Measuring weathering and nanoparticle coating impact on surface roughness of natural stones

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Measuring weathering and nanoparticle coating impact on surface roughness of natural stones

The surface texture of a stone represents a sensitive parameter in evaluating its conservation state. In monuments and sculptures, in fact, external agents continuously alter the appearance of stones, determining peculiar weathering patterns and modifying properties as retention of water and particles, interaction with light, color and finishing. The application of protective coatings also determines changes in surface appearance of a stone, usually evaluated and monitored by color change tests. Surface metrology methods offer the possibility to quantify these changes, evaluating the impact of external agents (natural, i.e. weathering, and artificially, i.e. protective coatings) on natural stones. In this research, we demonstrate the potential of surface areal measurements in describing the evolution of weathering processes and the effects of protective treatments on porous stone materials. The obtained results suggest that the extent of the modifications is related to the scale of observation (small vs large-scale undulations, i.e. roughness and waviness, respectively), with an overall increase of surface roughness as the weathering proceeds. Unexpectedly, coatings based on nanoparticle dispersions increase the topographic height parameters, due to the absence of a homogeneous film.

Keywords: roughness; weathering; **TiO_2**coating; natural stones.

Introduction

Surface texture is a physical feature of materials usually described by roughness parameters, extracted from linear profiles and/or areal maps by applying surface metrology methods. It represents a relevant feature in studying weathering process of stone materials (Turkington and Paradise 2005; Moses et al. 2014; Comite et al. 2017); in fact, being the direct interface with atmosphere, the roughness of a stone surface affects the interaction with weathering agents, namely water solutions, organic and inorganic particles, organism (biodeteriogens) (Korkanc and Savran 2015; Vazquez et al. 2016), thus involving its durability.

Generally speaking, rougher is a material, higher is the surface specific area exposed to weathering agents (Vazquez-Calvo et al. 2012).Therefore, an increase of surface roughness implies a possible high susceptibility of stone materials to be attacked by microorganisms, inorganic and organic compounds (Graziani, Quagliarini and D'Orazio2016):a rough surface retains a lot of running water and absorbs sun's radiation more than a smooth one, with direct growth of humidity and temperature of stone surface. Roughness has a direct impact also on the color of stone materials (Benavente et al. 2003); due to aesthetical requirements, such a characteristic is of a great relevance in built environment. Different surface finishing or chromatic alterations of a stone surface can determine undesirable roughness changes.

Modifications of surface texture can be determined also by cleaning actions or by protective coatings (Della Volpe et al. 2000;Vazquez-Calvo et al. 2012). In this sense, monitoring the roughness changes due to the conservative treatments can greatly support restoration management actions.

Actually, studying cultural stones, roughness description is useful to provide numerical parameters able to measure and monitor changes of surface texture, and therefore the impact of weathering and micro-erosion processes. Mainly borrowed by geomorphology (Pope, Meierding and Paradise2002), several methods are used to estimate the stone surface recession caused by weathering.

Classical methods finalized to study the surface weathering are usually based on direct observation, thanks to which a description of extension and depth of different weathering patterns can be obtained. Among them, the most common in building stone researches is represented by the Fitzner method (Fitzner, Heinriehs and Kownatzki 1997; Fitzner, Heinrichs and La Bouchardiere 2002). However, it remains a strictly subjective analysis method, not allowing an objective quantification of weathering degree. In this framework, the recent development of non-destructive digital image techniques provides new tools for measuring changes in stone surfaces in response to weathering, assuring a high resolution and the possibility to monitor the measured parameters over the time.

In view of their suitability, imaging methods have been largely applied in different research fields, especially in geomorphology (Robinson and Williams 1994; Robinson and Williams 1999; Swantesson 1994; McCarroll and Nesje 1996) and in building stone conservation science (Robinson and Williams 1996). Being not destructive, digital imaging can be also used for in situ measuring of surface texture in monuments (Sharp et al.1982; Trudgill et al. 2001; Vázquez et al. 2011), as well as in laboratory set-ups in order to monitor surface change and decay of samples subjected to accelerated weathering tests (López-Arce et al. 2010; Birginieand Rivas 2005).

The acquisition of 2D and/or 3D digital images of exposed surfaces in natural stones allows highlighting their quite complex structure. For example, Fitzner (1993) used image analysis for the quantification of the rock porosity by direct observation and measurement of shape, size and sections of pores by optical and electron microscope images; Zezza (1991) applied digital image processing in the diagnosis of the of monument alteration; Aires-Barros et al. (1994)showed the surface alteration of stone by application of profilometry lines; Kapsalas et al. (2006) used digital imaging and surface parameters as decay indicators on black crusts; Vázquez et al. (2011) used digital image processing of efflorescence in weathered stone as a tool for mapping and evaluation of stone decay; Stephenson and Finlayson (2009) employed micro-erosion meters in measurements of building stone weathering rates; López-Arce et al. (2010) quantified weathering by examining the surface roughness of building stones, such as Spanish granites; Jaynes and Cooke (1987)attributed changes in surface roughness of building stones to the action of salts as well as to air pollution.

In spite of the abundant literature, some problems still remain, as the establishment of proper links between small scale experimental studies and larger scale built environment evolution (Moses, Robinson and Barlow (2014). Moreover, even by applying digital imaging methods, providing more and more information on rough surfaces and weathering rates, the possibility to scale the observed processes remains out of a comprehensive description. In this perspective, a useful parameter could be represented by the fractal dimension(Vazquez-Calvo et al. 2012). A fractal describes in fact a rough geometric shape that can be subdivided into parts, each of which, at least approximately, is a reduced size copy of the whole. Thus, fractal dimension could be used as **descriptor** of a process observed at micrometric scale, allowing to reasonably **predict some physical properties and possibly scale up them** to building environment **(Barbera et al. 2014; Bernal and López 2000; Bernal and López 2001; Pia et al. 2014; Pia 2016; Pia et al 2016)** . The application of such an approach enables the description of processes over an increasing range of spatial and temporal scales, supporting the validation of multi-scalar models to describe weathering surface patterns.

In this study, we attempt to support the studies on weathering and treatments impacts on surface texture of building stones by acquiring digital images on artificially degraded and coated stone samples. Images have been processed in order to obtain metric parameters and fractal dimension as a function of surface degradation patterns and protective coatings.

The study aims also to explore the potential of digital multi-focus microscopy in the framework of weathering monitoring and restoration action on building materials.

Materials and methods

Materials

The samples tested were cubes (4x4x4 cm^3) of a yellowish coarse grained Sabucina stone, a calcarenite largely employed as building stone and suffering a lot of weathering due to salt crystallization (Barone et al. 2015); **samples, six in total, were obtained from fresh quarry stone and subjected to artificial aging and protective treatment.**

To test the impact of protective coating on surface texture, TiO_2 nanosols have been synthesized and applied on stone surfaces. TiO_2 nanoparticles have been obtained by sol-gel techniques at two different pH (1.3-10.6) (Bergamonti et al. 2015**a**; **2017**). The acid sol (0.1M), named TiAcN was obtained by mixing a solution of titanium isopropoxide (97%, Sigma-Aldrich,) and acetic acid (99-100%,Riedel–de Haen) in molar ratio 1/1. The sol was stirred for 30 min. Then, distilled water and nitric acid (Carlo Erba, 65%), as peptizer, were added and the sol was refluxed at 100 °C for 3 hours. The resulting sol is lightly opalescent and free from precipitate. The basic sol, called TiMaA, was synthesized by mixing a solution of titanium isopropoxide with malonicacid (99%, Sigma-Aldrich,) in molar ratio 1/1. After stirring for 30 min, distilled water and triethylamine (>98%, Fluka), as peptizer, were added and the sol was refluxed at 100 °C for 3 hours. The resulting sol was pale yellow and free from precipitate. **Nanoparticles TiO_2 dimension was about 4–6 nm in TiAcN and 6–8 nm in TiMaA (Bergamonti et al. 2015b).**

Artificial aging and treatment of the surfaces

Accelerated aging tests have been carried out according to UNI EN 12370 rules (UNI EN, 2001) with the aim to obtain weathered samples representative of different degrees of damage due to salt crystallization. In detail, two cycles, consisting in immersion in decahydrate sodium sulphate solution at 14% v/v for 2 hours at 20 ± 5 °C and drying at 105 ± 5 °C for 16 hours, have been repeated fifteen times. Representative samples have been moved from the analyzed set **(at four, eight, ten and fifteen cycles)** and preserved for surface metrology analysis.

The two TiO_2 sols have been applied with a bristle brush**, three times,** directly on the stone samples. **After each application the sample were kept in ventilated oven at 80 °C for 1h.** Before the application of the coatings, the specimens were washed with deionized water in order to remove dust deposits, dried 24 h at 60 °C and then kept 3 h in a dry atmosphere and weighed. The procedure was repeated until constant weight (±0.1 %) was attained. After each treatment, the samples were kept again at 60 °C for 24 h and then dried in a desiccator and weighed, repeating the cycle up to weight stabilization. The stone samples were then stored in a desiccator at (25 ± 1) °C.**The amount of titania per unit surface (mg/cm^2) was calculated by the difference of the dry weight before and after the application of the coating: 0.69 ± 0.01 mg/cm^2 for TiAcN, 0.76 ± 0.01 mg/cm^2 for TiMaA.**

Roughness measurements and data processing

The surfaces of fresh reference samples, **before aging and coating, four** artificially degraded surfaces (at different aging steps, i.e. four, eight, twelve and fifteen salts crystallization cycles) and **two** surfaces coated with basic and acid TiO_2 nanosols (TiMaA and TiAcN, respectively) have been analyzed in order to visualize and quantify the possible modification of surface texture due to artificially weathering and application of coatings. **A total of six samples have been analysed before and after aging and coating processes.** A digital imaging technique has been selected for the analysis**; in detail, an Hirox KH-7700 digital microscope with MXG-10C body, OL-140II lens and AD-10S Directional Lighting Adapter (Arrighi et al. 2016; Oxilia et al. 2017; Ronchitelli et al. 2015) has been used. For each sample,** images have been acquired on three spots of about 3 x 1.5 mm^2**; moreover, multiple tests have been preliminary performed on reference fresh samples before aging and coating to verify that the possible surface variability into the same sample remains less than differences among reference, weathered and coated surfaces.** The magnification was 100x**; at that magnification, the nominal resolution along Z-axis is about 0.5**

micron. In this study, focal planes have been acquired in a Z-range of 2 mm; the AutoMultiFocus tool enabled the creation of a 3D image by the composition of sixty-four planes taken at different focus levels**, with vertical steps of about 25 micron**.

It is important to stress that the instrument is portable, and digital maps can be acquired directly on monuments, enabling the in situ evaluation and monitoring of a process over the time. Images have been processed to obtain roughness and waviness maps as well surface texture areal parameters (Blateyron 2013) according to ISO 25178. Moreover, fractal dimension of studied surfaces has been determined, in order to verify the potential use of fractals in describing how the surface features change due to weathering and coatings.

Waviness (i.e. undulations that are several times longer than deep) and roughness (i.e. undulations that are just a few times longer than deep) have been defined by a cut-off wavelength λc (Volk 2005). Usually, the length of the measured profile is six or seven times λc (Volk 2005); then, the unfiltered primary surface map has been filtered by using robust Gaussian filters having a radius corresponding to the lower structure size, represented by the wavelength λc. In this way, roughness and waviness images can be obtained, representing components having shorter-length and longer-length structures than the cut-off wavelength λc, respectively (Figure 1). In this study λc has been defined as about the sixth part of the length of the measured profiles. 3D topographical information has been finally processed and displayed using Hirox 3D visualization tools.

Color changes evaluation

To evaluate the changes of the stone surface appearance due to the TiO_2 based coatings and relate them with roughness features, colorimetric analysis has been performed by a

Techkon Spectrodens colorimeter. Ten spots of about 1 mm^2 have been examined and averaged on each stone sample, using one sample for each case (before and after the treatment). According to UNI EN 15886, the color differences (ΔE) due to TiO_2 applications with respect to the uncoated stone have been evaluated by:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad \textbf{(1)}$$

where ΔL^* is the change in lightness, $\Delta a^*$and Δb^* the change in hue (a^* is the red (>0)/green (<0) coordinate and b^* the yellow (>0)/blue (<0) coordinate, in the CIELAB notation).

Results and Discussion

Impact of weathering

In Figure 2 the 3D plots of studied surfaces are shown, as examples of changes in texture due to the artificial weathering process, while in Tables 1-2 the obtained parameters from the surface analyses are reported.

Unfiltered surface texture changes, described in term of Sq (root mean square height) and Sa (arithmetic mean height) variations, result in a global increase of roughness caused by the weathering process. However, a careful analysis of the two components (waviness and roughness) indicates that the trend is controlled by small-scale undulations, while large scale undulations initially increase then slightly decrease.

It is interesting to note that the deviation in waviness areal parameters trend corresponds to weathering mechanism change in the studied stone (Barone et al. 2016). The material selected for the test is indeed mainly interested by granular disintegration due to salts, which in a first stage of the process crystallize into pore throats, while in a second stage enlarge throat and pore spaces, increasing the porosity. In this perspective, the observed mechanism might act also close to the surface, removing small particles, increasing the exposed surface and simultaneously slowing down waviness component. Actually, the surface becomes more and more heterogeneous while weathering proceeds, with Str (texture aspect ratio) roughness values moving toward 1; on the contrary, the surface appears more homogeneous in term of waviness undulation, as testified by Str parameters decreasing toward zero. In accordance with the hypothesis about the removal of particles and the increasing heterogeneity of the surface, Vv roughness parameters (describing volume voids) seem to slightly increase, while in terms of waviness undulation a definite trend cannot be inferred.

The final finishing aspect, and thus the effective surface exposed, can be summarized by considering Ssk (skewness) parameters, directly related to the degree of bias and porosity and describing as well the topographically height distribution. Generally speaking, negative Ssk parameters account for a surface characterized by small and deep valleys with the majority of surface above the mean profile; on the contrary, positive parameters depict a surface with spiky peaks and large valleys under the mean surface profile. In this case, unfiltered surfaces always show negative parameters, with a trend toward positive values with increasing weathering. This can be explained by roughness and waviness Ssk values: the progressive removal of particles works by enlarging valleys and sharpening peaks, thus determining a final positive Ssk value in term of roughness and a consequent negative Ssk value for waviness.

Looking at the changes in surface areal parameters determined by the weathering process (Figure 3), it is interesting to note that the largest variations are registered in height parameters (Sp, highest point; Sv, lowest point; St, total height; Ssk, skewness; Sku, kurtosis) at small scale undulation (roughness areal values). This evidence implies that processes acting at small scale control the main variations in term of spikiness as well as of degree of bias.

In spite of the above-discussed changes in surface texture, fractal dimensions Ds seems to fluctuate over 2.5-2.6 values, without a specific trend.

Finally, it has to be stressed that the discussed trends are considered in the light of the global variation of the studied surfaces (from reference to final artificial weathering conditions): possible deviations of trends at the different steps could be related to slight heterogeneities of the analyzed areas of interests.

Impact of coating

Color differences on uncoated and coated surfaces have been evaluated, and the results are reported in Table 3.

According to literature on conservation of natural stones, **color change is acceptable if not visually detectable by human eye, for ΔE values** less than **3** (**Benavente et al. 2003; Delgado-Rodrigues & Grossi, 2007;** García and Malaga 2012**).**

However, changes in lightness and in color coordinates have to be noticed, especially for the acid preparation.

Surface maps acquired on coated samples (Figure 4) and processed according to the previous established method allow **discussing and adding insights on the morphology of TiO_2 NPs sols dispersed on porous stone surfaces**. **Actually, the literature in the field highlighted a not homogenous behaviour of such systems, pinpointing that the fulfilment of a continuous film with regular thickness on a surface it is dependent on both morphological properties of the substrate and NPs concentration into the formulation, in function of employed dispersing medium. In fact, on one side, homogeneity of the film depends on roughness and outermost porosity of the substrate, so that rougher is the surface more cracks are developed during the evaporation of the solvent (Lopez et al. 2013; Quagliarini et al. 2018). On the other**

side, the deposition of small amount of TiO_2 seems to produce less cracked layers if NPs are dispersed in water (Quagliarini et al. 2018), while the coverage of the surface is better guarantee for high NPs concentration dispersed in TEOS (Crupi et al.2018). In many cases, TiO_2 NPs coatings produce discontinuous films characterized by cracks and NPs aggregates (Goffredo et al. 2017; Quagliarini et al. 2012), with slight variation in coverage ability as function of dispersing medium, concentration of NPs and porosity of the substrate (Calia et al. 2017), sometimes turning in homogenous and continuous layers (Munafò et al. 2014).

In the matter in question, the presence of **TiO_2 NPs** coatings determines an increase in roughness parameters, both considering small and large-scale undulation; reflecting color changes, the largest parameters values have been observed for the acid preparation. Trying to quantify surface texture variations (Tables 4-5), the overall topography of coated surfaces appears more spiky and heterogeneous, as confirmed by Sku and Str changes (Figure 5). Actually, as testified by SEM images (Figure6), TiO_2 sols, and especially TiAcN, do not homogenously cover the surface with a thin protective layer, looking like irregularly distributed nanoparticle aggregates; this evidence might justify the measured surface topography values.

Finally, also in this case, fractal dimension does not exhibit relevant trends, confirming values between 2.5 and 2.6.

It is well known that the topography influences the final color of a surface; by correlating surface areal parameters and colorimetric data, it is possible to note that the greater ΔE variation are exhibited by surfaces coated with TiAcN TiO_2 sol, for which the highest Sq parameters have been measured (Figure 7).

According to Ssk and L* values changes, the surface become less bright with chromatic variations particularly for yellow tones.

Conclusions

This study is developed in the framework of the currently researches on the footsteps of the process involved in stones decay. Understanding the response of cultural stones to external agents (natural, i.e. weathering, and artificial, i.e. protective coatings) is fundamental in appropriately protecting monuments and adequately modelling and scale weathering processes. Apart from specific changes measured on the studied stone, and the interesting variations in calculated parameters, the present study evidenced several challenges.

First, the potential of a portable multi-focus microscope in monitoring the surface features of natural stones was explored and assessed; the instrument allows obtaining affordable data, detecting the possible relevant changes, in spite of heterogeneities of the surface, grain-size of particles on surfaces, and exposed porosity. The advantages in using such an equipment, able to give back areal maps on which calculate areal surface parameters, in not trivial: these studies are usually performed by collecting multiple profiles, so that the final areal description is the result of a mathematical interpolation.

Second, the inspection and the accurate evaluation of areal maps give indication in selecting relevant parameters in surface analysis of cultural stones and pinpointing the scale at which processes occur. In such coarse-grained materials, in which weathering acts by removing grains, one expects a general smoothing of the surface: the obtained results highlight that this is true looking at large scale undulation, while at a small scale the established trends are opposite. This implies that the effective surface exposed to external agents becomes more and more extended as the weathering proceeds.

Similarly, the application of a coating could smooth the surfaces, by creating a homogeneous layer on the treated stone; however, **as observed in the case of TiO_2 NPs**

with average dimension between 4 nm and 8 nm, the deposition of aggregates not homogeneously distributed can determine an increase of topographic height parameters. Third, the possible use of fractal dimension in describing the evolution of weathering process, i.e. from less to more heterogeneous surfaces characterized by higher exposed material, has been discarded. Calculated Ds ranges in fact between 2.5 and 2.6 regardless weathering degree and/or coating process. This might indicate that, in spite of small-scale variations (in term of roughness) and changes in the degree of bias of the surface, the overall self-similarity of surface texture is maintained. On the contrary, parameters as Ssk and Sku better account and describe the surface changes and features of natural stones subjected to weathering or coatings.

Of course, this study cannot be considered exhaustive and enough to allow a scaling-up of the observed processes; possibly, the comparison of the analyzed data with real cases might support modelling attempts, accurately taking into account the possible deviations of laboratory accelerated aging and treatments with respect to the in situ conditions. However, this investigation supplies a useful back-story to better understand relations between small and large-scale variations, relevant parameters to account for in the evaluation of surface changes, entity of exposed surface after weathering and/or coating, and last but not least the resolution required to appropriately evaluate changes at the observed scale. The final image processing obtained in this study is actually the result of a trial-error process, during which many scans have been acquired to finally assess the spatial resolution to resolve textural details, representative dimension of regions of interest, magnification and illumination to use. In this perspective, once standardized, the acquisition and image processing routine might be extended to different stone substrates, focusing the attention on the more efficient set-ups and parameters to describe surface changes and correlate them to the studied processes, both reproduced in laboratory or observed in situ.

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Table 1. Areal field parameters obtained on unfiltered studied surfaces (unweathered and artificially weathered).*Sq: Root mean square height of the surface; Ssk: Skewness of height distribution; Sku: Kurtosis of height distribution; Sp: Maximum height of peaks; Sv: Maximum height of valleys; Sz: Maximum height of the surface; Sa: Arithmetical mean height of the surface; Str: Texture aspect ratio of the surface; Sxp: Peak extreme height; Vm: Material volume at a given height; Vv: Void volume at a given height; Ds: fractal dimension.St. Dev.: standard deviation.*

Table 2. Areal field parameters obtained on roughness and waviness maps by applying a robust Gaussian filter on unweathered and artificially weathered surface acquisitions. *Sq: Root mean square height of the surface; Ssk: Skewness of height distribution; Sku: Kurtosis of height distribution; Sp: Maximum height of peaks; Sv: Maximum height of valleys; Sz: Maximum height of the surface; Sa: Arithmetical mean height of the surface; Str: Texture aspect ratio of the surface; Sxp: Peak extreme height; Vm: Material volume at a given height; Vv: Void volume at a given height; Ds: fractal dimension. St. Dev.: standard deviation.*

Table 3. Color difference ΔE values for each treatment.

Table 4. Areal field parameters obtained on unfiltered studied surfaces(uncoated and coated). *Sq: Root mean square height of the surface; Ssk: Skewness of height distribution; Sku: Kurtosis of height distribution; Sp: Maximum height of peaks; Sv: Maximum height of valleys; Sz: Maximum height of the surface; Sa: Arithmetical mean height of the surface; Str: Texture aspect ratio of the surface; Sxp: Peak extreme height;*

Vm: Material volume at a given height; Vv: Void volume at a given height; Ds: fractal dimension. St. Dev.: standard deviation.

Table 5. Areal field parameters obtained on roughness and waviness maps by applying a robust Gaussian filter on uncoated and coated surface acquisitions. *Sq: Root mean square height of the surface; Ssk: Skewness of height distribution; Sku: Kurtosis of height distribution; Sp: Maximum height of peaks; Sv: Maximum height of valleys; Sz: Maximum height of the surface; Sa: Arithmetical mean height of the surface; Str: Texture aspect ratio of the surface; Sxp: Peak extreme height; Vm: Material volume at a given height; Vv: Void volume at a given height; Ds: fractal dimension. St. Dev.: standard deviation.*

Figure 1. Example of workflow applied to filter the scanned surfaces.

Figure 2. 3D plot of studied surfaces. (a) Reference unweathered surface (b) surface after 4 cycles (c) surface after 15 cycles of artificial weathering.

Figure 3. Changes in surface areal parameters determined by weathering process. (a) Unfiltered, (b) waviness, and (c) roughness areal surface parameters.

Figure 4. 3D plot of studied surfaces. (a) Reference uncoated surface (b) surface coated with TiAcN and (c) TiMaA.

Figure 5. Changes in surface areal parameters determined by coating. Areal surface parameters changes referred to (a) unfiltered, (b) waviness, and (c) roughness maps.

Figure 6. SEM images (backscattering) on surfaces coated with (a) TiAcN and (b) TiMaA; details from TiAcN treated surface showing (c) coated and (d) not homogenous coated areas.

Figure 7. Relationship between surface texture and color changes. (a) Sq vs a* and b*, (b) Sq vs L*and (c) Sq vs ΔE.

Table

Table 1

Unfiltered surface	**Reference**	**St. Dev.**	**4 cycles**	**St. Dev.**	**8 cycles**	**St. Dev.**	**10 cycles**	**St. Dev.**	**15 cycles**	**St. Dev.**
Sq (mm)	0.13	0.00	0.15	0.03	0.14	0.05	0.16	0.05	0.16	0.02
Ssk (no unit)	-0.39	0.03	-0.52	0.20	-0.35	0.15	-0.38	0.08	-0.17	0.19
Sku (no unit)	3.16	0.25	3.55	0.58	3.21	0.67	3.56	0.29	4.25	0.24
Sp (mm)	0.55	0.04	0.52	0.09	0.53	0.18	0.63	0.15	0.91	0.08
Sv (mm)	0.58	0.07	0.74	0.17	0.59	0.24	0.82	0.24	0.73	0.08
Sz (mm)	1.13	0.11	1.26	0.26	1.11	0.39	1.45	0.39	1.64	0.15
Sa (mm)	0.10	0.00	0.12	0.02	0.11	0.04	0.13	0.04	0.12	0.01
Sxp (mm, p = 50%, q = 97.5%)	0.25	0.07	0.33	0.06	0.30	0.12	0.35	0.11	0.35	0.07
Str (no unit, s = 0.2)	0.51	0.12	0.48	0.05	0.63	0.08	0.63	0.08	0.77	0.09
Vm (mm^3/mm^2, p = 10%)	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Vv (mm^3/mm^2, p = 10%)	0.15	0.03	0.19	0.04	0.19	0.07	0.21	0.06	0.19	0.02
Ds	2.53	0.01	2.60	0.01	2.54	0.00	2.44	0.01	2.55	0.01

Table 2

Roughness component	Reference	St. Dev.	4 cycles	St. Dev.	8 cycles	St. Dev.	10 cycles	St. Dev.	15 cycles	St. Dev.
Sq (mm)	0.11	0.00	0.12	0.02	0.11	0.04	0.13	0.04	0.13	0.02
Ssk (no unit)	-0.41	0.03	-0.85	0.21	-0.33	0.17	-0.55	0.11	0.15	0.29
Sku (no unit)	3.82	0.06	4.70	0.87	3.86	0.39	4.72	0.65	5.21	0.64
Sp (mm)	0.58	0.03	0.60	0.06	0.59	0.17	0.73	0.16	1.00	0.15
Sv (mm)	0.50	0.02	0.68	0.18	0.52	0.17	0.76	0.17	0.65	0.11
Sz (mm)	1.08	0.05	1.27	0.24	1.11	0.34	1.49	0.32	1.66	0.24
Sa (mm)	0.08	0.00	0.09	0.02	0.08	0.03	0.10	0.03	0.10	0.01
Sxp (mm, p = 50%, q = 97.5%)	0.20	0.05	0.29	0.07	0.23	0.08	0.28	0.09	0.26	0.06
Str (no unit, s = 0.2)	0.69	0.03	0.63	0.27	0.68	0.04	0.74	0.08	0.76	0.08
Vm (mm³/mm², p = 10%)	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00
Vv (mm³/mm², p = 10%)	0.12	0.03	0.14	0.03	0.13	0.05	0.16	0.06	0.16	0.02
Ds	2.49	0.04	2.61	0.01	2.55	0.01	2.63	0.04	2.56	0.01
Waviness component	**Reference**	**St. Dev.**	**4 cycles**	**St. Dev.**	**8 cycles**	**St. Dev.**	**10 cycles**	**St. Dev.**	**15 cycles**	**St. Dev.**
Sq (µm)	50.55	7.12	67.96	7.63	86.84	22.90	75.15	17.41	62.33	5.86
Ssk (no unit)	-0.24	0.22	0.32	0.44	0.07	0.56	0.32	0.31	-0.30	0.50
Sku (no unit)	2.81	0.71	2.69	0.62	3.37	0.65	2.59	1.07	3.35	0.82
Sp (µm)	108.53	36.92	182.57	53.21	231.67	12.46	201.17	94.90	189.15	33.94
Sv (µm)	143.97	52.89	139.30	12.87	240.53	74.96	180.08	55.17	201.82	66.81
Sz (µm)	252.50	89.71	321.87	61.48	472.20	62.49	381.25	149.75	390.96	96.43
Sa (µm)	40.42	4.88	55.19	3.69	66.67	19.42	61.45	12.39	49.22	4.16
Sxp (µm, p = 50%, q = 97.5%)	108.61	23.03	110.67	6.20	181.24	80.52	131.06	37.40	138.14	36.70
Str (no unit, s = 0.2)	0.59	0.10	0.54	0.19	0.61	0.04	0.52	0.13	0.35	0.16
Vm (mm³/mm², p = 10%)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vv (mm³/mm², p = 10%)	0.07	0.01	0.10	0.01	0.10	0.04	0.10	0.02	0.08	0.01
Ds	2.08	0.01	2.07	0.01	2.08	0.01	2.27	0.01	2.07	0.01

Table 3

Samples	**L***	**a***	**b***	**ΔE**
untreated	65,59	9,03	26,95	3,43
TiAcN	64,48	8,57	23,75	
untreated	65,20	9,05	26,04	1,50
TiMaA	63,94	9,04	25,22	

Table 4

Unfiltered surface	Reference	St. Dev.	TiAcN	St. Dev.	TiMaA	St. Dev.
Sq (mm)	0.13	0.00	0.17	0.06	0.20	0.07
Ssk (no unit)	-0.39	0.03	-0.37	0.31	-0.11	0.08
Sku (no unit)	3.16	0.25	3.29	0.92	3.33	0.69
Sp (mm)	0.55	0.04	0.64	0.27	0.83	0.25
Sv (mm)	0.58	0.07	0.71	0.18	0.86	0.07
Sz (mm)	1.13	0.11	1.34	0.45	1.69	0.30
Sa (mm)	0.10	0.00	0.14	0.05	0.16	0.06
Sxp (mm, p = 50%, q = 97.5%)	0.25	0.07	0.36	0.11	0.39	0.12
Str (no unit, s = 0.2)	0.51	0.12	0.58	0.18	0.76	0.06
Vm (mm^3/mm^2, p = 10%)	0.00	0.00	0.00	0.00	0.01	0.00
Vv (mm^3/mm^2, p = 10%)	0.15	0.03	0.23	0.09	0.26	0.09
Ds	2.53	0.01	2.57	0.01	2.60	0.01

Table 5

Roughness component	**Reference**	**St. Dev.**	**TiAcN**	**St. Dev.**	**TiMaA**	**St. Dev.**
Sq (mm)	0.11	0.00	0.13	0.05	0.15	0.04
Ssk (no unit)	-0.41	0.03	-0.39	0.61	0.12	0.20
Sku (no unit)	3.82	0.06	4.69	1.77	4.76	0.74
Sp (mm)	0.58	0.03	0.81	0.34	1.01	0.31
Sv (mm)	0.50	0.02	0.63	0.14	0.79	0.08
Sz (mm)	1.08	0.05	1.44	0.48	1.80	0.37
Sa (mm)	0.08	0.00	0.10	0.04	0.12	0.03
Sxp (mm, p = 50%, q = 97.5%)	0.20	0.05	0.28	0.07	0.30	0.08
Str (no unit, s = 0.2)	0.69	0.03	0.76	0.18	0.85	0.03
Vm (mm³/mm², p = 10%)	0.00	0.00	0.01	0.00	0.01	0.00
Vv (mm³/mm², p = 10%)	0.12	0.03	0.17	0.06	0.19	0.06
Ds	2.49	0.04	2.58	0.01	2.60	0.01
Waviness component	**Reference**	**St. Dev.**	**TiAcN**	**St. Dev.**	**TiMaA**	**St. Dev.**
Sq (µm)	50.55	7.12	110.65	6.14	117.39	22.32
Ssk (no unit)	-0.24	0.22	0.17	0.16	0.21	0.29
Sku (no unit)	2.81	0.71	2.66	0.55	3.03	1.13
Sp (µm)	108.53	36.92	262.92	31.89	269.39	82.23
Sv (µm)	143.97	52.89	256.70	10.38	218.60	71.30
Sz (µm)	252.50	89.71	519.62	42.27	487.98	153.50
Sa (µm)	40.42	4.88	88.23	10.51	77.09	37.42
Sxp (µm, p = 50%, q = 97.5%)	108.61	23.03	156.80	70.90	175.74	66.38
Str (no unit, s = 0.2)	0.59	0.10	0.45	0.06	0.54	0.27
Vm (mm³/mm², p = 10%)	0.00	0.00	0.00	0.00	0.00	0.00
Vv (mm³/mm², p = 10%)	0.07	0.01	0.13	0.06	0.13	0.06
Ds	2.08	0.01	2.06	0.01	2.08	0.01

Figure 1

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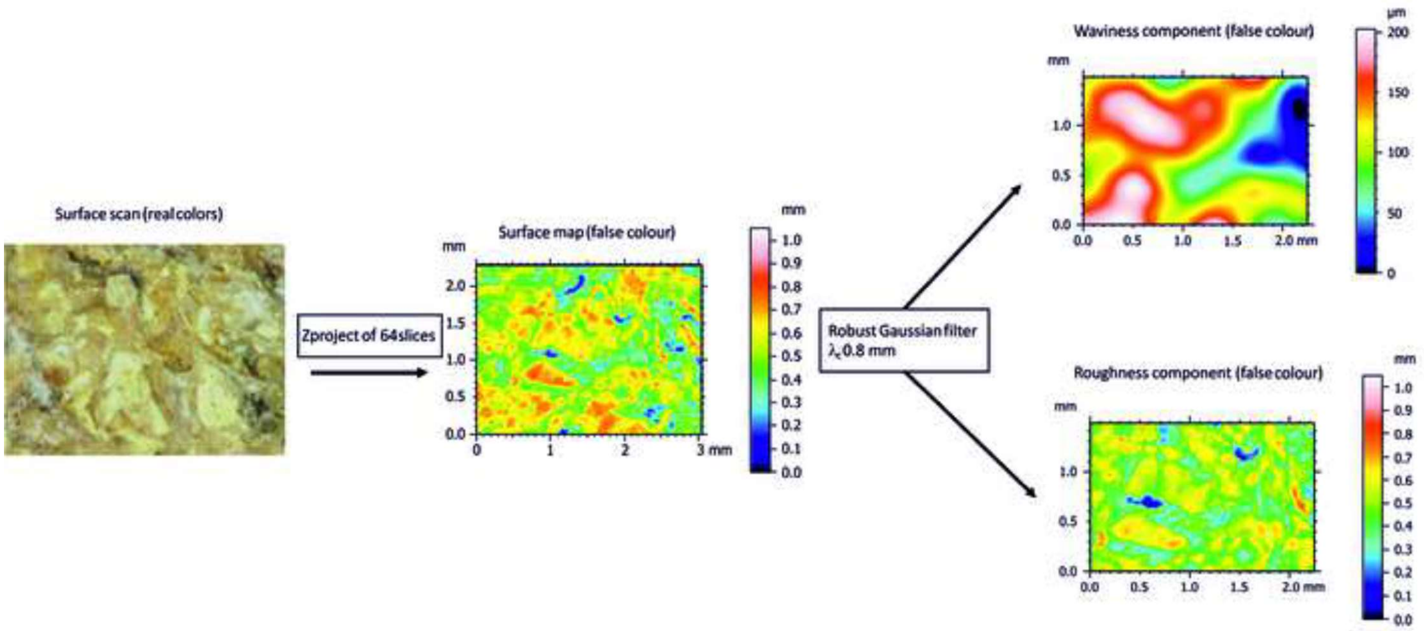

Figure 2

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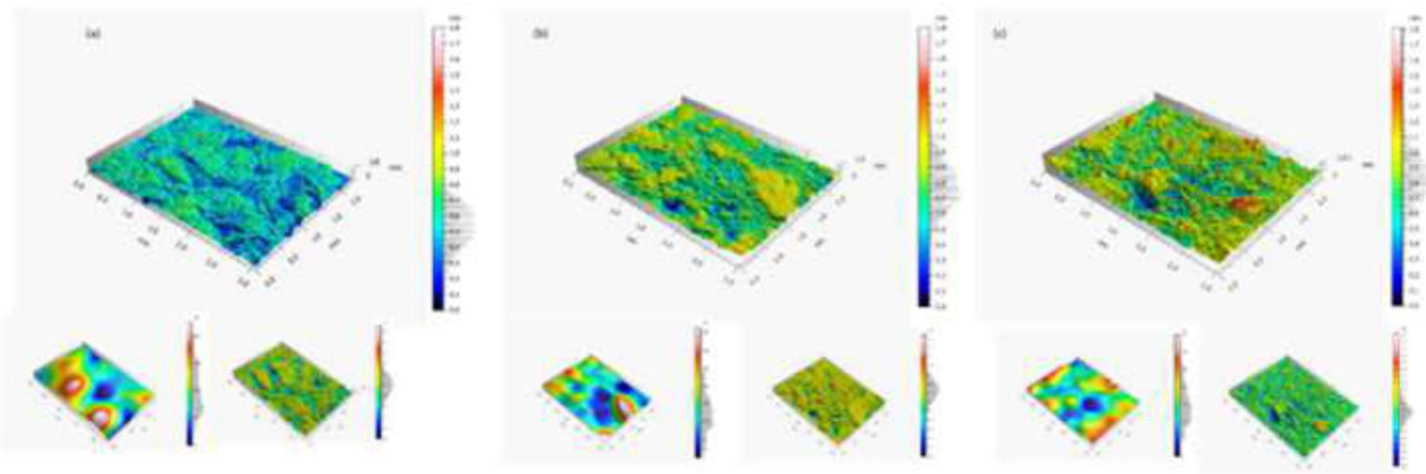

Figure 3

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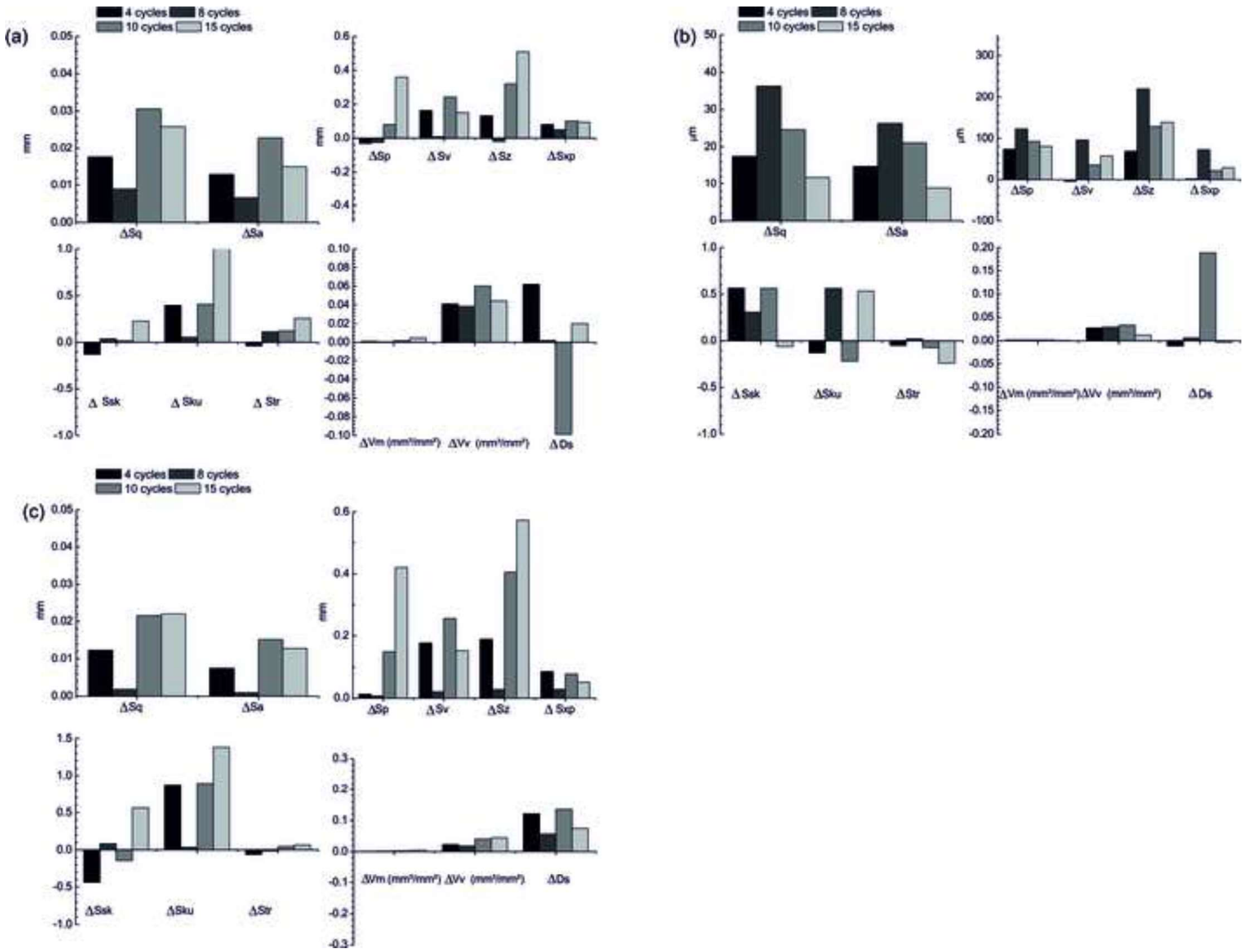

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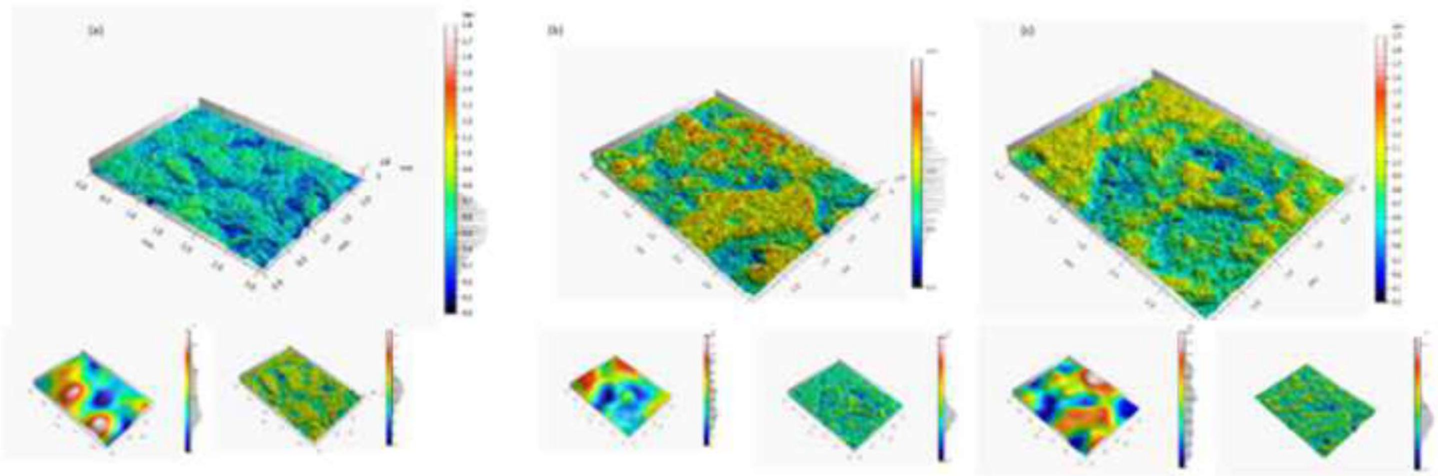

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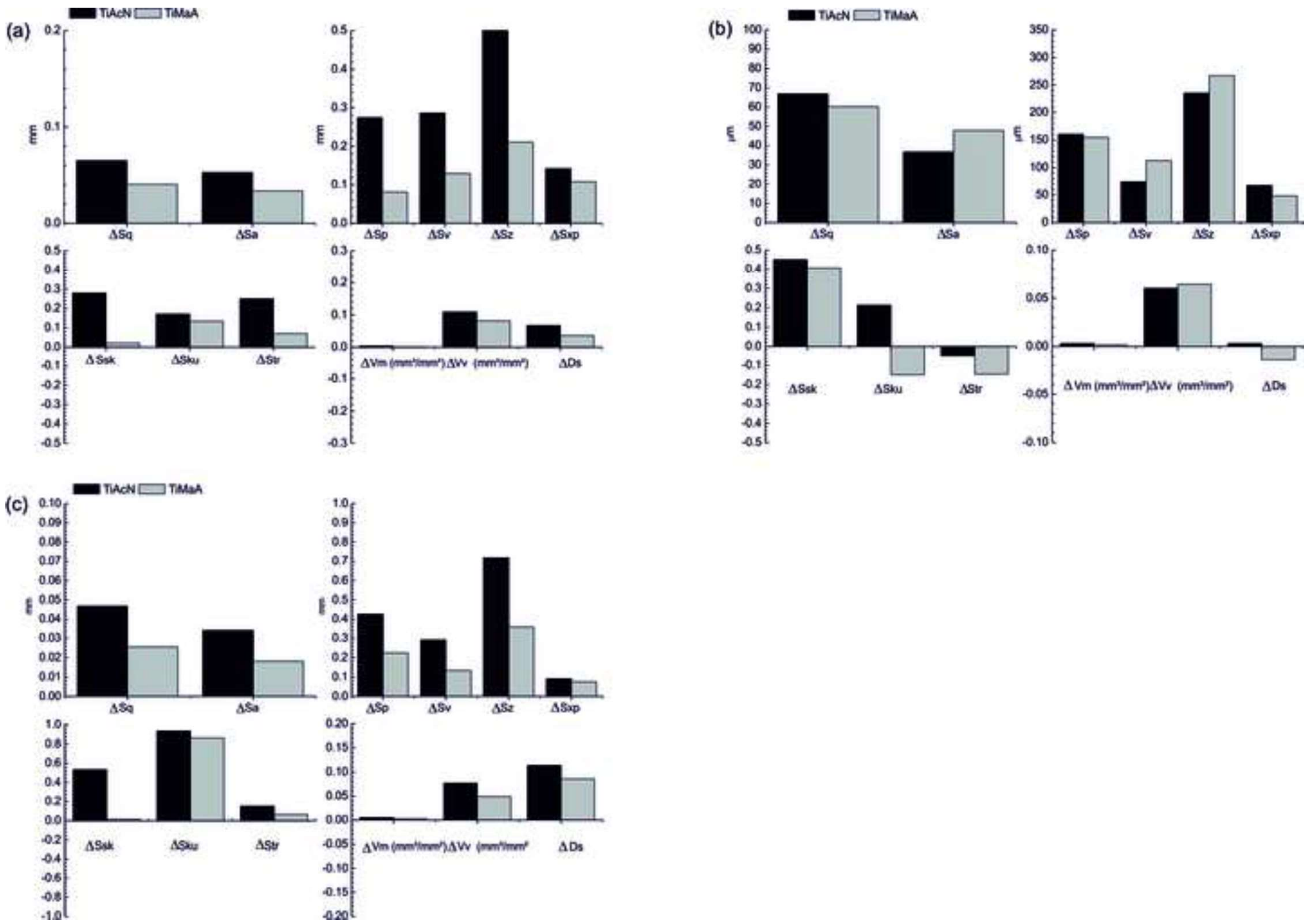

TiAcN
TiMaA
(a)
(b)
(c)
mm
μm
ΔSq
ΔSa
ΔSp
ΔSv
ΔSz
ΔSxp
ΔSsk
ΔSku
ΔStr
ΔVm (mm³/mm²)
ΔVv (mm³/mm²)
ΔDs

Figure 6

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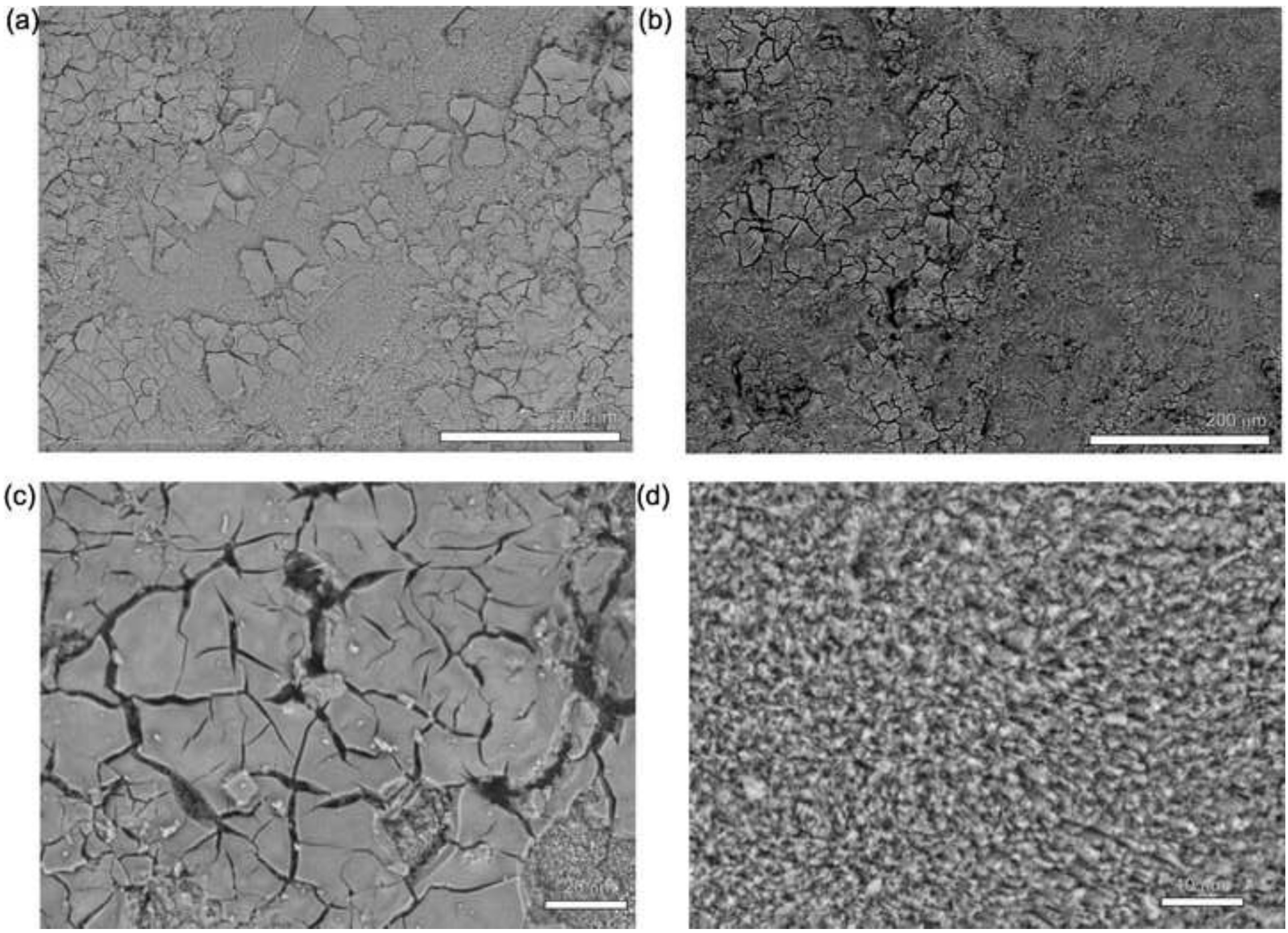

Figure 7

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