRD pattern of as-cast alloys: (**A**) Mg-4Al, (**B**) Mg-4Al-1Nd, and (**C**) Mg-4Al-4Nd.

Figure 2 shows the FESEM micrograph of the as-cast alloys. The presence of α-Mg and the discontinuously precipitated γ ($Mg_{17}Al_{12}$) phase along the grain boundaries is observed in Mg-4Al alloy (Figure 2a). The α-Mg grains are mostly equiaxed and have a rosette morphology. In contrast, Mg-4Al-1Nd alloy consists of small, irregularly shaped Al_2Nd homogeneously distributed throughout the matrix (Figure 2b), while both Al_2Nd and $Al_{11}Nd_3$ particles are seen in Mg-4Al-4Nd alloy (Figure 2c). Due to Nd in the Mg-4Al alloy, the γ ($Mg_{17}Al_{12}$) phase was completely suppressed and two additional intermetallic (Al_2Nd and $Al_{11}Nd_3$) phases evolved.

The histogram in Figure 3 shows the particle size distribution of Al_2Nd particles in the as-cast Mg-4Al-1Nd alloy (Figure 3a) and after 24 h of aging at 180 °C (Figure 3b). In the as-cast alloy, a major fraction of Al_2Nd particles are in the range of 2–4 μm and with an average particle size of 2.9 μm. Meanwhile, in the heat-treated alloy, the majority of Al_2Nd particles are in the size range of 1–2 μm.

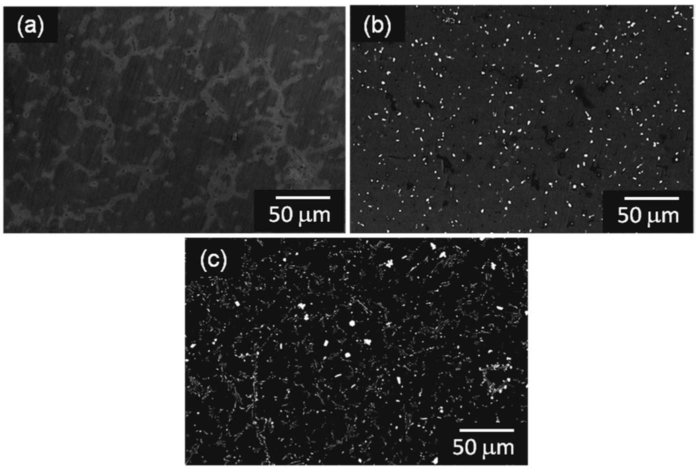

Figure 2. FESEM micrographs of the as-cast alloys showing the distribution of different intermetallic particles in the Mg-Al matrix: (**a**) Mg-4Al, (**b**) Mg-4Al-1Nd, and (**c**) Mg-4Al-4Nd.

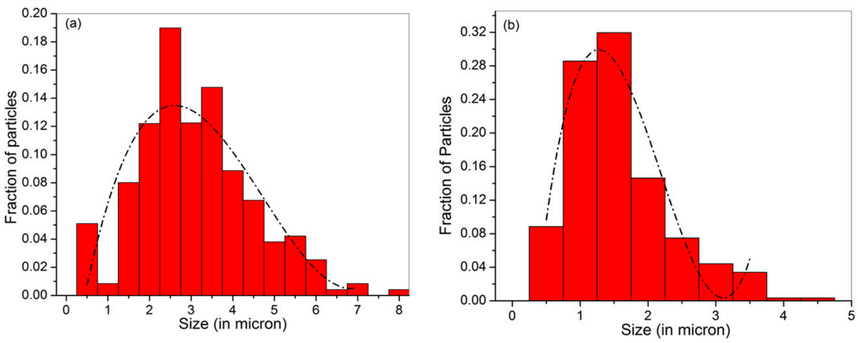

Figure 3. Particle size distribution of Al_2Nd particles in Mg-4Al-1Nd alloy (**a**) as-cast condition, and (**b**) aged at 180 °C for 24 h.

In Mg-4Al-4Nd alloy, four different morphologies of Al and Nd intermetallics were identified: large quadrangle, small polygonal, rod-like and dendritic (labelled in Figure 4). Large quadrangular and small polygon particles are identified as Al_2Nd while the particles with dendritic morphology are identified as $Al_{11}Nd_3$. The rod-shaped particles have a length of about 8.7 μm are identified as $Al_{11}Nd_3$ particles. Al_2Nd particles are coarser as they were observed in the first phase to solidify, while $Al_{11}Nd_3$ particles are fine as they were formed at later stage of solidification. The formation of the fine $Al_{11}Nd_3$ phase could be the result of the dissolution of coarse Al_2Nd particles due to the peritectic reaction with Al.

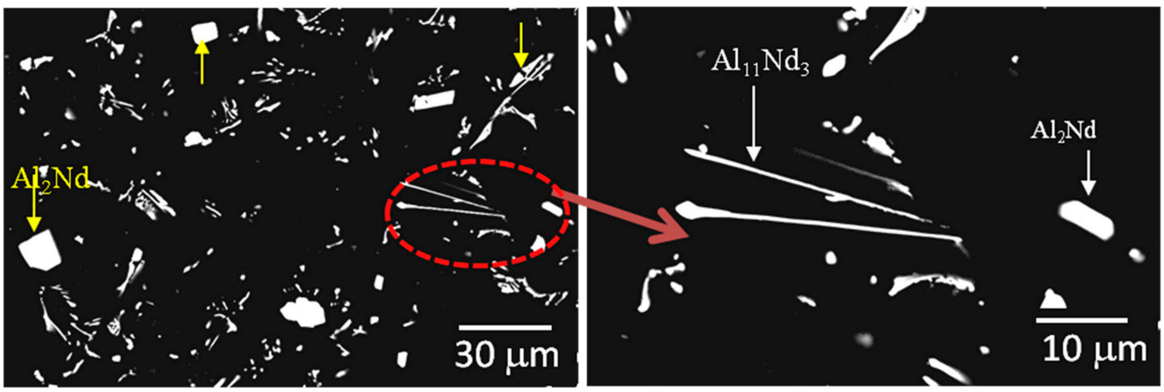

Figure 4. FESEM micrograph of Mg-4Al-4Nd at higher magnifications.

Figure 5 shows the microstructure of Mg-4Al-1Nd and Mg-4Al-4Nd after solutionizing at 400 °C for 8 h followed by artificial aging at 180 °C for 24 h. The Al_2Nd particles in Mg-4Al-1Nd alloy show marginal size reduction (1–2 µm) with irregular morphology persisting throughout the microstructure, similar to those found in the as-cast alloys (2.86 µm). Likewise, the morphology of Al_2Nd and $Al_{11}Nd_3$ particles in Mg-4Al-4Nd alloy after heat treatment was not altered. The rod-shaped $Al_{11}Nd_3$ particles in Mg-4Al-4Nd alloy are found to be 6.5 µm as compared to the cast alloys (8.7 µm). Also, it was found that T6 treatment resulted in a more homogeneous distribution of phases in Nd-containing alloys compared to as-cast condition.

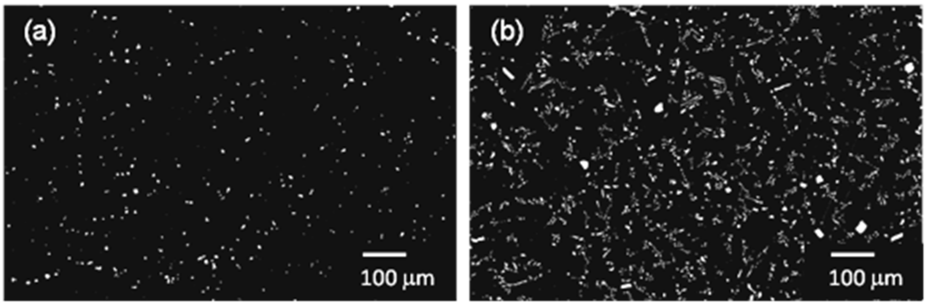

Figure 5. FESEM micrograph after 24 h aging: (**a**) Mg-4Al-1Nd alloy and (**b**) Mg-4Al-4Nd alloy.

The ratio of phases in different alloys after 24 h of aging was estimated from the XRD pattern (using the relative intensities of the maximum peak height of phases), as shown in Figure 6. The fraction of the γ ($Mg_{17}Al_{12}$) phase in Mg-4Al alloys is 0.022, while in Mg-4Al-1Nd alloy, the ratio of the α-Mg and Al_2Nd phases is 0.92:0.08. The fraction of the α-Mg, $Al_{11}Nd_3$ and Al_2Nd phases in Mg-4Al-4Nd alloy are respectively 0.788, 0.075 and 0.137. Thus, it can be inferred that the alloys containing Nd show higher fractions of Al_2Nd phases, almost 2–3 times as much as the cast alloys, formed after aging for 24 h. This could be one of the reasons for the increase in hardness of Nd-containing alloys at peak aged conditions. Further, the XRD also confirmed the complete suppression of the γ phase in Nd-containing alloys.

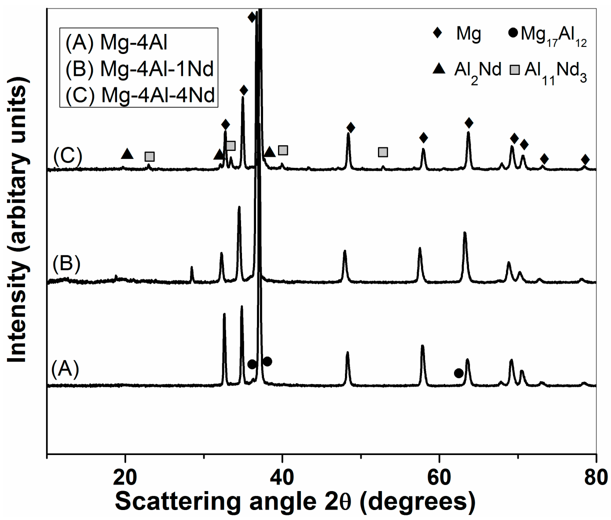

Figure 6. XRD pattern of T6-treated alloys in peak aged conditions.

3.2. Hardness

The average hardness of as-cast Mg-4Al, Mg-4Al-1Nd and Mg-4Al-4Nd alloys are 57.1 ± 4.1 Hv, 62.6 ± 4.8 Hv, and 66.5 ± 2.6 Hv, respectively. As expected, the hardness of the as-cast alloys increased as a function of Nd content due to the increase in the volume fraction of Al_2Nd and $Al_{11}Nd_3$ intermetallics, depending on the alloy composition. Also, it can be noted that the standard deviation in Mg-4Al-4Nd alloy is the maximum which suggests the inhomogeneous distribution of phases in the microstructure.

Figure 7 represents the Vickers micro hardness of Mg-4Al, Mg-4Al-1Nd and Mg-4Al-4Nd alloys isothermally aged at 180 °C up to 96 h [16,17]. It is interesting to note that the hardness of all of the alloys reaches peak value after 24 h of aging. This warrants a further detailed investigation of the microstructure of peak aged samples.

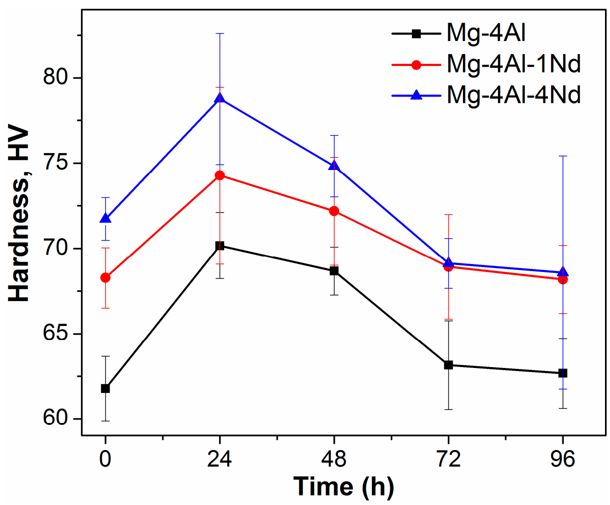

Figure 7. Vickers micro hardness of heat-treated alloys.

The hardness of the relatively coarse Al_2Nd particles in Mg-4Al-1Nd and Mg-4Al-4Nd alloys is 120.8 Hv and 144.1 Hv, respectively. However, the hardness of $Al_{11}Nd_3$ particles could not be measured due to their finer size as compared to Al_2Nd particles. These intermetallic particles have significantly higher hardness than that of the matrix, and hence contribute to the overall hardness of the alloy by dispersion hardening. It can be seen that in the initial stage of aging up to 24 h, the hardness increases steeply and thereafter the hardness decreases slowly after attaining the maximum value. The increase in hardness values at the peak aged condition of Mg-4Al alloy is attributed to the finer and even distribution of γ precipitates throughout the microstructure.

It is also interesting to note that the decrease in hardness of an alloy even in the overaged conditions between 72 and 96 h is not very significant (Figure 7), which suggests that the microstructure does not undergo significant coarsening (Figure 8a,b).

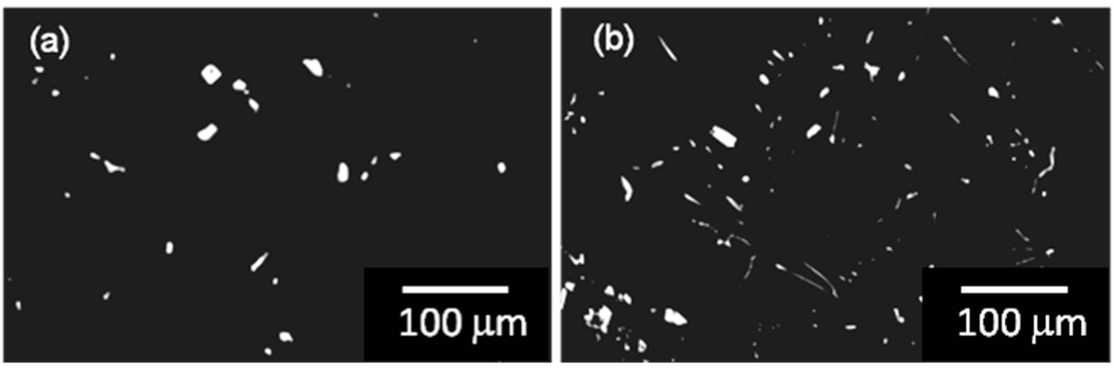

Figure 8. FESEM micrograph of alloys aged for 72 h: (**a**) Mg-4Al-1Nd and (**b**) Mg-4Al-4Nd alloy.

In Mg-4Al-1Nd alloy, though the microstructure reveals that there is no apparent change in the size of Al_2Nd particles, a detailed particle size analysis suggested that they undergo a size reduction on prolonged holding at 180 °C. The aged sample shows particle sizes in the range of 1–2 µm. After isothermal aging, the Al_2Nd particles size reduces to 1.3 µm and 0.7 µm after 24 h and 72 h, respectively. Thus, the particles seem to be significantly thermally modified in the overaged condition. However, in Mg-4Al-4Nd alloy, particle size analysis was not carried out as there were four different morphologies of two different kinds of particles in the same microstructure.

4. Conclusions

The microstructural evolution of Mg-4Al alloys modified by the addition of 1 wt.% Nd and 4 wt.% Nd was studied in the as-cast condition and after heat treatment. It was found that an addition of 1 wt.% Nd was sufficient to completely suppress the formation of the $Mg_{17}Al_{12}$ phase. The microstructure of Mg-4Al-1Nd alloy shows α-Mg and Al_2Nd phases, but Mg-4Al-4Nd alloy contains α-Mg and two intermetallic phases—Al_2Nd and $Al_{11}Nd_3$. The hardness of the as-cast alloy increases with the increase of Nd content, and reaches 66.5 ± 2.6 Hv for 4 wt.% Nd. It is interesting to note that peak hardness of all three alloys was attained after 24 h of aging time. The results also revealed that even after 72 h of aging at 180 °C the morphologies of Al_2Nd and $Al_{11}Nd_3$ phases do not change as compared to the as-cast alloys. However, subsequent isothermal aging at 180 °C led to the refinement of existing Nd-containing particles by thermal modification and an increase in amount of intermetallics, which could be due to precipitation of newer phases.

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Conflicts of Interest: The authors declare no conflict of interest.

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