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A mechanism-based study of the wettability transition of surface vaporization of nanosecond laser-treated titanium under various storage conditions

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ABSTRACT

Surface vaporization of metals is currently receiving significant attention as a wastewater treatment technique. This article examined the wettability transition of a treated titanium surface (so-called an evaporator) under varied storage conditions. Several aspects of the transition mechanism were evaluated, including contact angles, surface chemistry, and wetting dynamics. The titanium treated surface changed significantly in wettability when exposed to ambient air, going from highly water-attracting to ultra-hydrophobic after only 40 days of storage. The experiments conducted proved that the contaminants in the air absorbed on the Ti surface are responsible for this wettability shift. We found an increase in C/Ti ratios and C–C(H) (at. %) over time, which implied a nonpolar nature and showed a hydrophobic tendency. The samples kept in nitrogen and water, on the other hand, remained in their original state. In contrast, the sample stored in an open water environment increased its contact angles slowly over time, which could have been influenced by organic matter in the air. The results of this research are not only helpful in understanding the transition mechanism of nanosecond laser-treated titanium but also provide information that the wastewater industry can implement to store evaporators to avoid the rapid transition of wettability and produce super-hydrophilic surfaces with stability and durability.

1. Introduction

The wetting properties of solid substrates are critical both theoretically and in terms of manufacturing. The wettability transition of micro- and nanostructured metallic surfaces has been studied extensively, but no widely accepted theory appears to explain it [1]. In recent years, there has been an explosion of attention with regard to controlling the wetting condition of actual interfaces and fabricating nanostructures that are similar to surface vaporization but have extraordinary or unusual wetting properties [2]. The microstructural composition of the surfaces is typically the determining factor in wettability. The industrial or application requirements considerably affect the materials and technologies used to attain required wettability. To create surfaces with the necessary wettability, various approaches have been explored. Some investigations have focused on the modulation of surface roughness [3,4].

Several researchers employed optical techniques and electron irradiance to change the surface chemistry to swing from super hydrophilicity and super hydrophobicity [5,6]. In addition, the stability of surface super-hydrophobicity and super hydrophilicity, i.e., how they change with time, is a significant aspect to study to assure the useable duration of technological solutions [7,8]. Furthermore, in technology, the wettability of materials is very important. Self-cleaning engineered manufactured surfaces, for instance, could be utilized as solar panel coatings since these aid in the removal of accumulated dust and dirt, increasing light transmission and thermal energy efficiency. Such substrates could be divided into two categories, including hydrophobic and hydrophilic surfaces [9–11]. Besides, water droplets flow across hydrophobic surfaces, carrying dirt away with them. When water drops settle on hydrophilic surfaces, they expand and produce a thin water

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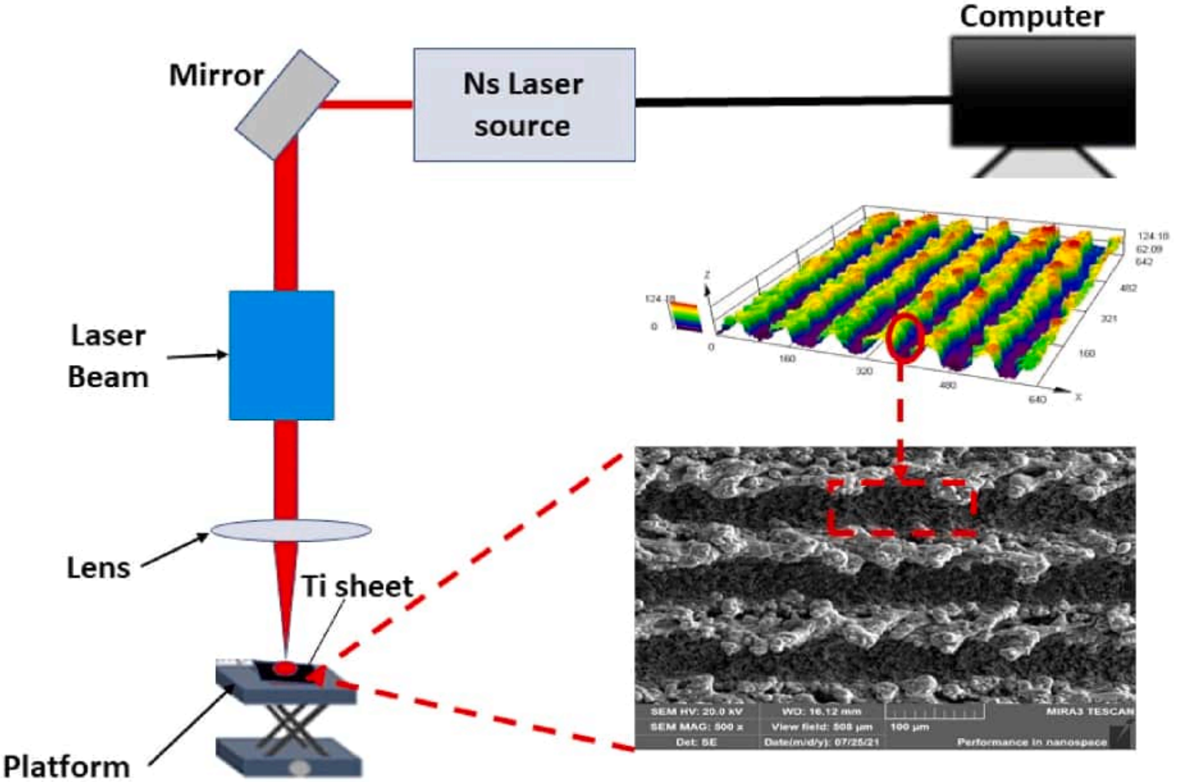

Fig. 1. Schematic of Nanosecond laser processing.

coating. The dirt is then wiped away during the expanding process [12].

Numerous investigations have demonstrated that originally hydrophilic nano- and micro-structured transition metal surfaces turn hydrophobic or, in some instances, superhydrophobic in the air over aging [1,10–13]. The quality of air in every laboratory largely depends upon the geographical and urban setting, whether it is cleaned or not, and the amount of human movement inside the facility, among other factors [17]. Furthermore, numerous earlier studies have found that the freshly ablated metal surface was hydrophilic or super-hydrophilic with the occurrence of micro/nanostructures shortly after pulsed laser deposition. The wettability shift from super-hydrophilic to superhydrophobic was discovered when the laser-ablated surface was subjected to atmospheric air for a long time [15–17].

The elucidation of the wettability transition process has been the subject of current studies. For instance, Yang et al. discussed the wettability transition mechanism of nanoseconds laser-treated surface and subjected to the air. They found that the slow superhydrophobic transformation was aided by chemisorption of hydrophobic molecules airborne compounds via humid air [19]. In addition, Long et al. conducted a similar study on a picosecond laser micro-structured exposed to the air. Similarly, they concluded that the adsorption of organic molecules from the surrounding environment over metal substrate was the principal reason for the wettability change. Besides, in the nitrogen and oxygen conditions, the hydrophilic state of the material was stable [1]. Moreover, Kietzig et al. hypothesized that the wettability change from hydrophilicity to hydrophobicity could be caused by the breakdown of CO_2 into carbon with active magnetite produced during the laser ablation process [21]. Although substantial improvements have been achieved in wettability transition on metal-based surfaces, as evidenced by the earlier studies, there is still much space for improvement in our comprehension of the wettability transition mechanism. Furthermore, identifying an appropriate environment to store hydrophilic surfaces for long-term wettability resilience is a more challenging task. Because of the high demand for Ti-based products, research on this subject is still in its early stages and merits further investigation.

The wettability transition of a nanosecond laser micro-structured titanium surface process was explored in detail in this work by examining the surface microchemical - structural contents of surface vaporization treated titanium specimens maintained in three different environments: water (open and airtight conditions), nitrogen, and ambient air for three different ages (10, 20 and 40 days). We monitored the wettability transition and evaluated their surface compositions to determine what constituent in the air is accountable for the wettability shift and discover the suitable environment for a long-term stable hydrophilic condition for the surface vaporization. The static contact angles, wetting dynamics, and the change in surface chemistry were systematically monitored over time as a function of storage conditions. The measurements of XPS, XRD, SEM, and Contact angle were used to determine the wettability transition mechanism. Consequently, our findings show that organic substances' adsorption from the atmosphere is the most accountable for the wettability transition. In addition, nitrogen and water (airtight) environments are the ideal storage conditions for surface vaporization.

2. Experimental content

2.1. Materials

Pieces of pure and shining titanium (Ti) with dimensions of 25 × 30 × 2 mm were purchased from Baoji Yinggao Metal Materials Co., Ltd. (Shanghai, China) and used to investigate the effect of storage environment on the wettability evolution of the treated Ti surfaces.

2.2. Surface modification

Nanosecond pulse lasers were used to modify titanium surfaces, as schematically illustrated in Fig. 1. A nanosecond scanner (SPI G3 20 W/R.M., U.K.) with a wavelength of 1064 nm, a pulse repetition rate of 25

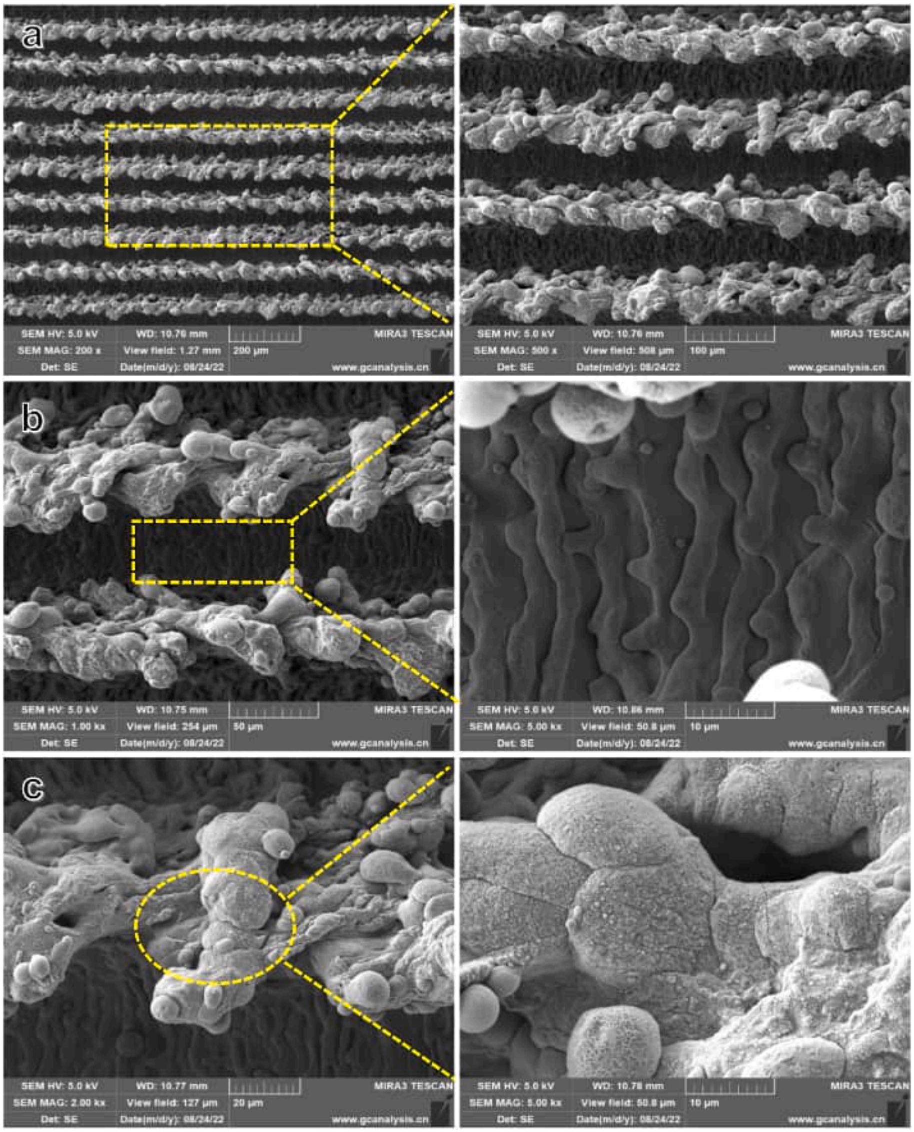

Fig. 2. SEM micrographs at various magnifications depicting the hierarchical microstructures and nanostructures of the treated titanium surface. (a) groove, (b) bottom of the groove, (c) edge of the groove.

kHz, a frequency range of 25–100 kHz, and a pulse width of 0.8 mJ was used to scan titanium plates. Under normal atmospheric conditions, laser scanning experiments were performed with the laser beam incident at an angle of 90°. In order to focus a laser beam on the titanium surface, an electrometric scanner with a two-mirror configuration and an F-Theta objective ($f = 100$ mm) was used. More laser processing parameters are presented in Table S1. After treating the sheets, they were stored in three different storage settings: ambient air, water (in a sealed and open environment), and nitrogen, all exposed to laboratory conditions, including atmospheric pressure and ambient temperature.

2.3. Surface characterization

The resulting surfaces of the laser processing were evaluated to assess the surface features. SEM analysis of the treated Ti was performed using the SEM-TESCAN MIRA3, Czech Republic, and confocal laser microscopic (OLS4100 3D measurement laser confocal microscope, Olympus of Japan) to investigate the morphology and the microstructure of the surface. The surface chemistry of the Ti sheet was studied by x-ray photoelectron spectroscopy (XPS-Thermo fisher Scientific EscaLab 250Xi, U.K.) the type, thermos fisher scientific K-Alpha with the following parameters: source of radiation (Al Kalpha source), test energy (1486.8 ev), test spot area (0.5 mm), test tube voltage (15 kv), tube current (10 mA), analysis chamber background vacuum (2.10^{-9}mbar), and electron emission angle (90°). A sputter-etch was not applied to the samples' surfaces and the charge neutralizer was not used. For a reliable binding energy (BE) referencing, as recommended by Greczynski et al. [22], the BE of the C 1s peak was set at 289.58- φ_{SA} eV (φ_{SA} is the work function determined by UPS) and then applied to all other core levels accordingly. The obtained work function and C 1s peak position were 3.62 eV and 285.96 eV, respectively. X-ray diffractometer (XRD) patterns were measured on a Rigaku UltimaIV X-ray diffractometer (Cu Kα, $\lambda = 1.54056$ Å) using the standard 2Θ-Θ mode with 2Θ ranging from 20° to 100° at the scan speed of 2°/min with a step of 0.02°under the condition of 40 kV (voltage) and 30 mA (current). Besides, the EDS analysis was performed using the Model: AZtec X-Max N80 (Oxford Company) with the following configuration and technical parameters: main configuration and technical parameters: resolution: better than 127 eV (MnKα); electrical refrigeration; analytical element range: Be4 ~ Cf98; collection methods: point, line, surface; Sampling time: >60 s; X-Max N80 large area analytical SDD Silicon Drift Detector. In addition, the cross-sectional TEM was performed using TEM Model: JOEL 2100f,

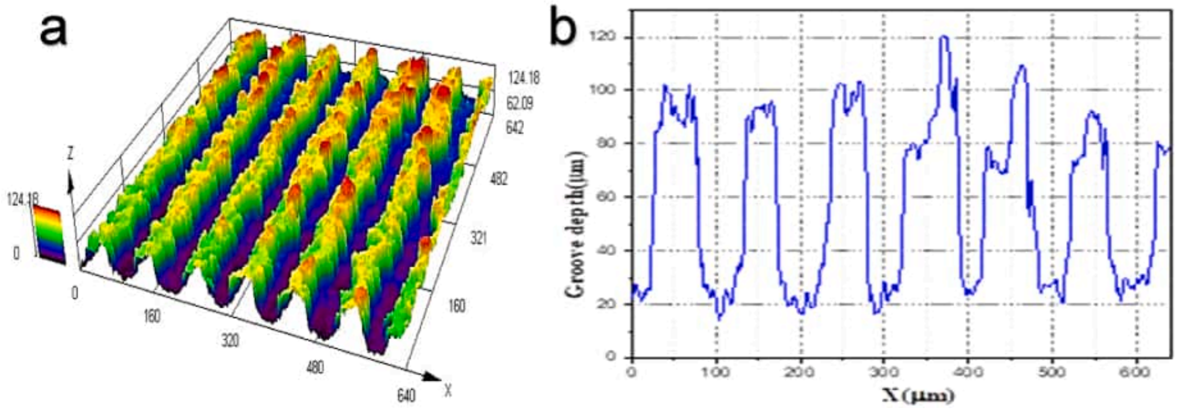

Fig. 3. 3D confocal laser microscopic image for treated Ti surface topography. (a) laser scanning optical microscopic image of the treated surface profile, and (b) depth profile of the parallel grooves.

JOEL Ltd., Tokyo, Japan. The FIB model (Model: HELIOS NanoLab 600i; Manufacturer: American FEI Company; Technical parameters: Secondary electron image resolution: 0.9 nm (15 kV), 1.4 nm (1 kV); Magnification multiple: 40–600000; Acceleration voltage: 0.5–30 kV; Ion imaging resolution: 4 nm (30 kV); Acceleration voltage: 0.5–30 kV) was used to prepare the samples. As part of the investigation, the static contact angle (Kino SL250, USA) and wetting dynamics of the material were measured by fixing it vertically on a platform, then dropping 60 μL of distilled water on its bottom to observe the wicking motion. The experiment was carried out in ambient conditions.

2.4. Storage setting

The nanosecond laser micro-structured titanium (Ti) sheets were stored in three different environments: water, nitrogen (N_2), and ambient air. An empty bottle was used to create the nitrogen atmosphere. A machine provided nitrogen with high purity. Two types of conditions were selected for the water environment, including hermetically sealed and non-hermetically sealed. After immersing the treated Ti sheets in the container filled with clean water, the lid was sealed. One must point out that only half of the titanium sheets were submerged in water. Under the final condition (air), treated Ti surfaces were placed in glass tubes without any lids and exposed to the lab setting at 25 °C and RH = 60% without any protective objects exposed to air. The facility was situated in Shanghai's Pudong district, China. In order to reduce convection airflow, the specimens were placed in a low-traffic area of the lab. Moreover, both samples were maintained in their respective atmospheres for three distinct periods, 10, 20, and 40 days, to investigate the effects of storage conditions on the wettability transition of titanium treated surfaces. The samples were placed in relative storage conditions 20 h after laser ablation due to the distance between our laboratory and the laser institute. The treated Ti sheets were still highly hydrophilic, with contact angles ranging from 2 to 5°. As a result of their thickness (2 mm) which required further preparation, all Ti sheets were exposed to atmospheric conditions after the storage periods for about 11 h before the analysis.

3. Results and discussion

3.1. Surface characterization

This research aimed to look at the shift from super-hydrophilic to hydrophobic or superhydrophobic behavior and the stability of the initial state of titanium surfaces stored in three distinct storage conditions over time. Serious modifications in various physical and chemical characteristics of a surface are possible based upon the physics of a nanosecond pulsing laser beam contact with metals and the likelihood of occurrences including shockwave creation, tensions, strains, thermal effects, and hydrodynamic disturbances [23]. Parallel patterning structures were produced by laser ablating in two orthogonal directions with laser at focal during the scanning. Peripheral channels were designed in a single scan to generate microcells quickly.

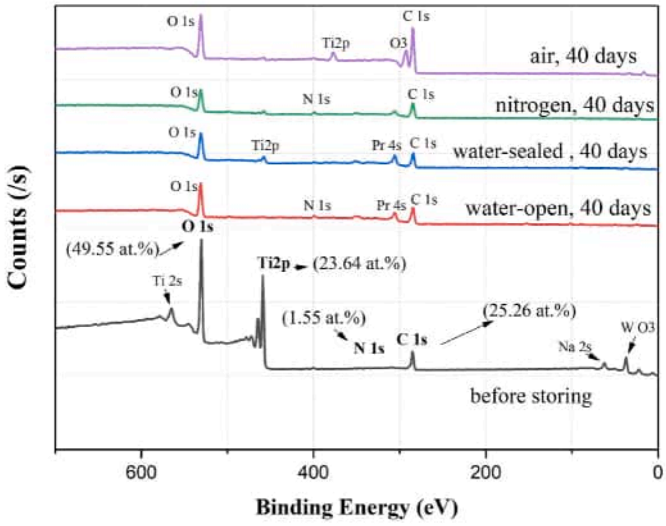

Fig. 4. XPS spectra of the treated titanium surface and stored in nitrogen, water and ambient air.

Fig. 2(a–c) illustrate the SEM micrographs of the treated Ti surface at different magnifications. This figure shows that parallel structures were obtained, referred to as grooves. As reported in Fig. 3(a–b), three-dimensional confocal laser microscopic images demonstrate hierarchical mono-structures linked in a network-like configuration. In addition, the grooves had a width of about 60 μm. The tops of the microgrooves were found to have microcavities, and the entire edges of the grooves were randomly coated with tiny irregular particles, as illustrated in Fig. 2(c). Hydrodynamic motion within the pulsed melted layer creates those nanostructures [24–26]. According to previous characteristics, these nanostructures are made up of tiny metallic nanoparticles with less than 10 nm. The redeposition of laser-ablated materials results in creating all these nanoparticles [27].

Following laser treatment of the treated Ti surface, a series of XPS analyses were performed in order to determine its surface chemistry. Fig. 4 illustrates a complete scan for XPS signals up to binding energy of 1200 eV. Carbon (25.26%), nitrogen (1.55%), Oxygen (49.55%), and Ti2p (23.64%) are the dominant chemistries present on the surface, with the remaining components contributing in smaller amounts and whose

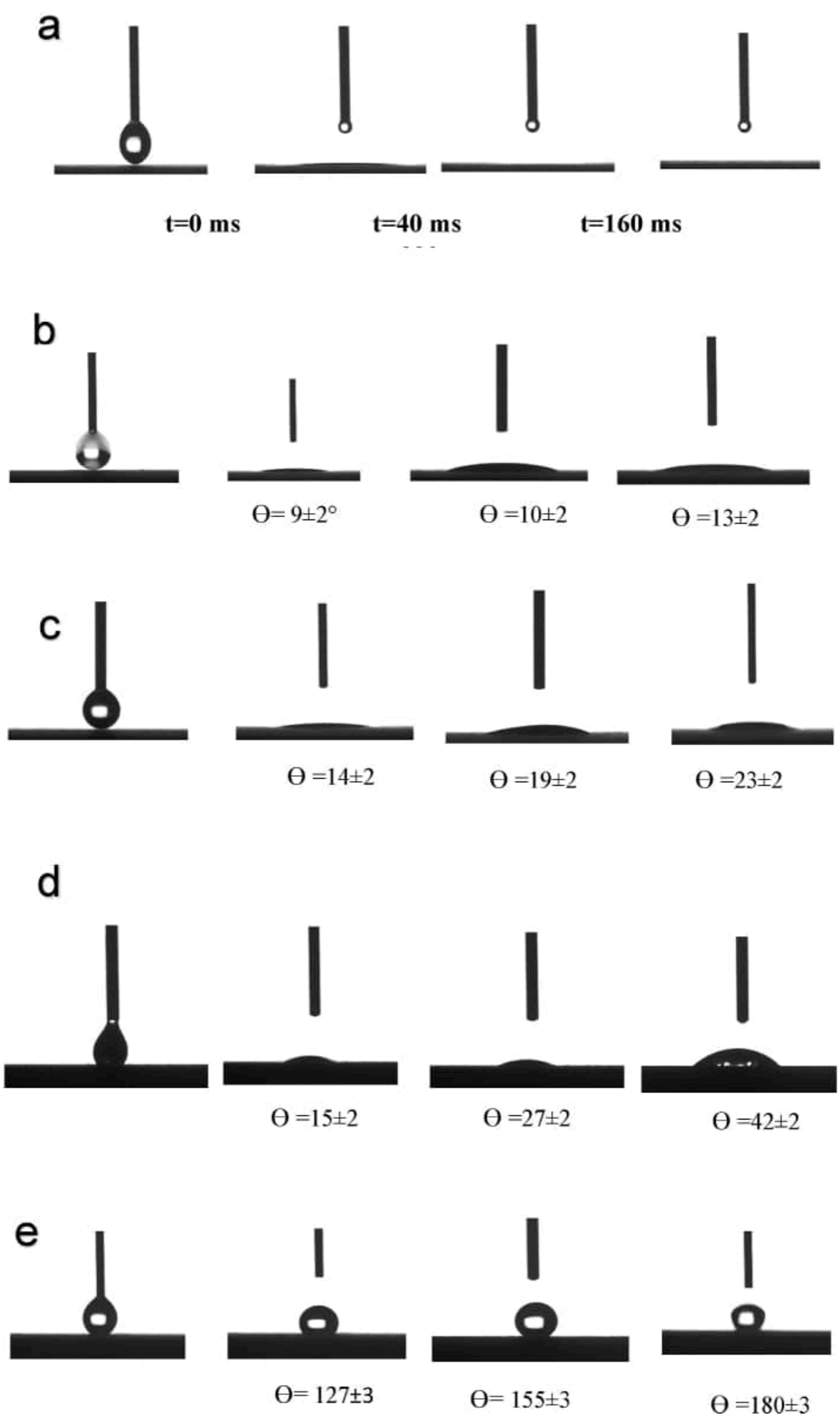

Fig. 5. Contact angles. (a) initially treated Ti before storage. (b) stored in nitrogen condition for three segments of periods (10, 20 and 40, respectively). (c) stored in water airtight (Water-A). (d) kept in water open environment (water-O), (e) stored in ambient air.

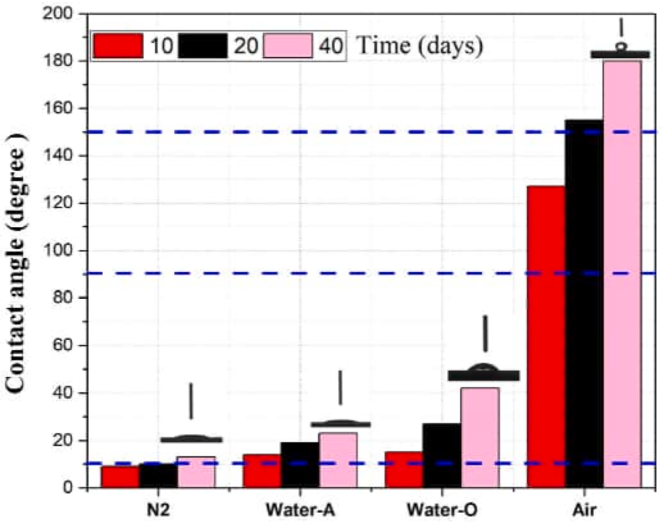

Fig. 6. Changes in contact angles as function of time and storage setting.

effects can be neglected. Furthermore, the treated samples had a contact angle of 0 ± 2° as measured after the laser processing was completed, as indicated in Fig. 5(a). Additionally, the XRD patterns of the sample shown in Fig. S4(c) (black line), Supplementary Materials, before storage indicate that the laser-treated titanium is composed primarily of titanium oxide (Ti_2O) and anatase (TiO_2), which correspond to 34.72° and 37.89° for anatase and 39.81° for Ti_2O. The treated samples initially possess super-hydrophilic properties and a low carbon content, accompanied by a high oxygen content after the laser processing with a shallow contact angle.

3.2. Wettability transition mechanism

As a function of time, the contact angles, the wetting dynamics in the treated Ti capillaries, and changes in the chemical surface of the treated Ti surface as a function of the atmosphere were examined to identify the mechanism of the wettability transition.

3.2.1. Contact angles analysis

The contact angles experiment is a crucial factor in understanding the wettability transition mechanism of treated surfaces. The storage time is heavily influenced by sample storage conditions, laser ablation, and the material's composition. The static contact angle is standard to test wettability qualities [28]. In this study, the static contact angles (SCAs) were monitored during 40 days of samples surfaces exposed in distinct environments.

Fig. 5(b–e) depicts the variation in contact angles of the treated Ti sheets stored in nitrogen, water, and ambient air over time. During the first 20 days, the samples stored in nitrogen condition maintained their super hydrophilic status with SCA ranging from 9° to 10 ± 2° for 10 and 20 days, respectively. In spite of this, after 40 days of storage, the SCAs remained hydrophilic, as evidenced by Video S2. Long et al. investigated the wettability transition of picosecond laser surface micro-structured Al kept in nitrogen for 8 and 30 days. Accordingly, the researchers found a similar result claiming that the material surface remains super hydrophilic [29].

Monitoring the wettability transition in the water environment consisted of two steps, including the storage of treated Ti samples in a hermetic environment (water-A) filled with clean water and the second in an open tube containing clean water (water-O). In both samples, shown in Fig. 5(c–d), the hydrophilicity was maintained under the whole monitoring protocol. Nevertheless, the values of SCAs for these samples were quite different. During 40 days of observation, the SCAs of the sample stored in an airtight environment ranged from 14° to 23 ± 2°. Conversely, the one kept in an open environment had a contact angle ranging from 15° to 42 ± 2°. The organic matter in the air could accelerate this increase in SCAs in open conditions. Furthermore, Jennissen et al. concluded that the hydrophilicity of material surfaces could be preserved by storing them in pure water [30]. That study, however, did not mention whether it was in an airtight or open environment. As shown in Fig. 5, along with time, the treated Ti sheet kept in an open environment water could remain hydrophilic despite the slow wettability transition.

Table 1
Chemical composition of the treated Ti surface, before and after storing in various conditions during 40 days.

	Ti (at %)	O (at %)	C (at %)	N (at %)	C/Ti	O/Ti	C/O
Before storing	23.64	49.55	25.26	1.55	1.06	2.09	0.51
Nitrogen (N2)	5.05	46.75	36.13	2.39	7.15	9.26	0.77
Water-A	2.8	41.8	33.2	2.86	11.86	14.9	0.79
Water-O	2.55	43.57	39.07	4.41	15.32	17.08	0.90
Air	0.89	26.23	71.05	2.04	79.83	29.47	2.7

Finally, the changes in contact angles of the treated Ti surfaces kept in the air were observed for 40 days. It could be seen in Fig. 5 (e) that after 10 days of storage, the sample presented a hydrophobic character with SCAs reaching 127 ± 3°, which continued to increase over time and became super hydrophobic just after 20 and 40 days of storage with SCAs comprised between 155 ± 3° to 180 ± 3°, respectively. This drastic increase in contact angles and ultimately leading to a super-hydrophobic is attributed to the air contents, including organic matters, which with sequence levels of active organic substances in the gaseous state mainly exhaled by people and animals, and released by manufacturing processes that adsorb upon the solid surface and alter the wettability qualities of the surface, particularly metallic materials. Many studies have proven this paradox for distinct materials, such as Cao et al., which investigated the impact of surface oxide and mono-structures on the wettability change of Cu surfaces. They found that Cu samples stored in the air had the highest SCAs and claimed that the VOCs in the air atmosphere is responsible and accelerating the wettability transition from super hydrophilic to super hydrophobic [31]. In addition, Yan et al. have demonstrated that after 30 days of storing Al sheet in the air, the wetting contact angle reached 153.3° and discussed that the chemisorbed nonpolar airborne hydro-carbons in the air are responsible for the gradual wettability transition [19], which is in congruence with our study.

Fig. 6 summarizes the contact angles changes during the three periods, including 10, 20, and 40 days of samples stored in nitrogen, water, and ambient air. The surface morphology, which does not vary over time, cannot justify such dependence on the contact angle on time. An alteration in surface chemistry appears to be sufficient to reveal such a transition.

3.2.2. Chemical surface investigation

The surface chemical changes were studied to deeply determine the wettability transition of the treated Ti surfaces. To achieve this experiment, the XPS and XRD analyses were performed on both surfaces, including the initial laser structured Ti surfaces, and after being stored in various environments for 10, 20, and 40 days. Also, samples initially laser structured and stored in the air for 7 and 15 days were analyzed to determine their elemental composition using cross sectional TEM/EDS elemental mapping. Afterward, the relationship between C/Ti and O/Ti ratios with the transition from ultra-hydrophilic to super hydrophobic state was discussed to understand the transition mechanism fully.

Table 1 shows the chemical composition of the treated Ti surface before and after storage. After laser processing, it is evident that the treated Ti was ultra-hydrophilic with a carbon content of only 25.26%.

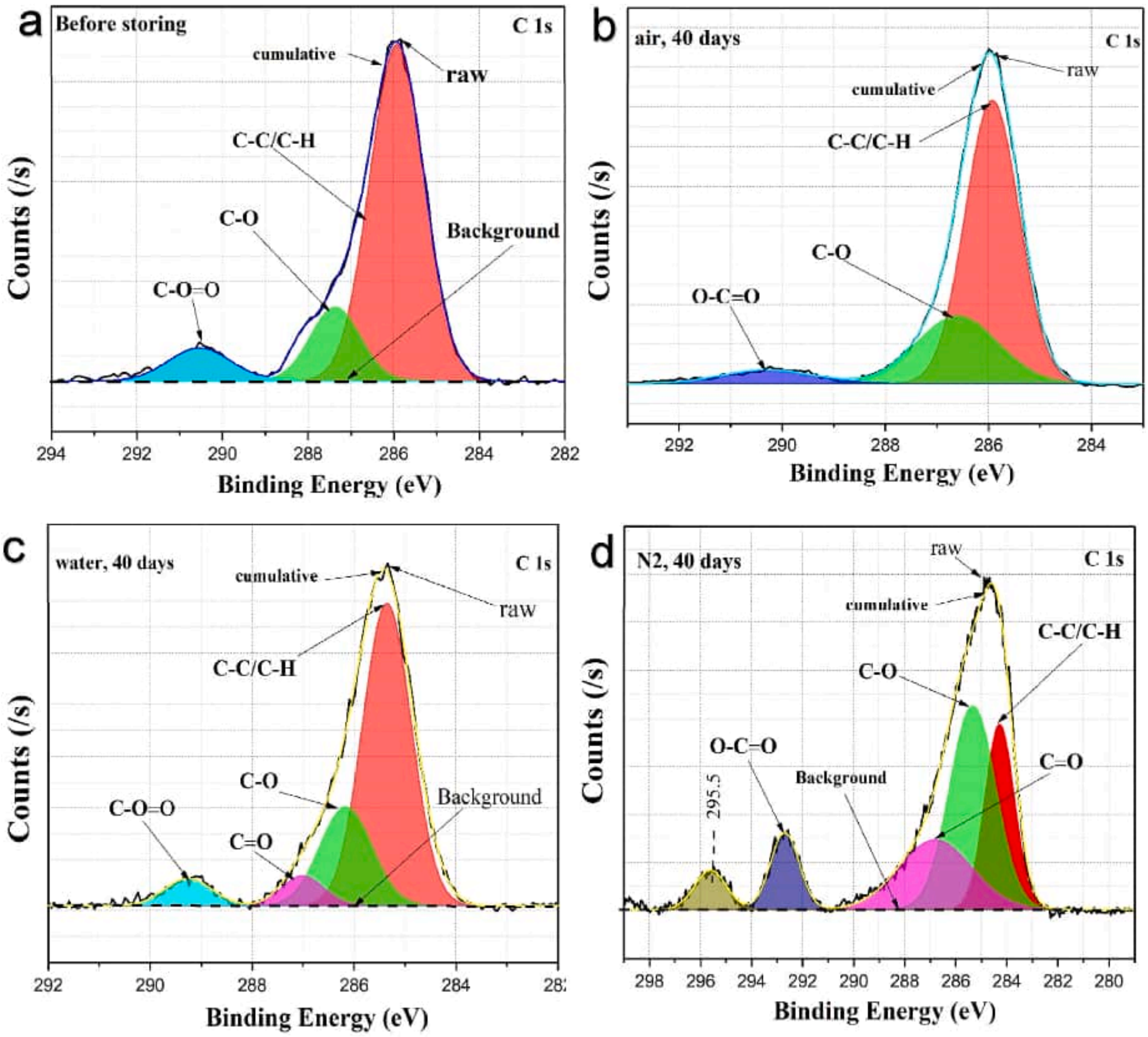

Fig. 7. Deconvolution of the XPS C 1s peaks of the samples kept in different storage setting for 40 days.

Compared to the one exposed to ambient air, the carbon content reached 71% after 40 days of storage, which is three times the one obtained directly after the laser treatment. Alternatively, the carbon contents of the treated Ti sheets stored in nitrogen and water environments increased only slightly over time with 36.03% and 39.07%, respectively. This chemical composition clearly proved a link between the carbon content and the wettability transition, and most cogently with the storage setting. Numerous studies on different materials have demonstrated the role of the ambient air composition, including organic matters, in the wettability change. To prove this, Long et al. stored treated aluminum sheets under two different conditions, one in Oxygen (O_2) and another in an organic-rich environment. Similarly, they found that the one kept in the rich organic condition had the highest carbon content [29].

Because the hydroxylation reaction is rapid, and initial contact angle tests proved that hydrophobic characteristics were gradually acquired once specimens were subjected to ambient atmosphere and because hydroxides have a strong attraction for molecules of water, and since the ambient atmosphere in our laboratory where the samples were stored openly was characterized by a low temperature ranging from 15 to 18 °C with high humidity demonstrating the high content of vapor in the air. Hydrophobicity had not been driven primarily by the hydroxylation phase. Another critical consideration is the possibility of a two-step adsorption process for organic matters in the air. Past research has shown that when a newly generated super-hydrophilic surface is exposed to the air, it is coated by a thin water film that draws organics and surface-active pollutants [32]. The absorbed organics may undermine the water layer after sufficient uptake on a layer of water film, subjecting the solid surface to them. The organic matter subsequently chemisorbs upon that surface, progressively generating a cross-linked monolayer structure that reduces the specific surface area of surface nanostructures and improves eventual physisorption. Even though it is commonly established that absorbing atmospheric volatile organic compounds cause spontaneous wettability change, the adsorption process is unknown. A monolayer molecular is formed by chemical adsorption in most cases; nevertheless, physisorption requires the production of several molecular layers [27]. Furthermore, Once subjected to a lab setting, a freshly produced hydrophilic material reaches the minimum energy state via immediate changes at the surface. Chemisorption of molecules of water or organic pollutants, for example. For many materials, contamination of the hydrophilic surface and, as a result, a loss in surface energy occurs spontaneously [32].

Fig. S1, Supplementary Materials, depicts the change in C/Ti, O/Ti, and C/O ratios as a function of the storage conditions. The treated Ti sheets' original C/Ti and O/Ti ratios were, respectively, 1.06 and 2.09. This initial carbon content on the freshly treated Ti surface could be attributed to the short exposure of the sheet to the ambient atmosphere before storing, or the contamination might have been caused by the XPS

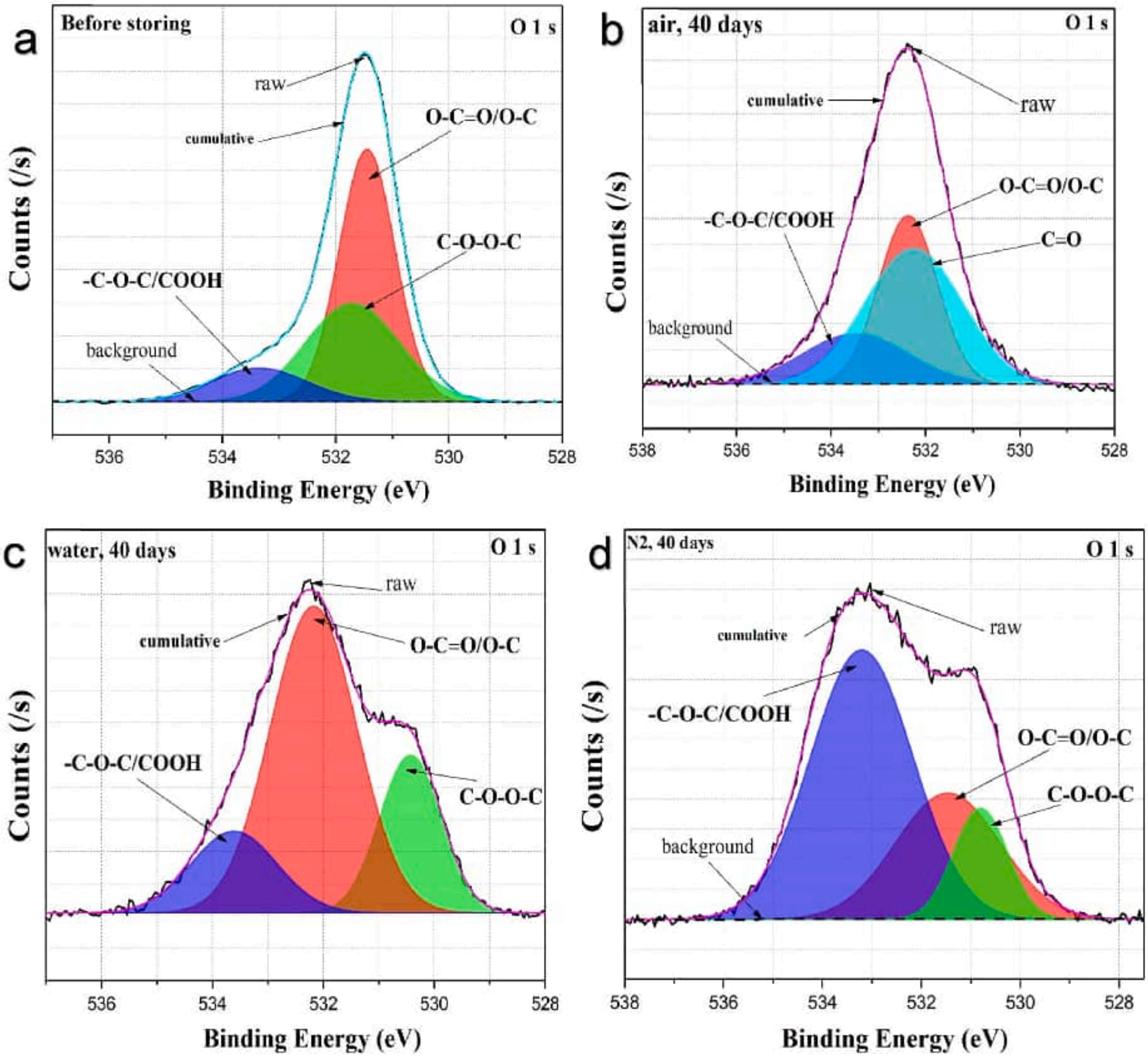

Fig. 8. Deconvolution of the XPS O 1s peaks of the samples kept in different storage setting for 40 days.

or XRD machine during the prior testing. As demonstrated earlier, the carbon content dependency of the storage setting is evident and significant. It could be noticed that after 40 days of storage, the C/Ti ratio reached 79.8, which is drastically higher than those in nitrogen and water, respectively, 7.15 and 11.8. Interestingly, the atomic percentage of the Ti2p of the sample kept in the air for 40 days is 0.89%, almost absent compared to the initial ablated Ti with 23.64%. Nevertheless, this study does not associate that absence with the wettability transition. However, we believe the absence of the Ti2p is due to the long exposure of the treated surface to organic contamination. Besides, the C/Ti ratio in the water conditions differs after 40 days, as shown in Fig. S1. The one kept in water airtight had the lowest value compared to the one in the open environment with 15.32. This difference shows clearly that the organic matter in the air is responsible for increasing carbon content, ultimately leading to the wettability transition. The trends in the C/Ti ratio of different samples appear to correlate well to the changes in respective contact angles. It is worth noting that samples with a significant contact angle always have a high C/Ti value. The previously discussed section confirms this paradox. In addition, the quantity of surface adsorbed organic molecules determines the C/Ti ratio, which is used to assess surface polarity. A greater C/Ti ratio produces a nonpolar surface.

Moreover, the changed surfaces have a high C/Ti ratio, indicating that long-chain alkanes coat them. Similarly, Long et al. schematically demonstrated that on an aluminum surface, the high C/Al is related to a nonpolar surface, which stands for the hydrophobic condition [29]. The initial laser-treated sample has lower carbon content, implying few organic adsorbates on the surface. So, because the alkyl group, the principal element among most organic compounds, is nonpolar, we assume that the presence of organic entities on the treated surface is a more practical approach to diminish the surface polarization. In addition, the polarity of absorbed organic compounds is closely proportional to the relative amount of the C–C(H) bond. Due to multiple organic substances adsorbing onto the surface and reducing surface polarity, the wettability change occurs. The exact figure illustrates the trend of the C/O ratio, which demonstrates that for all hydrophilic conditions, including nitrogen and water, the carbon content is low compared to the oxygen content.

Figs. 7 and 8 display, respectively, the decomposition of C 1s and O 1 s speaks for both storage settings for 40 days to deepen our understanding of the carbon state upon the treated Ti surfaces. Similar to Kawashita et al. [24,28], after subtracting a basic Shirley-type background, all peaks were deconvolved using a confined fitting approach. Within every base level, the FWHM of all peaks was limited toward being identical. Every one of the peaks' forms was likewise set to be Gaussian. The most critical parameters to be observed here are the changes in the treated Ti surface functional groups. As illustrated in Fig. 7, the surface chemical bonds of samples maintained in various environments significantly varied over their previous condition. The

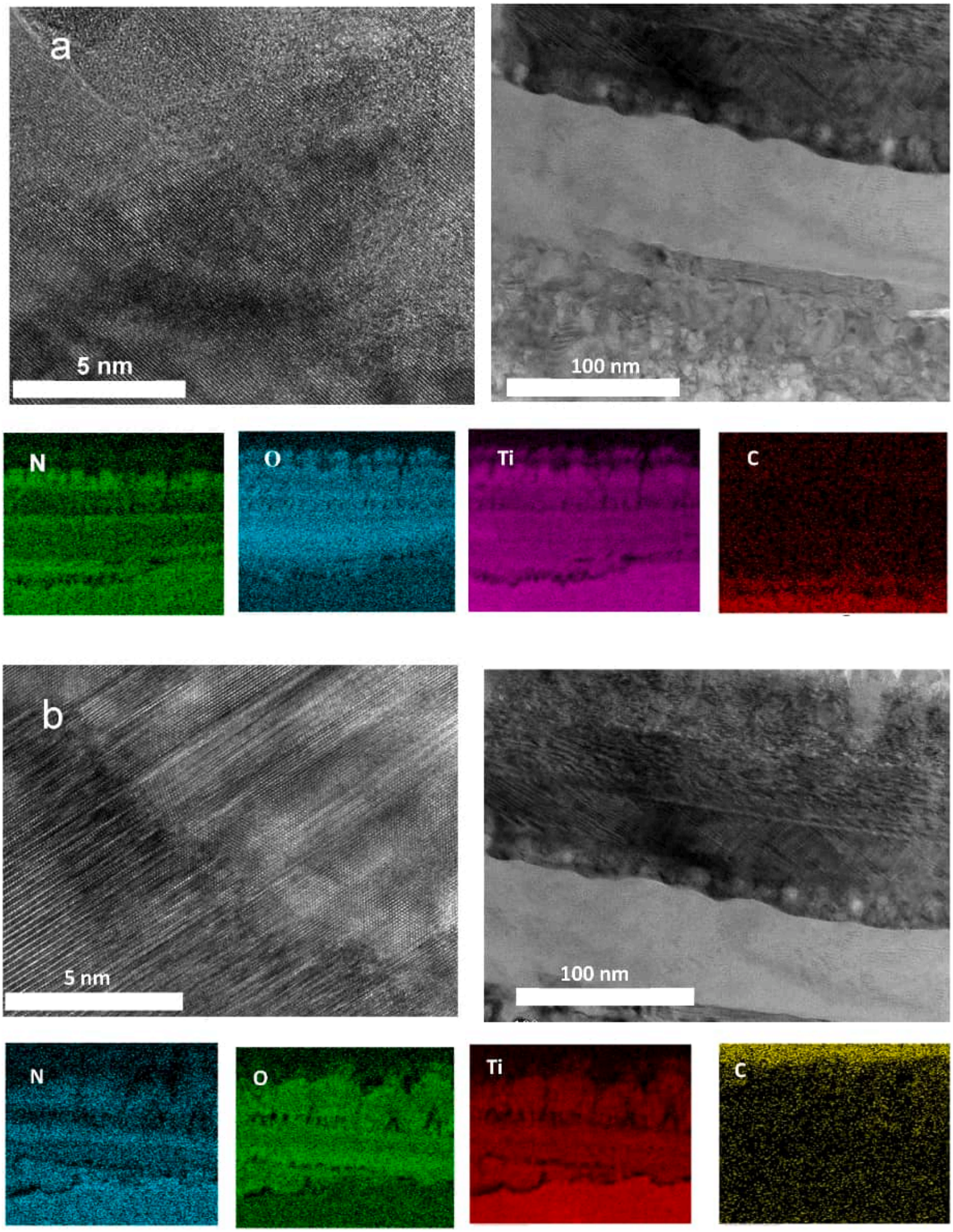

Fig. 9. Cross-sectional TEM and EDX mapping of treated Ti. (a) Cross-sectional TEM image of sample exposed to the air for 7 days. (b) Similar TEM images of a sample exposed to the air for 15 days. Insets show EDX elemental mapping showing the distribution of nitrogen (N), oxygen (O), titanium (Ti), and carbon (C).

Table 2
Chemical composition of the annealed Ti surface.

	Ti (at %)	O (at %)	C (at %)	N (at %)	C/Ti	O/Ti	C/O
Annealed sample	4.89	32.35	57.12	5.64	11.68	6.6	1.77

chemical state of the C 1s spectrum is dominated by C–C/C–H, C–O, C=O, C–O=O, and O–C=O at 285.96, 286.16, 287.05. 289.26 and 290.29 eV, respectively. Regardless of the substrates, greater exposure durations are necessary for the production of O–C=O. Additionally, it appears that a longer exposure time causes the O–C=O and C–C/C–H peaks to increase more quickly [34]. This figure shows that the treated Ti sheet exposed to the ambient air for 40 days of storage had a strong C–C (H) bond located at 285.35 (eV), which is known to be hydrophobic owing to its nonpolar state. The main functional groups observed on the samples stored in water and nitrogen were dominated by carbonyl or carboxylic groups in the hydrophilic region. Fig. 8 displays the oxygen content of the treated Ti surfaces stored in the same environments for 40 days. The relevant chemical states were identified in the O 1s core-level spectra measured from the treated Ti surfaces as a function of water, nitrogen, and air exposure period, including, C=O, O–C=O/O–C, and C–O–C/COOH at 531.8, 532.45, and 533.67, respectively. The peak positions found in the initially treated Ti are located at 531.47 eV (Fig. 8 before storing), which could be related to the lattice oxygen peak. For those kept in the nitrogen, water environments, and air, most of the oxygen peaks were high and located at 531.5 or 532 eV, which are acknowledged to be linked to hydroxy groups or carboxyl.

As illustrated in Fig. S2, Supplementary Materials, the EDS elemental mapping shows the chemical composition of samples stored in the air for 7 and 15 days. It is evident that the oxygen and carbon content has changed. The oxygen content declined from 18.60 wt% of the initially treated Ti surface to 16.60 and 13.31 wt% after 7 and 15 days of storage in the air, respectively. The EDS elemental mapping confirmed the XPS results, demonstrating that the oxygen content decreased when the treated surface turned to a hydrophobic state. The deconvolution of the XPS Ti2p and N 1s peaks of the samples kept in various storage conditions for 40 days is shown in Fig. S3, Supplementary Materials,. In the sample that was stored in water for 40 days, Ti2P was found to be dominant in terms of atomic percentage compared to the other samples kept in air and nitrogen conditions. It is consistent with C/Ti ratios, which showed that the Ti concentration declines with time when maintained in the air. Besides, the Ti 2p spectrum of the treated titanium sample stored in water for 40 days was characterized by a pair of spin-split peaks at 458.8 (Ti 2p3/2) and 464.5 eV (Ti 2p1/2), respectively. The two spin-split peaks are separated by an energy splitting of 5.7 eV (see Fig. S3), indicative of TiO2 phase [34,35]. Furthermore, the N-1s spectrum consisted of peaks located at 401.3, 403.25, and 408.53 eV corresponding to N–O, N–H4 or N–O2, N–O3, respectively [36,37]. The XRD analysis was performed to investigate further the role of the surface modification in the wettability transition of the vaporization surface. Fig. S4, Supplementary Materials, shows the XRD patterns of the samples stored in both storage conditions for the three chosen segment storage periods. Titanium dioxide was found to be the dominant phase on the treated Ti surface in the form of rutile or anatase. Additionally, anatase was mainly detected on samples that were kept in water and nitrogen. Further, rutile was only observed on the sample exposed to air for 40 days. Rutile is known to be hydrophobic, whereas anatase is hydrophilic [29,30]. Also, the air-stored sample exhibited different phases that may have been caused by oxidation, including Ti6O and Ti3O. Interestingly, the laser-textured Ti sample exhibited a wettability change showing that spontaneous surface oxidation occurred on the Ti surfaces during storage in the ambient environment. The TEM cross-sectional and EDS elemental mapping of samples stored in the air for 7 and 15 days, as shown in Fig. 9, corroborated this conclusion.

3.2.3. *Wetting dynamics analysis*

Supplementary video related to this article can be found at https://doi.org/10.1016/j.vacuum.2022.111773

The following are the supplementary data related to this article:

3.3. *Hydrophilicity rehabilitation*

The hydrophilic surface must be free of pollutants such as airborne organics, moisture, and particulate matter to maintain its wetting properties. Metal surfaces have been widely annealed to restore their hydrophilicity even at low temperatures. An annealing procedure was conducted to restore the hydrophilic property of the material after 40 days in ambient air. An annealing temperature of 250 °C and 30% of power frequency for 20 min were sufficient to restore the hydrophilic properties of the treated Ti. Long et al. have used the same parameters previously mentioned to recover the hydrophilicity of aluminum surface [29]. It is believed that the temperature plays a role in removing the contaminants chemisorbed during storage. In addition, Drelich et al. claimed that nonpolar vapors of benzene and hexane chemisorbed on metal surfaces could be removed by simply raising the temperature to 100 °C [32].

Supplementary video related to this article can be found at https://doi.org/10.1016/j.vacuum.2022.111773

4. Conclusion

In this research, the titanium plates were micro-structured by a nanoseconds laser. Immediately following laser processing, the ablated plates were stored in varying storage conditions for three-time segments. After 40 days of storage, it was found that the initially treated surface and super-hydrophilic could maintain their wettability state in water and nitrogen conditions. In comparison, samples stored in the air significantly changed from super hydrophilicity to ultra-hydrophobicity. As a result of contaminants in the air, this change has occurred. Over time, the increasing ratio of C/Ti and the C–C(H) functional group demonstrates this paradox. Results of XRD revealed that only the sample kept in the air for 40 days had the rutile phase, which is known to be hydrophobic. Furthermore, contact angles gradually increased, reaching 180° over time. After 40 days of storage, wetting dynamics demonstrated that water could not spread over the surface of the sample. In addition, thermal annealing strongly supported the theory that the wettability transition is caused by surface contamination. Based on this study, wettability transition occurs as a result of organic compounds being absorbed upon the treated titanium surface over time. Additionally, nitrogen and water maintain super-hydrophilic conditions, a critical element in surface vaporization.

The following main conclusions have been drawn:

1) XPS and EDS demonstrate that the surface chemistry changes drastically over time when exposed to air, compared to those stored in water and nitrogen, leading to a shift in wettability due to pollutants.
2) The C/Ti, O/Ti, and C/O ratios are important indicators for predicting the wettability transition.
3) Wetting dynamic analysis of treated Ti surfaces exposed to ambient air shows that increased surface hydrophobicity decreases water flow capability or water transport efficiency over hierarchical surfaces.

CRediT authorship contribution statement

Alseny Bah: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Zhenhui Chen:** Software, Investigation, Data curation. **Phan Dinh Tuan:** Writing – review & editing. **Daolun Feng:** Writing – review

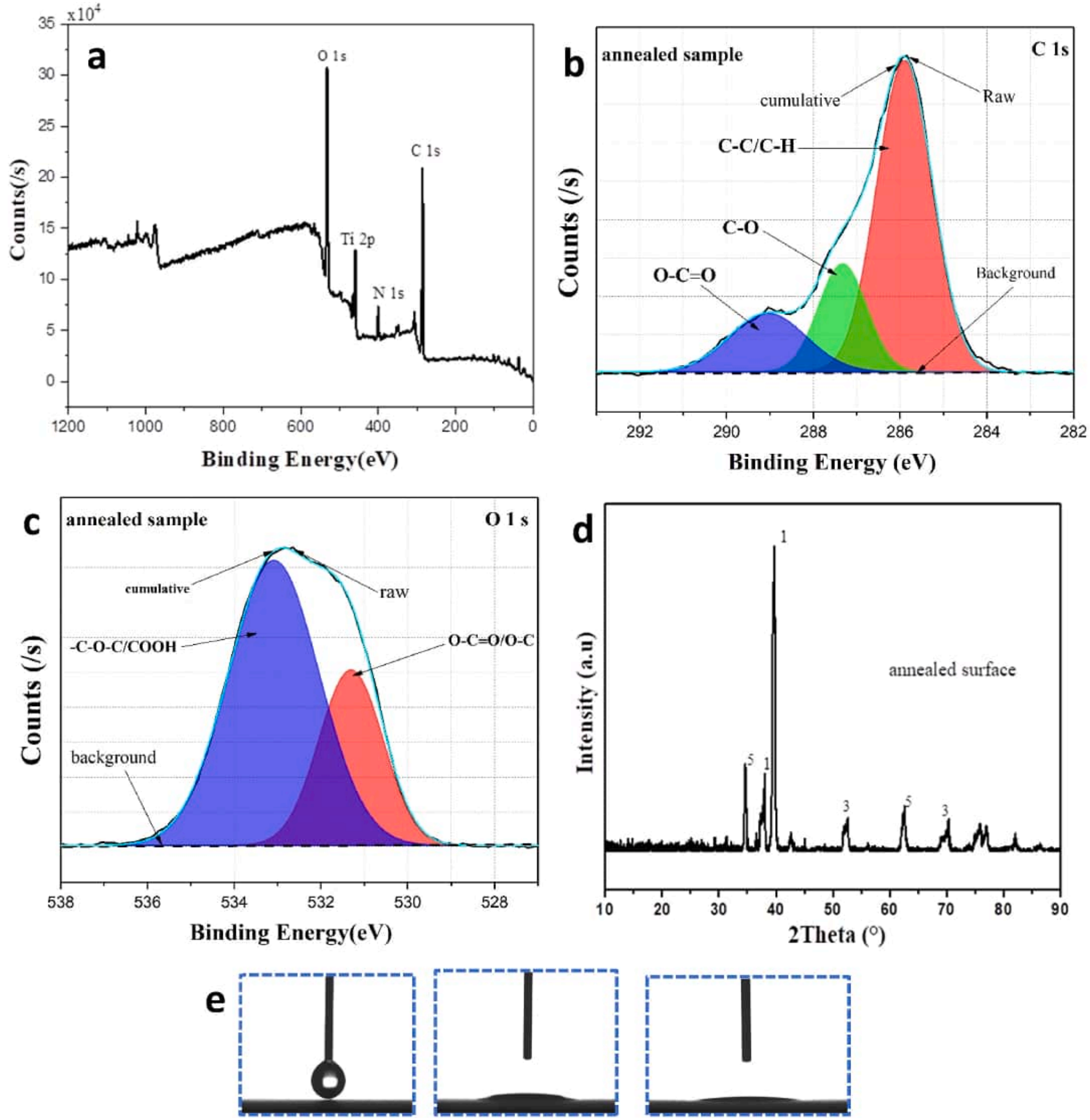

Fig. 10. (a) XPS spectra, (b) Deconvolution of the XPS C 1s peaks, (c) Deconvolution of the XPS O 1s peaks, (d) XRD phase composition of the annealed sample, and (e) contact angles of the annealed sample.

& editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

[1] J. Long, M. Zhong, H. Zhang, P. Fan, Superhydrophilicity to superhydrophobicity transition of picosecond laser microstructured aluminum in ambient air, J. Colloid Interface Sci. 441 (2015) 1–9, https://doi.org/10.1016/j.jcis.2014.11.015.
[2] C.G. Jothi Prakash, R. Prasanth, Approaches to design a surface with tunable wettability: a review on surface properties, J. Mater. Sci. 56 (1) (2021) 108–135, https://doi.org/10.1007/s10853-020-05116-1.
[3] Z. Liu, H. Wang, E. Wang, X. Zhang, R. Yuan, Y. Zhu, Superhydrophobic poly (vinylidene fluoride) membranes with controllable structure and tunable wettability prepared by one-step electrospinning, Polymer 82 (Jan. 2016) 105–113, https://doi.org/10.1016/j.polymer.2015.11.045.
[4] C. Kallweit, M. Bremer, D. Smazna, T. Karrock, R. Adelung, M. Gerken, Photoresponsive hierarchical ZnO-PDMS surfaces with azobenzene-polydopamine coated nanoparticles for reversible wettability tuning, Vacuum 146 (2017) 386–395, https://doi.org/10.1016/j.vacuum.2017.03.023.
[5] D. Scharnweber, F. Schlottig, S. Oswald, K. Becker, H. Worch, How is wettability of titanium surfaces influenced by their preparation and storage conditions? J. Mater. Sci. Mater. Med. 21 (2) (2010) 525–532, https://doi.org/10.1007/s10856-009-3908-9.
[6] A.O. Ijaola, et al., Wettability transition for laser textured surfaces: a comprehensive review, Surface. Interfac. 21 (September) (2020), 100802, https://doi.org/10.1016/j.surfin.2020.100802.
[7] R.A. Fleming, M. Zou, Silica nanoparticle-based films on titanium substrates with long-term superhydrophilic and superhydrophobic stability, Appl. Surf. Sci. 280 (2013) 820–827, https://doi.org/10.1016/j.apsusc.2013.05.068.
[8] B. jia Li, H. Li, L. jing Huang, N. fei Ren, X. Kong, Femtosecond pulsed laser textured titanium surfaces with stable superhydrophilicity and superhydrophobicity, Appl. Surf. Sci. 389 (2016) 585–593, https://doi.org/10.1016/j.apsusc.2016.07.137.
[9] Z. Lei, et al., MnO2-x nanowires on carbon cloth based superamphiphilic and under-oil superhydrophilic filtration membrane for oil/water separation with robust anti-oil fouling performance, Compos. B Eng. 199 (2020), https://doi.org/10.1016/j.compositesb.2020.108286.
[10] Q. Wang, H. Wang, Z. Zhu, N. Xiang, Z. Wang, G. Sun, Switchable wettability control of titanium via facile nanosecond laser-based surface texturing, Surface. Interfac. 24 (2021), 101122, https://doi.org/10.1016/j.surfin.2021.101122.
[11] J. Wang, M. Wu, X. Hou, Study on the influencing factors of spontaneous wettability transition behaviour on metallic-based surfaces, Vacuum 200 (2022), 111048, https://doi.org/10.1016/j.vacuum.2022.111048. November 2021.
[12] S.H. Mohamed, et al., Optical, water splitting and wettability of titanium nitride/titanium oxynitride bilayer films for hydrogen generation and solar cells applications, Mater. Sci. Semicond. Process. 105 (2020), 104704, https://doi.org/10.1016/j.mssp.2019.104704.
[13] J. Long, P. Fan, M. Zhong, H. Zhang, Y. Xie, C. Lin, Superhydrophobic and colorful copper surfaces fabricated by picosecond laser induced periodic nanostructures, Appl. Surf. Sci. 311 (2014) 461–467, https://doi.org/10.1016/j.apsusc.2014.05.090.
[15] Z. Liu, H. Wang, E. Wang, X. Zhang, R. Yuan, Y. Zhu, Superhydrophobic poly (vinylidene fluoride) membranes with controllable structure and tunable wettability prepared by one-step electrospinning, Polymer 82 (2016) 105–113, https://doi.org/10.1016/j.polymer.2015.11.045.
[16] G. Rosaz, A. Bartkowska, C.P.A. Carlos, T. Richard, M. Taborelli, Niobium thin film thickness profile tailoring on complex shape substrates using unbalanced biased High Power Impulse Magnetron Sputtering, Surf. Coating. Technol. 436 (2022), 128306, https://doi.org/10.1016/j.surfcoat.2022.128306. February.
[17] J. Drelich, A. Marmur, Physics and applications of superhydrophobic and superhydrophilic surfaces and coatings, Surf. Innov. 2 (4) (2014) 211–227, https://doi.org/10.1680/si.13.00017.
[19] Z. Yang, X. Liu, Y. Tian, Insights into the wettability transition of nanosecond laser ablated surface under ambient air exposure, J. Colloid Interface Sci. 533 (2019) 268–277, https://doi.org/10.1016/j.jcis.2018.08.082.
[21] A.M. Kietzig, S.G. Hatzikiriakos, P. Englezos, Patterned superhydrophobic metallic surfaces, Langmuir 25 (8) (2009) 4821–4827, https://doi.org/10.1021/la8037582.
[22] G. Greczynski, L. Hultman, Reliable determination of chemical state in x-ray photoelectron spectroscopy based on sample-work-function referencing to adventitious carbon: resolving the myth of apparent constant binding energy of the C 1s peak, Appl. Surf. Sci. 451 (2018) 99–103, https://doi.org/10.1016/j.apsusc.2018.04.226.
[23] S. Razi, K. Madanipour, M. Mollabashi, Improving the hydrophilicity of metallic surfaces by nanosecond pulsed laser surface modification, J. Laser Appl. 27 (4) (2015), 042006, https://doi.org/10.2351/1.4928290.
[24] E. György, I.N. Mihailescu, P. Serra, A. Pérez del Pino, J.L. Morenza, Crown-like structure development on titanium exposed to multipulse Nd:YAG laser irradiation, Appl. Phys. Mater. Sci. Process 74 (6) (2002) 755–759, https://doi.org/10.1007/s003390201307.
[25] B. jia Li, H. Li, L. jing Huang, N. fei Ren, X. Kong, Femtosecond pulsed laser textured titanium surfaces with stable superhydrophilicity and superhydrophobicity, Appl. Surf. Sci. 389 (2016) 585–593, https://doi.org/10.1016/j.apsusc.2016.07.137.
[26] A. Bah, Q. Qian, Z. Chen, P. Dinh, D. Feng, Concentration of landfill leachate by solar driven surface vaporization performed on nanosecond-laser-treated titanium surface, J. Environ. Chem. Eng. 10 (6) (2022), 108909, https://doi.org/10.1016/j.jece.2022.108909.
[27] Z. Cao, et al., Effects of surface oxides and nanostructures on the spontaneous wettability transition of laser-textured copper surfaces, Appl. Surf. Sci. 560 (January) (2021), 150021, https://doi.org/10.1016/j.apsusc.2021.150021.
[28] J.T. Cardoso, et al., Influence of ambient conditions on the evolution of wettability properties of an IR-, ns-laser textured aluminium alloy, RSC Adv. 7 (63) (2017) 39617–39627, https://doi.org/10.1039/c7ra07421b.
[29] J. Long, M. Zhong, H. Zhang, P. Fan, Superhydrophilicity to superhydrophobicity transition of picosecond laser microstructured aluminum in ambient air, J. Colloid Interface Sci. 441 (2015) 1–9, https://doi.org/10.1016/j.jcis.2014.11.015.
[30] H.P. Jennissen, D. Lattner, Preparation and properties of ultra-hydrophilic surfaces on titanium and steel, Mater. Werkst. 40 (1–2) (2009) 108–116, https://doi.org/10.1002/mawe.200800416.
[31] Z. Cao, et al., Effects of surface oxides and nanostructures on the spontaneous wettability transition of laser-textured copper surfaces, Appl. Surf. Sci. 560 (April) (Sep. 2021), 150021, https://doi.org/10.1016/j.apsusc.2021.150021.
[32] J. Drelich, E. Chibowski, D.D. Meng, K. Terpilowski, Hydrophilic and superhydrophilic surfaces and materials, Soft Matter 7 (21) (2011) 9804–9828, https://doi.org/10.1039/c1sm05849e. Nov.
[34] G. Greczynski, L. Hultman, X-ray photoelectron spectroscopy: towards reliable binding energy referencing, Prog. Mater. Sci. 107 (2020), 100591, https://doi.org/10.1016/j.pmatsci.2019.100591. June 2018.
[35] S.S. Cetin, B. Cristina-mihaela, R.R. Nigmatullin, B. Dumitru, S. Ozcelik, Chemical bonding structure of TiO 2 thin fi lms grown on n-type Si, Thin Solid Films 519 (2011) 5712–5719, https://doi.org/10.1016/j.tsf.2011.04.021.
[36] V. Natu, M. Benchakar, C. Canaff, A. Habrioux, S. Célérier, M.W. Barsoum, A critical analysis of the X-ray photoelectron spectra of Ti3C2Tz MXenes, Matter 4 (4) (2021) 1224–1251, https://doi.org/10.1016/j.matt.2021.01.015.
[37] B.V. Crist, XPS in industry – problems with binding energies in journals and binding energy databases, J. Electron. Spectrosc. Relat. Phenom. (2018), https://doi.org/10.1016/j.elspec.2018.02.005.
[41] M. Pegueroles, F.J. Gil, J.A. Planell, C. Aparicio, The influence of blasting and sterilization on static and time-related wettability and surface-energy properties of titanium surfaces, Surf. Coating. Technol. 202 (15) (2008) 3470–3479, https://doi.org/10.1016/j.surfcoat.2007.12.021.