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Correction of small imperfections on white glazed china surfaces by laser radiation

I. Képíró [1], K. Osvay *, M. Divall [2]

Department of Optics and Quantum Electronics, University of Szeged, PO Box. 406, Szeged H-6701, Hungary

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Abstract

A laser-assisted technique has been developed for correction of small diameter (1 mm) and shallow (0.5 mm) imperfections on the surface of gloss fired porcelain. To study the physics and establish the important parameters, artificially made holes in a porcelain sample have been first filled with correction material, then covered with raw glaze and treated by a pulsed, 7 kHz repetition rate CO_2 laser at 10.6 μm. The modification of the surface and the surrounding area have been quantified and studied with a large range of parameters of incident laser power (1–10 W), width of the laser pulses (10–125 μs) and duration of laser heating (60–480 s). Although the shine of the treated area, defined as the distribution of micro-droplets on the surface, is very similar to the untreated surfaces, the surroundings of the treated area usually show cracks. The measurement of both the spatial temperature distribution and the temporal cooling rate of the treated surface has revealed that a simple melting process always results in high gradient temperature distribution within the irradiated zone. Its inhomogeneous and fast cooling always generate at least micro-cracks on the surface within a few seconds after the laser was turned off. The duration and intensity of the laser irradiation have been then optimized in order to achieve the fastest possible melting of the surface, but without producing such high temperature gradients. To eliminate the cracks, more elaborated pre-heating and slowed-cooling-rate processes have been tried with prosperous results. These achievements complete our previous study, making possible to repair the most common surface imperfections and holes of gloss fired china samples.

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Keywords: Porcelain; Spatial temperature distribution; Micro-cracks

1. Introduction

One of the main problems in the production line of high quality china samples and figures is that smaller–larger imperfections on their surface occur after the gloss firing process [1]. The point-like defects and scratches on the shiny white surface usually originate in the imperfect coating of the raw goods with glaze material. These small size (typically 0.1–0.5 mm) and very shallow (depth is <0.1 mm) defects are traditionally corrected such that they are recovered with raw glaze and fired again. Due to the particularities of the technological process, there are considerably larger defects on the surface of unique china figures. Namely, the raw clay goods are usually not able to mechanically support themselves before the biscuit firing process, hence additional carriers or crutches need to be applied. Thus, the footprint of these supporters leave a deeper (0.5 mm) and larger diameter (1–3 mm) pit on the surface which, of course, cannot be covered with glaze. In the traditional repairing process, these pits are first filled with a so-called correction material, then painted with raw glaze material and fired again.

Laser-assisted techniques for welding and cladding of various ceramic materials have been developed and are widely used [2–8]. Efforts have been also made to develop theoretical models for explanation of the related melting and phase transition phenomena, including glazing modification and crack formation mainly in dental and architectural ceramics [9–14]. In our previous research [15] a CO_2-laser-based technique was introduced for correction of small and shallow defects. It

* Corresponding author. Tel.: +36 62 544273; fax: +36 62 544658.
E-mail address: osvay@physx.u-szeged.hu (K. Osvay).
[1] Present address: Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BW, UK.
[2] Present address: Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0NX, UK.

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was shown that under certain conditions of laser induced melting, a perfectly shining glaze with a diameter of 1.5 mm could be produced on the surface of a white porcelain sample covered with raw glaze.

In this paper we aim to further develop the technique of laser-assisted porcelain correction towards the treatment of larger and deeper imperfections. Since this is a more complex process including interaction of three materials (the porcelain carrier, the correction material and the raw glaze), first we extend our previous study for the correction material, then measure the spatial heat distribution around the treated porcelain surface, and finally discuss how to achieve a perfect correction of the holes.

We rely strongly on our previous paper, where not only the experimental setup, the radiation process, but also the definitions and notations have been introduced. Thus, in the present work we concentrate on the new findings and point out the dissimilarities, while only the essential descriptions and explanations are repeated.

2. Experimental

A pulsed Synrad CO_2 laser with a repetition rate of 7 kHz was used to heat the samples in a simple setup described earlier. The power of the laser, measured in the target position, was changed between 1 W and 10 W by varying the duration of the pulses between 10 μs and 125 μs. The diameter of the beam on the target was 2 mm.

For melting the sample, a certain amount of absorbed energy is needed. Although this is proportional to the irradiated laser energy which is a product of laser power and irradiation time, due to heat transfer and conduction, the melting process depends non-linearly on the absorbed laser energy [2,3]. Hence, in the experiment both the laser power and irradiation time have been recorded.

The shine of the porcelain was characterized by the size and distribution of micro-droplets. The laser induced melting and the subsequent solidification was regarded optimal when the shine of the melted area was similar to the untreated porcelain. The treated surface is characterized by the diameter of the melted area (inner ring), the diameter of the area with high temperature gradient (outer ring), and the radial cracks across the once melted area (see Fig. 6 of Ref. [15]).

The china samples were treated in the grid of points of a matrix, spaced 1 cm × 1 cm, each point representing different pairs of power and duration of irradiation. For the first study, a few samples were covered with correction material at even thickness. For the imitation of the correction process itself, others were prepared by a diamond borer drilling holes with a diameter and depth of 1 mm and 0.5 mm, respectively.

3. Correction material on white porcelain surface

The correction material is a particular mixture of clay and raw glaze material, having very similar spectroscopic features as the components described in [2]. In order to gain comparable data as for the raw glaze and porcelain materials studied earlier, the structural transformations have been first investigated for the correction material in the form of surface layers applied on the white porcelain samples.

The transformation phases of the correction material proceed in a very similar way to that of raw glaze material presented in [15]. Porcelain is about a 2:1:1 mixture of kaolin, feldspar and quartz. Correction material and raw glaze have in their mixture significantly more kaolin and quartz, respectively, than the mixture of porcelain. Following from the absorption measurements carried out in a similar way as described in [15], their relative absorption at 10.6 μm is 17:14. As the thermo-physical and spectroscopic characteristics, such as the absorption coefficient and surface tension vary depending whether correction material or raw glaze is applied, the transformation processes starts at different irradiation doses.

The processes, described by the diameter of the inner ring, occurring at exposure durations of 1, 2, 4 and 8 min are shown in Fig. 1. The surface of the correction material starts to discolor when a dose of 4 W over 2 min is applied. This indicates the starting point of melting process at molecular level. The first appearance of a small, contiguous and smooth area, that is the first physical indication of the melting process, could be observed at the dose of 7 W over 8 min (Fig. 1a). The translucid

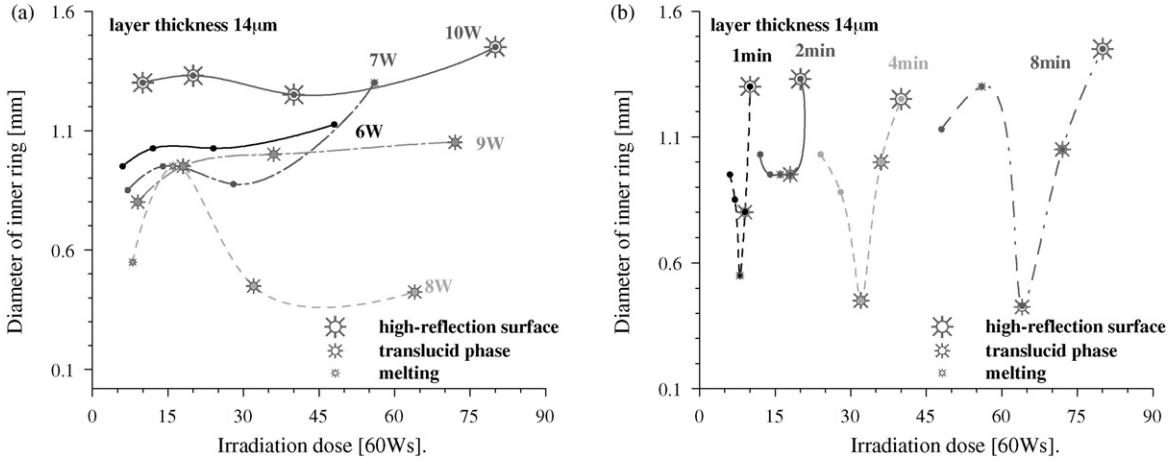

Fig. 1. Diameter of the inner ring vs. the irradiation dose for correction material of 14 μm thickness described at constant laser power (a) and irradiation time (b).