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.**

Keywords—hydrophobicity, hydrophilicity, static contact angle, laser texturing, heating

I. Introduction

Recently, the number of publications devoted to the description of new methods for obtaining surface structures with unique functional properties, as well as controllable wetting, spreading and evaporation of droplets has increased significantly [1-3].

Laser processing is the most promising way to obtain such surfaces: applicable to metallic and non-metallic surfaces, easily scaled for details of a complex profile, has low capital and operating costs, a fast and simple process. 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 [4-6]. 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 [6-11]. Consequently, superhydrophobicity can be achieved on laser-textured metal surfaces when stored their in the ambient condition. For different metals, the inversion time is different. For example, aluminum exposed to a nanosecond or picosecond laser takes about 40 days [12], whereas copper or brass textured by a nanosecond laser takes about 11–14 days [13,14]. Stainless steel treated with a femtosecond laser requires more time than other metals (52–60 days) to become superhydrophobic [15, 16].

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. [17] used nanosecond pulsed laser to texture pure copper plate, and then low-temperature annealing (100 ° C), thereby reducing the wettability transition time from 2 weeks to several hours [17].

The reported study was supported by RFBR, research project No. 18-38-00315 mol_a.

The aim of this work is to establish the effect of low-temperature heating on the wetting inversion time from super-hydrophilicity to hydrophobicity on aluminum-magnesium alloy surfaces textured by nanosecond laser radiation.

II. 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". Contaminants were removed with chemically pure isopropyl alcohol (C3H8O) and deionized water Milli-Q. The microrelief of the samples was investigated on the "MicroMesure 3D station" profilometric unit.

The laser texturing procedure was carried out in air at a temperature of 22-23 ° C, atmospheric pressure, and relative humidity of 40-45% with an IPG-Photonics ytterbium nanosecond pulsed fiber laser with a wavelength of 1064 nm as part of the MiniMarker-2 Laser Center. The samples were affected by single laser pulses with a duration of 200 ns, high average power of 20 W, and frequency of 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 I). The texture of sample No 3 formed at v = 2800 mm/s and n = 7.1 mm^{-1} is characterized by elements in the form of craters located at a certain distance from each other. When such a texture was formed, the light spots do not overlap on the surface. When the linear speed was reduced and the number of lines was increased, the nearest craters edges on the surface contact with each other (sample No 2). With a further change in these parameters, a partial overlap of the light spots occur, 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 3) and anisotropic (sample No 1).

TABLE I. 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 Fig. 1.

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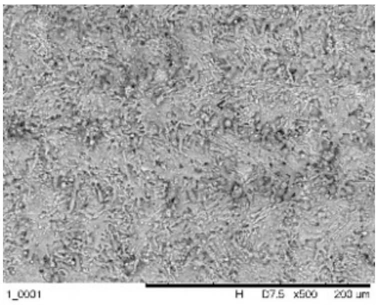
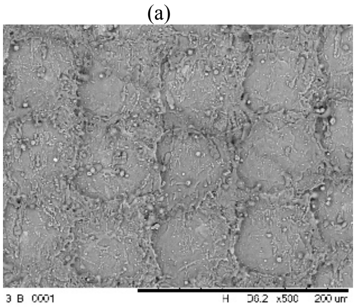
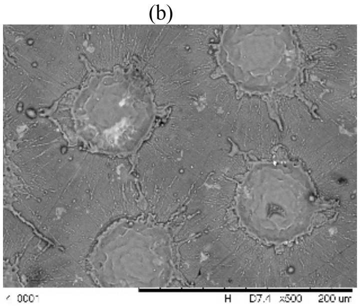


(a)



(b)



(c)

Fig. 1. Surfaces microstructure images obtained with a scanning electron microscope. Sample Number: (a) 1; (b) 2; (c) 3.

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

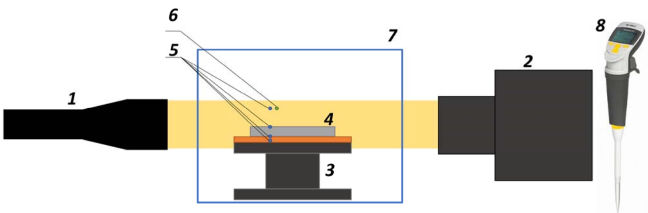


Fig. 2. Experimental setup: 1 - light source; 2 - high-speed video camera; 3 - goniometer; 4 - substrate; 5 - thermocouples; 6 - humidity sensor; 7 - transparent box; 8 – dispensing device.

Low-temperature heating used to reduce the time of wetting inversion (from superhydrophilicity to hydrophobicity) of samples in this study differs from low-temperature annealing [18] in the following: in our case, the sample is heated from its bottom side due to thermal conductivity. In the case of annealing [18], the sample was completely placed in the oven and was heated by mutual effect of convection and conduction.

The substrate was placed in a laboratory box made of 3 mm thick polymer glass for isolation from external influences (convection, radiation). Then it was fixed on the working area, 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.

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. Photographs of droplets were obtained by high-speed video camera with a macro lens. Static contact angles were obtained after processing received photographic images by goniometry methods. The random error in determining the angles was not more than 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.

III. Result and Discussion

The contact angle was measured after laser texturing. Then samples were heated to 100 ˚C. The heating led with contact angle measurement for six hours with interval of one hour. Each measurement was performed by placing a droplet on a previously unwetted surface area. The measurement results are presented in Fig. 3.

The static contact angle of polished surface of aluminum-magnesium alloy (before laser texturing) was 88.1°.

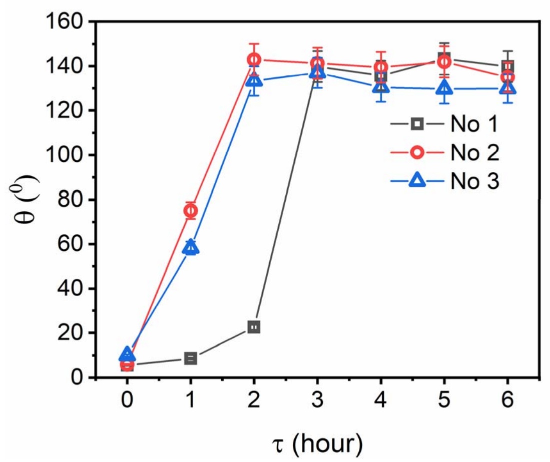


Fig. 3. Dependence of the static contact angle on the heating time of textured samples.

From Fig. 3 it can be seen that immediately after texturing ($\tau = 0$), all samples remained hydrophilic. The static contact angle at $\tau = 0$ 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 τ=3 hours, the wetting inversion of sample No 1 from hydrophilicity to hydrophobicity was registered, i.e. wettability properties on this surface stabilized more slowly than that on other one. A similar conclusion 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 was obtained in [18].

In the range from 3 to 6 hours of heating, when all surfaces showed hydrophobic properties, θ increased in a sequence from sample No 3 to sample No 1. In addition, this range (3–6 hours) is characterized by angles constancy over the heating time. In Fig. 4 shows typical photographs of water droplets before and after heating the substrate for six hours.

(a) (b)

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

In addition, the static contact angles on samples subjected to 6-hour heating were measured for 1 month after heating. Table II 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 II. 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	137.3	135.7	137.2
2	7.3	144.2	144.6	142.4
3	11.8	130.8	132.6	121.3

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 [18], 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 III presents the mass elemental composition in percent for samples No 1 and 3 before and after heating

TABLE III. 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 III for sample No 3 correspond to the measurements of the elemental composition in the center of the crater (Fig. 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.

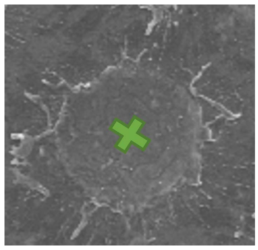


Fig. 5. SEM image of the texture element of sample No. 3 with the designation of the point at which the elemental composition was determined by EDS method.

Table III 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).

IV. CONCLUSIONS

- 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.

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