

# Effect of Nitriding Temperature and Nitriding Time on MgAZ91D Alloy

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## ABSTRACT

*Magnesium and its alloys are widely applied in the automotive industries, electronic and telecommunication industries due to its low densities and excellent strength to the weight ratio. However, it possesses a low surface hardness which can weaken the adhesion properties, especially when hard coating is applied. The need of hard coating is crucial to enhance its corrosion resistance. In this work, nitriding process was carried out to modify the surface properties of MgAZ91D in enhancing its corrosion resistance. The nitriding process was conducted using a high-temperature furnace with the nitrogen gas flow at a constant rate of 5scfh. Three nitriding temperatures were set which were at 300°C, 400°C, and 500°C, for a nitriding period of 1 and 2 hours respectively. Analysis on the surface roughness of the nitrided MgAZ91D was then conducted using MitutoyoSJ410 profilometer. Surface hardness and case depth of the nitride MgAZ91D was analyzed using MitutoyoVicker's microhardness testing machine. The results showed that the surface hardness, surface roughness, grain size and the case depth of the nitrided MgAZ91D increased through the increase as the process temperature and time. However, the effect of grain size on the case depth hardness is not significant. Thus, the process temperature and time of nitriding MgAZ91D is crucial to be investigated to obtain the right combinations between the surface hardness, surface roughness and case depth for corrosion applications.*

**Keywords:** Nitriding, MgAZ91D, Case Depth, Grain Size.

## Introduction

Magnesium (Mg) and its alloys, such as MgAZ91D are receiving more consideration, especially in telecommunication industries and automotive industry [1, 2] because of its high dimensional stability, good machinability, and easily recycled, which allow Mg and its alloys to be formed into more complex shape. Unfortunately, the poor wear and corrosion resistance of Mg and its alloys [3, 4] have limit its potential to be used in a severe mechanical application. Thus, surface modification could become a solution to Mg and its alloys, especially the MgAZ91D if it is to be exposed to wear environment.

Among the many techniques available under surface modification, nitriding is one of the conventional but easiest techniques that should be considered. Nitriding can modify a surface of metal to increase its surface hardness, fatigue strength, wear and corrosion resistance [5, 6]. However, in this process, the choice of source gases to supply the  $N^+$ ,  $N^{2+}$ ,  $NH^+$ ,  $NH^{2+}$  in nitriding are worth to consider [3, 7]. For an example, the use of ammonia as the source gas in conventional nitriding can cause toxicity issues that need higher precaution. Another alternative is to use plasma in nitriding which is more efficient, especially in avoiding a thicker compound zone [8].

However, plasma nitriding is unsuitable for metals having a low melting temperature, such as magnesium alloy and aluminium alloy. Therefore, the combination of both techniques known as duplex technique (combining nitriding and plasma in a control environment) can be imparted as an attempt to enhance the corrosion and wear resistance of Mg and its alloys. Before the duplex technique can be carried out, the optimum nitriding process parameters with the desired properties to be developed have to be investigated. In this study, the work is focused solely on nitriding in which the conventional gas nitriding process is carried out to nitride MgAZ91D by carefully selecting the nitriding process parameters (the gas flow rate, temperature, and time) to investigate its relation with the phases, surface hardness, case depth and grain growth of the desired MgAZ91D.

## Experimental Set Up

### Sample Preparation

Commercially cast MgAZ91D were cut into 20 mm×10mm×3 mm and is used as a substrate. Composition of the MgAZ91D substrates is shown in Table 1 for reference.

Table 1: Chemical Composition of AZ91D Magnesium alloy.

Mg	Al	Zn	Mn	Si	Cu	Fe	Ni
90	8.3 – 9.7	0.35 - 1	≥ 0.13	≤ 0.1	≤ 0.03	≤ 0.005	≤ 0.002

Prior to nitriding, all MgAZ91D samples were ground with SiC abrasive paper grit of 800 and 1200. Then the substrates were polished with fine alumina paste (average size 0.05  $\mu\text{m}$ ). The polished substrates were then, immersed in pure ethanol for 10 minutes in an ultrasonic bath for cleaning. Then, the samples were stored in an airtight container containing silica gel to prevent oxidization.

**Nitriding Process**

The nitriding process was conducted using the Naberthem gas furnace equipped with inlet and outlet gas flow socket. The gas flow rate during the nitriding process was set to be constant at 5scfh. Table 2 summaries the nitriding process parameters.

Table 2:Nitriding process parameter.

Time, (Hour)	Temperature, ( $^{\circ}\text{C}$ )	$\text{N}_2$ Gas Flow rate, (scfh)
1	300	5
	400	
	500	
2	300	
	400	
	500	

**Phases and microstructure analysis**

X-ray diffractometer (XRD) model, Expert Pro Panalytical with 1.54060  $\text{\AA}$  wavelengths is used to verify the phase composition of the nitrided MgAZ91D. The working voltage used was 40 kV and the working current was set at 30 mA with a step size of 0.008 $^{\circ}$ /s in the  $2\theta$  range of  $10^{\circ} - 90^{\circ}$ . The microstructure of MgAZ91D is analyzed using Zeiss Axioskop 2 MAT optical microscope.

**Surface roughness, surface hardness and case depth analysis**

Surface roughness are measured using a Mitutoyo SJ410 profilometer. All measurements were taken according to ISO 1997 standard with an evaluation length of 4mm with waviness profile filter cut-off,  $\lambda_c = 0.8\text{mm}$  and waviness profile filter cut-off,  $\lambda_s = 2.5\text{mm}$ . The surface hardness of the nitride MgAZ91D is measured using Mitutoyo Vicker’s microhardness testing machine with a load of 5 gf and duration of 15 s.

For accuracy, each sample was indented with 20 scattered points and the average value was recorded. For the case depth analysis, similar load of 5 gf is used with duration of 15 s and repeated 20 times at different points.

**Results and Discussion**

Figure 1 shows the XRD patterns of the nitrided MgAZ91D compare to the untreated MgAZ91D with regard to the selected temperatures. All of the nitrided

MgAZ91D reveal the existence of  $Mg_3N_2$  and AlN hard phases for all of the selected temperatures and the nitriding time. As seen in the figures, the distinct (002) plane of Mg is replaced with AlN plane of (002) during the nitriding process. As the temperatures increased, the intensity of AlN phase of (002) plane is also increased. The intensity of  $Mg_3N_2$  phase of (222) plane, however, slowly dissappeared as the temperature increased. At 500°C, most of the Mg phases had receded and the nitrided MgAZ91D is consisted of AlN and  $Mg_3N_2$  hard phases. The same trend is observed for both nitriding time.

Figure 2 shows the cross section image of the untreated and the nitrided MgAZ91D with regard to its temperatures and nitriding time. It can be clearly seen that the size of MgAZ91D grain growth as the temperature increased. However, the effect of nitriding time on the size of MgAZ91D grain is negligible and insignificant. The nitrided compound layer developed on the MgAZ91D surface, however, is very thin as revealed by the optical microscope image in Figure 2. The evidence on the formation of the nitride compound layer is further supported by the case depth measurement taken as shown in Figure 3.

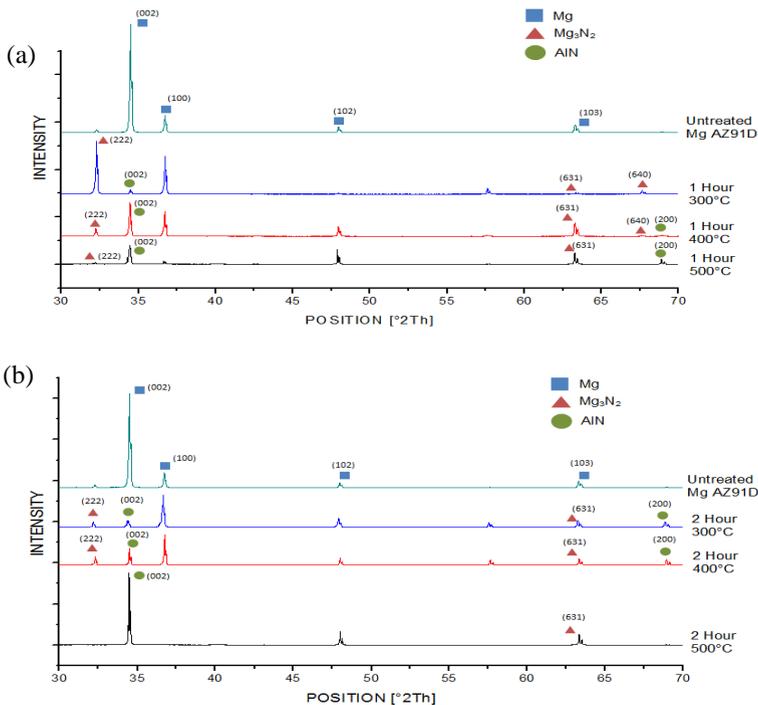


Figure 1: XRD pattern of the nitride MgAZ91D vs untreated MgAZ91D at 1 Hour, b) 2 Hours

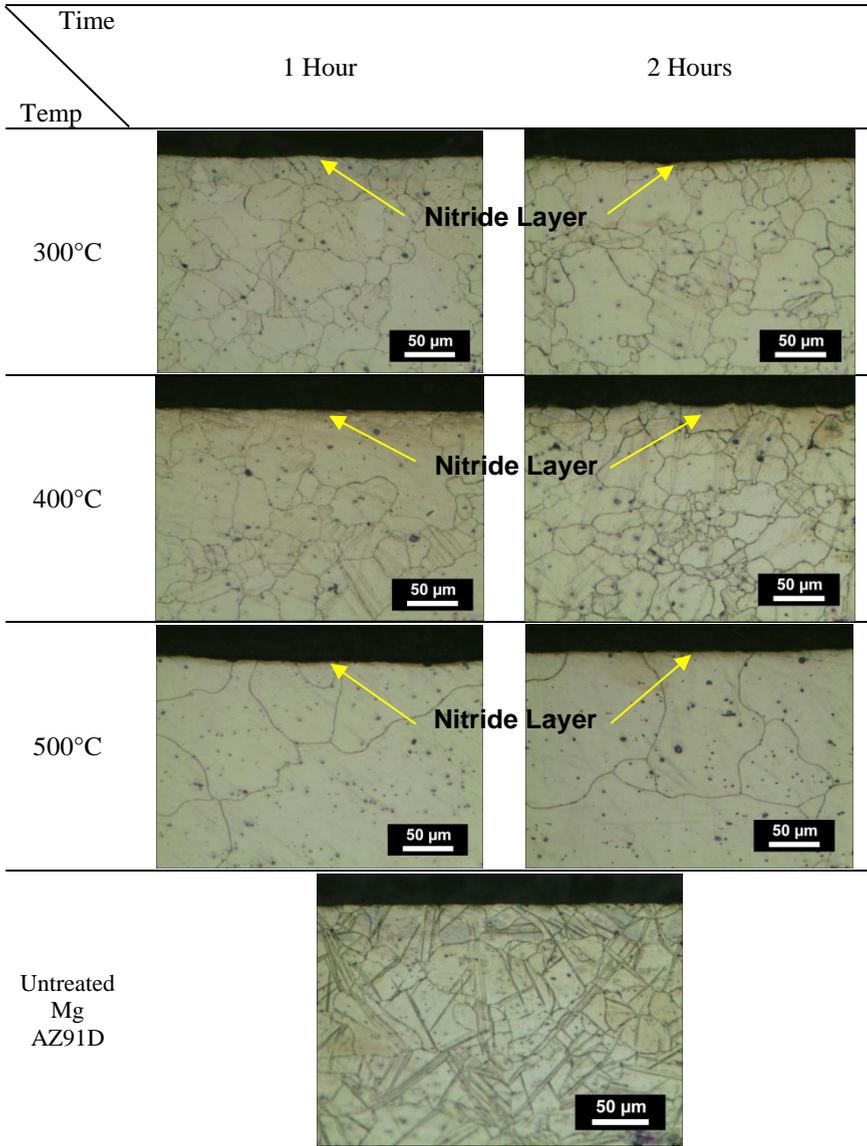


Figure 2: Optical microscope cross section image of the untreated and the nitrided MgAZ91D with regard to temperatures and nitriding time.

The case depth profiles shown in Figure 3 demonstrated that nitrogen managed to diffuse further to more than 20 µm underneath the surface as both process

parameters (the temperature and the nitriding time) increased. At 500°C, the surface of the nitrided MgAZ91D is the hardest compare to the MgAZ91D nitrided at 300°C and 400°C which indicating a thicker compound layer had established. Interestingly, that the case depth hardness is found to increase even though the grain size increased. This observation could be related to the development of the thin compound layer comprises as well as the existence of the Mg<sub>3</sub>N<sub>2</sub> and AlN hard phases underneath the MgAZ91D surface as nitrogen diffused deeper during the nitriding process. Therefore, the effect of grain size on the case depth hardness for the nitride MgAZ91D has been reversed by the presence of these hard phases.

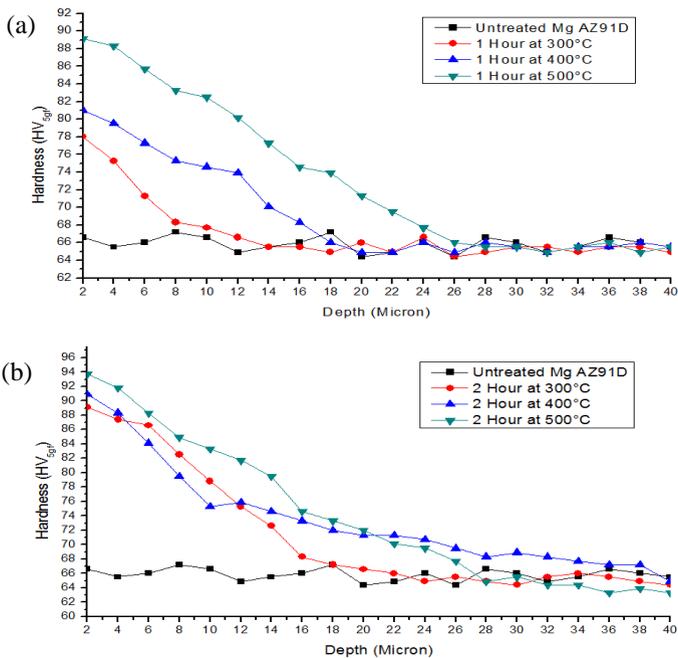


Figure 3: Comparison of case depths profile for the untreated MgAZ91D vs nitrided MgAZ91D at a) 1 Hour, b) 2 Hours with regard to its nitriding temperature.

Similar results are also observed for the surface hardness of the nitride MgAZ91D compared to the untreated sample to indicate the formation of compound layer as shown in Figure 4. All of the surface hardness values for the nitrided MgAZ91D are higher compared to the untreated sample. The surface hardness increased as the temperatures and the nitriding time increased which shows that the development of the compound layer at the surface. The surface

roughness is also increased as increasing the temperatures and the nitriding time. However, the effect of compound layer development on surface roughness is negligible and not significant except for the sample nitride at 500°C for 2 hours as shown in Figure 5.

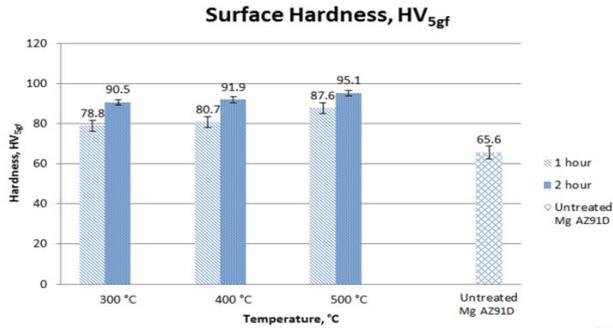


Figure 4: Surface hardness of the untreated MgAZ91D as compared to the nitrided MgAZ91D with its temperatures and nitriding time.

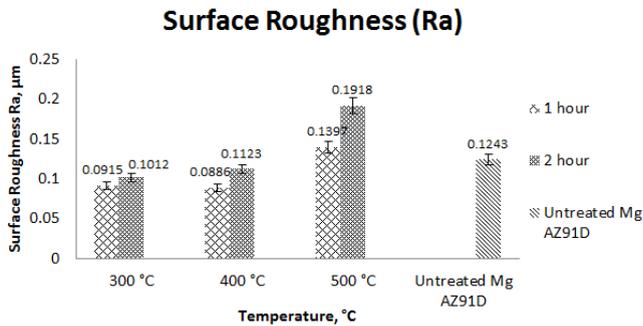


Figure 5: Surface roughness of the untreated MgAZ91D vs nitrided Mg AZ91D with its temperatures and nitriding time.

## Conclusion

The MgAZ91D has been successfully nitrided within the selected process parameters using modified gas furnace. The XRD results show that the Mg<sub>3</sub>N<sub>2</sub> and AlN hard phases appear for all temperatures used. For the grain growth effect, the increase in temperature and nitriding time increased the grain size. Conversely, the effect of grain size growth toward the case depth hardness of the nitrided MgAZ91D has been reversed due to the attendance of these two hard phases. The case depth hardness increase even though the size of the grain increased. Results of surface hardness strengthen the evident of compound layer establishment at the surface of the nitride MgAZ91D. All of the nitrided

MgAZ91D possess higher surface hardness values than the untreated MgAZ91D. However, the effect of compound layer formation towards surface roughness of the nitrided MgAZ91D is negligible and not significant.

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