Studies on azulejo glaze welding by means of laser irradiation

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SUMMARY: This communication discloses a preliminary study about the effects of CO_2 laser irradiation on the surface of historic glazed tiles in order to test its potential for their restoration. The influence of the processing parameters (working distance, linear scanning velocity and number of laser scans) of a 25W CO_2 laser upon the welding of ceramic glazed surfaces was studied. Tile replicas simulating 17^{th} -18^{th} century historic Portuguese tiles of different glaze compositions and pigmented – non-pigmented glazes, have been irradiated. Optical reflection microscopy and SEM have been used to study the resulting morphological alterations. The welded glaze surface appears to be greatly affected by the employed lased parameters but also the different composition of the glaze and the presence of pigments. In general at optimized conditions the welding of the glaze is obtained even if newly formed macro and micro- cracks are usually observed in the vicinity or at the irradiated area. Initial results are encouraging and further work is necessary before the on-site and real-case implementation of this methodology.

KEY-WORDS: laser, azulejo, restoration

INTRODUCTION

Glazed ceramics are important items of cultural heritage interest which can constitute decorative and structural materials, often monumental in scope. Portuguese azulejos for example, are almost ubiquitously found as decoration in interior and exterior architecture and constitute one of the country most important expressions of a national artistic heritage. Their acknowledged resistance in external and moisty conditions have made them one of the preferred materials to protect and decorate Portuguese architectural structures. These characteristics have nevertheless the shortcoming that tiles are in many cases set in harsh environments subject to pernicious weathering conditions. In those conditions their weathering-resistance capacity is limited and decreased during time when compared to their possibly "eternal" life when placed in non-moisture stable conditions [1]. This can be alarmingly observed by the increased degradation state that many historic tiles present nowadays. The harsh environmental conditions where many tile panels are placed; together with the restrictions as regards their move and/or transportation or the desire to leave them *insitu* increases also the demand upon their conservation and restoration treatments. A good restoration treatment for a tile panel in a museum environment for instance, will not necessarily be a good one for in-situ (sometimes outdoor) restoration since they need to be able to endure much harsher conditions. The lack of adequate conservation treatments to be applied in those settings is also a major issue and a constant complain of many professionals working in the field [2-4]. This lack has led us to the search for more efficient, compatible and durable conservation procedures leading us to explore the possible use of lasers for their conservation-restoration.

This article deals with a preliminary work on the innovative study of the potentials of using CO_2 lasers for the conservation and restoration of glazed ceramics. Therefore, the application of laser radiation based on the controlled thermal fusion of the glaze is presented and its potential is discussed.

On the use of lasers

Lasers have been established as most valuable tools for the study and conservation of Cultural Heritage objects and monuments, through spectroscopic and laser cleaning processes respectively [5]. The use of lasers for the cleaning of ceramic glazed surfaces is a field with limited research and applications. However, past works by Stratoudaki´s et al [6] and Huet et al [7] have elaborated about the potential of using Nd:YAG and KrF lasers for removing pollutants from outdoor ceramics of the 19th century.

The cleaning processes which are up to now the only laser-based conservation processes, are based on the laser-ablation of materials by selective interaction between a laser beam and the unwanted material, leaving the core object untouched. During the interaction of the laser beam and the material a number of effects take place based on photothermal, photochemical and photomechanical mechanisms while the final result depends closely to the material properties and the laser parameters. An optimum laser cleaning result should ensure that only the desired mechanism will dominate and no unwanted effects would take place i.e. no melting, fracturing or chemical alteration will occur to the substrate (authentic surface) after cleaning. Nevertheless these undesirable effects may be of some use in the conservation field and in this respect the capacity of lasers to melt materials has been considered in this study.

The laser-induced thermal processing of materials has been already used since the eighties in industrial applications on utilitarian glass and ceramic materials. Specifically, in 1980 a patent has been issued on the use of CO_2 lasers to repair small defects on glass [8] and in 1987 another patent was issued on the repair of high melting temperature ceramic coatings such as in heat engines by injection and melting of a powered material [9]. Later on, the use of lasers on the repair of whiteware ceramic articles has also been released [10-12]. Significant work has also been done on the engraving, by melting of a pigmented layer, on top of a ceramic material [13 - 17]. A Nd:YAG laser (λ = 10.64 μm in continuous wave mode) has also been used to print coloured patterns on tiles [18].

Up to now little has been researched on the use of the thermal and melting potential of lasers in the conservation of cultural heritage ceramic artefacts. In 2014 Ristić *et al* have studied the impact of pulsed lasers on cleaning ceramics of historical importance [19]. Later Polić at al has studied the effect of pulsed lasers on the glaze surface also for restoration purposes [20]. After the research made by FORTH and LNEC in 2016 a patent application (PCT/GR2016/000011) has been issued on the "Restoration of vitreous surfaces using laser technology" [21].

The possibility to heat and melt a small zone of the glaze without affecting the remaining tile is a great advantage compared to techniques such as re-firing [22, 23]. In re-firing the entire tile needs to be removed from the wall and is subject to a new firing cycle. Therefore the information regarding the production techniques that was stored in the materials is irreversibly altered. When re-firing - even when selecting a presumably appropriate firing program - due to the heterogeneity of the tiles and other unpredictable factors provides a certain risk to the procedure mainly because the final results can only be verified at the end while opening of the kiln. With localized welding the material is only affected locally in a range and a real-time operation where a more controllable procedure can be applied.

This article elaborates on preliminary studies made by these two institutions on the use of the above mentioned technique, namely the impact of the laser radiation upon glazed ceramic surfaces. The aim at this initial stage is to investigate the range of effects that may be caused on the glaze upon its irradiation at different laser parameters. This knowledge will allows us in the next stage to be able to determine the most appropriate irradiation conditions that would favour a "clean" melting without undesired results such as cracking and fracture, discoloration effects and other damages.

MATERIALS AND METHODS

Samples

Glazed ceramic tile replica samples with chemical glaze compositions similar to 17^{th}-18^{th} century Portuguese historical tiles [24] were made using two tin lead white glaze recipes (R1 and R2, Table 1). For the glazes preparation Tr29 and LT599 powdered frits from Ferro have been used and the chemical composition modified by adding silica powder (FPS 180 from Areipor), SnO_2 (Merck), K_2CO_3 (VWR chemicals), Na_2CO_3 (Riedel de Haen) and $CaCO_3$ (VRW prolabo).

The resulting powders have been mixed and fired at 980ºC to make a frit. The frit has been then crushed to a lower than 106 µm granulometry, suspended in water and applied by immersion to the ceramic body. Part of the R1 samples (R1_b) where painted blue on top of the dry powder frit layer using a Cobalt Oxide pigment (Casa Viana). All samples have then been fired at 980ºC for 30 min letting the kiln to cool down naturally.

Table 1: Theoretical elemental chemical composition of the replicas (based on the recipes)

	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	K_2O (%)	CaO (%)	TiO_2 (%)	Fe_2O_3 (%)	PbO (%)	SnO_2 (%)
R1	1.2	0.5	3.8	47.7	6.7	1.1	0.1	0.1	30.9	7.8
R2	2.0	0.2	0.9	61.1	7.0	1.3	0.1	0.2	21.6	5.8

Experimental setup and methodologies

Laser processing

Preliminary tests with various laser types available at IESL-FORTH proved that Continuous Wave (CW) CO_2 lasers are the most suitable for this application. This was expected since CO_2 lasers emit in the far infrared (10.6 µm) thus causing only thermal effects on materials while the

CW operation does not allow high fluencies, as in the case of pulsed lasers, which may lead to ablation phenomena.

A custom made laser system was used for the irradiation of the samples. The main components of the system (Figure 1) were a) a 25W CW CO_2 laser (10.6 μm, Gaussian beam profile), b) an optical system for shaping and finally focusing the beam at 180mm c) flying optics (galvo system) to move the laser beam into the desired area and "draw" on the target the desired pattern and d) an elevation stage where the tiles were positioned in order to locate their glazed surface at the desired working distance.

The tiles were then irradiated with the following parameters: a) 12 W laser power (fixed value at which the laser was found to be more stable), b) working distance (wd), that is the distance from the sample/tile to the lens (Figure 2), varying from 135 to 180 mm (focus), c) scan speeds varying of 2.00, 26.81 to 53.62 mm/s and d) 1 up to 100 scans along the same irradiation line. On each sample a series of line-scans was performed, the scanning travel was larger than the tile width, starting and ending outside the tile to ensure uniform irradiation along the whole irradiated line.

Evaluation methods

SEM-EDS: A JEOL JSM 6390 scanning electron microscope was used for the evaluation of the samples irradiation. The SEM was operating at 20KV and a tungsten filament was used as an electron gun.

Reflection Optical microscope: A Olympus PMG3 reflection microscope has been used to observe the influence of the irradiation on the surface of the glazed ceramics.

μ- Raman: A compact portable Raman system with a diode laser (λ_{exc}: 785 nm) was used. The beam was focused on the surface of the sample to be analyzed by objective lens (x20) and the irradiation area had a diameter of about 20 μm. The beam power on the samples was 30mW. The typical exposure time was 5s, while 2scans were averaged.

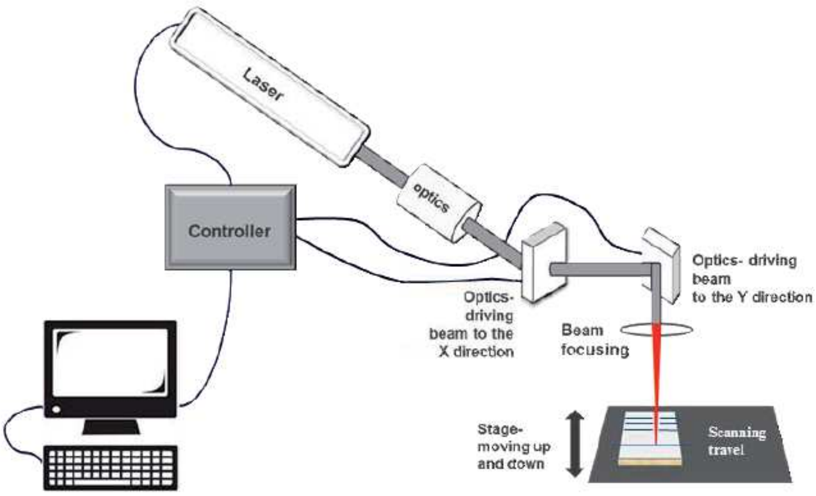


Figure 1: CO_2 laser set-up

RESULTS AND DISCUSSION

By visual inspection and depending on the irradiation parameters a number of effects could be recorded on the irradiated surfaces such as no observable effect, areas with increased gloss, craquelure, loss of material and in some cases discoloration (yellowing). Fig. 2 shows microscope image of the type of resulting glaze welding effects observed at the surface of the tiles.

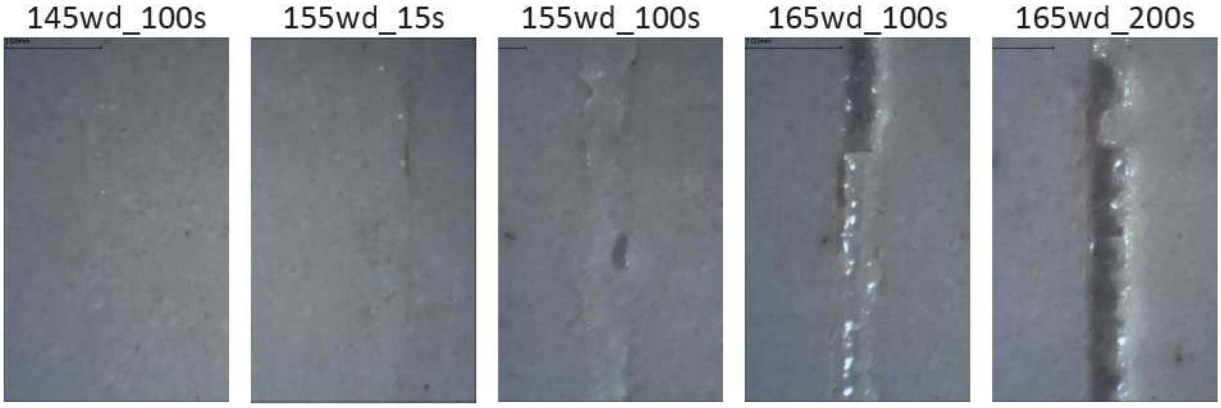


Figure 2: Microscopic observation of laser irradiation welding effects on the glazed surface for 53.62 mm/s velocity. a) No evident effect (145wd_100s); b) Crack along the irradiation line (155wd_15s); Multiple crack along the line (155wd_100s); Glaze welding and partial detachment (165wd_100s); Almost total detachment (165wd_200s). Where 'wd' is the working distance and the 's' the number of scans.

When looking in detail, whenever melting occurred, a constant crack network was observed both in the interface and the vicinity of the melted and non-melted glaze (Figure 2 and Figure 5). This crazing, was probably the result of the high temperature differences and inefficient heat exchange leading high thermal stresses between the two areas. At the surface of the melted lines a thin network of cracks was also developed. This was probably resulting from the different cooling rate and therefore due to the high temperature gradient between the melted surface and the melted inner-layers [11]. For working distances (wd) close to focus or lower velocities, besides melting, evaporation can be observed during the laser processing [20, 18]. The evaporation of glaze components, will also certainly affect the melted glaze composition. When irradiating, for instance glass bottles, it has been stated that alkaline and alkaline earth metal oxides were released leading to the decrease of the expansion coefficient of the melted glaze [25]. The resulting composition of the evaporated materials has not been analysed yet in our system but we would expect also an alteration of the melted glaze composition. A slight yellowing discoloration at the edges of the melted lines could also be observed. Through μ - Raman analysis yellow lead monoxide (β-PbO) could be detected (Raman shifts at 98, 158, 304 and 351 cm^{-1}) on the glaze irradiated samples (Figure 3).

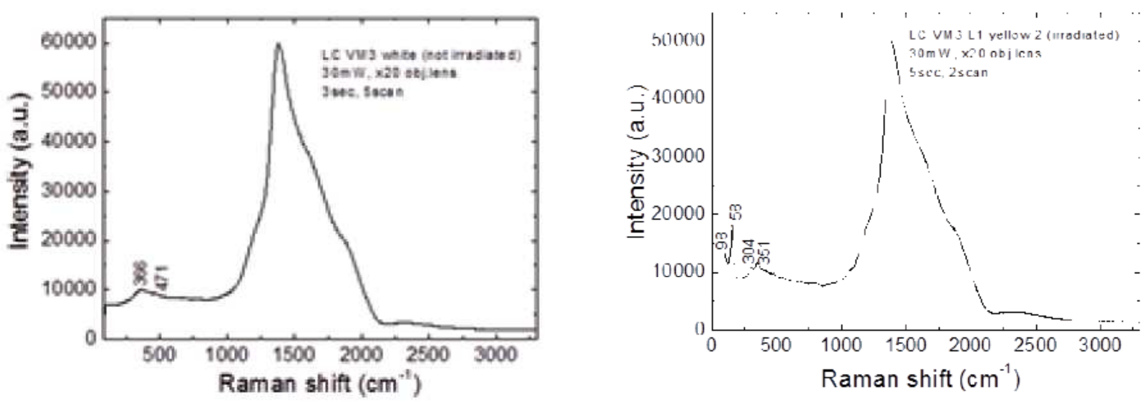


Figure 3: μ-Raman analysis of a non –irradiated and irradiated R1 glaze samples.

Through the observation of the samples by SEM the profile of the fissure system is more clearly observed (Figure 4). However, the depth of the melted glaze was not easily distinguished from the non-melted glaze and could only be estimated when a fissure occurred between both due to the thermal stress. As expected, in general, the melted zone was deeper and wider with increased energy density (close to focus, slow velocity and higher number of scans) It was also observed that within the tested conditions (laser parameters, glaze composition and thickness- around 200-500 μm)) the melted glaze pool seemed not to reach the interface between the glaze and ceramic body.

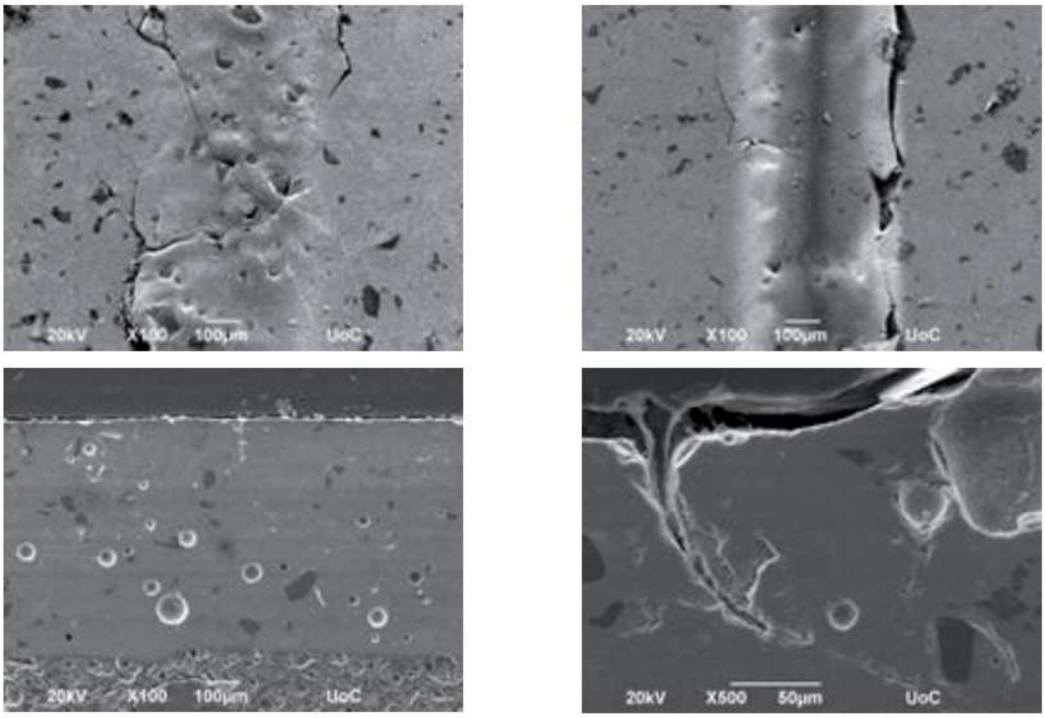


Figure 4: SEM analysis of R1 samples irradiated with a working distance/scans of 155wd/50s and 165wd/50s. Depending on the local the cross section is made the fissure between the melted and non-melted glaze can be seen or not.

Working distance and number of scans

Table 2 resumes the glaze surface alterations observed through reflection microscopy after irradiation at different working distances and number of scans at a constant velocity of 53.62 mm/s. It is observed that with a working distance of 135 mm (far away from focus) the glaze shows no visible alteration (Figure 5). When increasing the working distance to 145 mm a crazing network is already observable along the irradiated line with a higher crack density generally with increased number of laser beam scans. Apparently the energy delivered by the laser beam using this focal distance and speed is not enough to melt it but the crack network is still formed from the resulting thermal shock. Only when closer to focus (around 155 mm up to 180 mm - on focus) the glaze is melting. On average the melted line width increases when closer to the laser focus due to the delivery of higher amount of Energy. With 1 scan, only after 165 mm focal distance we could detect some minor glaze welding, but at the focus (180mm) a relatively homogeneous melted line was already observed. A large increase in line width is achieved from 1 to 15 laser scans while after this number this increase is lower (Figure 5).

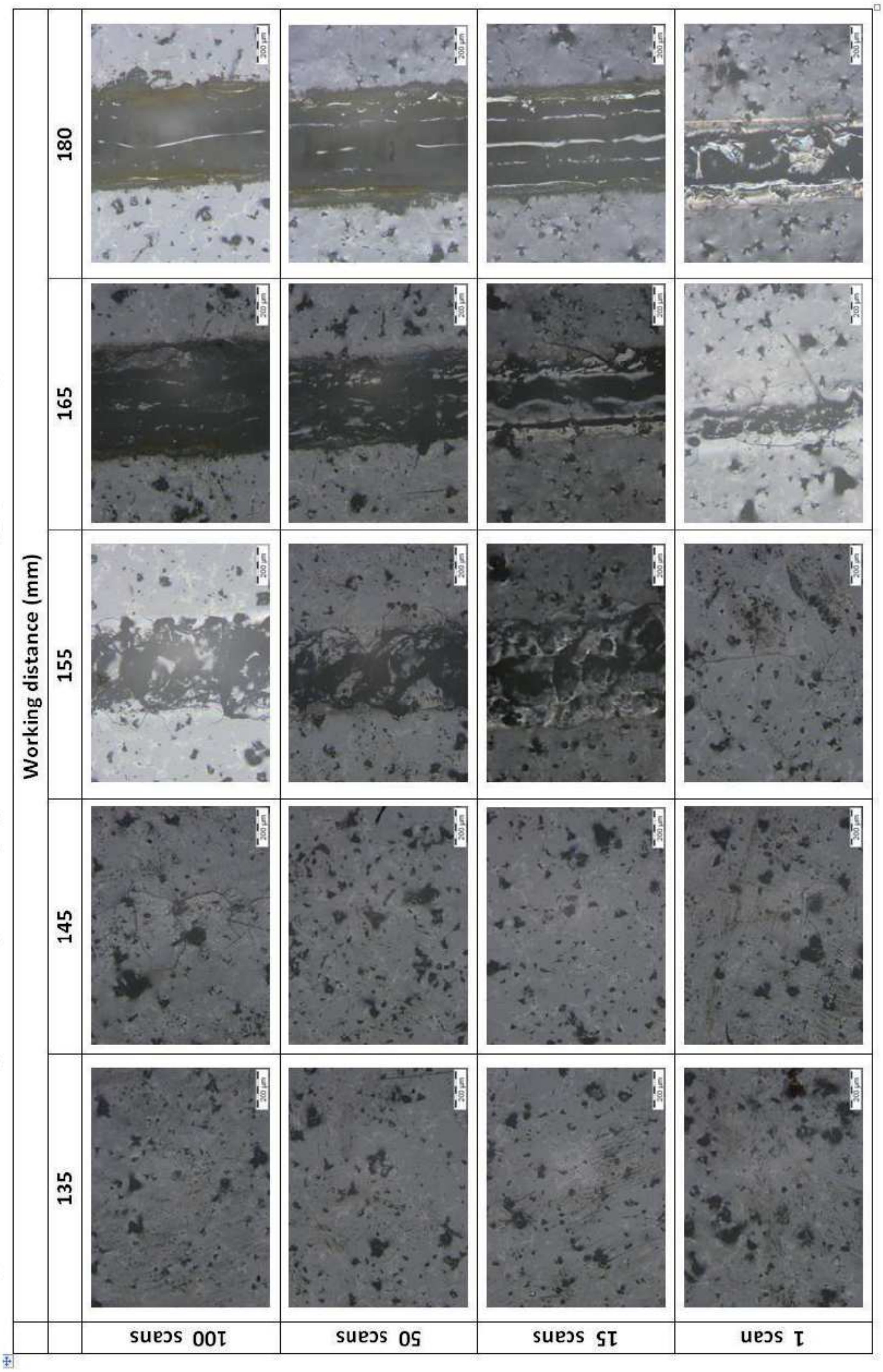


Figure 5: Surface analysis of sample R1 by optical reflection microscopy (53.62mm/s)

Irradiating velocity

When decreasing approximately to half the scanning velocity (from 53.62 to 26.81 mm/s) an average increase of the melted line width is observed. This effect can be specially observed at 1 scan irradiation (Figure 5, 6, 7 and 8).

At 2mm/s and 1 scan, melting is observed at 145 working distance while at 26.81 and 53.62 mm/s melting is observed only at 155 and 165 lens-tile distance respectively. The higher energy resultant from a slower velocity allows the glaze to fuse at further away from the focus and at the velocity of 2mm/s the amplitude of the crack network is observed to be extremely high (Figure 7 and 8).

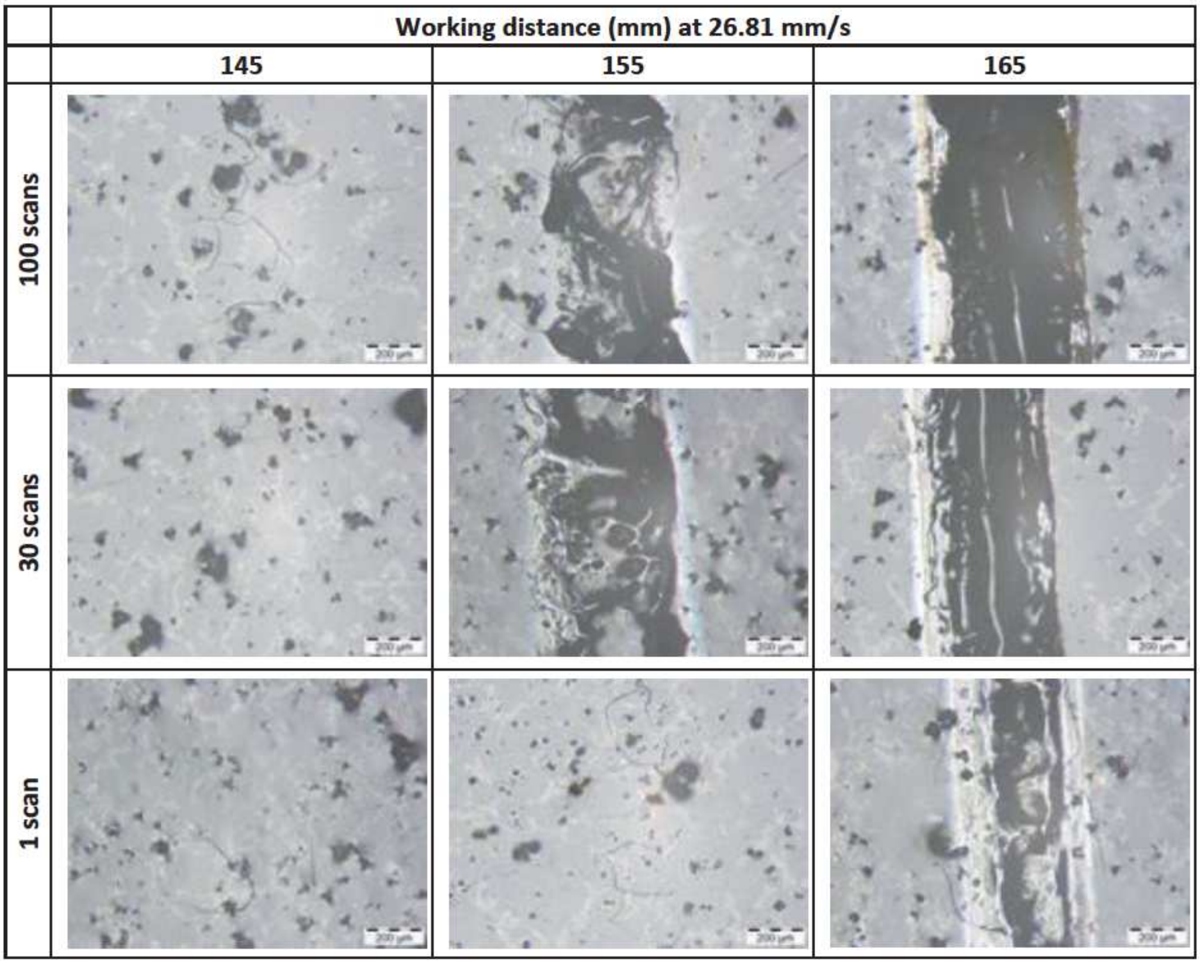


Figure 6: Surface analysis of R1 by optical reflection microscopy irradiated at 26.81 mm/s

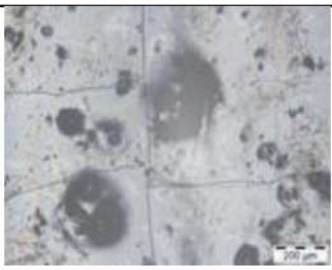
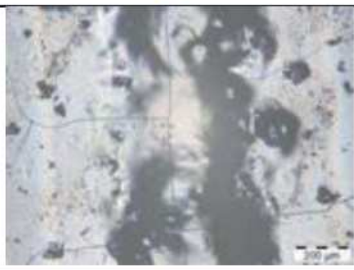
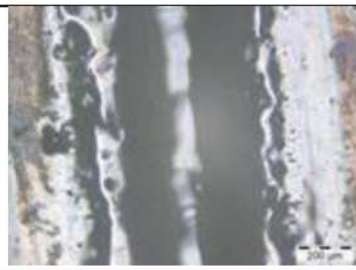
	Working distance (mm)		
	135	145	155
1 scan			

Figure 7: Surface analysis of R1 by optical reflection microscopy irradiated at 2 mm/s, 1 scan at 135, 145 and 155 working distance.

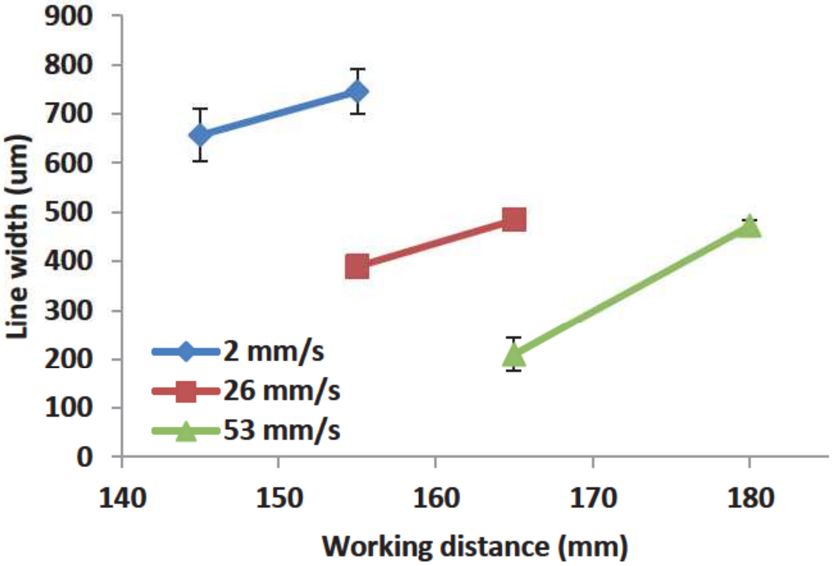


Figure 8: Effect of beam velocity and working distance on the melted line width after 1 beam scan.

Painted surfaces

Tiles are usually painted in one or more colours. Traditionally the pigments are applied as a liquid suspension to the raw glaze layer and then fired. When firing the pigments are mixed and integrated into the glaze layer showing usually a decreasing content from the surface of the resulting glaze layer (Figure 11) to the glaze-ceramic interface.

The pigments will certainly change the glaze properties such as its melting point. Cobalt oxide, responsible for the blue colour in tiles it is known to be a fusing agent and therefore the effect of the irradiation at the painted areas was largely enhanced. The average melting width was larger the results obtained for lower speed irradiation (Figure 6 and 10) and melting of the glaze was even observed for working distances of 145 and 50 scans (Figure 10).

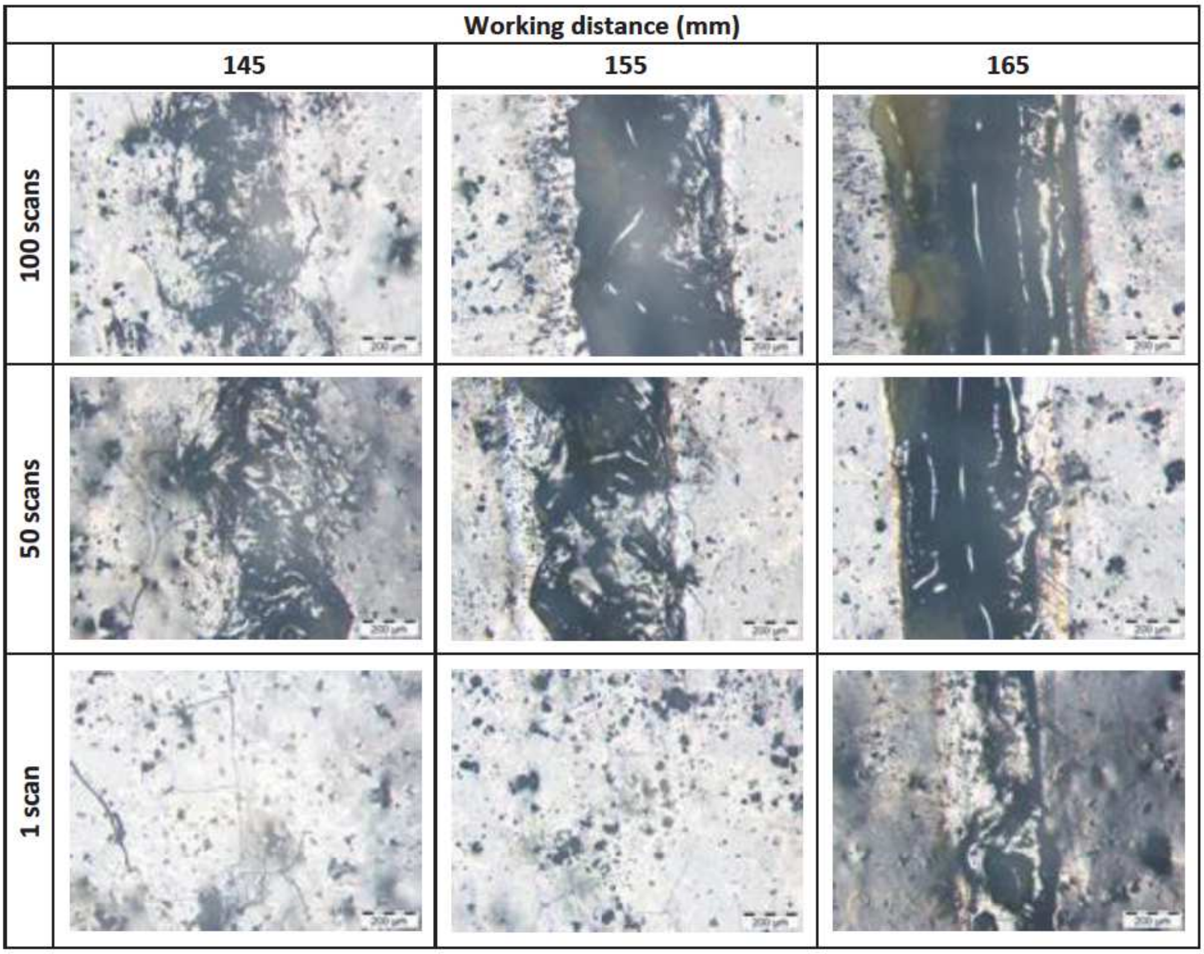


Figure 10: Surface analysis of R1 painted with blue with a Cobalt Oxide pigment by optical reflection microscopy irradiated at 53.62 mm/s

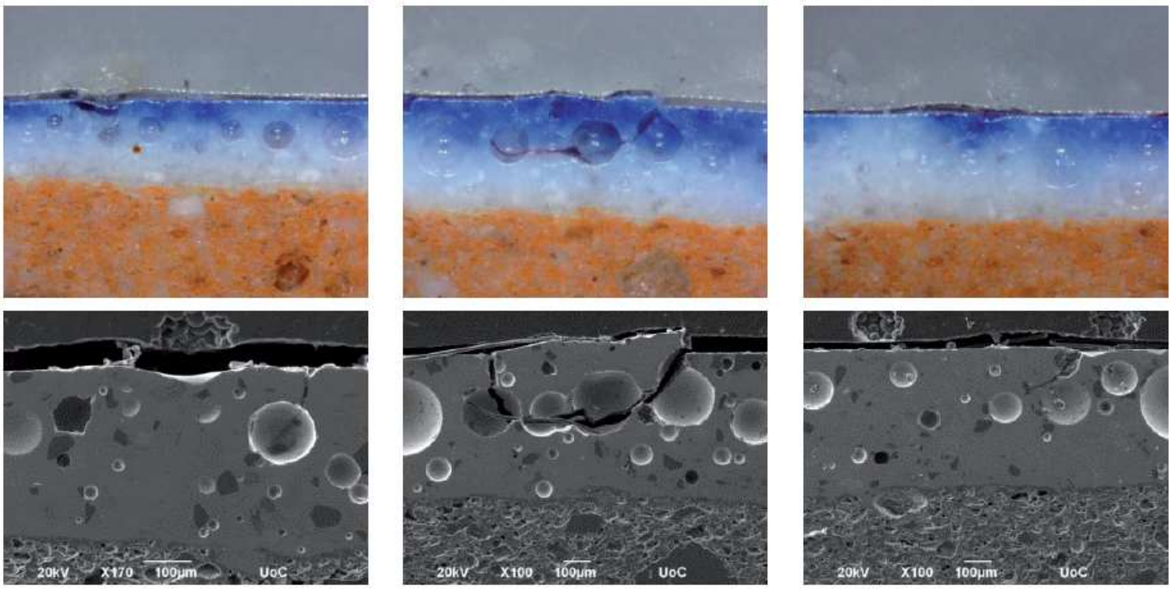


Figure 11: Optical microscopy and SEM analysis. From left to right: Working distance 165/1 scan with a small fissure, 155wd/50 scans with complete detachment, and 165wd/100 scans with a small detachment. Depending on the cross section zone it can be observed the fissure of the previously melted glaze or not.

Different glaze type

When different glaze compositions are used, a different resulting melting point of the glaze can affect its melting by laser irradiation. In this Case the R2 glaze originated on average a stronger glaze melting with melted glaze even at 155 working distance and 1 scan (Figure 12). These results show that the irradiation conditions would need to be tuned whenever a different tile glaze would be treated.

Figure 13 depicts the average width results for 50 scans and several working distances.

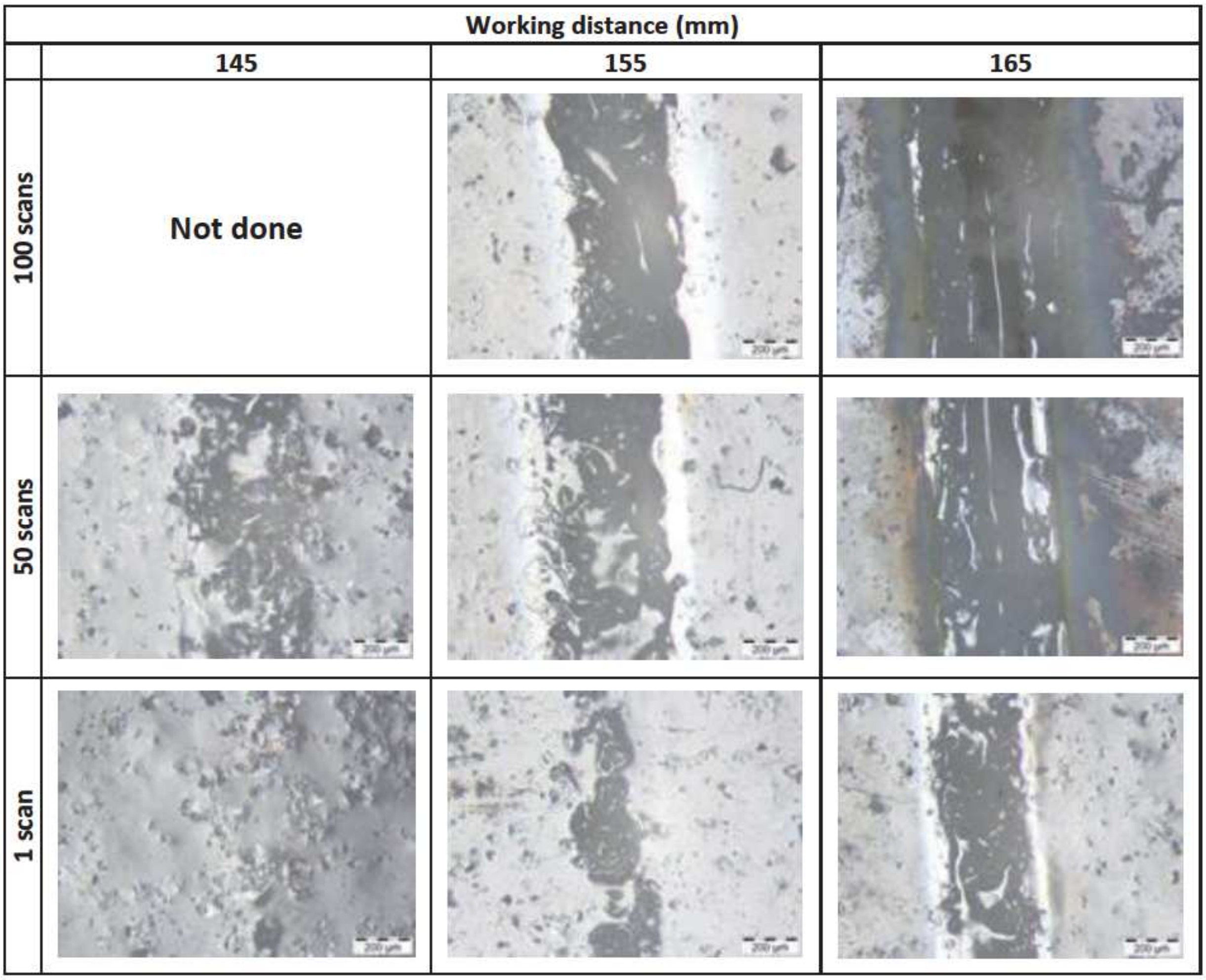


Figure 12: Surface analysis of R2 by optical reflection microscopy irradiated at 53.62 mm/s

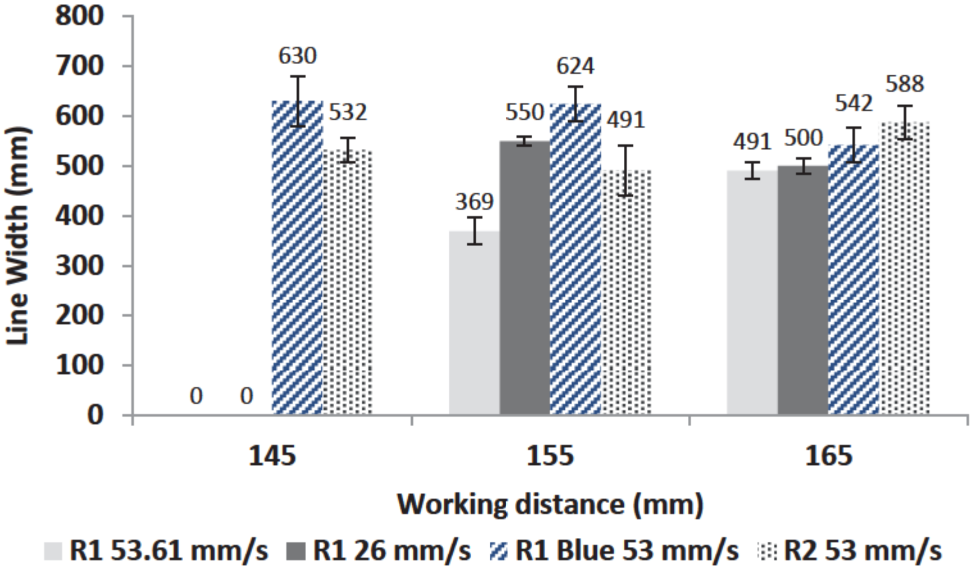


Figure 13: Effect of beam velocity and focal distance on the melted line width after 50 beam scans.

CONCLUSIONS

This present article is part of the common effort of two institutions to study the potential use of lasers in the restoration of glazed ceramics and dwells upon on the effect of the CO_2 laser irradiation on the glazed surface of historic tiles.

The laser was able to melt the irradiated areas while in certain cases undesired affects such as increased glossy appearance, crazing and in some cases yellowing was observed in the irradiated areas associated mainly with accumulated energy density.

In general the lines irradiated with higher accumulated energy (slower speeds and closer to the focus) are wider but the composition and presence of pigments of the glaze (due to differences in the melting point) are shown to also greatly affect the melted pool. The number of scans seems to be determinant up to a certain point (15- 50 scans) after which no substantial gain is observed. Advanced methods would need to be tested to decrease and ideally eliminate the resulting crazing.

The results obtained show that great care should be put in the selection of the laser parameters; the distance to the glaze surface plays a great role, but also velocity and number of scans. This optimization of parameters varies however when applying the irradiation on variations of types of glaze and even in different pigmented areas of the same glazed tile. An initial optimization would need to be made and the laser parameters adapted to the specific glaze on and pigments of the substrate.

Notwithstanding the necessary optimizations, CO_2 laser welding is a promising technique to treat ceramic tile and is a methodology that needs and deserves to be better researched.

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