Effect of processing environment on laser-induced darkening evolution in magnesium alloy

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2013

Guan, Y. C., Zhou, W., Li, Z. L., & Zheng, H. Y, (2013). Effect of processing environment on laser-induced darkening evolution in magnesium alloy. Optics and Lasers in Engineering, 52, 35-40.

<https://hdl.handle.net/10356/85037>

<https://doi.org/10.1016/j.optlaseng.2013.07.018>

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Abstract

Laser-induced darkening effect is an important phenomenon for Mg alloys to provide potential engineering applications in product identification, photocatalysts, and bio-optical implants. This work reports darkening evolution on Mg alloy by KrF excimer laser irradiation. Effort **was** made to study how processing environment influence morphological evolution and chemical variation of **laser**-irradiated surface. All irradiated surfaces **were** characterized using Talysurf surface profiler, atomic force microscope, scanning electron microscope and energy dispersive X-ray spectrometer. The results **showed** that oxygen content **played** a critical role in determining darkening effect on the Mg alloy, and surface morphology **transferred** from network structures to granular structures and protruding oxide particles when darkening **occurred**. Mechanism of laser-induced darkening in Mg alloy **was** further discussed.

Key words: Darkening; Excimer laser; Magnesium Alloy; Oxidation.

1. Introduction

Laser-induced coloration of material surfaces provides many promising engineering applications including decorations, photocatalysts, product identification, and biocompatible implants, and it also offers an alternative approach to understanding of coloration theory [1-9]. Zhao *et al.* [1] and He *et al.* [6] ascribed laser-induced coloration of WO₃ to photoinduced thermochromism, **which** was different from ordinary photochromism induced by UV light. Zheng *et al.* [7-9] studied color change of different material surfaces following laser irradiation, and they found that color generation was result of controlled surface oxidation during laser beam interaction with metal surfaces. Qian *et al.* [10] demonstrated formation of different oxides layer on **laser**-irradiated Ti surface, and they proposed that

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morphological change of irradiated area played an important role in determining the laser-induced coloration.

Nowadays, driven by energy and environmental concerns, Mg alloys have been increasingly used in industries due to their low density and high specific strength. However, actual use of Mg alloys has been limited in many applications because of poor surface properties [11-18]. Recent studies have showed that application of Mg alloys can be explored to more fields on basis of advanced surface engineering technology [12, 13]. As one of the most promising processes, laser surface engineering has been widely considered to improve surface performance without altering global properties of bulk materials [14-18]. In our previous work, improved corrosion resistance of AZ91D Mg alloy following laser surface melting was associated with microstructure refinement and Al concentration enrichment in the molten pool [16, 18]. Wettability of laser-melt Mg alloy was also enhanced, and this was useful to improve adhesion of Mg alloy substrates for better coating quality [19].

In this paper, surface darkening was achieved on AZ31B Mg alloy following by KrF excimer laser irradiation. The objective of current research is to understand how laser processing environment affects darkening evolution of Mg alloy. Special attention was made to study morphological difference and chemical variation of the irradiated areas in different environment.

2. Experimental Procedures

The material studied was wrought AZ31B Mg alloy with following chemical composition (in wt. %): Al 2.89, Zn 0.87, Mn 0.39, Si 0.015, Cu 0.001, Ni 0.0005 and Mg balance. The specimens of dimensions 20 mm by 30 mm by 3 mm were ground with progressively finer SiC paper (180, 400, 800, 1200, 2400 and 4000 grit), cleaned with alcohol, and then irradiated with laser at atmospheric pressure and room temperature.

The krypton-fluorine (KrF) excimer laser (with wavelength of 248 nm and pulse duration 25 ns) was used by following parameters: laser fluence 655 mJ/cm^2 and repetition rate 10 Hz. Laser beam was operated with a square beam spot of 3 mm side length, and number of laser pulses was varied from 100 to 800. In order to demonstrate effect of oxygen in processing environment on irradiated surface, the specimens were irradiated in air, under 0.5 bar Ar using jet nozzles and 2.0 bar Ar in well-sealed chamber, respectively, as shown in Fig. 1.

After laser irradiation, microstructural features of irradiated areas were investigated using JEOL 5600 LV SEM, equipped with an energy-dispersive X-ray spectrometer (EDS). The EDS measurements provided information on chemical composition. Surface topography with low laser pulses was measured using AFM in tapping mode. The surfaces produced with large number of laser pulses were too rough to be characterized with AFM, so their topography was characterized using a Taylor Hobson Precision Talysurf profiler.

3. Results and Discussion

Observation of AZ31B Mg alloy surface after Excimer laser irradiation by naked eyes is shown in Fig. 2. **Darkening effect** was obtained at most of laser-irradiated **surfaces** both in air and under Ar nozzles. With the increasing **number of** laser pulses, the color became darker significantly. Compared to the specimens irradiated in air, color transition on the surface was slower under Ar nozzles. When laser irradiated **Mg alloy** in Ar chamber, evolution of color change was not obvious, only partially darkening occurred at the irradiated area under large laser pulses.

Morphological evolution of all **surfaces** before and after laser **processing** was investigated using SEM. Before laser irradiation, surface of AZ31B Mg alloy was smooth due to fine grinding and polishing mechanically. After laser irradiation, the surfaces were roughened significantly with the increasing number of laser pulses. **In order to study color transition of irradiated areas, SEM results were presented to show the morphological evolution with progressive laser pulses under Ar nozzles**, as shown in Fig. 3. Fig. 3 (a) and (b) displays network structures at the surface when the number of laser pulses was 100 and 200. When laser pulses increased to 300, granular structures together with small particles were observed, as shown in Fig. 3 (c). At large number of laser pulses from 400 to 800, the amount of particles increased significantly, and surface features became coarse and poorly defined, as shown in Fig. 3 (d) to (f). Morphological evolution of irradiated surfaces both in air and in Ar chamber was also observed. SEM results **of laser pulses 800** are shown in Fig. 4. Fig. 4 (a) presents a large amount of particles at the coarse surface after laser irradiation in air. Fig. 4 (b) displays network structures and few granular structures as well as few particles at the smooth surface after laser irradiation in Ar chamber. It should be noted that the surface features of three irradiated areas were

similar, thus subsequent study will be mainly focused on the transition results obtained using Ar nozzles.

Since SEM images cannot reveal all information of morphological evolution in the irradiated area when laser pulses are low (Fig. 3 (a) and Fig. 3 (b)), those areas were further characterized using AFM. Fig. 5 shows clearly that surface topography of the irradiated areas changed from network structures when laser pulses were 100, to granular structures together with small particles when laser pulses were 200. Fig. 6 presents the distinct boundary between irradiated area and non-irradiated area in the periphery region, and the irradiated area was found to be above the non-irradiated area based on line profile drawn from AFM image, as shown in Fig. 6 (b).

When laser pulses increased to 300, granular structures and small particles totally replaced network structures at the irradiated areas, as shown in Fig. 3 (c) to Fig. 3 (f). However, such area was too rough to be characterized with AFM, so the Talysurf surface profiler was used to study the surface topography. Fig. 7 shows that the small particles were protruded above the surface of irradiated area. This observation lends support to assumption that these small white particles formed as a result of material redeposition during laser irradiation according to previous findings [7, 10, 19, 20]. According to Talysurf profiler measurement, surface roughness Ra of the irradiated areas was found to be increased linearly from 382 nm to 641 nm with laser pulses from 100 to 800, as shown in Table 1. It is also found that surface roughness of irradiated areas in air increased much more significantly than that of using Ar nozzles, while Ra in Ar chamber was the smallest. This is in good agreement with the SEM results of Fig. 3 and Fig. 4.

Investigation of chemical composition of irradiated areas was carried out using EDS. Quantitative analyses of small white particles found that O and Mg contents were about 38 wt% and 59 wt%, respectively, which was believed to be magnesium oxide (MgO). This indicated that oxidation could not be eliminated completely during laser irradiation using Ar nozzles. Fig. 8 shows the distribution of O element in the periphery region of the irradiated area when laser pulses were 800, and O concentration increased significantly from non-irradiated area to irradiated area. In addition, the distribution of average O concentration at all irradiated areas as a function of laser pulses was shown in Table 2. O concentration was found to be increased linearly with the number of laser pulses in three media, and transition of darkening occurred when it was above 8 %. O concentration at the area irradiated in Ar chamber was much less than that in air and under Ar nozzles. This indicates that the

darkening effect of AZ31B Mg alloy surface was accompanied by laser-induced oxide formation. Further effort is needed to analyze chemical state of O as well as formation of oxides by advanced techniques, such as X-ray photoelectron spectroscopy.

After a few initial laser pulses under the current laser fluence, the surface of AZ31B Mg alloy was heat treated and molted due to high thermal conductivity (77 W/m K at 20° and 102 W/m K at 250°) and low melting point as 632° [11]. Subsequently, surface tension of the liquid led to surface curling, thereby resulting in the formation of network structures at the irradiated area, as shown in Fig. 3 (a) and Fig. 5 (a). It is known that both melted volume and plasma/plume is involved during nanosecond pulse laser irradiation of material surface [13, 21]. Previous study has been reported that the major advantage of nanosecond laser pulses is the presence of laser-ejected small species during laser material processing [22, 23]. Therefore, Mg alloy surface would be strongly excited with the increasing laser pulses, causing rapid ejection of species [24, 25].

In the presence of oxygen in processing environment, oxidation would happen inside the ablated material plume, resulted in formation of oxides. The oxides would deposit to the surface during rapid cooling condensation and plume collapse process [7-10, 19], resulting in protruded oxides particles at the surface, as shown in Fig. 6. When laser pulses were very large, the network structures and the oxide particles further interacted with each other [1, 26], leading to coarse surface features in the form of droplets, thus isolated melt as granular structures companied with more oxide particles were formed at the irradiated area. The oxidation level and surface roughness of irradiated areas increased with oxygen content in the processing environment, as shown in Fig. 3 (c)-(f), Fig. 4 (a), Table 1 and Table 2. However, when laser irradiated AZ31B Mg alloy in well-sealed chamber with 2.0 bar Ar gas flow, few oxide particles and granular structures were investigated at the surface due to less oxidation as well as hydrodynamic ablation [27], as shown in Fig. 4 (b).

4. Conclusions

Darkening evolution of AZ31B Mg alloy caused by processing environment was investigated after KrF excimer laser irradiation upon with progressive pulses. With the increasing number of laser pulses in the presence of oxygen, color of irradiated areas became dark rapidly, and oxidation as well as surface roughness increased significantly. Transition of darkening occurred when surface morphology

changed from network structures to granular structures as well as protruding oxide particles, and average oxygen concentration was above 8 %. The mechanism of surface darkening was proposed to be as a result of combined effect of morphological difference and compositional variation. The current study indicates that laser-induced darkening in Mg alloy has potential application in many fields, such as photocatalysts, product identification and biocompatible implants.

Acknowledgements

Support by Nanyang Technological University, Ph.D. scholarship and Singapore Institute of Manufacturing Technology, A*STAR (Agency for Science, Technology and Research, Singapore), Collaborative Research Project U11-M-030AU is gratefully acknowledged. The authors would like to express grateful thanks to Dr. Wang Xincan, Dr. Wang Zhongke, Mr. Teh Kim Ming, and Mr. Tan Chi Wai from SIMTech for their guidance and help in this work.

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Figures captions

Fig. 1 Schematic diagram of experimental setup for Excimer laser on AZ31B Mg alloy in air (a), under 0.5 bar Ar using jet nozzles (b) and 2.0 bar Ar in well-sealed chamber (c), respectively.

Fig. 2 Photo showing darkening evolution of irradiated areas with progressive laser pulses on AZ31B Mg alloy in air, under Ar nozzles and in Ar chamber, respectively.

Fig. 3 SEM images showing morphological evolution of AZ31B Mg alloy surface after irradiation with progressive laser pulses under Ar nozzles: (a) 100 pulses; (b) 200 pulses; (c) 300 pulses; (d) 400 pulses; (e) 500 pulses; (f) 800 pulses.

Fig. 4 SEM images showing surface morphology of AZ31B Mg alloy after irradiation with 800 laser pulses in air (a) and in Ar chamber (b).

Fig. 5 AFM images showing surface topography of AZ31B Mg alloy after irradiation under Ar nozzles with (a) 100 pulses and (b) 200 pulses.

Fig. 6 AFM images showing irradiated areas of AZ31B Mg alloy after irradiation with 200 laser pulses under Ar nozzles: (a) AFM image at the boundary between irradiated area and non-irradiated area. (b) Line profile of AFM image shown in (a).

Fig. 7 3D surface profiler image showing irradiated area of AZ31B Mg alloy after irradiation with 300 laser pulses under Ar nozzles.

Fig. 8 Distribution of oxygen element in the boundary between irradiated area and non-irradiated area of AZ31B Mg alloy after irradiation with 800 laser pulses under Ar nozzles.

Fig. 1

Fig. 2

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 3

(a)

(b)

Fig. 4

(a)

(b)

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Table 1 Surface roughness Ra (nm) of irradiated AZ31B Mg alloy as a function of laser pulses in air, under Ar nozzles and in Ar chamber, respectively.

Environment	Air	Ar nozzles	Ar chamber
Laser pulses			
100	411	382	102
200	503	447	138
300	627	535	204
400	702	566	219
500	825	603	249
800	966	641	278

Table 2 Average oxygen content (wt.%) at the irradiated area of AZ31B Mg alloy as a function of laser pulses in air, under Ar nozzles and in Ar chamber, respectively.

Environment	Air	Ar nozzles	Ar chamber
Laser pulses			
100	7.12	6.41	5.03
200	12.38	8.26	5.98
300	16.26	10.75	6.41
400	18.64	13.68	7.36
500	21.75	15.46	8.52
800	26.52	19.72	10.08