Treatment Techniques on Aluminum to Modify the Surface Wetting Properties

L. Torrisi* and C. Scolaro

Dipartimento di Fisica e S.d.T., V. le F.S. D'Alcontres 31, 98166 S. Agata, Messina, Italy

Different techniques of surface treatment are employed to modify the physical properties of aluminum surfaces. Experimental data report measurements of water wetting ability in aluminum surfaces treated with six different techniques: polishing, sanding, acid attach, laser ablation, ion implantation and nanoparticle deposition. Surfaces can be modified as a function of the different treatment parameters. Treatment duration, roughness and morphology play an important role in determining the properties from hydrophobic to hydrophilic behavior.

1. Introduction

Different chemical and physical treatments can be employed to modify the wetting ability of Al surfaces, such as thermal oxidation, mechanical rolling, ion implantation, laser ablation, and chemical etching. In this study the wet ability of the Al surface as a function of different treatments is investigated and discussed.

Aluminum is a soft and ductile metal, with a white color; it is the third most abundant element in the Earth crust; it is highly reactive and generally is found as aluminum oxides and sulfates. It has a low density of 2.7 g/cm^3, a melting point of 660°C, a thermal conductivity of 237 W/mK, an electrical resistivity at room temperature of 28 nΩm, a Mohs hardness of 2.75 and a Young's modulus of 70 GPa [1]. It is able to resist to corrosion due to the phenomenon of oxygen passivation. The excellent corrosion resistance is due to a thin surface layer of Al_2O_3 that forms when the metal is exposed to air. The corrosion resistance is also often greatly reduced by aqueous salts, particularly in the presence of dissimilar metals. Structural components made from aluminum and its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials. The aluminum coverage of different materials is used as anti-corrosion of surfaces. Aluminum foil is widely regarded as the most effective material in flexible packaging, giving almost perfect protection against light and suppressing any transport of matter through the film. A polished film of aluminum serves as a good reflector (approximately 92%) of visible light and an excellent reflector (as much as 98%) of medium and far infrared radiation [2].

Aluminum can be used in several fields: transportation (automobiles, aircraft, railway, bicycles, etc.), packaging, building construction (windows, doors, etc.), household items (cooking utensils), electronics (transmission lines, substrate materials, LED support, etc.), chemistry, optical coating and mirrors.

The wet ability of Al surface is important for all of these applications, such as the request of hydrophobic (contact angle higher than 90°) Al surfaces for food container, the hydrophilic (contact angle lower than 90°) surfaces for Al–Al and Al–other materials welding and interface preparation [3].

2. Experimental section

Experiments were conducted on pristine aluminium obtained by mechanical rolling to a final thickness of 300 μm characterized by a mean roughness of 0.1 μm.

In these investigations six treatments were studied to modify the surface wetting ability. They are based on: polishing, sandblasting, chemical etching, laser ablation, ion implantation and deposition of metallic nanoparticles on the surface.

The polishing was obtained mechanically with high-speed rotary polisher up to obtain a mirror finished surface; the sandblasting was used with 10 μm sized silica powder fluxed by air at about 100 m/s final velocity; chemical etching was obtained using HCl at 10% concentration in water deposited for a fixed time on the surface followed by water removing; for the laser ablation experiments, an Nd:YAG laser operating at 1064 nm wavelength, 200 mJ maximum pulse energy, 3 ns pulse duration, 10 Hz repetition rate and 1 cm^2 spot surface; ion implantation uses 2 keV Ar$^+$ ions at 20 μA current emitted by an ion gun. Ti, Cu, Ag and Au nanoparticles with 50–100 nm in diameter and a concentration of 5 mg/10 ml in water have been deposited as water drops on the Al samples. Nanoparticles were obtained by laser ablation of the different elements in water at the Laser Laboratory of Plasma Physics of Messina University.

The method used for the measurement of the contact angles is the "sessile drop" method which involves the measurement of the profile of a drop of liquid resting on a solid surface [4]. It consists essentially in the measure

_____

*corresponding author; e-mail: lorenzo.torrisi@unime.it

of the contact angle between the tangent to the profile of a distilled water drop, deposited on the sample surface, and the surface itself. The contact angles of liquid droplets (1 μl water deposited on the surface by means of a micro-liter syringe) were measured directly using a webcam aligned to the eyepiece of an optical microscope that records video and captures photos of the system formed by the solid sample (housed in a movable sample holder) and the liquid drop. Suitable software permits to measure the contact angle using the line fitting the surface level and the line tangent to the deposited drop in the initial curvature points from the horizontal surface. The contact angle measurement is performed 10 times before to give the average final value. Generally measurements are affected by an error of about 10%.

The roughness measurements were performed using a Tencor P-10 surface profiler using a micrometric mobile tip with 1 mg force scanning the sample surface. The system has a 10 nm depth resolution and 1 μm lateral resolution during the scanning of the sample surface. The surface roughness was measured using the average peak-to-peak distance of the roughness profile.

Scanning electron microscopy (SEM) was performed by using a 20 keV electron beam produced by a Fei Quanta — model Inspect S microscope at the Physics Department of Messina University.

The evaluation on the ion range and sputtering yield due to the Ar ion implantation treatment was obtained using the international SRIM Code of Ziegler [5].
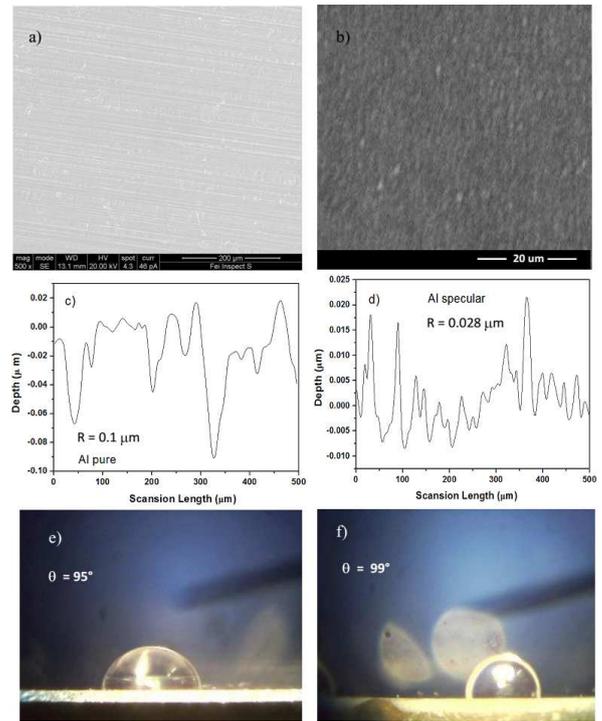

Fig. 1. Comparison of a SEM image in pristine (a) and polished surface (b), typical roughness profile in the pristine (c) and polished (d) surface, and comparison between the water drop photo on the pristine (e) and on the polished surface (f).

3. Results

Polishing treatment. The process used to polish aluminum has to match the amount of tarnish and roughness of a given surface removing the hard oxidized aluminum patina. Mechanical polishing techniques using hard abrasives tend to scratch, smear, or even embed abrasive particles in the material surface [6]. We have adopted abrasive silicate grains from micrometric to sub-micrometric sized dispersed in a chemical-mechanical polishing solution employed to polish optical components. The polishing of Al surface prolonger for some hours has transformed it in a very reflective surface becoming it so as a mirror. Figure 1 shows a comparison of a SEM image in pristine (a) and polished surface (b). The same figure shows the typical roughness profile in the pristine (c) and polished (d) surface, valuated of 0.1 μm and 0.028 μm, respectively. In the figure bottom it is possible to observe the photo comparison between the water drop on the pristine (e) and on the polished surface (f). The measured contact angle at room temperature was 95° and 99° for pristine and polished surface, respectively. Thus the treatment increases the contact angle enhancing the hydrophobicity of the Al surface.

Sandblasting treatment. The sandblasting process has been obtained spraying SiO_2 micrometric particles, less than 10 μm in diameter, against the Al surface in air [7]. The abrasive microparticles were accelerated by a fast

nitrogen flux to about 100 m/s and they hit the substrate orthogonally to its surface. The treatment time was varied from 30 s up to 3 min and a surface cleaning in high pressure air was performed at the end of the process. Figure 2 shows a comparison between the SEM images of an Al surface treated using sandblasting for 30 s (a) and 3 min (b), their profile of surface roughness at 1 min (c) and 3 min (d) and the optical images of the water drop for minor (d) and prolonger treatment (e) from which it is possible to measure the wetting ability. The average roughness is 3 μm and 4.5 μm for 30 s and 3 min sandblasting, respectively, while the contact angle from the initial 95° measured in the pristine surface decreases to 85° at 30 s sandblasting treatment and up to 63° at 3 min sandblasting, demonstrating that the long treatment increases the hydrophilicity of the Al surface.

Chemical etching treatment. HCl at 10% in water volume was deposited on the Al surface at room temperature (22 °C) for different times from 30 s up to 10 min and just after removed with water. The reactions

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2;$$
$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \qquad (1)$$
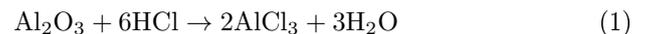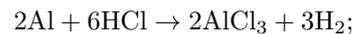
may occur at the surface, removing the aluminium oxide and the first Al layers [8]. The surface is chemically etched in preferential points from which the reactions start to diffuse superficially. Figure 3 shows a typical SEM image, of the centres of initial chemical attaches,
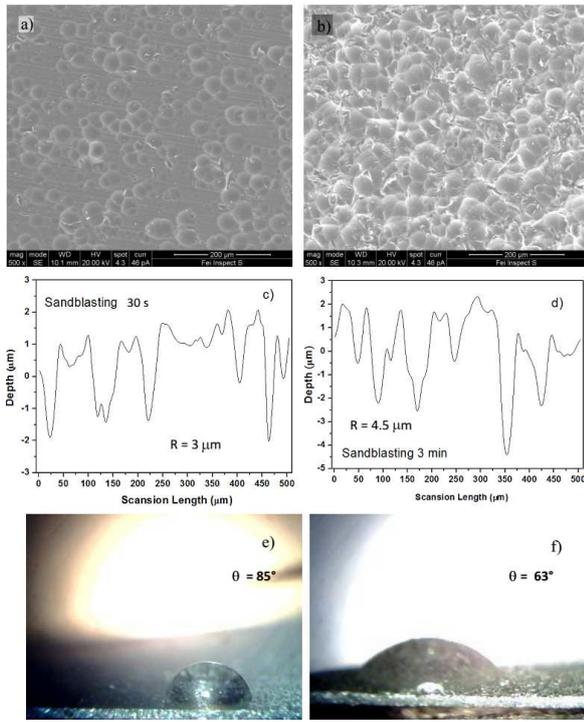
Fig. 2. Comparison between the SEM images of an Al surface treated using sandblasting for 30 s (a) and 3 min (b), the profile of surface roughness at 30 s (c) and 3 min (d) and the optical images of the water drop for the minor (d) and the prolonger treatment (e).
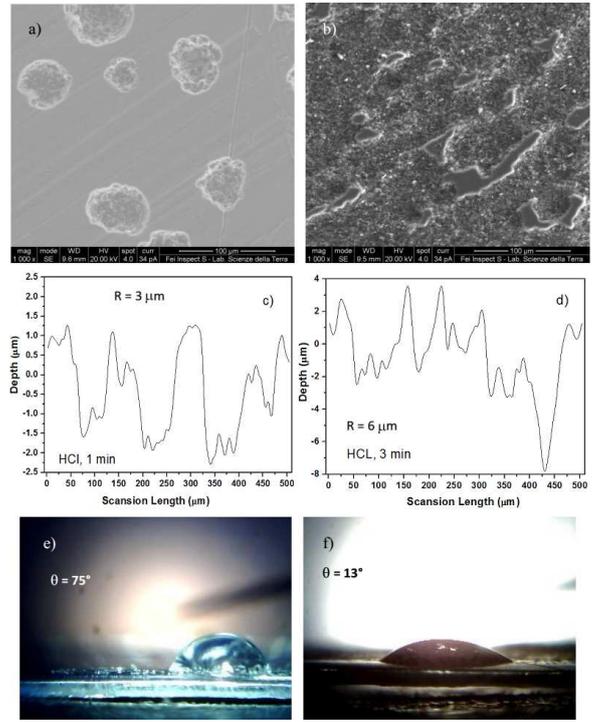

Fig. 3. Typical SEM image obtained for chemical HCl attack in the first 1 min (a) and of its progression at 3 min (b), surface roughness profile at 1 min (c) and 3 min (d) and measurement of contact angle for attack at 1 min (e) and 3 min (f).

obtained in the first 60 s (a) and of their progression after 3 min (b). The same figure shows the surface roughness profile which is about 3 μm (c) and 6 μm (d) in the two cases, respectively. The wet ability of the two cases is observable from the photos reported in Fig. 3e and f, indicating a contact angle decreasing to 75° and 13° at 1 min and 3 min HCl etching. Thus this treatment induces high hydrophilicity of the Al surface.

Laser ablation treatment. The 1064 nm laser radiation without any focalization on the Al surface, with a spot of 1 cm^2 and 10 Hz repetition rate, produces removing of the first superficial layers as a function of the pulse energy and of the irradiation time [9]. The ablated surface shows more roughness with respect to the pristine one. Figure 4 shows a SEM comparison of the ablated surface due to 50 laser shots at 50 mJ (a) and 200 mJ (b) pulse energy, the corresponding surface roughness was evaluated to 0.7 μm (c) and 0.8 μm (d), respectively. The figure shows also the comparison of the optical images of the drop wetting ability for the low energy irradiation (e) and high energy irradiation (f), at which the contact angle is 92° and 45° for low and high laser energy, respectively, both using an irradiation with 50 laser shots. Results indicate that low laser energy may decrease the contact angle from the pristine value of 95° up to about 92° (using 50 laser shots at pulse energy of 50 mJ); at high laser energy and high shots number (≈1000) the contact angle decreases up to 45° showing that the laser treatment

produces hydrophilicity of the Al surface.

Ion implantation treatment. Ar$^+$ ions accelerated at 2 keV energy and emitted from an ion gun with a current density of 20 μA/cm^2 have been employed to irradiate in high vacuum, at 45° incidence angle, the surface of the pristine Al surface for different times accumulating different ion doses, from 10^{14} ions/cm^2 up to 10^{16} ions/cm^2 [10]. For normal incidence the ion range is 44 Å with a straggle of 19 Å, as reported in the SRIM simulation of Fig. 5a, and the energy transferred to recoil atoms is maximum at the target surface where it assumes a value of about 40 eV/ion/Å, and decreases of about one order of magnitude at about 65 Å depth, as reported in the SRIM simulation of Fig. 5b. At 45° incidence angle the sputtering yield of Al surface is 4 atoms/ion and the average energy transferred is about 20 eV. Thus ion implantation removes atoms from the Al surface, especially at high incidence angle (> 45°); generally it reduces the roughness of the Al surface and increases little the contact angle of the implanted surface as a function of the implanted dose, similarly to a polishing effect. Figure 5 shows the roughness profile of the implanted surface at a dose of 10^{16} ions/cm^2 (c), of about 0.08 μm, and the optical image of the wetting ability measurement indicating an angle of 96.5° (d).

Treatment with metallic nanoparticles. Metallic nanoparticles of Ti, Cu, Ag, and Au have been prepared via laser ablation in water for different applica-
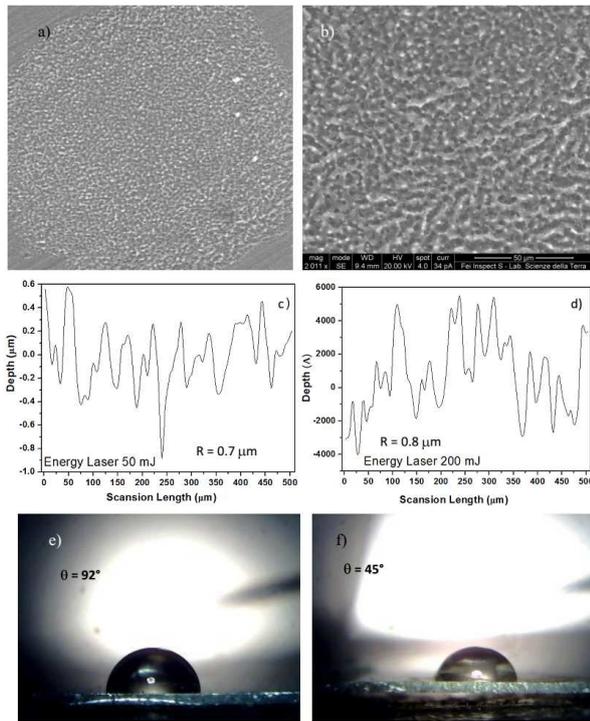
Fig. 4. SEM comparison of the laser ablated surface due to 50 laser shots at 50 mJ (a) and 200 mJ (b) pulse energy, corresponding surface roughness at low (c) and high energy (d) an optical images of the drop wetting ability for the low energy (e) and high energy irradiation (f).

tions [11, 12]. The concentration of the prepared solution containing the nanoparticles was 5 mg/10 ml. The average dimensions of the produced nanoparticles was in the range 50–100 nm, according to the visible absorption measurements of the produced solution performed in our laboratory and according to the literature data [13]. Drops of solution were deposited on the Al pristine substrate and left to dry. After 24 h drying, nanoparticles remain deposited on the pristine Al surface, as SEM images of Fig. 6 demonstrated for Ti (a), Cu (b), Ag (c), and Au (d). Successively the wetting was performed. The wet ability becomes function of the used nanoparticles as confirm the optical images reported in Fig. 6 for Ti (a′), Cu (b′), Ag (c′) and Au (d′) indicating a contact angle of 67°, 91°, 37°, and 53°, respectively. Thus, in general the nanoparticles decrease the water absorbance as a function of the substrate nature, as obtained for Ti (−36%), Cu (−4%), Ag (−61%) and Au (−44%).

In conclusion, the measurements demonstrated that the wetting ability of Al surface may be increased as a function of the kind of treatment at which it is submitted. Moreover, the roughness of the surface is a crucial parameter that controls the contact angle. High wetting ability is obtained using liquids containing nanoparticles and depositing NP on the investigated surface. Surface treatments based on laser irradiation, sandblasting and chemical etching, as a function of the time surface treat-
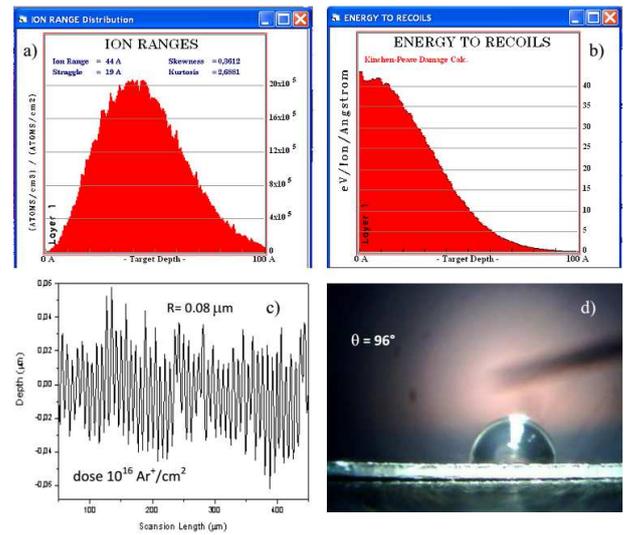

Fig. 5. SRIM simulation for the Ar^+ ion range in Al (a) and for the energy transferred to recoil atoms (b), roughness profile of the implanted surface at a dose of 10^{16} ions/cm^2 (c), and the optical image of the contact angle of 96.5° (d).
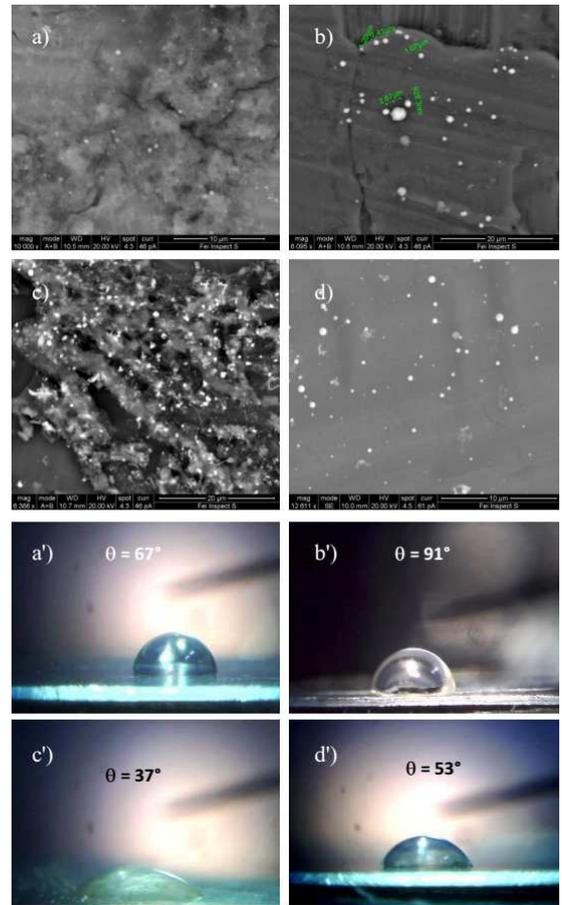

Fig. 6. SEM images of nanoparticles of Ti (a), Cu (b), Ag (c) and Au (d) deposited on aluminum and contact angle measurements for water on the Al surfaces covered with Ti (a′), Cu (b′), Ag (c′) and Au (d′) nanoparticles.
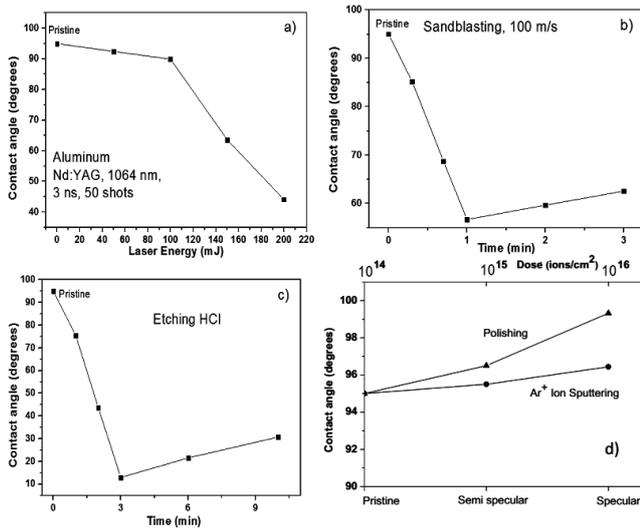
Fig. 7. Contact angle of the Al surface treated with 50 laser shots as a function of the laser energy (a), with sandblasting vs. time (b), with HCl etching vs. time (c) and with polishing and ion sputtering vs. ion dose and of type of treatment (d).

ment, demonstrate that the wetting ability of the surfaces increases, as reported in the summary plots of Fig. 7a–c, respectively. Low wetting ability, i.e. hydrophobic surfaces, are obtained using surface mirror polishing and ion sputtering, as reported in the summary plot of Fig. 7d.

3. Discussion and conclusions

Six different methods for creating controlled micro-scale morphology by varying the Al surface roughness have been presented, and the effects of these surface features on wetting and droplet retention have been quantified. Results show that the contact angle of water on aluminum is a function of the kind of surface treatment used and of the roughness produced. A summary of obtained
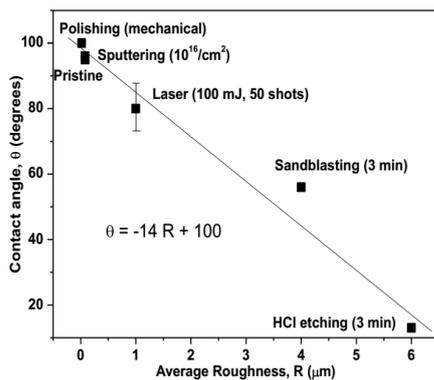

Fig. 8. Contact angle as a function of the average roughness for different methods of Al surface treatments and empirical relation between the two parameters.

results is observable in the plot of Fig. 8 reporting the contact angle as a function of the roughness for different

methods of Al surface treatment, going from polishing, inducing low roughness and high hydrophobicity, to HCl etching, inducing high roughness and high hydrophilicity. In other words the contact angle, θ (degree), using opportune treatments, is approximately linearly dependent on the average roughness, R (μm), according to the empirical relation

$$\theta° = -14R[\mu\text{m}] + 100. \qquad (2)$$

This linear trend was obtained with measurement with errors within about 15%. Aluminum surface can be well-prepared for efficient wetting, coating and durability. Coatings of Al surfaces provide the most important pre-requisite for durability, if they are completely spread on the foil surface. Since the surface of aluminum acts as a barrier in a laminate, migrating compounds can enrich or react there. In this sense the hydrophobicity enhances the durability of the aluminum sheet. Plastic, ceramic and metallic coatings can be well adherent to the Al substrate if treatments increasing the wet ability are previously employed.

The techniques presented in this paper have broad applicability for metals other than aluminum, and their accompanying effect on wettability is of special relevance in applications concerning the Al–Al welding and Al/fuse interface preparation.

High roughness of Al surface and porous structures induce high wetting ability, thus a liquid can penetrate very well inside the microcavities and the Al surface can result well adherent to other materials while very polished surfaces showing a minor contact area induce low liquid absorbance and material do not adhere to coverage films reducing eventual diffusion of elements through the interface. In this last case hydrophobic property characterize the prepared Al surfaces increasing the contact angle to about 100°. All the presented treatments are simple, not expensive and can be applied with successfully to control the morphology and the physical-chemical characteristic of the Al surfaces.

References

[1] *Handbook of Aluminum, Physical Metallurgy and Processes*, Eds. G.E. Totten, G.S. MacKenzie, Vol. 1, USA 2003.
[2] J.E. Hatch, *Aluminum: Properties and Physical Metallurgy*, American Society for Metals, Metals Park Ohio 1984.
[3] A.J. Klinter, G. Mendoza-Suarez, R.A.L. Drew, *Mater. Sci. Eng. A* **495**, 147 (2008).

[4] C. Scolaro, L. Torrisi, M. Cutroneo, L. Velardi, *J. Physics: Conf. Series* **508**, 012030 (2014).

[5] J.F. Ziegler, *Nucl. Instrum. Methods Phys. Res. B* **219–220**, 1027 (2004).

[6] L.E. Samuels, *Metallographic Polishing by Mechanical Methods*, 4th ed., ASM International, Materials Park, USA 2003.

[7] L. Slatineanu, S. Potarniche, M. Coteata, I. Grigoras, L. Gherman, F. Negoescu, *Proc. Manufact. Syst.* **6**, 69 (2011).

[8] H. Oh, J. Lee, H. Ahn, Y. Jeong, N. Park, S. Kim, C. Chi, *Mater. Sci. Eng. A* **449–451**, 348 (2007).

[9] A. Picciotto, L. Torrisi, A.M. Mezzasalma, E. Amato, C. Gentile, in: *Proc. PPLA2003, Messina (Italy)*, Eds. S. Gammino, A.M. Mezzasalma, F. Neri, L. Torrisi, World Sci. Publ., Singapore 2003, p. 191.

[10] O. Gautsch, *The Sputtering of Aluminum Oxide by Argon Ions*, Joint Research Centre, Brussels 1993.

[11] V. Piriyawong, V. Thongpool, P. Asanithi, P. Limsuwan, *Procedia Eng.* **32**, 1107 (2012).

[12] L. Torrisi, M. Cutroneo, G. Ceccio, *Phys. Scr.* **9**, 015603 (2015).

[13] Nano Composix Europe, Chicago (2014), nanocomposix.eu/pages/ gold-nanoparticles-optical-properties.