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Modification of Aluminium Surface Using Picosecond Laser for Printing Applications

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ABSTRACT

Ultrafast picosecond laser pulses of wavelength of 1064nm have allowed the surface modification of anodised aluminium plate for potential industrial application. The interaction of the laser with the substrate created a hydrophilic surface, giving a contact angle of less than 10 degrees. On examination under a Scanning Electron Microscope (SEM), it was observed that these surfaces have an interesting 'lotus-leaf' like structure. It has been found that these laser processed hydrophilic surfaces revert with time. The potential for application in the printing industry is strong due to the reusability and sustainability of the process materials; initial trials confirm this. This technology would offer extra advantages as a non-chemical process without the need for developer, thereby reducing the overall cost and time of printing.

INTRODUCTION

In today's fast moving technological world, it has been realized that modifying the surface wettability of solid substrate is important in various situations. There are many applications where highly hydrophilic (water contact angle < 10) and hydrophobic (water contact angle > 100) materials are highly desirable [1]. There is a considerable amount of literature available on photoresponsive or photoinduced surface wettability of different materials, mainly TiO_2, by using various forms of light source and dark storage to switch from a hydrophilic to a hydrophobic state or vice-versa [1-7]. Two excellent review articles on photoresponsive surfaces and controlled switchable surfaces have been written by Kong *et al.* and Jiang *et al.* [8, 9]. The use of an ultraviolet (UV) and a green lasers to change surface wettability of polymers has been recently reported by Athanassiou *et al*. [10, 11]. To the author's knowledge, no work has been reported on the use of ultra short picosecond Infra-Red (IR) laser pulses to create hydrophilicity on aluminium (Al) and aluminium oxide.

In the present study, Al is chosen because it is a material of choice in the printing industry due to its properties and is cheap and readily available. After printing, the plate is either recycled (but is not reusable for lithographic plates) or is disposed of. An estimated 0.5 million tonnes of lithographic grade Al is produced annually requiring a power of 10^{10} kWh/annum; that is the equivalent of the annual power demand of 2 million homes. Also, the Al smelting process results in emissions of hydrofluoric acid (HF), inorganic fluorides and perfluorocarbons, up to 500 tons/year. Environmentally unacceptable chemicals are used to 'develop' the lithographic plates, i.e. nearly 2000 tonnes of caustic, 4000 tonnes of metasilicate and 3500 tonnes of surfactants. For sustainable development, these figures need to be reduced drastically.

The aim of this work is to eliminate the use of any surface coatings and developers for printing plates, and to create plates that can be reused, thereby reducing the cost of production of the plates, their transportation from the manufacturing to the print sites, removing the cost of disposal of developers, hence saving on total time and cost. To achieve these goals, a picosecond pulsed laser was employed on grained and anodised Al to make the necessary change in morphological structure resulting in the substrate becoming hydrophilic. This laser exposed hydrophilic substrate was used to print. After printing, the inks were removed and the substrate heated in an oven to revert/switch the substrate back to a hydrophobic state. Once this was achieved, the next cycle of laser exposure was carried out and print test repeated. In this way a processless, switchable and re-writable plate was produced which could be reused several times.

EXPERIMENTAL METHODS

The 1001 grade Aluminium sheet (99.4%) is manufactured by Sumitomo. The sheets were degreased, grained and anodized as described by Ansari *et al.* [12]. The freshly prepared anodized Al is hydrophilic after manufacture but then becomes hydrophobic after period of exposure to air.

For control experiments, ungrained unanodised Al was used while ungrained but anodized Al was used to investigate weight loss.

The laser used in this work was a High Q IC-355-800 Nd:VAN regenerative amplifier picosecond (ps) laser system (High Q, Photonics Solutions) capable of running at up to 50kHz with output wavelengths at 1064nm [13]. The laser can output up to 2.5W at 20kHz was controlled by dedicated software. The temporal pulse width τ_p = 10ps (FWHM), was confirmed with an autocorrelator, while measured pulse-to-pulse stability was excellent, <0.5%. An internal attenuator, software controlled, was used to vary the output pulse energy. Figure 1 shows the schematic of the experimental set-up. The output beam traversed a beam expander and was then directed to a scanning galvanometer with a 100 mm focal length f -theta lens. Focused spot size was observed to be ~22μm, almost diffraction limited.

The substrate was positioned on the horizontal surface of an Aerotech computer-controlled 5-axis stage (x, y, z and a goniometer). By synchronizing the scanning galvonometer with the stage, a large sample could be processed, providing great flexibility and accuracy. The laser exposure patterns were controlled by software (SCAPS GmbH).

The Al substrate used for experimental analysis had the dimension 20 mm x 20 mm x 0.3 mm while the substrate used for print test had the dimension 400 mm x 510 mm x 0.15 mm, which could fit the industrial printing machine that was used.

The laser exposed plates were characterized using a KRŰSS Drop Shape Analysis System to measure contact angle. Once the desired change to hydrophilicity was achieved, the substrate was examined under a JEOL JSM 7100F Scanning Electron Microscope (SEM) to study the morphology. A concurrent study of different elements present in the substrate was carried out by employing Energy Dispersive X-rays (EDX) on the substrate.

Once the substrate had changed to hydrophilic state after the laser exposure, print tests were carried out using an industrial printing machine. Several recycle print tests were carried out in order to determine that the substrate would print satisfactorily after going through cycles of reversion to hydrophobic-hydrophilic-hydrophobic states.

DISCUSSION

Preliminary laser exposure tests were carried out with different laser exposure energies, repetition rate and scanning speed. It was found that at 5kHz repetition rate, the threshold energy for inducing hydrophilicity on the substrate was Ep = 9μJ/pulse when the scan speed was 100mm/s, causing minimum damage to the anodic film. In order to get reproducible results, an energy, Ep = 10μJ/pulse was determined as the optimized energy for laser exposure with acceptable damage to the anodic film. A square pattern of 12mmx12mm was exposed using 10μJ, 100mm/sec scan speed and a hatch of distance 0.02 mm (i.e. the separation between line scans). The contact angle was measured and was found to be $<10^{o}$ (i.e. hydrophilic). Table 1 shows the contact angle after laser exposure and the time taken to revert back to the initial hydrophobic state. It was found that the sample become hydrophobic again in 4-5 hrs.

In order to study the morphological structure, SEM and EDX were carried out. Prior to examination under the SEM, the laser exposed substrate was sputter coated with gold. A control Al substrate (i.e. ungrained, unanodised) was also laser exposed in the same way and examined after gold sputter coating. Figure 2(a) and (b) shows the morphology of the control Al while figure 3(a) and (b) shows the morphology of grained and anodized Al substrate.

In the case of the control Al, after the laser exposure, it was found that the substrate did not become hydrophilic. The morphology of the control substrate, seen in figure 2, supports this observation as it shows the extremely pitted structure, caused by the Gaussian beam of the laser; and substantial damage to the Al substrate itself. The surface shows evidence of surface melting on Al with formation of tiny globules on resolidification with structuring greatest at the centre as a result of the higher intensity there.

In contrast to this, figure 3(a) and (b) shows a significantly different morphology. It is seen that at some places the anodic film is still very much intact after the laser exposure. It is thought this is due to the interaction of the laser pulses with the substrate. The alumina film is essentially transparent to the IR laser wavelength, the pulses couple into the metal at the metal/oxide layer interface, ablating the metal, resulting in the spallation of the substrate on laser exposure. This results in the surface roughening shown and the microstructure responsible for the changing of the substrate to a hydrophilic condition. It has been shown that the surface roughness can be an effective tool for changing the contact angle [14]. A similar structure here is believed to be created, and that this causes the change to hydrophilicity as it is supported by figure 3 (a) and (b). This very much resembles to the morphology reported by Patankar [15] and Bhushan *et al.* [16]. It is in agreement with the earlier findings that by increasing the surface roughness, a reversible surface switching between superhydrophobic and superhydrophilic states was realized on flower-like nanostructured titanium dioxide films [17, 18]. The control Al does not become hydrophilic after laser exposure, while the grained and anodized Al does become hydrophilic after laser exposure, so to achieve a hydrophilic change using a short pulse picosecond laser, it is necessary that the Al substrate be grained and anodized.

Figure 4(a) shows the site where the EDX was carried out on the grained and anodized Al while figure 4(b) shows the resulting spectrum. It can be seen that the spectrum lines 2 and 3 in figure 4(b) have high oxygen content and low in Al content, confirming the presence of anodic film after the laser exposure. The higher content of Al and negligible oxygen in spectrum lines 1 shown in figure 4(b) confirms the removal of anodic film from that area of the substrate.

It can be concluded that the laser exposed sample loses the surface oxide and forms hydroxide and that this is responsible for the hydrophilic change. This compliments earlier

theories that the oxygen atoms gradually replaced hydroxyl when stored in the dark, because the hydroxyl was energetically unstable and the oxygen adsorption is thermodynamically favored. As a result, the surface was returned to its original state and became highly hydrophobic [19].

With this knowledge of the process, control on the reversion time was achieved in the subsequent print tests to be carried out. After first laser exposure, the print plates were placed in an oven at 150^{o}C for 1h, and then rested at room temperature for 30 mins. This turns the hydrophilic Al plate back to its initial hydrophobic state (i.e. as it was before any laser exposure). In this way, several cycles were carried out to assess their reusability.

For this evaluation, a large grained and anodized Al substrate that could fit the industrial printing machine was exposed with the laser. Figure 5(a) shows the resulting printed pattern, 2000th print impression. The grey color is the area which was laser exposed which did not take up the ink and the surrounding black area is the background. After this initial print trial, further print tests were carried out with a slightly different print pattern. As mentioned above, this time after the first laser exposure the grained and anodized print plate was placed in an oven at 150^{o}C for 1h, rested for 30 mins and then laser exposed for a second time. In this way, the plates were recycled up to 4 times by re-exposing the same plate after each print test. Figure 5(b) shows the print test after the fourth laser exposure. This shows successful demonstration of good quality prints with up to 2000 impressions from a single laser exposure. It is also demonstrated that the same plate can be recycled up to 4 times.

CONCLUSIONS

In conclusion, a totally new technology in Computer to Plate lithographic printing has been developed by employing ultra short picosecond laser processing on anodized Al. This developed technology is 'green', has many environmental benefits and is extremely sustainable. As demonstrated in this study, the reuse of the plate up to 4 times without use of any developer, offers reduction in the overall cost and time by up to 80%. The technology has been submitted for two GB patents [20, 21]. There is great incentive for the entire industry to take this new technology up and considerable interest has been shown by the print industry in this future, green technology.

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20. GB patent application No. 0910791.3 (June 2009)
21. GB patent application No. 0816697.7 (September 2008)

Figures:

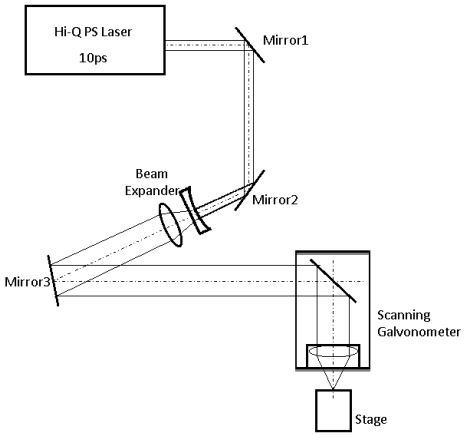

Figure 1. Schematic diagram of laser experimental set-up

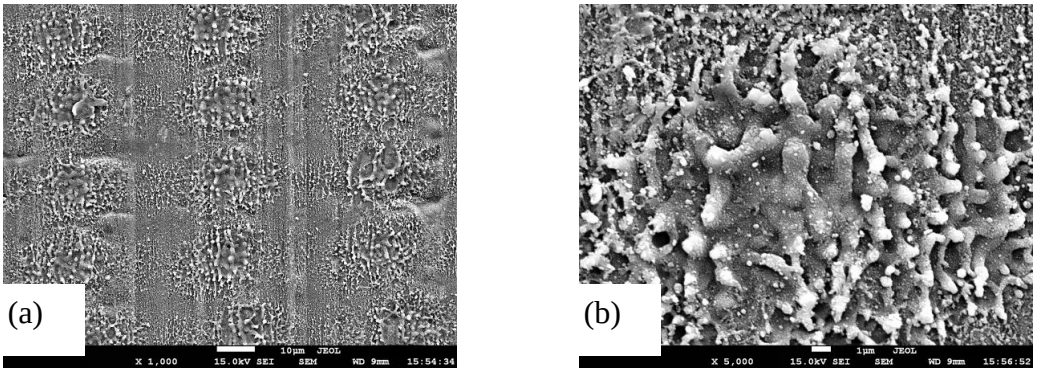

Figure 2. Scanning Electron Micrograph of Control Al (a) and (b)

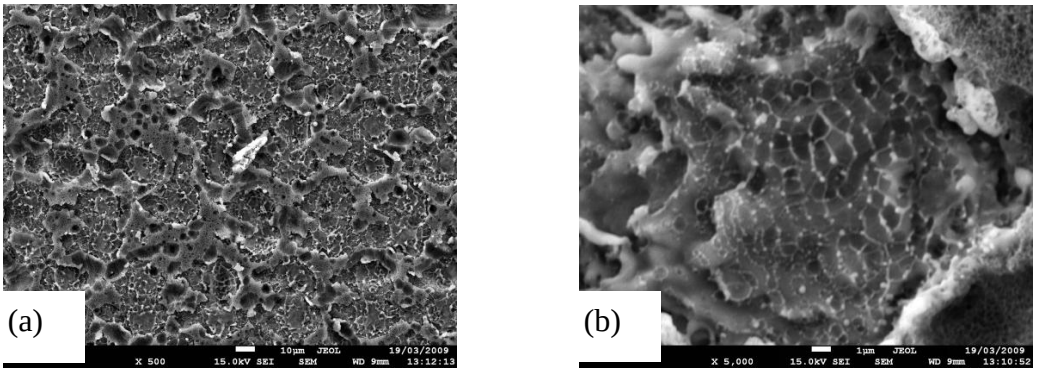

Figure 3. Scanning Electron Micrograph of grained and anodized Al (a) and (b)

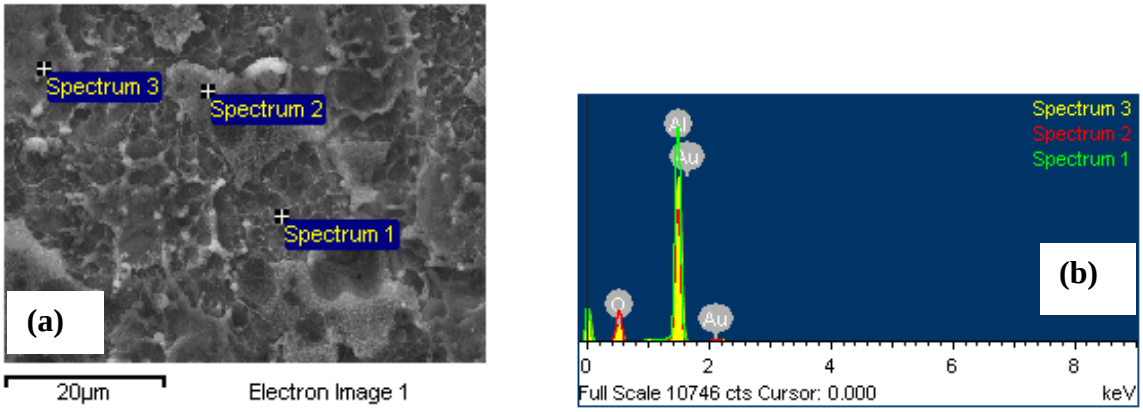

Figure 4. Scanning Electron Micrograph (a) EDX site, (b) EDX showing presence of elements at sites shown in Figure 4(a)

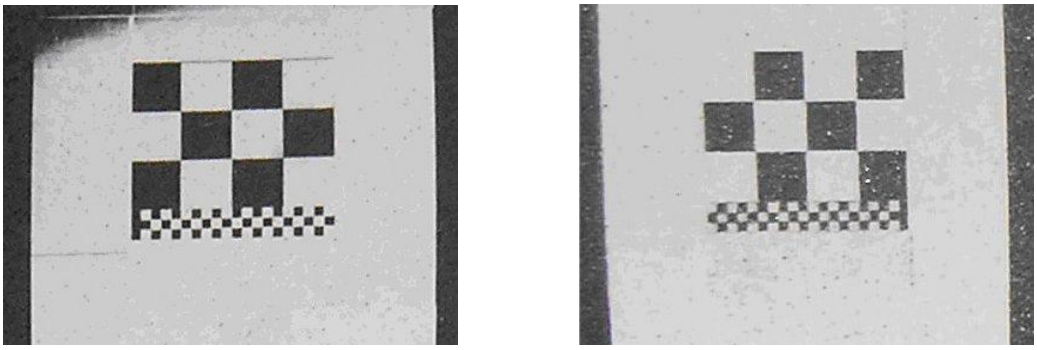

Figure 5. Printed pattern after (a) 1st laser exposure, (b) 4th laser exposure

Tables:

Table 1: Contact angle after laser exposure

Time (mins)	0	5	10	20	30	60	120	180	240	300
Contact Angle (degrees)	<10	20	31	40	48	58	60	65	74	74