Effect of solution treatment on microstructure and corrosion behaviour of Mg-9Al-1Zn alloys

R Naldi and A Anawati*
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

*E-mail: anawati@sci.ui.ac.id

Abstract. The effect of solution treatment on the microstructure and corrosion behavior of cast Mg-9Al-1Zn (AZ91) were studied by using electro-optical microscopy, X-ray diffraction (XRD) technique, and weight loss method. The solution treatment was done at 415°C for 2 h followed by a water quench. The as-cast AZ91 alloy composed of α-Mg phase and β-phase (Mg17Al12). Most of the β-phase was segregated along the grain boundaries. A significant reduction in the volume fraction of β-phase was obtained as a result of solution treatment. The β-phase precipitate was distributed randomly both at grain boundaries and in the grain interior as discrete particles of a few µm sizes. The solution treatment induced grain growth resulting in a significantly larger equiaxed grain in the range 100-500 µm. A higher corrosion rate was obtained for the solution treated alloy than the untreated one. The β-phase precipitate played a dual role in the corrosion of AZ91 alloy depending on its volume fraction in the alloy. A nearly continuous distribution of β-phase along grain boundaries in the as-cast alloy served as a barrier for corrosion across grain while the distribution of discrete particles in the solution-treated alloy accelerated corrosion in the surrounding matrix.

1. Introduction
Magnesium (Mg) has attracted considerable attention in engineering application particularly in the automotive and aerospace industry where the high strength to weight ratio is demanding [1]. Mg is the lightest metal on earth with a low density of 1.7 g/cm³ having a high strength, great damping capability, and excellent fluidity in casting [2]. Mg is usually used in the form of an alloy which exhibited an improved in the mechanical and corrosion properties. The conventional Mg alloys typically contain alloying elements Al, Zn, Mn, Fe, Cu, and Si [2]. The recent development of Mg alloy uses rare earth elements to boost the mechanical and heat properties [3, 4]. The AZ91 alloy which composed of 9% Al and 1% Zn is widely investigated considering the potential application for low-temperature application [5, 6].

The microstructure affects the mechanical properties and corrosion behavior of Mg alloys. The conventional AZ series alloys typically consist of an α-Mg matrix which is decorated by intermetallic precipitates β-phase (Mg17Al12). The strengthening and hardening of Mg alloys are performed by solution treatment [6-8]. The strengthening and hardening mechanism was controlled by the number, size, and distribution of the intermetallic particles in the alloy [8]. From the corrosion viewpoint, the intermetallic precipitates existed in Mg alloys play role in either accelerating the corrosion rate or reducing the corrosion propagation depending on the distribution and the volume fraction of the intermetallic precipitates [7-9]. The precipitates which mostly are more cathodic than the Mg matrix...
induced potential gradient which accelerated local corrosion in the surrounding matrix. The microgalvanic corrosion is the common type of corrosion occurred in the Mg alloy [7, 10].

This work is aimed to throw lights on the effect of solution treatment on the development of microstructure in the alloy and its role in determining the mechanical hardness and corrosion behavior of as-cast Mg-9Al-1Zn. The corrosion behavior was studied by measuring weight loss as a result of immersion in NaCl solution.

2. Experimental procedure

The material used was as-cast Mg-9Al-1Zn prepared by gravity casting producing a cylindrical ingot of 15 cm long and 2 cm in diameter. The as-cast alloy was cut into a disk with 1 cm thickness. Some of the specimens were heat treated. The solution treatment was conducted in a furnace at a temperature of 415°C for 2 h followed by water quenching. Prior further used, the specimens were ground with #600, #800, and #1000 grit papers followed by polishing with alumina paste to give a mirror reflection. The polished specimens were then degreased in acetone and subsequently in ethanol in an ultrasonic bath for 3 min for each step.

For observing the metallurgical microstructure, the specimen was etched in 4% HNO₃ solution for 20 s to reveal the metallic grain. The specimen was then rinsed in DI water and then dried in an air stream. The microstructure was studied by an optical microscope of CX31 from Olympus. The alloy composition was analyzed by X-ray diffraction spectroscopy (XRD, Panalytical X’Pert Pro MPD). The mechanical hardness was determined by Vickers Microhardness tester (Struers DuraScan) by using 2 kgf load. The average hardness was obtained from 5 measurement points on the specimen.

The corrosion behavior of both as-cast and solution-treated specimens was studied by conducting an immersion test in 3.5% NaCl solution at 30°C. The specimen was immersed individually in 10 ml solution in a glass bottle inside a water bath controller. The average corrosion rate was determined based on the weight loss measured after 24, 48, and 72 h immersion.

3. Results and Discussion

The microstructure of the as-cast and solution-treated Mg-9Al-1Zn alloys was investigated by an optical microscope. The results are presented in Fig. 1. The as-cast alloy consisted of α-Mg, α-eutectic, and intermetallic precipitate β-phase (Mg₁₇Al₁₂). The as-cast alloy showed a relatively small metallic grain boundary below 100 µm size. The grain boundaries were occupied by a nearly continuous β-phase (Mg₁₇Al₁₂) which surrounded by the α-eutectic phase, while the matrix composed of α-Mg phase. The grain size became significantly larger in the range 200-600 µm after solution treatment as shown in Fig. 1b. Enlargement of grain size as a result of heat treatment was reported [6]. Most of the β-phase dissolved in the solid solution matrix as a result of solution treatment. The remaining β-phase intermetallic segregated at the grain boundaries and decorated the grain interior as small spherical particles. The solution treatment resulted in a remarkably lower volume fraction of β-phase relative to the as-cast.

Confirming the microstructure observation, the XRD patterns of the as-cast and solution-treated Mg-9Al-1Zn alloys revealed that the main composition of the alloys was α-Mg and β-Mg₁₇Al₁₂ phases as shown in figure 2. The existence of α-phase was recognized by the serial distinct peaks at the angles 32.6°, 34.7°, 37.0°, 48.4°, 58.1°, 63.8°, 68.3°, 69.4°, 70.9°, and 79.0° in the XRD curves for both as-cast and solution-treated alloys. The peaks intensity of the α-phase was higher for the solution-treated alloy indicating larger crystalline phase than that for the as-cast one which confirmed the microstructure observation in figure 1. The peaks corresponded to β-phase was rather small although unambiguously resolved at the angles of 34.4°, 36.1°, 40.4°, 44.8°, and 65.4° for the as-cast alloy. Some peaks for β-phase did not arise in the curve of solution-treated alloy indicating less number of β-phase. The solution treatment reduced the number of β-phase precipitates similar to the reported work in ref [6].
Figure 1. The optical microscope images showing the microstructure of a) as-cast and b) solution-treated Mg-9Al-1Zn alloys.

Figure 2. X-ray diffraction pattern of as-cast and solution-treated Mg-9Al-1Zn alloys.

The effect of solution treatment on the mechanical hardness of as-cast Mg-9Al-1Zn alloy was not significant. The hardness decreased slightly as a result of solution-treated as displayed in figure 3. The as-cast alloy exhibited an average hardness of 61.86 HV while the solution-treated alloy showed a hardness value of 60.66 HV. Reduction of hardness as a result of solution treatment was due to the dissolution of intermetallic precipitate β-phase into solid solution matrix. The precipitate played a role as a hardening phase in the alloy. The release of residual stress during solution treatment also contributed to the reduction of the mechanical hardness of the alloy [11].

Figure 3. The mechanical hardness of as-cast and solution-treated Mg-9Al-1Zn alloys.
Figure 4 shows the results of the corrosion test by measuring weight loss after 24, 48, and 72 h immersion in 3.5% NaCl solution at 30°C. Both specimens showed a linear increase in weight loss with exposure time but at a different slope. The solution treated alloy consistently showed higher material loss than that of the as-cast alloy. The as-cast alloy exhibited weight loss rate of 0.045 g.cm\(^{-2}\).h\(^{-1}\) while the rate for solution-treated specimen was higher at 0.056 g.cm\(^{-2}\).h\(^{-1}\) indicating higher dissolution than the as-cast one.

Figure 5 shows the specimen appearance after the immersion test for 24, 48, and 72 h in 3.5% NaCl solution at 30°C. The as-polished surface which exhibited a metallic reflection turned to a whitish rough surface after immersion for 24 h and longer. In agreement with the weight loss data presented in figure 4, the specimen already suffered from harsh corrosion attack after 24 h immersion. The material loss increased significantly with extension immersion time as indicated by decreasing in the specimen thickness and diameter. The specimen dimension decreased faster in the solution-treated specimen than in the as-cast one. Significant material dissolution occurred during immersion as indicated by the accumulation of white deposit in the solution at the bottom of the glass. During drying of the specimen
after the 72 h test was terminated, the specimen was easily disintegrated into powder. The specimen became spongy after 48 and 72 h immersion. The spongy structure was obtained as a result of selective corrosion of the α-Mg matrix leaving the β-phase. The corrosion test results demonstrated that the Mg-9Al-1Zn was susceptible to micro galvanic corrosion due to the potential gradient between the α-Mg matrix and the β-phase intermetallic precipitate. However, the β-phase precipitate also contributed to providing a barrier for corrosion propagation across the grain when forming a continuous network along grain boundaries. Therefore, the as-cast alloy had a lower weight loss rate relative to the as-cast alloy. The dual role of β-phase precipitates had been observed in AZ series alloys [1].

4. Conclusion
The effect of solution treatment on the microstructure development and the weight loss rate during the corrosion test of as-cast Mg-9Al-1Zn alloy has been investigated. The metallographic observation revealed that the solution treatment enhanced dissolution of the intermetallic precipitate β-phase in the α-Mg matrix. The reticular distribution observed in the as-cast alloy disappeared after solution-treatment leaving a random distribution of the β-phase intermetallic. Since the metallic grain size became significantly larger (10x), the volume fraction of β-phase precipitate decreased significantly as a result of solution treatment. The reticular distribution of β-phase precipitate existed in the as-cast alloy was beneficial in stopping the corrosion propagation across the grain. The weight loss rate of the as-cast alloy was hence lower than that of the solution-treated alloy.

References
[1] Song G 2011 Woodhead Pub. 117-260
[2] Pekguleryuz M O, Kainer K U, Kaya A A 2013 Woodhead Pub. 125-189
[3] Esmaily M, Svensson J E, Fajardo S, Birbilis N, Frankel G S, Virtanen S, Arrabal R, Thomas S, Johansson L G 2017 Prog. Mater. Sci. 89 92-193
[4] Jin X, Xu W, Li K, Zeng X, Shan D 2018 Mater. Sci. Eng. A 729 219-229
[5] Liu Q, Ma Q, Chen G, Cao X, Zhang S, Pan J, Zhang G, Shi Q 2018 Corros. Sci. 138 284-296
[6] Yuan G, You G, Bai S, Guo W 2018 J. Alloys and Compd. 766 410-416
[7] Li J, Jiang Q, Sun H, Li Y 2016 Corros. Sci. 111 288-301
[8] Barylski A, Kupka M, Aniolek K, Rak J 2017 Vacuum 77-86
[9] Anawati A, Asoh H, Ono S 2016 AIP conference Proc. 1725 020002
[10] Anawati A, Asoh H, Ono S 2018 International Journal of Technology 3 622-631
[11] Wang C, Luo T, Zhou J, Yang Y 2018 Mater. Sci. Eng. A 722 14-19

Acknowledgement
This work was fully supported by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA) Universitas Indonesia with contract no. 2226/UN2.R3.1/HKP.05.00/2018. The authors would like to thank to Adi Ganda Putra for helping with the casting process.