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Laser-Induced Color Marking of Titanium Alloy

Li Chunling*[1], Lu Changhou[2]
[1,2]Key Laboratory of High-efficiency and Clean Mechanical Manufacture, Ministry of Education,
School of Mechanical Engineering, Shandong University,
17923 Jingshi Road, Jinan, Shandong Province, China, 0531-88392118
[1]School of Mechanical and Automotive Engineering, Qilu University of Technology
3501 Daxue Road, Jinan, Shandong Province, China, 0531-89631132
*Corresponding author, e-mail: lcl_Alice@126.com[1], luchh@sdu.edu.cn[2]

Abstract

A Nd:YAG nanosecond laser was utilized in the laser color marking of titanium alloy substrates. It was focused on how several laser parameters, such as pumping current, delay between the effective vector step, laser line spacing, Q-switch frequency and focal plane offset, affected the resulting colors, and the influence of the resulting colors on the substrate. Firstly, single-factor experiments were carried out. Then the dark blue square pattern and two samples were analyzed using an environmental scanning electron microscope (ESEM) and X-ray diffractometer (XRD) respectively. Results clearly showed that the Nd:YAG nanosecond laser can induce multiple colors on titanium alloy substrates and all the five parameters had an effect on the resulting colors significantly. The dark blue square pattern didn't induce internal stresses within the substrate material, so the influence of the resulting colors on the substrate is negligible.

Keywords: *laser color marking, titanium alloy, surface oxidation, laser processing parameter*

1. Introduction

Color markings on metal surfaces are made by the traditional technologies such as printing, electroplating, painting and so on. However, these processes have some limitations in practical applications [1]. The poor scratch and wear of printing coatings and complexity of electroplating processes and high cost of paintings are recognized problems. So the traditional color marking technologies are gradually replaced by the laser color marking technology which requires a laser to scan the metal surface and give rise to surface oxidation to create a permanent color marking on a metal surface and does not use any chemicals, coatings or tools [2]. The laser-induced color patterns can make the metal surface visually more attractive and are gaining interest for consumer products [3, 4].

A lot of investigations have been carried out to better understand the laser color marking process. The color patterns were marked on stainless steel by an infrared laser [5,6], or fiber laser [7-12] or KrF excimer laser [13] or UV laser [14] and marked on titanium by a fiber laser [15, 16]. These studies mainly focused on the influence of laser processing parameters on the resulting colors and the analysis of laser induced oxide films on metal surfaces. It has been proved that the laser-induced colors are sensitive to laser processing parameters which consistently appear in these studies are laser power, scanning speed, and focal plane offset. But the controlled parameters differ in various laser marking systems. The effect of other parameters on the laser-induced colors was not reported, such as pumping current, Q-switch frequency, laser line spacing, Q release time etc. Regarding the analysis of oxide films, the surface morphology and optical properties of the oxide films and their thickness were mainly studied. But as the laser beam generates intense heat, internal stresses may occur, which may cause distortion of the substrates outside its limits. It is must be avoided in industrial applications of laser coloring marking technology. So far the related researches haven't been reported.

In this study, a Nd:YAG nanosecond laser was used to mark several color square patterns of 5mm×5mm on titanium alloy substrates in air. The influence of selected laser processing parameters on the obtained colors was investigated by One-Factor-at-a-Time (OFAT) experiments. As well as the influence of the resulting colors on the substrate was

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explored by analyzing the laser treated area and two samples using an environmental scanning electron microscope (ESEM) and X-ray diffractometer (XRD) respectively. The researches have greatly improved the industrial applications of laser color marking technology.

2. Research Method

2.1. Experimental Setup

A HAN'S Q-switched lamp pumped neodymium-doped, yittrium-aluminium-garnet (Nd :YAG) laser was used in the laser color marking process of titanium alloy. The technical parameters of the laser are shown in Table 1.

Table 1. Technical parameters of the HAN'S YAG-T80C laser

Technical Parameters	Specification	Technical Parameters	Specification
Maximum Average Power/W	80	Operating Frequency/kHz	0-20
Beam Quality Factor	10	Laser Spot Diameter/mm	0.010~0.150
Supply Voltage/V	380	Machine Power(MAX)/kW	7.5
Supply Current/A	25	Maximum Q-Switched Laser Power/W	70
Supply Frequency/Hz	50	Pulse Duration/ns	80~260
Supply Phase	three-phase	Laser Wavelength/nm	1064
Laser Beam Divergence Angle/mrad	5.5	Marking Depth/mm	<2.0
Peak Power(MAX)/kW	140	Marking Linear Velocity/($mm \cdot s^{-1}$)	≤7000

The laser-induced colors were analyzed by means of a Quanta 200 environmental scanning electron microscope (ESEM) whose resolution is 3.5nm. The internal micro-stresses of the laser marked blue area were analyzed using a D8-ADVANCE X-ray diffractometer (XRD) which is copper (Cu) target X-ray tube. The XRD was equiped with a θ/θ goniometer whose angle repeatability is 0.0001º and degree of accuracy is ±0.001º [17].

2.2. Substrate Materials

Experiments were conducted for plates of commonly used TC4 titanium alloy (chemical composition Fe=0.3%$_{max}$, C=0.1%$_{max}$, N=0.05%$_{max}$, H=0.015%$_{max}$, O=0.2%$_{max}$, Al=5.5%~6.8%, V=3.5%~4.5%, the rest is Ti) with thickness of 2mm. The plates were rinsed using ethyl alcohol to remove any oil and dust residues before the experiments.

2.3. Experimental Procedure

The laser tool path pattern was one-way raster scanning which was depicted in Figure 1. The triangle and circle represented the starting and ending point of laser beam respectively. The laser scanned the first line along the x direction, then waited for the galvanometric scanner back to the starting point of the second line. The dotted line represented the return route where no laser was emited. The worktable was adjustable in three dimension.

The controlled processing parameters in HAN'S laser marking system 2000 were up to 12 which was shown in Table 2. The laser energy can be controlled by adjusting the pumping current, Q-switch frequency and Q release time. The pumping current referred to the current of the pumping source of the laser (i. e. the krypton lamp) [18]. The output power can be regulated directly when the pumping current is changed. The relationship between the pumping current and output power is shown in Table 3 [19]. The laser step can be controlled by the four parameters, i.e. effective vector step, delay between the effective vector step, empty vector step, and delay between the empty vector step. Adjusting the effective vector step and delay between the effective vector step, the laser scanning speed can be changed [20]. The empty vector step and delay between the empty vector step were related to the empty stroke corresponding to the dotted line in Figure 1, during which no laser was emitted. so the two parameters had no significant effect on the laser-induced colors. There is no laser stroke connection problem in color marking, so the four parameters (i.e. delay of laser on, delay of laser off, delay of jumping, delay of turning) are related to the laser stroke connection, which had no significant effect on the laser-induced colors. The laser line spacing refers to the spacing between laser lines, namely *s* in Figure 1. This parameter can affect the accumulation of laser heat in the substrates, and then affect the resulting colors. The focal plane offset refers to the distance between the focal point and the substrate position. The substrate materials are easy to be burned at the focal plane owing to the high laser power density [21], so the focal plane offset had an important impact on the laser-induced colors.

On the basis of above analysis, the 5 processing parameters (i.e. pumping current, delay between the effective vector step, Q-switch frequency, laser line spacing, focal plane offset) were selected to carry out the laser color marking experiments. Many color square patterns of 5mm×5mm were marked on titanium alloy substrates by OFAT experiments. In addition, two samples with the same dimensions were analyzed by the X-ray diffractometer (XRD). One was unmaked sample, the other was maked a dark blue square pattern.

Table 2. Controlled processing parameters in HAN'S laser marking system 2000

Controlled Processing Parameters	Range	Default values	Controlled Processing Parameters	Range	Default values
Effective Vector Step/mm	0.001~0.03	0.01	Empty Vector Step/mm	0.03~0.08	0.06
Delay between the Effective Vector Step/μs	8~60	20	Delay between the Empty Vector Step/μs	4~20	8
Q-switch Frequency/kHz	1~20	3	Delay of laser on/step	1~60	2
Q Release Time/μs	1~40	12	Delay of laser off/μs	0~1000	300
Pumping current/A	7.2~30	16	Delay of jumping/μs	200~1500	400
Laser Line Spacing/mm	0.01~0.15	0.01	Delay of turning/μs	0~6	5

Table 3. Relationship between pumping current and output power

Pumping current/A	Output power/W	Pumping current/A	Output power/W	Pumping current/A	Output power/W	Pumping current/A	Output power/W
11	1.0	16	10.2	21	37.8	26	47.5
12	2.0	17	12.5	22	36.4	27	52.7
13	3.8	18	16.0	23	39.4	28	59.0
14	5.4	19	21.5	24	35.1	29	68.5
15	7.4	20	33.2	25	41.0	30	78.3

3. Experimental Results

Laser-induced color patterns on the titanium alloy are shown in Figure 2, Figure 3, Figure 4, Figure 5 and Figure 6 by varying some parameters as indicated in the figure, and the values of other parameters are taken in Table 4. The ESEM analysis results of Figure 6 are shown in Figure 7. The XRD analysis results of the two samples are shown in Figure 8.

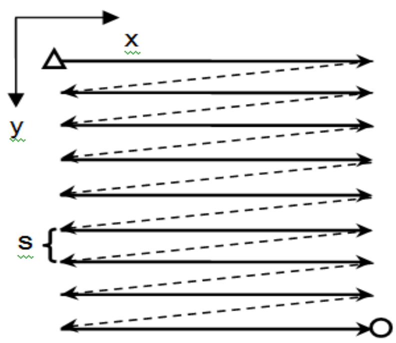


Figure 1. One-way raster scanning

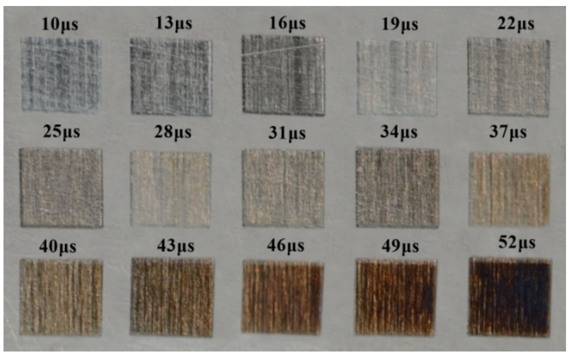
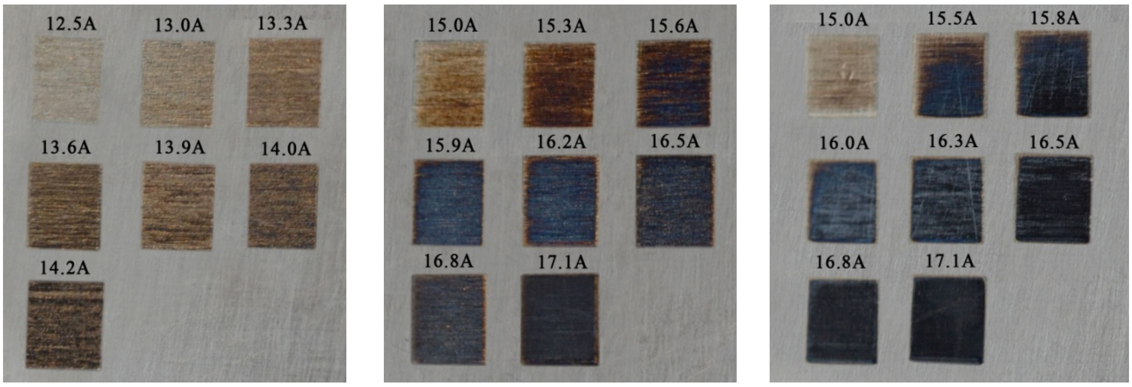
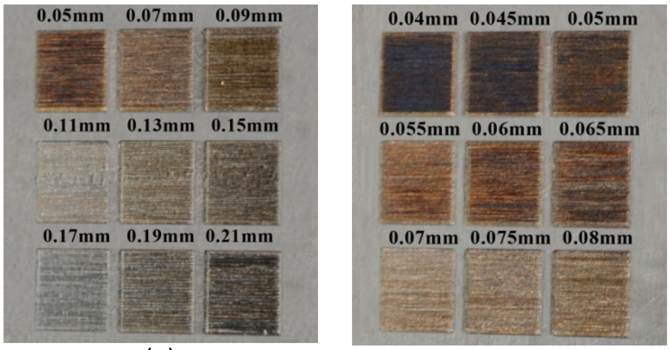


Figure 2. Effect of delay between the effective vector step on the laser-induced colors



(a) (b) (c)

Figure 3. Effect of pumping current and focal plane offset on the laser-induced colors: (a) focal plane offset 3.0, (b) focal plane offset 4.6mm, (c) focal plane offset 5.9mm



(a) (b)

Figure 4. Effect of laser line spacing on the laser-induced colors

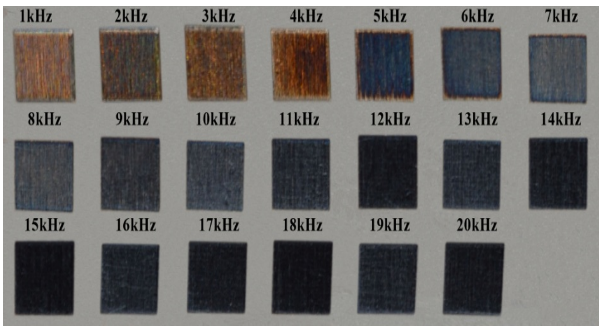


Figure 5. Effect of Q-switch frequency on the colors

Figure 6. The blue pattern

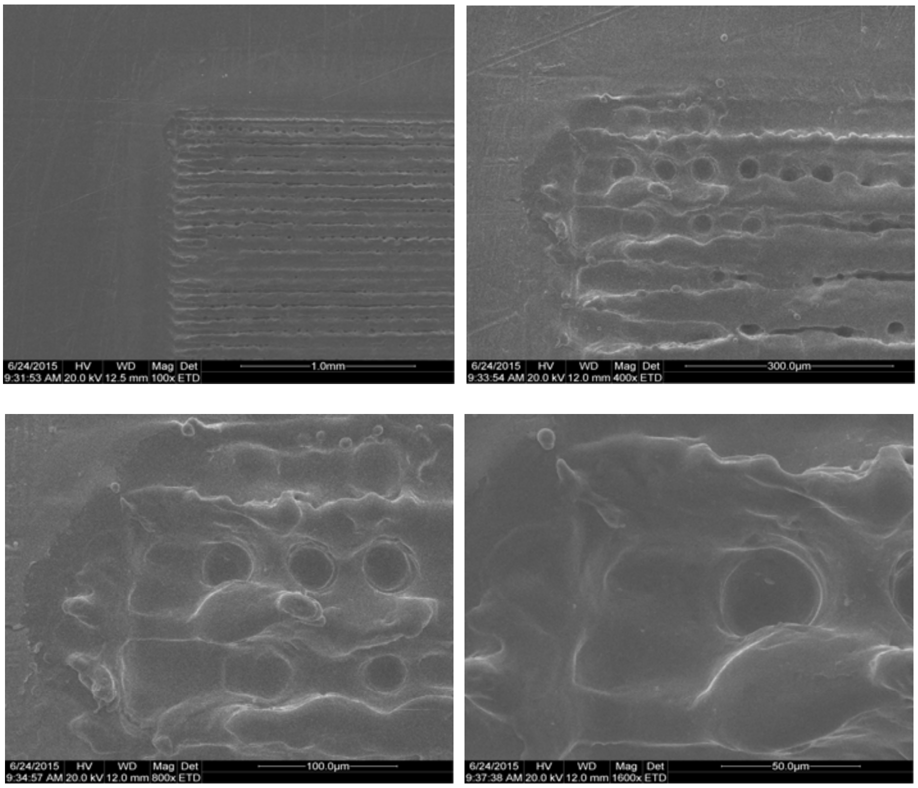


Figure 7. ESEM photographs of the blue pattern

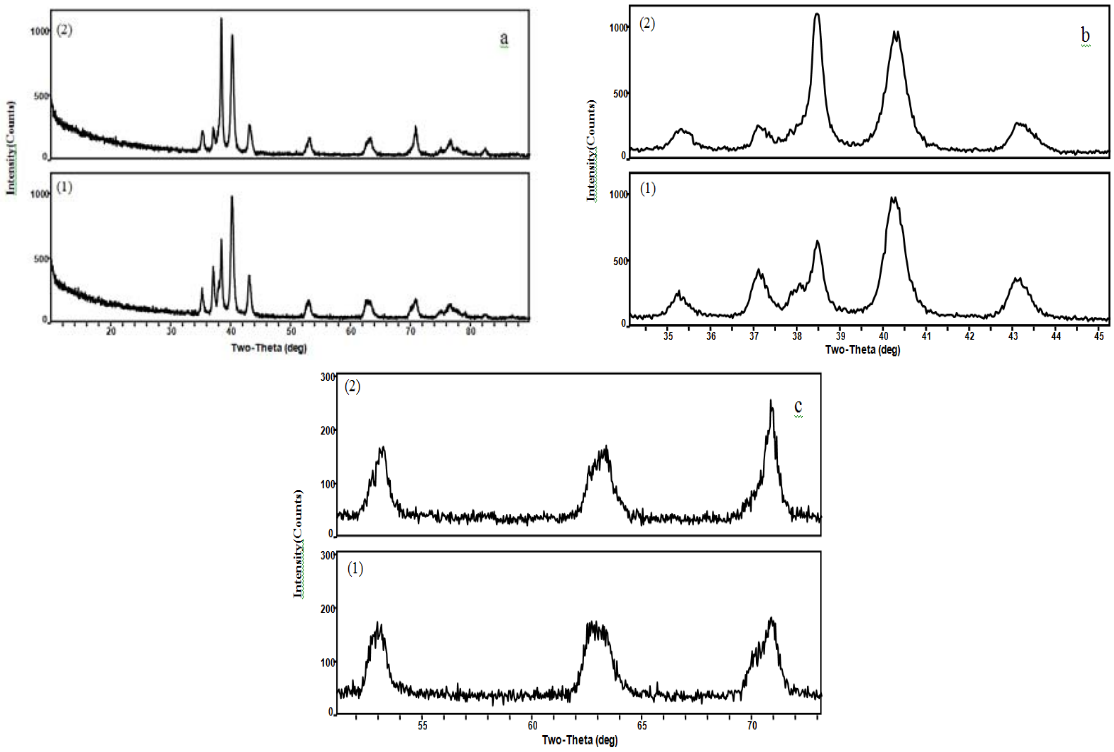


Figure 8. XRD analysis results, with 2θ between 10° and 90° (a) , 35° - 45° (b) and 55° - 70° (c): (1) unmarked sample, (2) sample with the blue square pattern.

Table 4. Laser parameter values in each experiment

Controlled Processing Parameters	Figure 2 Values	Figure 3 Values	Figure 4 Values	Figure 5 Values	Figure 6 Values
Effective Vector Step/mm	0.001	0.001	0.001	0.001	0.001
Delay between the Effective Vector Step/μs	variable	40	30	40	42
Q-switch Frequency/kHz	5	5	4	variable	5
Laser Line Spacing/mm	0.08	0.08	variable	0.08	0.08
Pumping Current/A	15.0	variable	15.5	16.0	16.0
Focal Plane Offset/mm	5.2	variable	5.2	5.2	5.0
Q Release Time/μs	12	12	12	12	12
Empty Vector Step/mm	0.06	0.06	0.06	0.06	0.06
Delay between the Empty Vector Step/μs	8	8	8	8	8
Delay of laser on/step	2	2	2	2	2
Delay of laser off/μs	300	300	300	300	300
Delay of jumping/μs	400	400	400	400	400
Delay of turning/μs	5	5	5	5	5

4. Discussions

On the whole, the laser-induced colors gradually deepen even burning black with the increase in the delay between the effective vector step, pumping current, and Q-switch frequency as shown in Figure 2, Figure 3, and Figure 5 respectively, while the colors became light gradually with the increase in the laser line spacing and focal plane offset as shown in Figure 4 and Figure 3 respectively. The reason may be as follows. When a color square pattern was being marked, a transparent oxide film was formed on the surface of the titanium alloy [13]. The resulting colors were formed owing to the interference effect in the thin film, so the thickness of the film determined the colors. The accumulated laser heat determined the thickness of the film, because the influence of the parameters on the obtained colors are based on heat treatment.

The output power increases with the increase of pumping current as shown in Table 3, so the laser power density in the laser treated area increases correspondingly when the focal plane offset is kept constant. The focal plane offset is also closely related to the laser power density in the laser treated area. The smaller the focal plane offset, the smaller the laser spot radius on the substrate, the higher the laser power density, so the deeper the resulting colors. It can be seen from Figure 3 that there is a suitable laser power density range, some colors cann’t be obtained if the laser power density is too high or too low.

The delay between the effective vector step refers to the preset time for each effective vector step. The laser scanning speed decreases gradually with the increase of the delay between the effective vector step. When laser scanned on the metal surface due to the movement of the galvanometer, many continuous linear markings were obtained as a result of the overlap of laser pulse spot. The distance between the two adjacent laser linear markings is called laser line spacing, namely the *s* in Figure 1. The wider the laser line spacing, the less the laser line needed for marking a square pattern, the less the laser heat accumulation, and so the lighter the obtained colors. The fact that the resultant colors produced by the same processing parameters exist color difference are also observed in Figure 4. It is mainly caused by the instability of the laser color marking process.

Figure 10 indicates two adjacent pulses are marking on metal surface at a certain time interval and spacing. The relationship between them is to be:

$$\Delta t = \frac{1}{f} \qquad \Delta s = \frac{v}{f}$$

Where: Δt is the time interval of two adjacent pulses
Δs is the spacing of two adjacent pulses
f is the Q-switch frequency
v is the laser scanning speed

This shows the heat accumulation process will be affected by the time interval and spacing of two adjacent pulses and the extent of the impact depends on the Q-switch frequency and the laser scanning speed. The slower the laser scanning speed, the smaller the pulse spacing, the more the heat accumulation effect, and so the deeper the colors. Similarly, the bigger the Q-switch frequency, the deeper the colors. But Figure 5 shows that there is little color difference when the Q-switch frequency is more than 10kHz. The phenomena are caused by the change of laser output power and pulse width. Obviously, effective vector step and Q release time also significantly affect the obtained colors, but they were kept constant in experiments. In practice, the influence of the two processing parameters on the resulting colors can be derived from delay between the effective vector step and Q-switch frequency respectively. The influence of laser processing parameters on the obtained colors was based on the combination of heat accumulation and oxidation of substrate materials. So the same color can be marked by different sets of parameters.

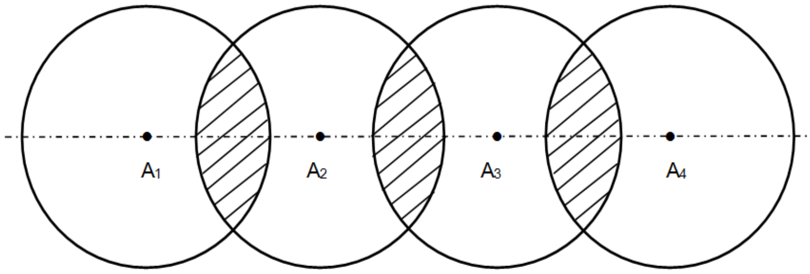


Figure 10. Schematic diagram of laser pulse overlap regions

The blue square in Figure 6 isn't a flush or smooth mark and there are many obvious continuous linear markings and circular dents under ESEM with 100 and 400 times magnification respectively as shown in Figure 7. These circular dents can be seen clearly under ESEM with 800 and 1600 times magnification. This illustrates that the surface of the laser marked blue square has been molten and resolidified to form larger clusters of crystals. As can be seen in Figure 8 (a), (b) and (c), within the range of diffraction angle between 10° and 90°, there is no evident increase in the width of the diffraction peak for the laser color marked sample and no appearance of new diffraction peak or the displacement of those initially recorded on the unmarked sample. So the nature of the phases and the structure of the substrate haven't been modified, then one can say laser color marking didn't induce internal stresses within the substrate material.

5. Conclusion

Based on the obtained results and discussions, the main conclusions are: The Nd:YAG nanosecond laser can induce several colors on titanium alloy substrates, such as yellow, gray, blue and so on. The same color can be marked by different sets of parameters; All the selected parameters (i.e. pumping current, delay between the effective vector step, Q-switch frequency, laser line spacing, focal plane offset) had an effect on the resulting colors significantly. But the resultant colors produced by the same parameters exist color difference owing to the instability of the laser color marking process; There is a suitable laser power density range, some colors cann't be obtained if the laser power density is too high or too low; and The surface of the laser marked blue square has been molten, but laser color marking didn't induce internal stresses within the substrate material.

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