ABLATION METHOD OF GRINDING A LEATHER SPLIT UNDER THE INFLUENCE OF LASER RADIATION

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ABSTRACT. Using scanning electron microscopy, the surface morphology of a split leather sample was studied under the action of laser radiation from the front and backsides. It has been established that the effect of laser skin resurfacing is achieved in the range of input energies of 40 J and exposure times of 40 sec. It was found that laser exposure from the front and backsides leads to polishing of splits. Skin resurfacing from the front and leather split starts at different input energies from the front side from the split, which is associated with a looser structure of the leather from the split and its lower absorption of radiation.

KEY WORDS: leather tissue, pigment concentrate, protein, acrylic aldehyde, copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid, coating dyes, laser radiation, diffusion, split leather surface structure, collagen fibers, elemental analysis, hygroscopicity, moisture return

METODĂ DE ŞLEFUIRE A ŞPALTULUI DE PIELE UTILIZÂND ABLAȚIA LASER

REZUMAT. S-a studiat morfologia suprafeței unei probe de șpalt de piele sub acțiunea radiației laser pe ambele părți folosind microscopia electronică cu scanare. S-a stabilit că efectul de remodelare a suprafeței pielii cu laser are loc la o energie inițială de 40 J și la un timp de expunere de 40 de secunde. S-a descoperit că expunerea pielii la laser pe ambele părți conduce la șlefuirea suprafeței șpaltului. Procesul de remodelare a suprafeței șpaltului începe la energii inițiale diferite pe fața șpaltului, care este asociată cu o structură mai slabă a șpaltului și cu o absorbție mai scăzută a radiațiilor.

CUVINTE CHEIE: țesut de piele, pigment concentrat, proteine, aldehidă acrilică, emulsie de copolimer de acrilat de butil, metacrilat de metil și acid acrilic, coloranți de acoperire, radiații laser, difuzie, structura suprafeței șpaltului, fibre de colagen, analiză elementară, higroscopicitate, retur de umiditate

MÉTHODE DE POLISSAGE DE LA CROÛTE DE CUIR À L›AIDE D›UNE ABLATION AU LASER

RÉSUMÉ. La morphologie de surface d’un échantillon de croûte de cuir sous l’action d’un rayonnement laser des deux côtés a été étudiée par microscopie électronique à balayage. On a déterminé que l’effet de remodelage de la surface du cuir au laser se produit à une énergie initiale de 40 J et un temps d’exposition de 40 secondes. L’exposition du cuir au laser des deux côtés s’est avérée lisser la surface de la croûte. Le processus de remodelage de la surface de la croûte commence à différentes énergies initiales sur la face de la croûte, ce qui est associé à une structure de la croûte plus faible et à une absorption de rayonnement plus faible.

MOTS CLÉS : tissu de la peau, pigment concentré, protéine, aldéhyde acrylique, émulsion de copolymère d’acrylate de butyle, de méthacrylate de méthyle et d’acide acrylique, colorants de revêtement, rayonnement laser, diffusion, structure de surface de la croûte, fibres de collagène, analyse élémentaire, hygroscopicité, retour d’humidité

INTRODUCTION

The structural miracle of collagen makes natural skins. The skin matrix is superior to other synthetic matrices [1-3].

A technology has been developed for plasma-chemical finishing of natural leathers based on the use of silver nanoparticles and high-frequency low-pressure plasma radiation [4]. An induction high-frequency plasma torch has been developed for processing materials with nanoparticles under the conditions of an inductive discharge. It has been established that the use of this technology can significantly improve the quality of natural leathers, in particular, significantly improve their physical and mechanical properties.

In previous works [5-7] it was shown that the introduction of plasma treatment before liquid processes in the leather industry makes it possible to achieve results in improving the consumer properties of leather and intensifying liquid processes. However, the processing of leather material with a moisture content of more than 20% requires a long pumping time to create a pressure of the order of 1.33 Pa, in addition, constant monitoring of the moisture content of the processed material is necessary, because at a humidity of more than 50%, ice crystals form between the structural elements of the dermis.

The effect of plasma treatment and nano-finishing on the properties of leather was studied. O_2 and N_2 gases were used to activate the skin surface, on which thin layers of hexamethyldisiloxane and tetraethyloxysilanes were deposited [8]. The process of finishing with nanoparticles was carried out using a TiO_2-SiO_2 nanocomposite solution.

The surface properties of the treated leathers were characterized by scanning electron and atomic force microscopy. The results showed that the hydrophobicity of the skin was clearly improved after the treatment with hexamethyldisiloxane, while the treatment with tetraethyloxysilane increased its hydrophilic properties. In addition, the strength properties and water vapor permeability of the skin have been improved.

The structure and composition of titanium and hafnium nitride coatings on orthopedic skin, obtained by condensation from the vapor-plasma phase under ion bombardment, were studied by scanning electron microscopy and X-ray fluorescence analysis. The rate of condensation of combined coatings was calculated. The micro- and nanostructure of condensates was fixed, and the stages of formation of a multilayer nitride coating on the skin were shown [9].

With laser exposure in a two-pulse mode, the effect of laser polishing of a leather split is observed. There is an understanding that for each type of laser there is a certain energy and time area for optimal efficient processing of split leather.

For ablative resurfacing of split skin, lasers with a short pulse duration are most suitable. Such laser devices with a short pulse duration at a certain power density are able to effectively remove the surface layer of the derma structure split (up to 100 μm).

The mechanism and modes of exposure are determined by the properties of the splits, the characteristics of the radiation (irradiation mode: continuous or pulsed, wavelength, laser power, energy in the pulse, the absorption coefficient of this radiation by natural skin and its individual components. Thus, it is possible to remove its defects from the surface of the leather split: scars, etc. Scars on the skin of animals significantly change the overall relief of the skin. In the dermis, elastic fibers disappear, and collagen fibers grow.

This paper presents the results on the use of laser radiation for skin resurfacing from the front and a split sample.

The purpose of the work is to establish the features of laser modification (polishing) of the skin surface from the front and split in the dual pulse mode.

EXPERIMENTAL

Materials and Methods

Laser Radiation

In this work, we used laser processing in the regime of double pulses of a sample of genuine leather. An LS-2134D yttrium-aluminum grenade laser (LOTIS, Belarus) with a wavelength of 1064 nm was used, which generated in a two-pulse mode (pulses were separated by a time interval of 3 μs, pulse duration 10 ns). The sample was treated with laser radiation in the energy range 5–40 J at exposure times of 5–40 s [10].

SEM Research and Elemental Analysis

The study of the surface morphology of the leather was carried out using a MIRA-3 scanning electron microscope (Czech Republic) with a system of micro analyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously study the surface morphology of the material, determine the distribution of chemical elements of the sample, and also obtain an image of the object in a wide range of magnifications. The thickness of the leather sample is ~ 500 μm [10].

Tensile strength [11] is defined as the load at break of the skin or leather tissue of the fur, which falls on the unit cross-sectional area of the sample. This indicator to a greater extent characterizes the mechanical properties of the skin, the leather tissue of the fur and is normalized by state standards.

The tensile strength is determined on the scale of the loads of the tensile machine at the moment of destruction of the sample. Since the test specimen may have uneven thickness in the test area, the cross-sectional area at the rupture site is taken into account [11].

Tensile strength σr, Pa, is calculated by the formula:

$$\sigma p = \frac{P}{S} \quad (1)$$

where:

P is the load at break, N; S is the cross-sectional area of the specimen at the point of fracture, m^2.

The total elongation of the skin and leather tissue of the fur is set at a load at the moment of sample rupture or at a certain load per unit of cross section and is determined as a percentage of the initial length of the sample.

Relative elongation at break εp, %, is determined by the formula:

$$\varepsilon p = 100\frac{\Delta \mathrm{lp}}{I} \quad (2)$$

where:

is elongation at break of the sample, mm; lp is the absolute length of the sample at the moment of rupture, mm; l is the initial length of the sample, mm.

Hygroscopicity (G) [12] as a percentage is calculated by the formula:

$$G = \frac{m_1 - m}{m \times 100} \quad (3)$$

where:

m_1 is the mass of an elementary sample after moisture absorption, g;

m is the mass of the elementary sample before moisture absorption, g.

Moisture return (W) [13] as a percentage is calculated by the formula:

$$W = \frac{m_1 - m_2}{m \times 100} \quad (4)$$

where:

m is the mass of an elementary sample before moisture absorption, g;

m_1 is the mass of the elementary sample after moisture absorption, g;

m_2 is the mass of the elementary sample after moisture release, g.

Adhesion: The force required to lift a coating layer from the skin, applied evenly at an angle of about 90° to a solid bonding plate to which the finished skin is adhered [14]. The finished surface of the leather strip is glued to the bonding plate with a thermosetting adhesive. A force is applied to the free end of the skin strip to peel off the coating from it over a predetermined length. In this case, the coating remains on the bonding plate along with the adhesive layer. The force required to pull off is measured and recorded as the adhesion of the coating to the skin. The tests are carried out under conditions of normal relative humidity and temperature. If necessary, pre-moistened samples can be tested.

RESULTS AND DISCUSSION

In this work, we used laser processing of a split leather sample in the dual pulse mode. We used an LS-2134D yttrium aluminum garnet laser (LOTIS, Belarus) with a wavelength of 1064 nm, generating in a two-pulse mode (pulses separated by a time interval of 3 µs, pulse duration 10 ns). The sample was treated with laser radiation in the energy range of 40 J at exposure times of 40 sec. from front and back.

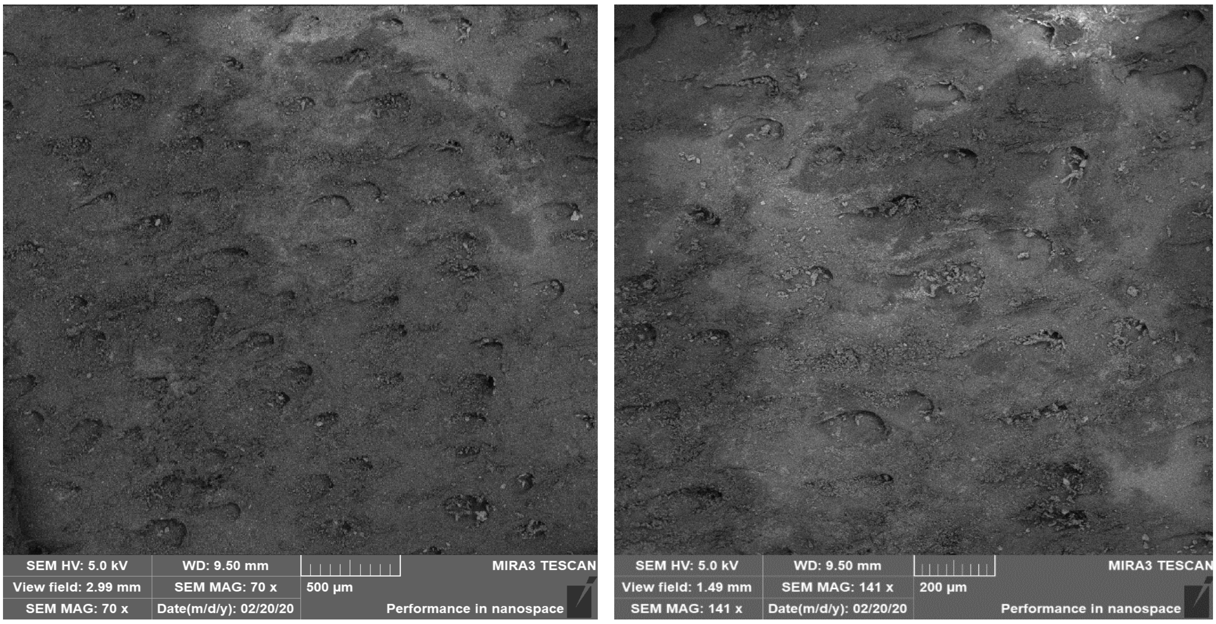
The study of the surface morphology of the leather split was carried out using a scanning electron microscope MIRA-3 (Czech Republic) with a system of microanalyzers from Oxford Instruments (Great Britain). The device allows you to simultaneously study the morphology of the surface of the material, determine the distribution of chemical elements of the sample under study, and also obtain an image of the object in a wide range of magnifications.

The leather split leather of chrome tanning (produced in Uzbekistan) was studied, unpainted chrome waste leather was used, with the following physical and chemical parameters. In %: humidity - 52.4; total ash - 4.8; fatty substances - 3.2; naked substance 76.83; chromium oxide - 5.2; and hydrothermal destruction 92.0 °C, the front side of the sample of leather splits, ~ 1.2 mm thick, was treated with laser radiation.

According to [15–16], under the influence of the first laser pulse, the substance evaporates, and a region with an increased temperature and a reduced density of air particles is formed in the near-surface layer, which leads to a more complete use of the energy of the second pulse for laser ablation [15]. The processes of nonequilibrium heating, melting, and ablation of a substance under the action of nanosecond pulses were studied in [15], however, the final stage of the ablation process, associated with the formation of the surface morphology of the coated polymer, has not been studied enough. It is known [15–18] that, under the action of a series of nanosecond pulses, the main mechanism of substance removal is thermomechanical ablation, which leads to the removal of the surface layer.

When exposed to IR laser radiation, energy is absorbed on the surface of the material, the layer depth can be from fractions to tens of micrometers. The nature of light erosion is determined to a large extent by the characteristics of the material itself: optical, thermophysical properties and structural inhomogeneities, etc.

Figure 1 a) and b) shows the morphology of the surface of the front side of a natural leather sample before and after laser resurfacing.

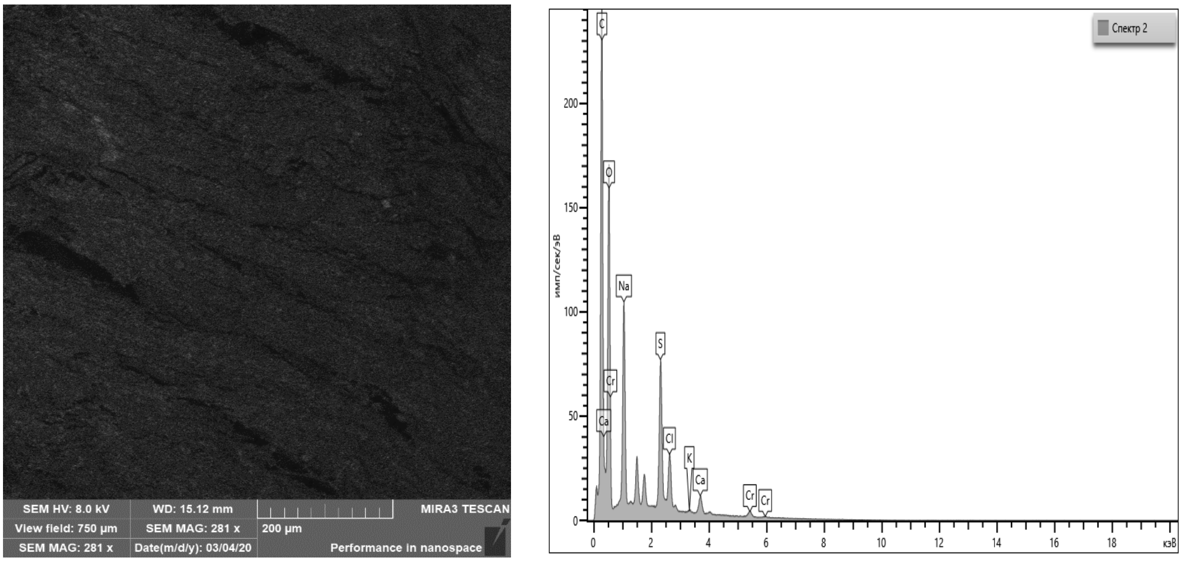


a) b)

Figure 1. Morphology of the surface of the front side of the skin before and after laser exposure: a) without exposure, b) after exposure (energy input 40 J, exposure time 40 sec)

Analysis of Figure 1 shows that in the process of laser ablation, the leather split is polished, the surface morphology of the leather split is changed, and the relief is smoothed out.

Figure 2 shows the morphology and elemental composition of the split leather before laser ablation.



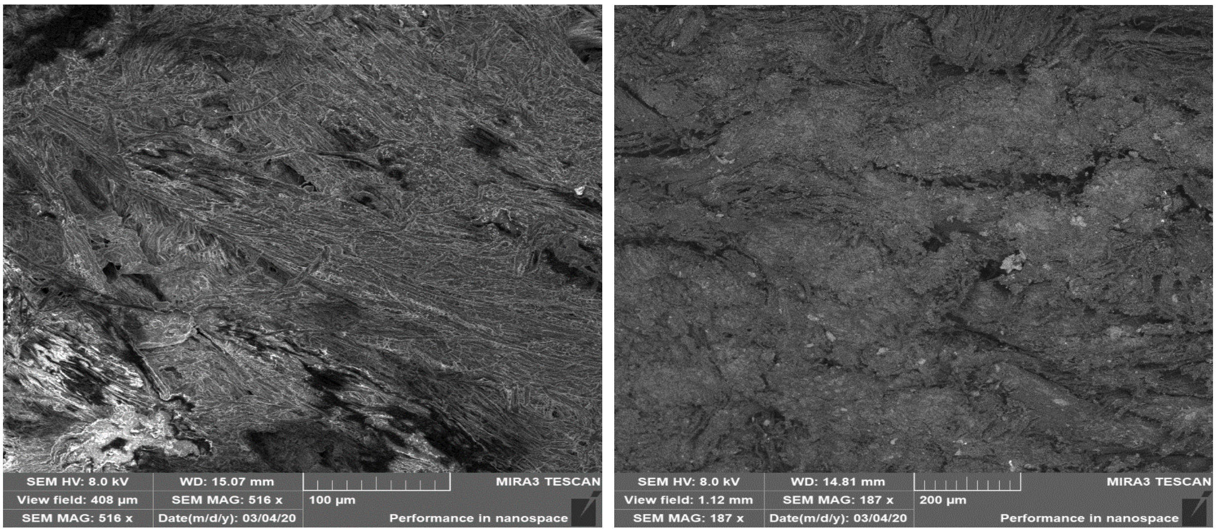
a) b)

Figure 2. Surface morphology of split leather before laser exposure

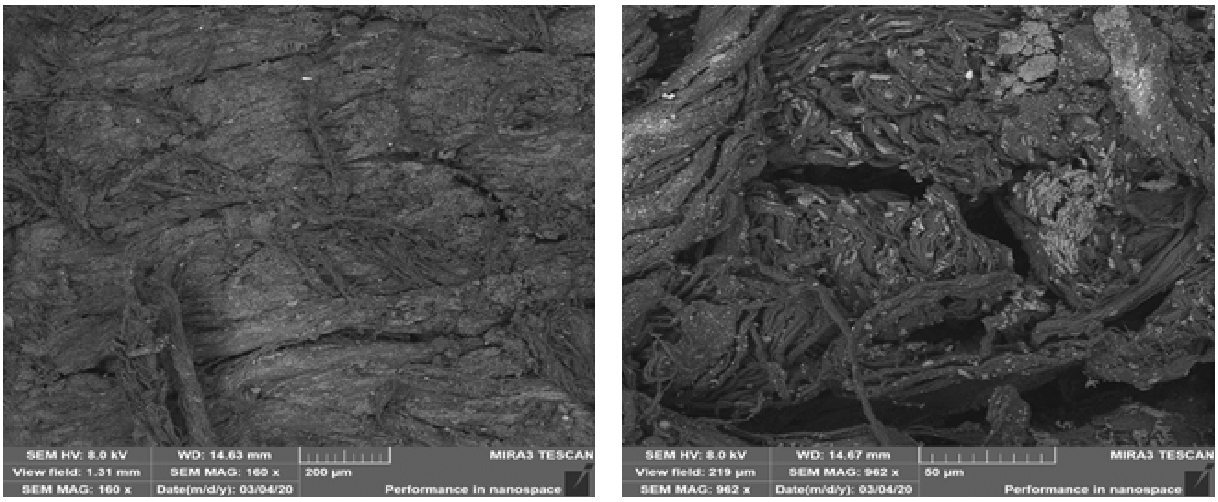
It should be noted (Figure 2) that the surface of the leather split is characterized by a heterogeneous structure and a loose structure.

Figure 3 shows the surface morphology of a leather split after laser exposure at various input energies and exposure times.

It should be noted that, in contrast to the front side, the laser exposure energy required to start the grinding process from a split leather sample increases. From the comparison of Figures 3 a), b), c), d) it follows that with an increase in the invested energy and exposure time, the surface relief of the skin splits is smoothed out, the skin structure appears better, on its surface (Figure 3 c), d)) are clearly visible separate collagen fibers with a thickness of 1-2 microns, the connections of these collagen fibers form bundles of fibers with a thickness of 30-50 microns, intertwining in different directions form a complex tissue of the dermis. Figure 3a) also clearly shows individual fibrils (thickness ~ 0.5 µm). It should be noted that the skin tissue on the reverse side of the sample has a fairly developed inner surface and has many empty spaces of various shapes, the sizes of which vary in a wide range from 7 to 40 µm.



a) b)



c) d)

Figure 3. Morphology of the surface of a leather split under various processing modes: a) input energy 25 J, exposure time 40 sec; b) input energy 30 J, exposure time 40 sec; c) input energy 35 J, exposure time 40 sec; d) input energy 40 J, exposure time 40 sec.

When obtaining and studying the properties of coating dyes, the problem of improving the physical and mechanical properties during long-term operation of products was solved. The non-pigmented primer contains 20% liquid rubber, a penetrator and water. The top coat contains a pigment concentrate, protein, aldehydes, a copolymer emulsion of butyl acrylate, methyl methacrylate and acrylic acid (in a ratio of 35.37:46.68:17.95, respectively) and water.

A distinctive feature of the new coating dyes is the use of the process of protein crosslinking with aldehyde, as well as the use of the product of emulsion copolymerization of butyl acrylate, methyl methacrylate and acrylic acid.

Laser processing of leather split, both with dense and loose coated structures, allows you to simultaneously modify the nanostructure of the leather tissue and the structure of the coating, as a result of which the area of mutual penetration of the two contacting polymers increases, leading to an improvement in the adhesion of the coating to the leather tissue up to 4 times, in addition, all physical and mechanical parameters are increased, as well as the hygienic properties of the composite material. Based on the results of this work, four pilot batches of leather fabric with a dense structure, 24 pieces each, and four pilot batches of leather with a loose structure, 16 pieces each, were produced, two batches of leather fabric with dense and loose structures were subjected to laser processing in the selected modes. The pigment concentrates included in the coating compositions were preliminarily modified. The results of changes in the physical and mechanical properties of batches of leather splits of dense and loose structures are presented in Table 1.

Table 1: Physical and mechanical properties of batches of coated leather split leather

№	Physical and mechanical indicators	Control	Experienced
	Dense structure		
1	Hygroscopicity, %	14,2	17,8
2	Moisture return, %	17,5	21,7
3	Tensile Strength, MPa	11,4	13,7
4	Elongation at stress 10 MPa, %	33,0	37,0
5	Coating resistance to repeated bending, points	3,0	5,0
6	Coating resistance to abrasion, revolutions	35,0	45,0
7	Coating adhesion to dry skin, N/m	570	1720

№	Physical and mechanical indicators	Control	Experienced
	Loose structure		
1	Hygroscopicity, %	16,3	20,1
2	Moisture yield, %	20,4	25,6
3	Tensile strength, MPa	8,8	10,9
4	Elongation at stress 10 MPa, %	36,0	41,0
5	Coating resistance to repeated bending, points	3,0	4,0
6	Coating resistance to abrasion, revolutions	32,0	40,0
7	Coating adhesion to dry skin, N/m	540	1640

As can be seen from the values given in the table, the leather split of a dense and loose structure with a coating, obtained using the developed technologies, improves the following indicators: hygroscopicity by 25.35 %; moisture return - 25.50%; skin strength by 20.17%; elongation by 12.12%; resistance of the coating to repeated bending by 33-66%; coating resistance to abrasion by 28.57%; adhesion of the coating to the skin up to 3 times.

CONCLUSIONS

For the first time, laser modification of a leather split surface sample from the front side was carried out using a laser generating in a two-pulse mode (pulses separated by a time interval of 3 µs, pulse duration 10 ns) with a wavelength of 1064 nm at an input energy of 40 J and an exposure time in the range of 40 sec.

It was found that laser exposure from the front and back sides leads to skin resurfacing. It is shown that resurfacing of the skin from the front and leather split starts at different input energies from the front side, from the split, which is associated with a looser structure of the skin from the split and its lower absorption of radiation.

The use of this technology for finishing split leather allows for high-quality sorting of finished products, i.e., if the coating is applied with large deviations, then the laser treatment after the final finishing increases the defectiveness of the coating.

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