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Wettability inversion of aluminum-magnesium alloy surfaces

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Abstract. The paper presents the experimental results on the use of low-temperature heating to reduce time of wetting inversion (from superhydrophilicity to hydrophobicity) of aluminum-magnesium alloy surfaces textured by laser radiation. Stable growth of the contact angle to 137.3–144.2° after heating surfaces (wettability properties deteriorate) was recorded. Wetting inversion from superhydrophilicity to hydrophobicity occurs in 2–3 hours of low-temperature heating of textured samples. The wettability inversion time depends on the type of texture. A significant increase in carbon content of elemental composition of the near-surface layer of samples after their low-temperature heating was registered.

1. Introduction
Laser processing is the most promising way to obtain surface structures with unique functional properties, as well as controllable wetting, spreading and evaporation of droplets [1,2]. Such surfaces are applied in aviation, energy, shipbuilding, medical equipment, biotechnology, microelectronics. It is used for non- and metallic surfaces, has low capital and operating costs, a fast and simple process easily scaled for details of a complex profile.

Many studies showed that immediately after laser texturing, the surface of the freshly treated metal was hydrophilic or superhydrophilic with the presence of micro / nanostructures [3–5]. When the laser-textured surface was exposed to ambient air for a relatively long time, it was possible to observe a transition of wettability from superhydrophilicity to superhydrophobicity [5–10]. Consequently, superhydrophobicity can be achieved on laser-textured metal surfaces when stored their in the ambient condition. The inversion time is different for different metals. For example, copper or brass textured by a nanosecond laser takes about 11–14 days to become superhydrophobic [11,12]. Jagdheesh et al. [13] reported that wettability inversion of laser ablated aluminum takes about 40 days. Whereas the wettability change of femtosecond laser ablated stainless steel requires more time than other metals (52–60 days) [14, 15].

To reduce the time required for the transition metal wettability from hydrophilic to superhydrophobic without using any chemical coating, it is proposed to use low-temperature annealing. D.-M. Chun et al. [16] reduced wettability transition time of pure copper plate treated by nanosecond pulsed laser from 2 weeks to several hours using low-temperature annealing (100 ° C).

In this work, we strive to find out the influence of low-temperature heating on the wetting inversion from super-hydrophilicity to hydrophobicity of laser-textured aluminum-magnesium alloy surfaces

2. Methods and materials
At present work, the aluminum-magnesium alloy is selected because of its widespread use in industry. Samples made of aluminum-magnesium alloy (Al 91.2, Mg 6.8, Mn 0.8, Fe 0.4, Si 0.4, Zn 0.2, Ti 0.1, Cu 0.1 in wt%) with a thickness of 5 mm and a diameter of 50 mm were used. Before texturing, the

surfaces were polished using the “Grinding Polishing Machine MP1B”. We used ultrasonic cleaner with distilled water and chemically pure isopropyl alcohol (C_3H_8O) for removing contaminants. Three-dimensional non-contact optical profilometer "MicroMesure 3D station" was used to investigate the texture of samples.

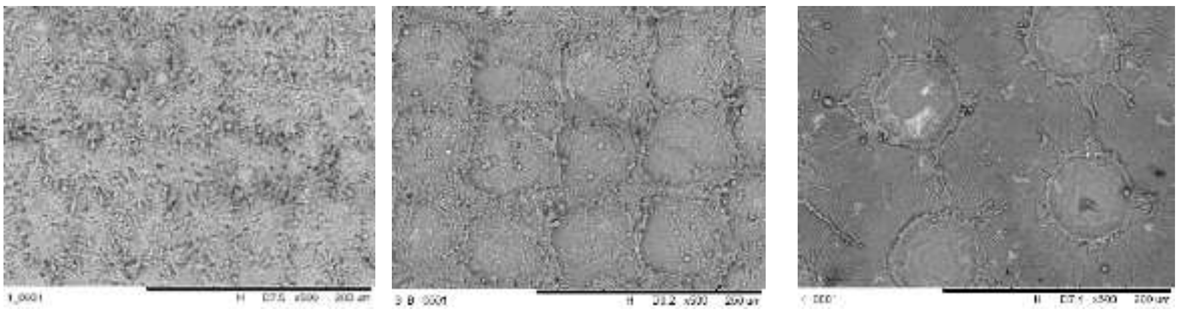
IPG-Photonics ytterbium nanosecond pulsed fiber laser (MiniMarker-2 Laser Center, 1064 nm wavelength) was used for laser texturing procedure. The procedure was carried out in air at a temperature of 20–22 °C, relative humidity of 35–40% and atmospheric pressure. The samples were affected by single laser pulses: duration is 200 ns, high average power – 20 W and frequency – 20 kHz. By varying the beam linear speed v (mm/s) and the number of lines n (mm^{-1}), three samples with different texture were created (table 1). The texture of sample No 3 formed at n = 7.1 mm^{-1} and v = 2800 mm/s is characterized by crater-like elements located at some distance from each other.

With such values of linear speed and number of lines, the light spots do not overlap on the surface. When v was reduced and n was increased, the nearest craters edges on the surface contact with each other (sample No 2). A partial overlap of the light spots occur with a further change in these parameters, and a texture of sample No 1 is formed with randomly located drops and jets of molten and solidified metal. Thus, two different types of textures were created: periodic (samples No 2 and No 3) and anisotropic (sample No 1).

Table 1. Laser parameters.

Parameters of Laser Beam Spatial Displacement	**Sample No**		
	1	***2***	***3***
n (mm^{-1})	20	15	7.1
v (mm/s)	1000	1320	2800

Images of the microstructure of aluminum-magnesium alloy surfaces textured with laser radiation were obtained using a scanning electron microscope (SEM) and are presented in Figure 1.



(a) (b) (c)

Figure 1. Surfaces microstructure images obtained with a scanning electron microscope. Sample Number: (a) No 1; (b) No 2; (c) No 3.

Experimental studies of wetting inversion were conducted on the setup with the use of shadow optical system (Figure 2).

We used low-temperature heating (heating of samples from their lower side by thermal conduction) for accelerating the wetting inversion process. This heating differs from low-temperature-annealing [17] implemented in the furnace where heat is transferrred by conduction, convection and radiation.

A polymer glass laboratory box (3 mm thick) was used to isolate experimental setup from external influences (convection). The substrate was mounted on the working cell, which consisted of a goniometer and a silicone heater connected to a laboratory autotransformer. The surface was heated to 100 ° C for six hours. The temperature under the substrate and on its surface was recorded by chromel-alumel thermocouples (with a measurement error of ± 0.1 ºC). The temperature difference did not exceed 0.1 ºC in the longitudinal coordinate direction. In addition, humidity inside the box was recorded.

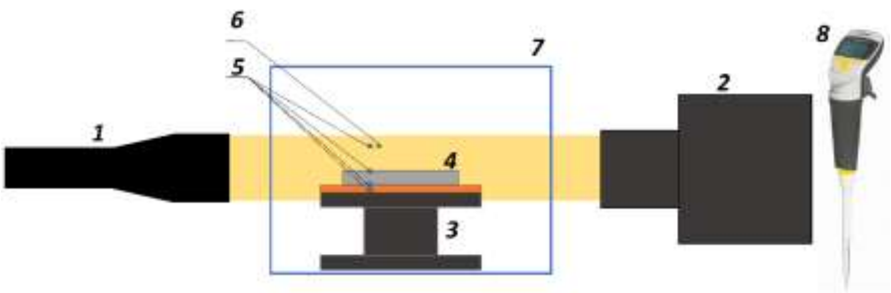


Figure 2. Experimental setup: 1 – light source; 2 – high-speed video camera; 3 – goniometer; 4 – substrate; 5 – thermocouples; 6 – humidity sensor; 7 – transparent box; 8 – dispensing device.

To measure the static contact angles, the shadow method was used. A beam of light from source passed through a fiber-optic illuminator, falling into a telecentric tube, where it was transformed into plane-parallel light. This light illuminated a droplet formed on the surface of the substrate with a dispensing device. Video camera with a macro lens was used to obtain photographs of droplets. The latter were processed by goniometry methods for determining contact angles. The random error of measuring contact angle did not exceed 5 %.

The elemental composition of the samples was analyzed on the Hitachi S-3400N scanning electron microscope using energy dispersive spectroscopy equipped with a Bruker XFlash 40 EDS chemical analysis unit. Studies were conducted before and after heating the samples.

3. Result and discussion

The contact angle was measured immediately after laser texturing. Then samples were heating for 6 hours at 100 ˚C, and contact angles were measured every hour. For each measurement, a droplet was placed on a previously unwetted surface area. The obtained results are presented in Figure 3. The static contact angle of polished surface of aluminum-magnesium alloy (before laser texturing) was 88.1°.

Figure 3 shows hydrophilicity of all samples that immediately after texturing ($\tau = 0$). At $\tau = 0$, the static contact angle increased in the sequence from sample No 1 to No 3. After two hours of heating, the contact angles on all samples increased: samples No 2, 3 showed hydrophobicity with $\theta = 142.9°$ and $\theta = 133.3°$, respectively, and sample No 1 remained hydrophilic ($\theta = 22.5°$).

At $\tau = 3$ hours, we registered the wetting inversion of sample No 1 from hydrophilicity to hydrophobicity. The wettability properties on sample No 1 stabilized more slowly than that on other one. Ngo and Chun obtained similar results that the decrease in the distance between the effects of light spots while texturing leads to an increase in the stabilization time of the static contact angle [17].

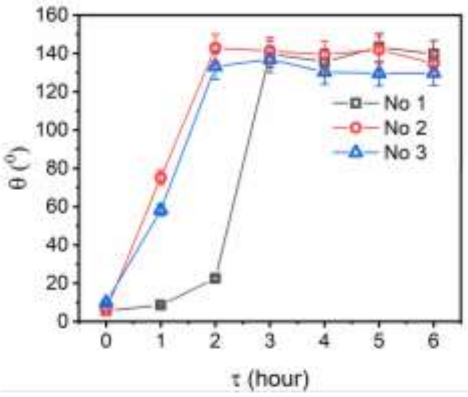


Figure 3. The static contact angle of textured samples at the heating time.

When all surfaces showed hydrophobic properties, in the range from 3 to 6 hours of heating, contact angle increased in the sequence from sample No 3 to sample No 1. In addition, 3–6 hours range is characterized by constant contact angles over heating. In Figure 4 shows typical photographs of water droplets before and after heating the substrate for six hours.

(a) (b)

Figure 4. Typical photographs of distilled water droplets on the surface immediately after texturing (a) and after six hours of heating (b).

In addition, for 1 month after heating the static contact angles on samples No 1–3 were measured. Table 2 shows the results of measurements of the static contact angle immediately after texturing with laser radiation, after 6 hours of heating and at 1 and 30 days after heating.

Table 2. Static contact angles measured on textured surfaces before and after heating.

Sample No	After Laser Texturing	After 6-hour Heating	One Day after Heating	Thirty Days after Heating
1	4.0±0.3	137.3±6.7	135.7±5.4	137.2±5.0
2	7.3±0.3	144.2±6.0	144.6±3.5	142.4±3.2
3	11.8±0.5	130.8±5.5	132.6±3.3	121.3±4.3

All samples retained hydrophobicity after heating, confirming the possibility of using low-temperature heating of an aluminum-magnesium alloy textured by laser radiation in order to reduce the time of wetting inversion from superhydrophilicity to hydrophobicity.

In [17], the change in the wettability properties of stainless steel treated with laser radiation after 6–20 hours is explained by an increase in carbon in the elemental composition of the samples. The latter is adsorbed from CO_2, which is part of the air. When samples are stored in the atmosphere, the reaction of CO_2 decomposition with carbon adsorption occurs slowly. Heating intensifies the decomposition process; the wetting inversion is accelerated.

Thus, the carbon adsorption can lead to a change in the wettability properties. To confirm this assumption, the elemental composition of the near-surface layer of anisotropic (sample No 1) and periodic (sample No 3) textures was analyzed using the EDS method. Table 3 presents the mass elemental composition in percent for samples No 1 and 3 before and after heating.

Table 3. Mass element composition.

	Al	**Mg**	**O**	**C**	**C/Al**
			wt %		
No 1 (before heating)	52.92	4.74	38.86	3.48	0.066
No 1 (after heating)	44.19	4.29	28.50	23.03	0.521
No 3 (before heating)	88.44	5.78	4.14	1.64	0.0185
No 3 (after heating)	55.18	4.60	13.21	27.01	0.489

The elemental composition of the near-surface layer of sample No 1 was obtained by averaging the percentage of Al, Mg, O, C over the area. The data presented in table 3 for sample No 3 correspond to the measurements of the elemental composition in the center of the crater (Figure 5). The elemental composition of sample No 2 was not analyzed since it was similar with that of sample No 3 since the conditions of the texture element formation was similar, the difference was in the parameters of laser beam spatial displacement.

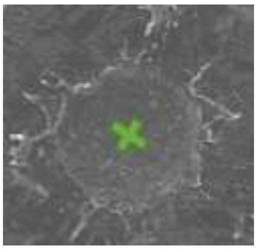


Figure 5. SEM image of the texture element of sample No 3 with the designation of the point at which the elemental composition was determined by EDS method.

Table 3 presents that after heating the samples, the carbon content in the elemental composition increases. The C/Al ratio for samples No 1 and 3 after heating increased significantly. It can be assumed that the adsorption of carbon leads to a significant change in the wettability properties in the process of heating the textured surfaces of the aluminum-magnesium alloy.

It should be noted that after heating the samples leading to the wetting inversion, their surface showed ultrahigh adhesion. It was not possible to register the roll-off angle (the droplet did not roll when turning the samples upside down).

4. Summary

It was established that after laser texturing all samples showed hydrophilic properties. With a decrease in the density of the arrangement of texture elements, which is controlled by the parameters of the spatial displacement of the laser beam, the static contact angle after texturing increases.

Wetting inversion from superhydrophilicity to hydrophobicity occurs in 2–3 hours of low-temperature heating of textured samples. The change time of wetting properties depends on the type of texture.

The samples with the static contact angles up to 137.3–144.2° were obtained after laser texturing and low-temperature heating.

A steady increase in the contact angle after low-temperature heating of samples was recorded (wettability properties deteriorate).

A significant increase in the carbon content in the elemental composition of the surface layer of the samples after their low-temperature heating was recorded.

Acknowledgments

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