

# Effects of Zirconium Incorporation on Corrosion Resistance of AZ91 Magnesium Alloy

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**Abstract**—This study aimed for improving wear resistance of AM60 magnesium alloy by Ti addition (0, 0.2, 0.5, 1wt%Ti). An electric resistance furnace was used to produce alloys. Pure Mg together with Al, Al-Ti and Al-Mn were melted at 750 °C in a stainless steel crucible under controlled Ar gas atmosphere and then poured into a metal mould preheated at 250 °C. Microstructure characterizations were performed by light optical (LOM) and scanning electron microscope (SEM) after the wear test. Wear rates and friction coefficients were measured with a pin-on-disk type UTS10 Tribometer test device under a load of 20N. The results showed that Ti addition altered the morphology and the amount of  $\text{Mg}_{17}\text{Al}_{12}$  phase in the microstructure of AM60 alloy.  $\text{Mg}_{17}\text{Al}_{12}$  phases on the grain boundaries were refined with increasing amount of Ti. An improvement in wear resistance of AM60 alloy was observed due to the alteration in the microstructure by Ti addition.

**Keywords**—Magnesium alloy, titanium, SEM, wear.

## I. INTRODUCTION

In recent years, there has been a considerable increase in the use of magnesium as a structural metal due to its unique high specific strength. The lightness of magnesium alloys makes them very promising materials to replace aluminum and its alloys in primarily automotive, aerospace and railway applications providing better fuel efficiency and higher performance. Magnesium alloys have also excellent castability, machinability, hot formability and damping capability [1]-[3]. Nevertheless, some properties of magnesium alloys such as strength, fatigue and creep resistance at elevated temperatures, ductility, hardness, corrosion resistance and wear properties remain low compared to other structural metals. As surface related drawbacks of magnesium alloys, wear and corrosion resistances are tough challenges for the use of magnesium alloys in commercial applications [2]-[5].

Many research studies were carried out in order to improve wear resistance of magnesium alloys by surface modification [4]-[7]. Wear mechanisms and wear transition maps of various magnesium alloys with no external process for alteration of surface were also investigated in numerous studies [8]-[12]. It was reported that [8], [9] oxidation and abrasion were observed at low sliding speeds and loads whereas oxidation,

delamination and adhesion mechanisms were dominant at higher sliding speeds and loads in AM50B and AM60B magnesium alloys. Wear resistance of magnesium alloys can be improved through alloying additions providing second phase formation or changing the morphology and volume fraction of second phases and several studies focused on the effect of alloying elements on wear behavior of magnesium alloys [13], [14]. It was reported that [13], Sr addition improved the wear resistance of Mg-6Zn-4Si alloy by 0.5wt% Sr and further addition of Sr led to a decrease in wear resistance due to the formation of needle-like SrMgSi compounds. Another study showed an improved wear resistance in AZ91 magnesium alloy by Ce-rich mish metal addition due to the formation of  $\text{Al}_{11}\text{RE}_3$  phase [14]. The main wear mechanisms were found as abrasion, delamination and plastic deformation.

Although some improvements on wear resistance of magnesium alloys were achieved by different alloying additions, there is limited number of studies investigating the effect of Ti addition on wear properties of magnesium alloys. However, numerous studies were carried out on the effect of Ti addition on microstructure, mechanical, corrosion properties of several magnesium alloys [15]-[23]. It was reported that Ti addition by 0.5 wt% increased both the mechanical properties and corrosion resistance of AZ91 magnesium alloys [15], [16]. Another study demonstrated that trace amount of Ti addition by 0.01 wt% significantly increased the corrosion resistance of AZ61 magnesium alloys [21]. A grain refining effect by Ti addition was observed in Mg-Zn-Zr-Ca alloy [22]. It was also demonstrated that minor Ti addition on Mg-3Sn-2Sr led to a refinement of primary  $\alpha$  grains and an increase in the tensile and creep properties [23].

Since the influence of Ti addition on microstructure and wear properties of magnesium alloys have not been well understood, this study focused on investigating the microstructure and wear properties of AM60 magnesium alloy which is one of the most used commercial magnesium alloys. Different amounts of Ti (0, 0.2, 0.5 and 1 wt%) were used to investigate how the wear resistance of AM60 magnesium alloy changes.

## II. EXPERIMENTAL

### A. Casting

The Mg-6%Al-0.6%Mn alloys with different Ti additions (0, 0.2, 0.5, 1 wt%) were processed by conventional gravity casting. High purity Mg (99.9%), Al-10%Mn and Al-10%Ti master alloys were used to prepare the studied alloys. The alloys were melted in stainless steel crucible placed in an electric resistance furnace under controlled Ar gas atmosphere. After holding the melt at 770 °C for 45 minutes and stirring for 15 minutes, the melt was poured

into a metal mould preheated to 250 °C. The chemical compositions of the studied alloys are given in Table I.

TABLE I  
CHEMICAL COMPOSITION OF THE ALLOYS (WT%)

Alloys	Compositions (wt%)				
	Al	Mn	Zn	Ti	Mg
AM60	6.0	0.50	0.2	-	Bal.
AM60+0.2Ti	6.0	0.68	0.21	0.28	Bal.
AM60+0.5Ti	6.1	0.68	0.21	0.68	Bal.
AM60+1Ti	6.2	0.68	0.21	1.34	Bal.

### B. Microstructure

The microstructure images of the samples were taken by LOM.

### C. Wear Test

Samples having 30 mm x 10 mm x 5 mm dimensions were machined for wear tests. Contact surfaces of the samples were ground with 1000 grit emery paper. Wear tests were performed by a pin-on-disk type UTS-10 Tribometer test device. Wear rates, wear depth and friction coefficients of the studied alloys were measured under a load of 20 N, a sliding speed of 0.08 m/s and a sliding distance of 1000 m. SEM was used for the investigation of worn surfaces and the determination of the wear mechanisms.

## III. RESULTS AND DISCUSSION

### A. Microstructural Characterization

Optical micrograph images of AM60, AM60+0.2Ti, AM60+0.5Ti and AM60+1Ti alloys are given in Fig. 1. It can be partially divorced, granular, fibrous and lamellar shaped eutectic phase can be formed in sequence [24].

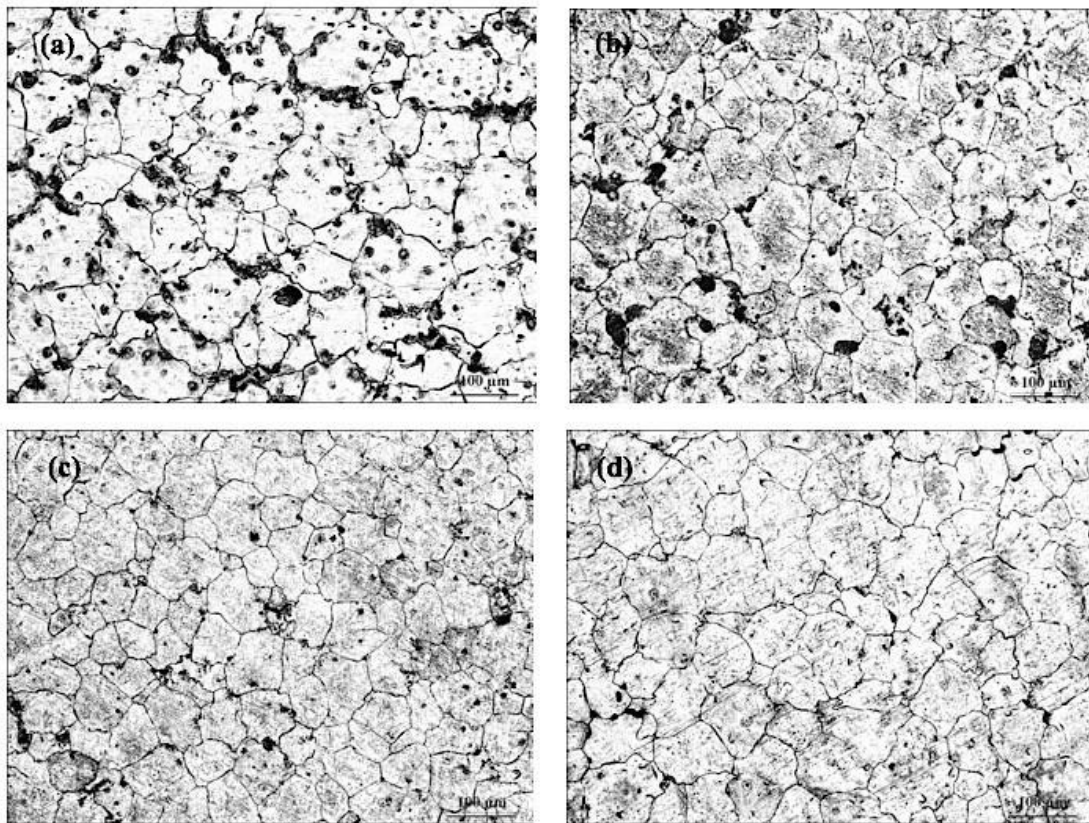


Fig. 1 Optical microstructures of (a) AM60, (b) AM60+0.2Ti, (c) AM60+0.5Ti, (d) AM60+1Ti

Before the microstructure analysis, all the samples were mechanically ground with 240, 400, 600, 800, 1000 and 1200 grit emery papers followed by polishing with 6 μm and 1 μm diamond paste. An etching solution of 50 ml picric acid, 20 ml glacial acetic acid, 10 ml distilled water and 10 ml ethanol was applied to the polished samples. After taking the optical microstructure images, average grain size measurements were performed on eight microstructures for each alloy by linear intercept method in accordance with ASTM E112 standard.

seen that all the studied alloys consisted of primary  $\square$ -Mg (white matrix) and  $\square$ -Mg<sub>17</sub>Al<sub>12</sub> intermetallic compound (dark regions). Essentially,  $\square$ -Mg<sub>17</sub>Al<sub>12</sub> eutectic phase appear in MgAl system under non-equilibrium cooling conditions during casting as little as 2 wt% Al even though the maximum solid solubility of Al in  $\square$ -Mg reaches 12 wt% [1], [24]. It was reported that both cooling conditions during casting process and alloying additions can significantly affect the morphology of eutectic phases in Mg-Al alloy. As the Al content increases or the cooling rate during casting decreases, fully divorced,

It was observed in Figs. 1 (a)-(d) that AM60 alloy contains high volume fraction of discontinuous  $\square$ -Mg<sub>17</sub>Al<sub>12</sub> eutectic phase and it significantly decreased with increasing amount of Ti. The morphology of the  $\square$ -Mg<sub>17</sub>Al<sub>12</sub> phase appeared to be changed from partially divorced to fully divorced structure. In a previous study [15], a considerable increase in Al content in  $\square$ -Mg solid solution was observed with increasing content of Ti from 0 to 1 wt%. This observed reduction in the volume fraction of  $\square$ -Mg<sub>17</sub>Al<sub>12</sub> phase is attributed to the higher Al content in the solid solution.

The effect of Ti addition on the average  $\square$ -Mg grain size in AM60 alloy is demonstrated in Fig. 2. It was observed that grain size of  $\square$ -Mg was refined with increasing amount of Ti addition. It can be said that Ti is an efficient grain refiner due to creation of new nucleation sites during solidification.

### B. Wear Properties

Wear tests were performed under a constant load, sliding speed and sliding distance of 20 N, 0.08 m/s and 1000 m respectively in order to investigate the effect of Ti addition on wear properties of AM60 magnesium alloy.

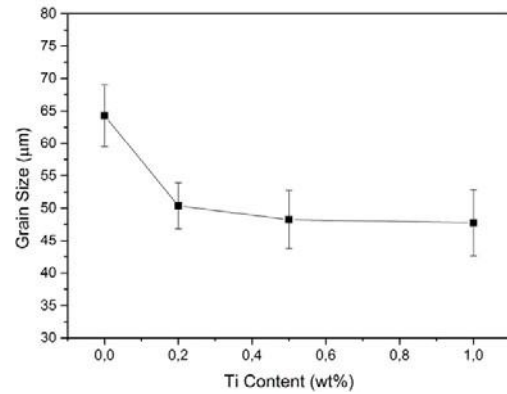


Fig. 2 Average  $\square$ -Mg grain size of AM60 as a function of Ti content

Wear depth graphs of the studied alloys given by the pinon-disk type wear test machine were presented in Figs. 3 (a)(d). It can be seen in Fig. 3 that the variability of wear depth changed as a function of Ti addition and the smallest wear depth was observed for AM60+0.2Ti as it is depicted in Fig. 4 with friction coefficient values.

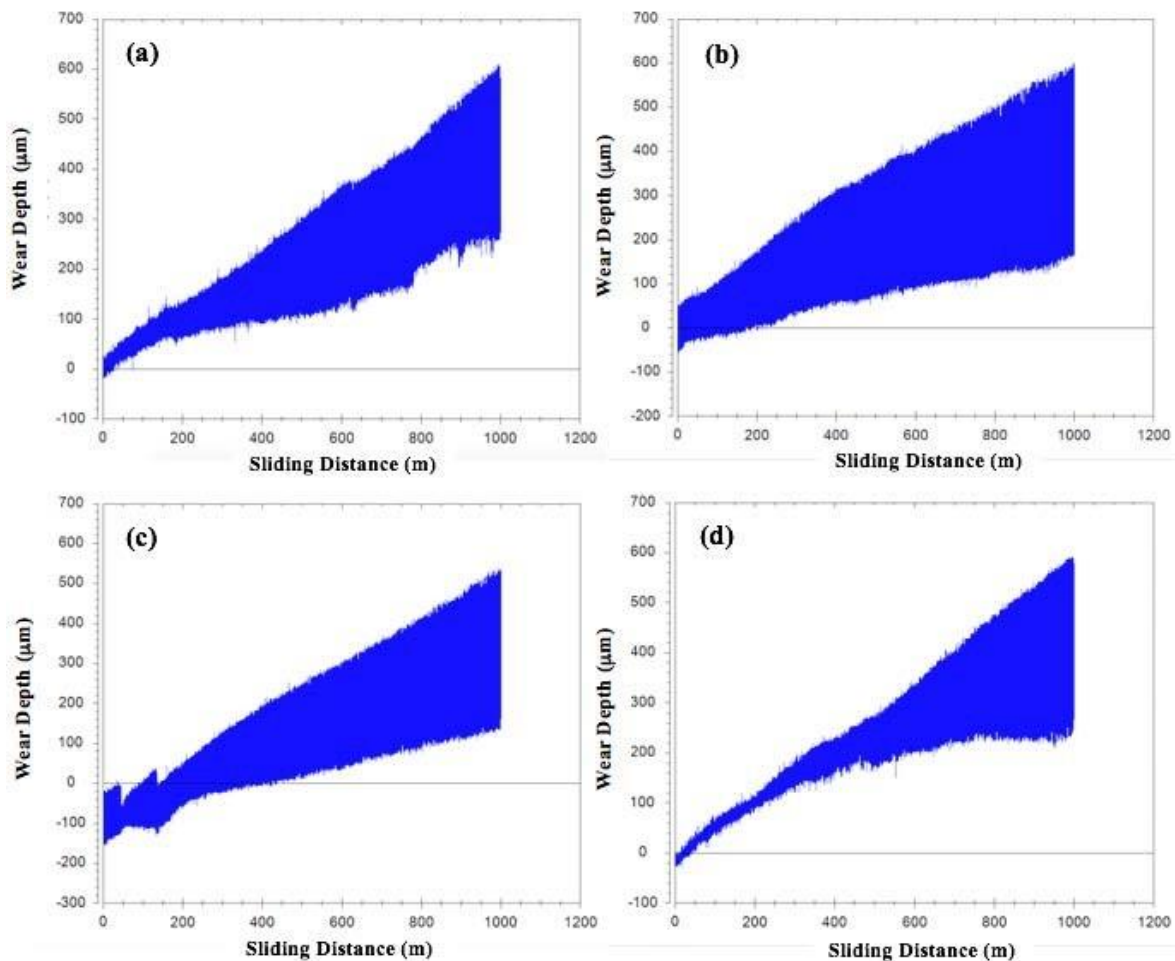


Fig. 3 Wear depth graphs of (a) AM60, (b) AM60+0.2Ti, (c) AM60+0.5Ti, (d) AM60+1Ti

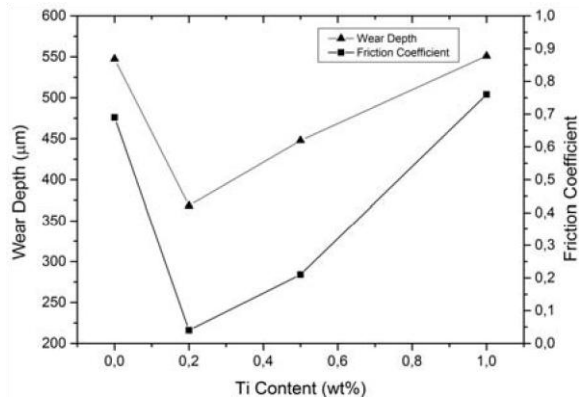


Fig. 4 Friction coefficient and wear depth value of AM60 as a function of Ti content

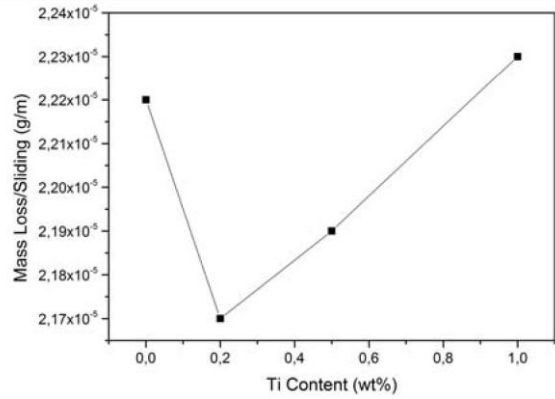


Fig. 5 Wear rate of AM60 as a function of Ti content

In accordance with the changes in the friction coefficients

It can be clearly seen in Fig. 4 that wear depth of AM60 and wear depth values, AM60+0.2Ti alloy exhibited the alloy significantly decreased with the addition of 0.2wt%Ti. lowest wear rate (mass loss/sliding distance) and as it is shown However, increasing amount of Ti led to an increase in wear in Fig. 5, increasing amount of Ti to 1wt% led to a depth and when the Ti addition was 1 wt%, the wear depth deterioration in wear resistance of AM60 alloy. Mg and Ti do became almost the same as AM60 alloy with no Ti addition. not form intermetallic compounds and Ti has a maximum Friction coefficients of the studied alloys were also indicated solid solubility in Mg by 0.24 wt% [25]. Therefore, the in Fig. 4 and a similar trend with wear depth was observed as decrease in the wear resistance of AM60 alloy above 0.2 wt% the smallest friction coefficient was found to be for

AM60+0.2Ti alloy. the matrix resulting in higher friction coefficient and mass loss

Ti addition can be attributed to the presence of Ti particles in between the contact surfaces during abrasion.

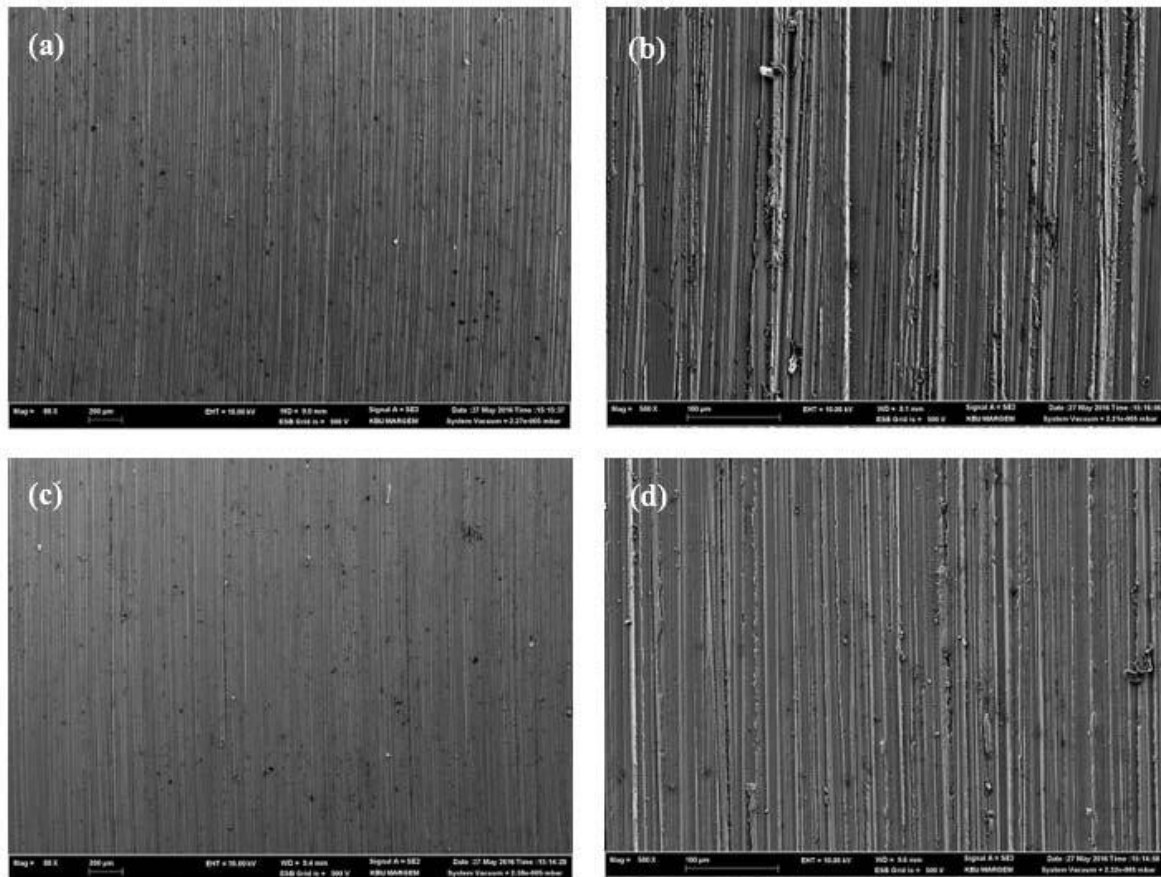


Fig. 6 SEM micrographs of the worn surfaces of (a) AM60 88X, (b) AM60 500X, (c) AM60+0.2Ti 88X and (d) AM60+0.2Ti 500X

Figs. 6 (a)-(d) show the worn surfaces of AM60 and AM60+0.2Ti alloys. The formation of fine wear grooves along the sliding direction was observed in both alloys. However, AM60 showed a rougher surface than AM60+0.2Ti alloy which can be associated with the presence of larger  $\square$ - $Mg_{17}Al_{12}$  eutectic phase in AM60 magnesium alloy. Hard  $\square$ - $Mg_{17}Al_{12}$  particles detached from the contact surface between the pin and the sample may bring about coarse scratches in AM60 alloy. As it was shown earlier in Fig. 1, Ti addition modified the morphology of  $\square$ - $Mg_{17}Al_{12}$  phase so that finer  $\square$ - $Mg_{17}Al_{12}$  phase led to a smooth worn surface in AM60+0.2Ti alloy as it is shown in Figs. 6 (c), (d). Nevertheless, above the maximum solid solubility of Ti in Mg solid solution (0.24 wt%), the presence of Ti particles in the matrix resulted in a decrease in the wear resistances of AM60+0.5Ti and AM60+1Ti alloys.

#### IV. CONCLUSION

The effect of Ti addition on the wear resistance of as-cast AM60 magnesium alloy was investigated and a relationship between the microstructure and wear behavior was presented. The following conclusion can be drawn:

- Ti addition can efficiently modify the microstructure of AM60 magnesium alloy by decreasing the amount of  $\square$ - $Mg_{17}Al_{12}$  phase and refining the  $\square$ -Mg grain size.  $\square$  A significant improvement in the wear resistance of AM60 magnesium alloy can be achieved by 0.2 wt% Ti addition. Going

up with the further addition of Ti led to a decrease in the wear resistance since those additions were above the maximum solid solubility limit of Ti in Mg.

- The main wear mechanism in modified and unmodified AM60 alloys was abrasion caused by the hard and oxidized particles and no delamination or strong adhesion wear mechanisms were observed since a low sliding speed of 0.08 m/s and a low load of 20 N were used in the wear test.

#### REFERENCES

- [1] M. M. Avedesian and H. Baker, *ASM Specialty Handbook: Magnesium and Magnesium Alloys*. ASM International, 1999.
- [2] A. A. Luo, "Magnesium casting technology for structural applications," *Journal of Magnesium and Alloys*, vol. 1, no. 1, pp. 2–22, Mar. 2013.
- [3] B. L. Mordike and T. Ebert, "Magnesium: Properties — applications — potential," *Materials Science and Engineering: A*, vol. 302, no. 1, pp. 37–45, Apr. 2001.
- [4] B. Carcel, J. Sampedro, A. Ruescas, and X. Toneu, "Corrosion and wear resistance improvement of magnesium alloys by laser cladding with Al-Si," *Physics Procedia*, vol. 12, Part A, pp. 353–363, 2011.
- [5] B. J. Zheng, X. M. Chen, and J. S. Lian, "Microstructure and wear property of laser cladding Al+SiC powders on AZ91D magnesium alloy," *Optics and Lasers in Engineering*, vol. 48, no. 5, pp. 526–532, May 2010.
- [6] M. K. Lei, P. Li, H. G. Yang, and X. M. Zhu, "Wear and corrosion resistance of Al ion implanted AZ31 magnesium alloy," *Surface and Coatings Technology*, vol. 201, no. 9–11, pp. 5182–5185, Feb. 2007.
- [7] J. Dutta Majumdar, R. Galun, B. L. Mordike, and I. Manna, "Effect of laser surface melting on corrosion and wear resistance of a commercial

- magnesium alloy,” *Materials Science and Engineering: A*, vol. 361, no. 1–2, pp. 119–129, Nov. 2003.
- [8] C. Taltavull, P. Rodrigo, B. Torres, A. J. López, and J. Rams, “Dry sliding wear behavior of AM50B magnesium alloy,” *Materials & Design*, vol. 56, pp. 549–556, Apr. 2014.
- [9] C. Taltavull, B. Torres, A. J. López, and J. Rams, “Dry sliding wear behavior of AM60B magnesium alloy,” *Wear*, vol. 301, no. 1–2, pp. 615–625, Apr. 2013.
- [10] S. Anbu selvan and S. Ramanathan, “Dry sliding wear behavior of ascast ZE41A magnesium alloy,” *Materials & Design*, vol. 31, no. 4, pp. 1930–1936, Apr. 2010.
- [11] H. Chen and A. T. Alpas, “Sliding wear map for the magnesium alloy Mg-9Al-0.9 Zn (AZ91),” *Wear*, vol. 246, no. 1–2, pp. 106–116, Nov. 2000.
- [12] J. An, R. G. Li, Y. Lu, C. M. Chen, Y. Xu, X. Chen, and L. M. Wang, “Dry sliding wear behavior of magnesium alloys,” *Wear*, vol. 265, no. 1–2, pp. 97–104, Jun. 2008.
- [13] M. Cong, Z. Li, J. Liu, and S. Li, “Effect of Sr on microstructure, tensile properties and wear behavior of as-cast Mg-6Zn-4Si alloy,” *Materials & Design*, vol. 53, pp. 430–434, Jan. 2014.
- [14] K. Meshinchi Asl, A. Masoudi, and F. Khomamizadeh, “The effect of different rare earth elements content on microstructure, mechanical and wear behavior of Mg-Al-Zn alloy,” *Materials Science and*
- [15] S. Candan, M. Unal, E. Koc, Y. Turen, and E. Candan, “Effects of titanium addition on mechanical and corrosion behaviours of AZ91 magnesium alloy,” *Journal of Alloys and Compounds*, vol. 509, no. 5, pp. 1958–1963, Feb. 2011.
- [16] X. Ai, “Effect of Ti on the Mechanical Properties and Corrosion of Cast AZ91 Magnesium Alloy,” *The Open Materials Science Journal*, vol. 6, no. 1, pp. 6–13, Feb. 2012.
- [17] P. Zhao, Q. Wang, C. Zhai, and Y. Zhu, “Effects of strontium and titanium on the microstructure, tensile properties and creep behavior of AM50 alloys,” *Materials Science and Engineering: A*, vol. 444, no. 1–2, pp. 318–326, Jan. 2007.
- [18] H. Y. Choi and W. J. Kim, “Development of the highly corrosion resistant AZ31 magnesium alloy by the addition of a trace amount of Ti,” *Journal of Alloys and Compounds*, vol. 664, pp. 25–37, Apr. 2016.
- [19] Z. Yu, A. Tang, L. Zhang, and F. Pan, “Effect of microalloying with titanium on microstructure and mechanical properties of AZ91 magnesium alloy,” *Materials Science and Technology*, vol. 30, no. 12, pp. 1441–1446, Oct. 2014.
- [20] T. J. Lee and W. J. Kim, “The significant effect of adding trace amounts of Ti on the high-temperature deformation behavior of finegrained Mg-6Al-1Zn magnesium alloys,” *Journal of Alloys and Compounds*, vol. 617, pp. 352–358, Dec. 2014.
- [21] J. Y. Choi and W. J. Kim, “Significant effects of adding trace amounts of Ti on the microstructure and corrosion properties of Mg-6Al-1Zn magnesium alloy,” *Journal of Alloys and Compounds*, vol. 614, pp. 49–55, Nov. 2014.
- [22] J. Chen, Y. Sun, J. Zhang, W. Cheng, X. Niu, and C. Xu, “Effects of Ti addition on the microstructure and mechanical properties of Mg-Zn-Zr-Ca alloys,” *Journal of Magnesium and Alloys*, vol. 3, no. 2, pp. 121–126, Jun. 2015.
- [23] M. Yang, H. Li, C. Duan, and J. Zhang, “Effects of minor Ti addition on as-cast microstructure and mechanical properties of Mg-3Sn-2Sr (wt.%) magnesium alloy,” *Journal of Alloys and Compounds*, vol. 579, pp. 92–99, Dec. 2013.
- [24] A. K. Dahle, Y. C. Lee, M. D. Nave, P. L. Schaffer, and D. H. StJohn, “Development of the as-cast microstructure in magnesium-aluminium alloys,” *Journal of Light Metals*, vol. 1, no. 1, pp. 61–72, Feb. 2001.
- [25] J. L. Murray, “The Mg-Ti (Magnesium-Titanium) system,” *Bulletin of Alloy Phase Diagrams*, vol. 7, no. 3, pp. 245–248, Jun. 1986.