Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Increasing the hydrophobicity degree of stonework by means of laser surface texturing: An application on Zimbabwe black granites

A. Chantada*, J. Penide, A. Riveiro, J. del Val, F. Quintero, M. Meixus, R. Soto, F. Lusquiños, J. Pou

Applied Physics Department, University of Vigo, EEI, Lagoas-Marcosende, Vigo, E- 36310, Spain

ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form 8 November 2016
Accepted 24 December 2016
Available online xxx

Keywords:
Laser texturing
Natural stone
Wettability
Roughness
Design of experiments

ABSTRACT

Tailoring the wetting characteristics of materials has gained much interest in applications related to surface cleaning in both industry and home.

Zimbabwe black granite is a middle-to-fine-grained natural stone commonly used as countertops in kitchens and bathrooms. In this study, the laser texturing of Zimbabwe black granite surfaces is investigated with the aim to enhance its hydrophobic character, thus reducing the attachment of contaminants on the surface. Two laser sources (λ = 1064 and 532 nm) were used for this purpose. The treatment is based on the irradiation of the stone by a laser focused on the surface of the targeting sample. The influence of different laser processing parameters on the surface characteristics of granite (wettability, roughness, and chemistry) was statistically assessed. Most suitable laser processing parameters required to obtain the highest hydrophobicity degree were identified. It has been possible to identify the 532 nm laser wavelength as the most effective one to increase the hydrophobic degree of Zimbabwe black granite surface. The phenomenon governing wettability changes was found to be the surface roughness patterns, given the unaltered chemical surface composition after laser processing.

1. Introduction

Natural stone is one of the most used materials in construction industry because of its capacity to withstand extreme weather conditions and its aesthetic appeal. The high production volume of natural stones is driven by its suitability for a wide range of applications related to construction industry. In 2014, indeed, the world trade of the natural stone sector recorded a 1.8% increase compared to the year before, reaching a value of 22.8 billion euros [1].

Granite represents the largest part of the production of natural stones used as building materials [1]. ASTM C119-95b defines as black granite those igneous rocks of dark appearance presenting crystalline texture. Unlike common granite, black granite barely contains quartz and alkaline feldspars. Instead, it is principally composed of calcic plagioclases, along with dark minerals, such as pyroxenes and biotite, among others. Within the industrial naming of black granites, Zimbabwe black granite, which is the subject of study, belongs to diorite variety. Its use as building material is not only restricted for outdoor constructions but also for countertops in the domestic environment, such as kitchens and bathrooms. In this case, this material is commonly exposed to the presence of microbial contamination [2]. Surface contamination in such places is not a minor problem, since it may result in disease transmission if the contaminants proportion exceeds a certain value [3].

Contamination is a surface phenomenon closely related to the wettability of surfaces, due to the fact that this is a parameter controlling the microbial adhesion. Wettability is a surface engineering phenomenon which is acquiring great relevance in biological and industrial processes because it is present in several fields, such as cell adhesion or surface cleaning [4], among others. In the recent years, a great volume of researches have been published confirming the use of hydrophobic surfaces to remove surface contamination due to the self-cleaning phenomenon [5–7]. This phenomenon, observed in hydrophobic surfaces, is based on the rolling of the liquid droplets which trap contaminant particles along the surface leading to the removal of the undesirable contamination [7]. To the present day, this phenomenon has been explored mainly in polymers [8,9], and metals [10–12], but not in such a heterogeneous material as natural stone.

Laser surface texturing is a well-known method to modify the wettability of a great range of materials [11–15]. Furthermore, it

* Corresponding author at: University of Vigo, Applied Physics Department, E.E. Industrial, Lagoas-Marcosende, 9, 36310, Vigo, Spain.
E-mail address: achantada@uvigo.es (A. Chantada).

http://dx.doi.org/10.1016/j.apsusc.2016.12.196

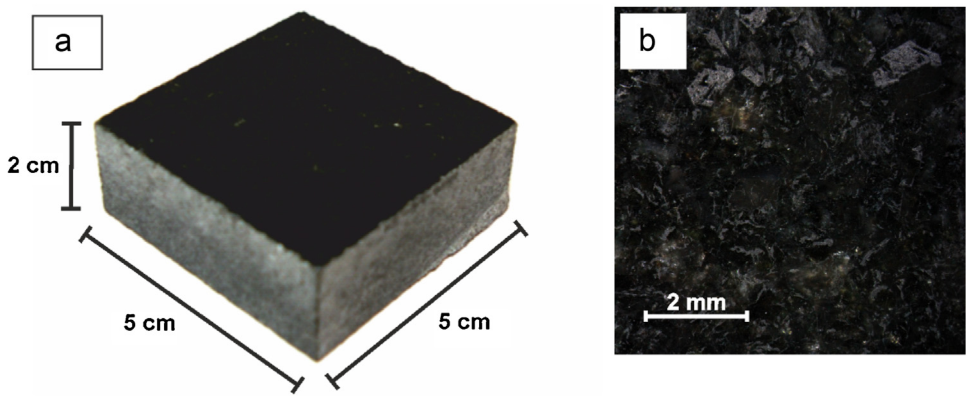

Fig. 1. Images of a fragment of Zimbabwe black granite: (a) overall view of the polished slab and (b) detailed view of its original and untreated surface.

offers advantages over other chemical techniques (e.g. silanization of post-textured surfaces) [16], such as its higher processing rate, due to the fact that there is no need to use prior or subsequent coatings [17,18]. Also, the laser treated resulting surface is free of contaminants without changing the bulk properties of the material. This technique is applicable to nearly all types of materials [10,19–21], as it is based on the radiation absorption by the matter and its subsequent thermalization, but, to the best of our knowledge, its use for tailoring wetting features of natural stones has not been reported in previous works.

In the present paper, laser surface texturing of Zimbabwe black granite is analysed. The effect of the laser processing parameters on the wettability and surface roughness was performed for two different wavelengths ($\lambda = 1064$ and 532 nm). The aim of this work is to increase the hydrophobic degree of the Zimbabwe black granite surface to make possible the control of contaminants and the presence of bacteria on its surface. The influence of the laser processing parameters (laser irradiance, scanning speed, pulse frequency, and spot overlapping) on the treated surfaces of granite was analysed by means of statistically planed experiments.

2. Materials and methods

2.1. Material

The base material used in this work was the Zimbabwe black granite. This middle-to-fine grained natural stone belongs to the family of igneous rocks and it is characterized by exhibiting a deep black appearance and small bright areas due to the presence of quartz in its morphology. It is principally composed of quartz, calcium-rich plagioclase feldspar and orthopyroxenes, containing also small proportions of biotite and diopsides. A more detailed petrographic examination of Zimbabwe black granite is shown in Table 1. Its aesthetical appearance and high specific gravity make it one of the most used material in indoor construction, specifically in countertops in kitchens and bathrooms.

All the experiments were carried out with square polished slabs of dimensions: $5 \times 5 \times 2\,cm^3$ (length × width × height) (Fig. 1). The initial average roughness (*Ra*) of the samples was 0.16 μm.

2.2. Laser treatment

Surface treatment was performed using two diode end-pumped $Nd:YVO_4$ lasers (Rofin-Sinar PowerLine E). Both lasers show similar beam quality ($M^2 < 1.2$), by emitting at different wavelengths: 1064, and 532 nm. The pulse durations are 20, and 14 ns, respectively. The laser beam was focused onto the surface of the workpiece using lenses with different focal length: 211 mm, and 365 mm. The spot diameters of the focused laser beam were 70, and 60 μm for 1064, and 532 nm wavelengths, respectively. In all cases, the laser surface treatment was performed in air at atmospheric pressure.

The laser-induced damage threshold for Zimbabwe black granite was estimated by performing diverse experiments varying laser processing parameters prior to establish those appropriate to accomplish the laser surface texturing. These irradiance values were found to be approximately of $2.6 \cdot 10^4\,W/cm^2$ (laser fluence of $1.2\,J/cm^2$), and $2.4 \cdot 10^4\,W/cm^2$ (laser fluence of $0.9\,J/cm^2$) for 1064, and 532 nm, respectively. Therefore, every treatment belonging to the statistically planned experiments was conducted with higher values of laser irradiance (and hence fluence).

2.3. Statistical design and analysis

In the present work, a 2^4 Full Factorial Design (FFD) of experiments was elaborated to find the laser processing parameters (key factors) that statistically influence on the dependent response variables (main outputs): average roughness of the treated areas (*Ra*) and the water contact angle (θ). Statistical analyses were performed using the computing environment *R* (*R* Development Core Team 2012). The laser irradiance (I), scanning speed (v), pulse frequency (f), and pass overlapping (s) were the selected processing parameters in this case of study [22]. This technique was analysed by assigning two levels, high and low, designated by "+" and "−",

Table 1
Composition analysis of Zimbabwe black granite.

Name	Chemical formula	Composition percentage [%]
Silica	$Si\,O_2$	40.4
Diopside	$Ca\,Mg\,(Si\,O_3)_2$	13
Albite (Feldspar)	$Na\,(Si_3\,Al)\,O_8$	11.1
Anortite (Feldspar)	$Ca\,Al_2\,Si_2\,O_8$	10.6
Biotite (Mica)	$K\,(Mg, Fe^{+2})_3\,(Al, Fe^{+3})\,Si_3\,O_{10}\,(O\,H, F)_2$	9.4
Magnesioferrite	$Mg\,Fe_2\,O_4$	8.5
Crossite	$(Na, Ca)_2\,(Fe, Mg, Al)_5\,(Si, Al)_8\,O_{22}\,(O\,H)_2$	5.5
Augite	$Ca\,(Mg, Fe)\,Si_2\,O_6$	1.3