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Laser-induced Microstructural Development and Phase Evolution in Magnesium Alloy

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Abstract:

Secondary phase plays an important role in determining [microstructures](#) and properties of magnesium alloys. This paper focuses on laser-induced microstructure development and secondary phase evolution in AZ91D Mg alloy studied by SEM, TEM and EDS [analyses](#). Compared to bulk shape and lamellar structure of [the](#) secondary phase in as-received cast material, rapid-solidified [microstructures](#) with various morphologies including nano-precipitates [were](#) observed in laser melt zone. Formation mechanisms of microstructural evolution and effect of phase development on surface properties were further discussed.

Key words: Laser processing; Secondary Phase; Rapid solidification; Magnesium alloy; Precipitation.

1. Introduction

Driven by energy and environmental concerns for lightweight structural as well as functional parts, magnesium alloys have been increasingly used in automotive, aerospace, and electronic industries due to [their](#) low [densities](#) and high specific [strengths](#) [1-5]. Unfortunately, practical application of Mg alloys has been largely limited due to poor surface-related properties [1, 2, 5]. Secondary phase in the microstructure normally helps to improve surface properties of [the](#) Mg alloys, but the effectiveness of such phase in improving surface performance depends on its amount and distribution in the matrix [1, 3]. It is believed that fine and homogeneous secondary phase provides [an](#) effective barrier for performance enhancement; however, the presence of coarse and non-homogeneously distributed microstructure could deteriorate surface performance [1, 2, 5].

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In recent years, laser processing of metallic materials including Mg alloys has attracted considerable attentions because the surface properties of laser-treated layer can be enhanced significantly [6-10]. As one of the most widely used Mg alloys AZ91D, previous studies show that wear and corrosion resistance of laser-melt AZ91D Mg alloy is improved significantly due to refined β -Mg₁₇Al₁₂ secondary phase and enriched alloying element concentration in the laser melt zone [9-12]. However, direct observation of laser irradiation on microstructural evolution of Mg alloy, in terms of phase transformation during rapid solidification, has not been fully reported, although it is well known that faster cooling rates produce finer microstructures. The formation mechanism of microstructure development is also open for debate. The objective of this study is to observe microstructural evolution of the β -Mg₁₇Al₁₂ secondary phase in AZ91D Mg alloy irradiated by a millisecond pulse Nd:YAG laser. Special attention is paid to understand effect of rapid solidification on phase transformation and phase precipitation induced by laser surface melting.

2. Experimental procedures

The material studied was an as-cast AZ91D Mg alloy with the following chemical composition (wt.%): Al 8.97, Zn 0.78, Mn 0.31, Si 0.023, Cu 0.002, Ni 0.0005 and Mg balance. The specimens of dimensions of 20 mm by 30 mm by 3 mm were extracted from an ingot, ground with progressively finer SiC papers (180, 400, 800, 1200, 2400 and 4000 grit), cleaned with alcohol, and then irradiated under Ar gas protection with an Nd:YAG laser system (wavelength of 1064 nm) using the following parameters: power density 3.82×10^4 W/cm², scanning speed 10 mm/s, repetition rate 100 Hz, pulse duration 1.0 ms, and spot overlap 50%. The laser was operated in a near TEM₀₀ mode, and the beam was defocused to 1 mm in diameter.

Microstructural features of as-received and laser-melted specimens were studied using a JEOL 5600 LV SEM and a JEOL 2010 TEM equipped with EDS. A selected area electron diffraction technique (SAD) in TEM was used to extract crystallographic information. The TEM thin foils were obtained first by polishing mechanically on one side of substrate until the samples were less than 30 μ m thick. Disks of 3 mm diameter were punched from the foils for subsequent jet electro-polishing in a solution composed of an electrolyte of 750 ml methanol, 150 ml butoxyethanol, 16.74 g magnesium perchlorate, and 7.95 g lithium chloride at -20 °C and an applied voltage of 40 V. Finally, ion beam

was used on a Gatan precision ion polishing system under conditions of 5.0 kV and an incident angle of 4-5°. An X-ray diffractometer (Philips PW1830 series) was used to identify phases in the as-received alloy and in the laser-melt zone.

3. Results

Figure 1 shows typical microstructural evolution of AZ91D Mg alloy before and after laser treatment. In the as-received microstructure, β -Mg₁₇Al₁₂ secondary phase indicated lamellar and bulk growth from the grain boundaries into α -Mg grain interior, as shown in Fig. 1 (a). After laser irradiation, the microstructure of AZ91D Mg alloy was much refined, as shown in Figs. 1(b) and (c). Typical cellular/dendrite structure was observed in the melt zone, and line-shape structure was also found. XRD analyses indicated that the solidification microstructure of laser melted AZ91D Mg alloy consisted of refined α -Mg matrix phase and β -Mg₁₇Al₁₂ secondary phase [11, 12].

Fig. 1 Typical microstructure of AZ91D Mg alloy before and after laser treatment: (a) as-received microstructure, showing bulk and lamellar β -Mg₁₇Al₁₂ phase distributed in the α -Mg matrix. (b) laser-melt microstructure, showing longitude view of the melted zone; (c) laser-melt microstructure, showing cross-section view of the melt zone.

The solidification microstructure in the laser-melted zone was further investigated by TEM, as shown in Figure 2, Figure 3 and Figure 4. Figs. 2(a) and (b) show the cellular/dendrite structures of β - $\text{Mg}_{17}\text{Al}_{12}$ secondary phase. Figure 2(b) reveals that many individual precipitates were distributed randomly inside the matrix, and the sizes of these precipitates were in the range of 50-200 nm. SAD patterns show that these particles exhibit BCC crystal structure. Quantitative elementary compositions in the particles were analyzed by EDS, including 63.11 wt% Mg, 32.83 wt% Al, 3.48 wt% Zn and 0.68 wt% Mn. Therefore, these nano-scale precipitates were identified as β - $\text{Mg}_{17}\text{Al}_{12}$ secondary phase. It should be noted that various types of Mg-Al, Mg-Mn, and Mg-Ca precipitates are generated in sizes ranging from nanometers to microns in Mg alloys processed by different methods [13, 14]. However, rapid solidification induced by laser treatment results in a more homogeneous distribution as well as a relatively more refined scale.

Figure 3 shows that the typical orientation relationship (OR) between the individual nano-particle and the matrix. The OR between the plate-shape β - $\text{Mg}_{17}\text{Al}_{12}$ secondary phase and the α -Mg matrix was found to be Burgers OR ($(0001)\alpha // (110)\beta$), as shown in Fig. 3(a). It has been known that Burgers OR was the predominant Burgers OR of β - $\text{Mg}_{17}\text{Al}_{12}$ precipitation in AZ91D Mg alloy [15-17]. Moire fringes were observed in the precipitates due to overlapping effect between the nano-crystal and α -Mg matrix[18]. The OR between the spherical-shaped β - $\text{Mg}_{17}\text{Al}_{12}$ secondary phase and the α -Mg matrix was found to be $(10\bar{1}2)_m // (113)_p$, as shown in Fig. 3(b).

Fig. 2 (a) Bright-field TEM image of laser-melted AZ91D Mg alloy, showing lath-shaped β - $\text{Mg}_{17}\text{Al}_{12}$ formed along the cellular/dendrite structure. (b) Bright-field TEM image of laser-melted AZ91D Mg alloy, showing β - $\text{Mg}_{17}\text{Al}_{12}$ formed along the cellular/dendrite structure and sub-

micron and nanometer scale particles being distributed within the matrix, SAD pattern from one of these particles exhibiting BCC structure.

Fig. 3 (a) Bright-field TEM image of one individual plate-shape nano-particle, SAD pattern showing Burgers OR $(0001)_\alpha // (110)_\beta$ between β -Mg₁₇Al₁₂ secondary phase and α -Mg matrix. (b) Bright-field TEM image of one individual spherical-shape nano-particle, SAD pattern showing OR $(10\bar{1}2)_\alpha // (113)_\beta$ between the secondary phase and the matrix.

A large amount of cluster-shaped precipitates were observed in the overlapped region of laser-melt AZ91D Mg alloy, as shown in Figure 4. Figure 4(a) shows cluster-shaped precipitates together with individual tiny precipitates in the matrix. The size of cluster-shaped particles was in the range of 200-400 nm, while the size of individual particles was in the range of 50-100 nm. Figure 4(b) shows the morphology of one of these cluster-shaped precipitates, and it can be found that the nucleation and development of small particles above the existing particles. SAD pattern and EDS result confirmed that such cluster-shaped particles were β -Mg₁₇Al₁₂ precipitation. However, it should be noted that further effort needs to study the specific OR among each crystal and the OR between single nano-crystal and the matrix.

Fig. 4 (a) Bright-field TEM image of nanoparticles in the overlapped region of laser-melted AZ91D Mg alloy, showing cluster-shaped particles together with individual particles in the matrix; (b) Magnified view of one of these cluster-shaped particles.

4. Discussion

Generally, solidification reaction sequence in AZ91D Mg alloy can be described qualitatively at initiation of solidification using projection of liquidus valleys for Mg-rich region in Mg-Al-Zn system [19, 20], as shown in Fig. 5. The first solid to form would be α -Mg matrix due to combined effect of thermodynamics and kinetics [21, 22]. On further cooling, depending on prevalent solidification condition, liquid composition in enriched Al region, such as grain boundary where supersaturated α -Mg region with high Al concentration [15-17], could intersect the line of twofold saturation between α -Mg phase and β -Mg₁₇Al₁₂ secondary phase. At this stage (represented by point P and Q, respectively in Fig. 5), the solubility limit of primary solidification phase, α -Mg matrix, would be exceeded, and secondary solidification constituents $\alpha + \beta$ would form simultaneously from the liquid by an eutectic-type reaction $L \rightarrow \alpha + \beta$ in the structures, indicating as the lamellar structure in Fig. 1(a). During casting process, β -Mg₁₇Al₁₂ phase would form in high enriched Al region due to heterogeneous chemical composition in the liquid, and it would be elongated in the direction of the easiest heat loss, indicating as the bulk shape in Fig. 1(a). The liquid would continue to be consumed by this reaction as its composition changes along the monovariant line of twofold saturation. Final solidification could occur by the monovariant eutectic-type reaction, at the invariant reaction point Q. According to the

liquidus surface projection, point Q corresponds to the lowest temperature of intersections of the liquidus valleys and thus, represents the temperature at which terminal solidification occurs in the system.

Fig. 5. Liquidus projection surface for Mg-rich region of Mg-Al-Zn system [20]

However, during laser surface melting, where the molten pool is moved along laser beam through the material, the growth rate and temperature gradient vary considerably across the molten pool [19]. Based on our previous work [11, 12], solidification occurs spontaneously by epitaxial growth on the partially melted β -Mg₁₇Al₁₂ grains, and conditions for the growth of cellular/dendrite structure as well as line-shape structure are optimum when one of the easy growth directions coincides with the heat-flow direction. This is due to heat-flow control rather than interface control, as shown in Figs. 1 (b) and (c). It is well known that chemical composition plays a key role in determining the final microstructure during rapid solidification. In laser-melt zone of AZ91D Mg alloy, the content of Al element increases significantly due to rapid solidification and selective vaporization. On one hand, under laser irradiation where rapid solidification occurs, the solute is ejected by the α -Mg matrix at the liquid/solid interface when α -Mg phase propagates into the liquid from the original interface into the molten pool, resulting in a supersaturation of Al in the α -Mg matrix due to very high cooling rates [11, 23, 24]. On the other hand, selective vaporization of Mg and Al elements takes place, causing Al content increasing in the melted zone due to the relatively stronger evaporation of Mg element [12, 25, 26]. Therefore, eutectic reaction takes place in the molten pool due to the combined effect of thermodynamics and kinetics, leading to cellular/dendrite and line-shape structure simultaneously, and the final morphology of

solidification microstructure is determined by the localized liquid-solid interface stability factor G (temperature gradient)/ R (solidification rate) [19]. Such refined cellular/dendrite and line-shape structure of $\beta\text{-Mg}_{17}\text{Al}_{12}$ secondary phase plays a crucial role in improving degradation behavior of laser-melt AZ91D Mg alloy in modified-simulated body fluid, and increasing polar component of surface energy thus enhancing wetting and adhesion of laser-melt surface significantly. The details of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase evolution and surface properties change of laser-melt AZ91D Mg alloy were analyzed in our previous work[11, 12].

High degree of supersaturated $\alpha\text{-Mg}$ matrix as well as fine and uniform microstructure in the melt zone results in accelerated aging kinetics for $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitation [16, 27]. When laser beam was fired, the temperature was high enough and nuclei formed because random atomic vibrations were continually making tiny crystals of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase. When temperature was lower, these tiny crystals were thermodynamically stable and grew as individual nano-particles, as shown in Fig. 2. The presence of specific orientation relationship between $\beta\text{-Mg}_{17}\text{Al}_{12}$ nano particles and $\alpha\text{-Mg}$ matrix substantiated the argument that these precipitates resulted from a solid-state transformation, as shown in Fig. 3. According to the typical ORs $(0001)_{\alpha} \parallel (110)_{\beta}$ and $(10\bar{1}2)_{\alpha} \parallel (113)_{\beta}$, we propose that the interface between plate-shape particles and matrix is coherent, while the interface between spherical-shape particles and matrix is incoherent. Such discrepancy is related to precipitation sequence during rapid solidification in the melt zone. In addition, due to re-heating during laser scanning, a driving force tended to make dispersions of those tiny crystals coarsening in the overlapped region as a result of “quench-hold-quench” process [28, 29]. During coarsening, such small precipitates shrunk and eventually vanished together, while large precipitates grew by solid-state diffusion. This results in cluster-shaped particles in the microstructure, as shown in Fig. 4. However, the effect of $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitates on surface performance of laser-melt AZ91D Mg alloy is still not clear because it is difficult to separate them from the overall solidification microstructure including cellular/dendrite and line-shape structure in the melt zone. Further effort is needed to elucidate the role of submicron secondary phase precipitates in the properties of laser-melt surface.

5. Conclusions

Various morphologies of β -Mg₁₇Al₁₂ secondary phase were developed in the laser-melted AZ91D Mg alloy due to rapid solidification and selective vaporization as well as laser re-heating. It showed potential applications of microstructure optimization to enhance surface properties after localized laser processing. Cellular/dendrite and line-shape structures were formed mainly based on the combined effect of heat flow control thermodynamics and kinetics. Mechanism of submicron and nano-scale precipitates formation was due to solid-state transformation as a result of accelerated aging kinetics in the melt zone, and they occurred in both overlapped and non-overlapped region. Cluster-shaped β -Mg₁₇Al₁₂ particles were found in the overlapped region due to precipitation coarsening. Refined β -Mg₁₇Al₁₂ secondary phase played an important role in optimizing the microstructure and properties of Mg-Al alloys.

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References

1. M.M. Avedesian, H. Baker, Magnesium and magnesium alloys, ASM handbook. Materials Information Society, Materials Park, (1999).
2. K. Matsubara, Y. Miyahara, Z. Horita, T.G. Langdon, Acta Mater. 51(2003):3073.
3. C.S. Wang, Y.L. Gao, M. Yao, Acta Metal. Sin. 43(2007):493.
4. Y.C. Guan, W. Zhou, Mater. Lett. 62(2008):4494.
5. R. Ambat, N.N. Aung, W. Zhou, Corr. Sci. 42 (2000):1433.
6. S. A. David, T. DebRoy, Science 257(1992): 497.
7. M. Lee, S. Moon, M. Hatano, K. Suzuki, C.P. Grigoropoulos, J. Appl. Phys. 88 (2000):4994.
8. S.P. Harimkar, A.N. Samant, A.A. Khangar, N.B. Dahotre, J. Phys. D. 39(2006):1642.
9. Y. Chen, A. Samant, K. Balani, N.B. Dahotre, A. Agarwal, Appl. Phys. A 94(2009):861.
10. Y.C. Guan, W. Zhou, H.Y. Zheng, J. Appl. Electrochem. 39(2009):1457.
11. Y.C. Guan, W. Zhou, Z.L. Li, H.Y. Zheng, Appl. Surf. Sci. 255 (2009):8235.

12. Y.C. Guan, W. Zhou, H.Y. Zheng, Z.L. Li, *Appl. Phys. A* 101(2010): 339.
13. N. Hort, Y.D. Huang, K.U. Kainer, *Adv. Eng. Mater.* 8 (2006):235.
14. R.S. Coelho, A. Kostka, H. Pinto, S. Riekehr, M. Kocak, A.R. Pyzalla, *Mater. Sci. Eng. A* 485(2008):20.
15. C.P. Luo, X.L. Xiao, J.W. Liu, J.F. Nie, B.C. Muddle, *Acta Metall. Sin.* 38 (2002):7097.
16. Y. Wang, G. Liu, Z. Fan, *Acta Mater.* 54 (2006):689.
17. J.P. Zhou, D.S. Zhao, R.H. Wang, Z.F. Sun, J.B. Wang, J.N. Gui, O. Zheng, *Mater. Lett.* 61(2007):4707.
18. W.Z. Zhang, G.C. Weatherly, *Prog. Mater. Sci.* 50 (2005):181.
19. W. Kurz, D.J. Fisher, *Fundamentals of Solidification*, Trans Tech Publications, (1998).
20. V. Raghavan, J. Phase Equilib. Diff. 28(2007):203.
21. R.G. Ding, O.A. Ojo, M.C. Chaturvedi, *Scr. Mater.* 54(2006):859.
22. P.B. Oliete, J.I. Pena, A. Larrea, V.M. Orera, J. LLorca, J.Y. Pastor, A. Martin, J. Segurado, *Adv. Mater.* 19(2007):2313.
23. Y.C. Liu, Q.Z. Shi, G.C. Yang, Y.H. Zhou, *Mater. Lett.* 59(2005):813.
24. A. Bag, W. Zhou, J. Mater. Sci. Lett. 20 (2001):457
25. X. Cao, W. Wallace, C. Poon, J.P. Immarigeon, *Mater. Manuf. Process* 18 (2003): 1.
26. W. Zhou, T.Z. Long, C.K. Mark, *Mater. Sci. Tech.* 23 (2007):1294.
27. E. Cerri, S. Barbagallo, M. Cabibbo, E. Evangelista, *Magnesium technology 2002*, Warrendale, TMS, (2002).
28. M.F. Ashby, D.R.H. Jones, *Engineering materials 2: an introduction to microstructures, processing and design*, (2006).
29. R. Banerjee, A. Genc, D. Hill, P.C. Collins, H.L. Fraser, *Scr. Mater.* 53 (2005):1433.