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Femtosecond Laser-induced Iridescent Effect on AZ31B Magnesium Alloy Surface

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Abstract:

Both micro-ripples and nano-ripples were firstly reported at AZ31B magnesium alloy surface irradiated by femtosecond laser in atmospheric environment. Iridescent effect was also demonstrated over a large area of the irradiated surface induced by scanning laser beam. Results revealed that the color effect was mainly attributed to the nano-ripples with broad distribution of periods acting as diffraction gratings, and intensity of the structural color was greatly influenced by morphology evolution of the micro-ripples with laser processing. It was suggested that near-field interference between surface plasmons polaritons and incident laser light determined the formation of the nano-ripples, and initial surface roughness combining with such interference lead to the formation of the micro-ripples. Potential applications of such effect on Mg alloys and how to apply the technique to other materials with different properties was further proposed.

Key words: Structural color; Periodic surface structures; Femtosecond laser; Diffraction and gratings; Magnesium alloy

1. Introduction

The generation of laser-induced periodic surface structures, also termed as ripples, is a universal phenomenon during laser irradiation [1-21]. According to previous studies, most of the ripples can be classified into two groups [7-14]. One is called low spatial frequency ripples, with a spatial period close to the wavelength of the incident light. The other is called high spatial frequency ripples, with a spatial period significantly smaller than the wavelength of the incident light. It has been widely accepted that surface plasmon polaritons as well as surface roughness plays significant role in formation of ripples based on investigations over the past 30 years [1-6]. Brueck and Ehrlich firstly discussed surface plasmon polaritons

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for explanation of the ripples [2]. Clark et al. [4] and Schmidt et al. [5] explained the interference between incident light field and electric field of plasma wave for ripples formation. Barnes et al. [6] further reported that interaction of surface plasmons with light could be tailored by altering the structure of a metal's surface.

In recent years, structured color caused by ripples acting as diffraction grating has attracted much attention due to unique surface properties [10, 12, 16, 19, 20]. Vorobyev and Guo [10, 12] produced ripples over an extended area by scanning a laser beam across a metal surface, and suggested that such technique could be an effective method to control optical properties of metals. Dusser et al. [16] demonstrated the possibility of achieving material modification using femtosecond laser irradiation to generate specific color patterns. Selectively decoration on steel using structural color with ripples has been examined by Yao et al. [20], and it shows potential applications in many fields, including anti-counterfeiting, color display, decoration, encryption and optical data storage. In nature, it is well known that structural color is responsible for the appearance of bird feathers, butterfly wings and beetle shells, and an iridescent effect occurs because reflected color depends on viewing angle, which is attributed to variation in the periods of these structures [22, 23].

Magnesium alloys have been widely used in the automobile, communication and aerospace fields due to low density and high specific strength [24], and also been considering as bio-medical materials due to bio-degradability and bio-absorbability [25]. Unfortunately, actual use of Mg alloys is limited due to inferior surface properties [22, 23]. Laser surface processing has been examined to further extend the applications of Mg alloys [26, 27], which offers the potential for developing new types of Mg-based materials and devices.

In this paper, we firstly report two types of ripples including micro-ripples and nano-ripples at surface of Mg alloy irradiated by femtosecond laser in atmospheric environment. We demonstrate how iridescent effect occur over a large area of irradiated surface and discuss the influence of ripples evolution with laser processing on wavelength as well as brightness of the structural color. We conclude by explaining the mechanism of two ripples formation during laser-material interaction, and indicate how it applies to other materials with different properties for potential applications.

2. Experimental procedures

The material studied was wrought AZ31B Mg alloy from Luoyang Hualing Magnesium CO., LTD. with the following chemical compositions (wt. %): Al 2.89, Zn 0.87, Mn 0.39, Si 0.015, Cu 0.001, Ni 0.0005 and Mg balance. The specimen at the dimensions of 30 mm × 30 mm × 3 mm were ground with progressively finer SiC papers (180, 400, 800, 1200, 2400 and 4000 grits), polished using 1.0 and 0.5 μm liquid diamond suspensions, and cleaned with alcohol. A Ti:Sapphire femtosecond laser (Clark-MXR, CPA-2010, wavelength 775 nm, pulse duration 150 fs, repetition rate 1000 Hz) was used in this study, as shown in Fig. 1 (a). The sample surface was irradiated under normal incidence by linearly polarized laser in air. The single pulse energy was 30 μJ at near-damage-threshold pulse energy, and laser-irradiated area was 20×20 mm² in square using hatched scanning mode in the program at speed of 50 mm/s. The laser scan number was varied from 1 to 100 using SCANLAB galvanometer scanner, and the beam spot size was focused as around 20 μm in diameter at the sample surface with a 4f optical system.

After the laser irradiation, optical reflection of the irradiated area was measured under normal incidence using Ocean optics DT-Mini-2 system and Spectrometer Operating Software. All specimens were exposed to Deuterium Halogen white light source via an adapter. Reflected light from the surface was guided to HR4000 High-Resolution spectrometer for characterization. Each reflection measuring test was repeated three times. Before each test, environment factor, such as fluorescent light and natural light, was excluded as reference. Microstructural feature of the irradiated area was examined by Scanning Electron Microscope (JEOL 5600 LV), and surface topography was inspected by Atomic Force Microscope (Veeco Nanoscope IIIa) in tapping mode. The probed areas were 10×10 μm² for all AFM measurements.

3. Results and Discussion

Fig. 1(b) displays iridescent effect on a typical surface of AZ31B Mg alloy following the femtosecond laser scanning. Compared to original metallic appearance of non-irradiated surface, optical performance of laser-irradiated regions was changed significantly. The laser-irradiated surface exhibits different colors, mainly including blue, green, orange and some yellow color in the transition region between green and orange, at different viewing angles by naked eyes, which is similar to the iridescent effect in nature as mentioned before [22, 23]. Such iridescent effect took place at all irradiated surfaces after laser scanning at different numbers of 10 to 100. When number of laser scanning was above 50, the brightness of the color by naked eyes was reduced largely with the increasing scanning number. No color but randomly spots or

small patterns were observed when scanning number is below 10.

Reflectance spectra of Mg alloy surfaces before and after the laser irradiation was examined, as shown in Fig. 1(c). Before the laser irradiation, the reflectance is nearly 100% in the visible spectral range from 475 nm to 750 nm due to non-irradiated surface being finely polished. After the laser irradiation, three dominant peaks appear in the spectra at 485 nm, 540 nm and 610 nm, which corresponds to the wavelength range of blue, green and orange color, respectively. Small and wide peaks can also be observed between 570 nm and 600 nm, and this belongs to yellow color wavelength range. This is in agreement with the observation of Fig. 1(b). The spectra patterns for all irradiated surfaces were the same, but the reflectance decreased to 10%-70% regarding to the non-irradiated surface when number of laser scanning increased from 10 to 50. The reduction of reflectance is possibly due to light trapping at rough surface when irradiation time increases [28]. The noise signal of the wavelength below 475 nm is attributed to environmental ambient light.

Fig. 1 (a) Femtosecond laser setup used for writing large-area structured color on AZ31B Mg alloy surface; (b) Photographs of typical iridescent effect on the irradiated surface by femtosecond laser scanning 30 times at pulse energy of 30 μ J and speed of 50 mm/s; (c) Reflectance of laser-irradiated surfaces at laser

scanning numbers as 10, 30, and 50 at pulse energy of 30 μJ and speed of 50 mm/s.

Morphological evolution of the above laser-irradiated surfaces was investigated by SEM. When the scanning number was 10, nano-sized ripples were produced on top of micro-size wavelike structures (micro-ripples) at the surface, as shown in Figs. 2(a)-(b). Orientation of the nano-ripples is perpendicular to laser polarization direction, and period is estimated in the range of 400-650 nm, which is appreciably smaller than laser wavelength at 775 nm. Orientation of micro-ripples is parallel to laser polarization direction (perpendicular to the nano-ripples), and period range is 1-3 μm . When number of laser scanning increased to 30 and 50, the micro-ripples expanded and clusters structure was developed inside the individual micro-ripple. The orientation of nano-ripples keeps the same as pervious direction, but the period decreases slightly (Figs. 2(b)-(f)). For number of laser scanning was more than 100, strong surface melting occurred and the micro-ripples and nano-ripples disappeared gradually. The structures of micro-ripples and nano-ripples are highly dependent on laser energy and material property. This is in according with the finding of Bonse et al. [29] (see Fig. 6 in Ref). Unfortunately, they did not give further explanation on the formation of micro-ripples.

Surface topography analyses of the nano-ripples and the micro-ripples were carried out by AFM. According to the surface profile in Figs. 3(f)-(h), the period of nano-ripples is in the range of 450 nm -620 nm. This is in agreement with SEM results in Fig. 2. It should be noted that the nano-ripples have a broad distribution of spatial periods smaller than laser wavelength, and their periodicity match the wavelengths of three dominant peaks as 485 nm, 540 nm and 610 nm from the reflectance spectra in Fig. 1(c). According to grating diffraction equation $d\sin\theta=n\lambda$ where n is refractive index, $d=n\lambda$ when the incident light angle is normal to the target surface. Therefore, we propose that structural color is responsible for iridescent effect on Mg alloy surface [22, 23], because ripples periodicity and wavelengths spectra follow grating diffraction equation very well when the sample material was irradiated under normal incidence by linearly polarized laser. However, further effort needs to study how the widely distributed nano-ripples lead to appearance of multiple peaks in the reflectance spectra. Figs. 3(a) and (e) show that shallow groves and randomly nano-protrusions are produced on the irradiated surface when numbers of laser scanning is low. With the increasing scanning number, the nano-ripples replace the nano-protrusions, and the period of such ripples is

in the same range (Figs. 3(b)-(h)). Fig. 3(f) reveals that the average period of such ripples is 530 nm at scanning number of 10. When number of laser scanning is 50, the average period of the nano-ripples decreases to 450 nm, as shown in Fig. 3(h). Micro-ripples are identified as valleys, and the depth increases with the scanning number. In addition, surface roughness Ra of all measured areas was measured as 113.3 nm, 136.9 nm, 164.5 nm, and 187.5 nm, respectively. It shows the irradiated surface is much rougher than original polished surface as 7.6 nm.

Fig. 2 Morphological evolution of AZ31B Mg alloy surfaces at laser scanning number of: (a)-(b) 10, (b) magnified image for (a); (c)-(d) 30, (d) magnified image for (c); (e)-(f) 50, (f) magnified image for (e). Laser pulse energy is 30 μ J and scanning speed is 50 mm/s.

Fig. 3 Profiles of topographical evolution on AZ31B Mg alloy surfaces at laser scanning number of: (a) and (e) 5; (b) and (f) 10; (c) and (g) 30; (d) and (h) 50. Laser pulse energy is 30 μJ and scanning speed is 50 mm/s.

Fig. 4 shows the formation of the micron-ripples and the nano-ripples on AZ31B Mg alloy surface by femtosecond laser irradiation schematically. When Mg alloy surface was initially irradiated by laser, rapid ejection of species including electrons, ions or atoms was excited strongly and the excited electrons transferred energy to metal lattice by electron-phonon coupling [30]. Meanwhile, plasma including the ejection of species was formed above the irradiated surface, as shown in Fig. 4(a). Figure 4(b) illustrates that nano-protrusions are produced randomly at the surface after a few laser pulses. Such nano-protrusions are mainly attributed to laser-ejected species, plasma confinement and material re-deposition within several picoseconds during rapid cooling condensation and plume collapse process [31]. When number of laser pulses increased, kinetic energy and temperature of the ejected species increased significantly [13]. Correspondingly, the expansion of high energy caused scattering of the ejected species, thereby leading to the nano-protrusions expanded and larger irradiated area occupied by these structures, as shown in Fig. 3(a). Meanwhile, surface plasmons (SP), both localized and propagating along the surface, would be excited by coupling the incident light to such-nano protrusions [13, 32], as shown in Fig. 4(c).

It is known that surface roughness plays a significant role for periodic structure formation [9, 12, 13],

thereby, the combined effect of initial surface roughness and the interference of laser and SP play an important role in forming micro-ripples. As shown in Fig. 3, the micro-ripples deepen and widen by more laser pulses, and this is caused by the efficient transfer of laser light to SP [13, 29]. According to one dimensional heat conduction model [34], maximum surface temperature of AZ31B Mg alloy was calculated as 1150 °C in this work, which was above its melting point as 632 °C [34]. Surface of Mg alloy was heat treated and molted due to high thermal conductivity at 75 W/mK [34]. Surface tension of the liquid lead to surface curling, and highly localized heating as well as large thermal gradients caused the development of severe strain fields, finally results in the formation of micro-ripples and their evolution on the surface (Figs. 2 and 3).

Subsequently, the developed nanostructures further excited the SP, and the SP interfered with the incident light [13, 31, 32, 34]. It has been suggested that the nano-ripples can be explained as the near-field interference between incident light field and the electric field of plasma wave [29, 30, 31, 34] due to the orientation of the nano-ripples being perpendicular to the direction of laser polarization. The final surface morphology including the micro-ripples and the nano-ripples is illustrated in Fig. 4(d).

Fig. 4 Schematic representation for the formation of laser-induced ripples on AZ31B Mg alloy during femtosecond laser irradiation: (a) surface absorption, ejected species and plasma; (b) nano-protrusions; (c) developed nano-protrusions and excited surface plasmons (SP); (d) micro-ripples and nano-ripples generation.

In this study, the period of the nano-ripples 450 nm-620 nm does not follow the classical relationship $\Lambda = \lambda / (1 \pm \sin \theta)$ obtained for sub-wavelength ripples [35]. Considering the effect of SP excitation, detailed and precise models were proposed by previous researchers [29, 36, 37]. λ_{sp} for metal/air interface can be

calculated based on dispersion relation $k_0[\epsilon_a\epsilon_b/(\epsilon_a+\epsilon_b)]^{1/2}$, where k_{sp} and k_0 are wave vectors of the SP and the incident light in vacuum, while ϵ_a and ϵ_b are relative dielectric constants of air and the metal, respectively. With the help of local field periodically enhanced by SPs, the interference fringes induce permanent ripples on material surface with Λ equal to λ_{sp} , which is smaller than λ . This is in good agreement with our observations of nanostructures in Figs. 2 and 3, which is the origin of sub-wavelength characteristic of the nano-ripples. Although dielectric constant of Mg alloy is not publically available to our best of knowledge, current nano-ripples have a broad distribution of spatial periods, and it indicates that the effective dielectric constants of both air and Mg alloy surfaces may vary significantly during laser processing, thus affect the overall effective refractive index of the SP and lead to the various periods of nano-ripples [3]. The average periods of the nano-ripples decreases slightly with laser scanning number, probably due to grating-assisted SP-laser coupling mechanism [13, 29]. Further effort is needed to elucidate the specific relationship between the SPs and these two ripples.

4. Conclusions

Micro-ripples and nano-ripples were formed at surface of AZ31B Mg alloy induced by femtosecond pulse laser irradiation. Iridescent effect was observed due to structured color caused by the nano-ripples as diffraction gratings. The formation of the nano-ripples was suggested to be caused by near-field interference between incident light and surface plasmons polaritons being excited in air and metal interface, while the formation of the micro-ripples was due to the combined effect of initial surface roughness and the near-field interference. By adjusting laser parameters according to thermal properties of materials, this technique can be applied in many applications, which offers the potential for developing new types of Mg-based bio-optical devices and color display.

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