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Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials

A.S. Fonseca [a,b,*], M. Viana [a], X. Querol [a], N. Moreno [a], I. de Francisco [c], C. Estepa [c], G.F. de la Fuente [c]

[a] Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain
[b] Universidad de Barcelona, Facultad de Química, Martí i Franquès 1-11, 08028 Barcelona, Spain
[c] Instituto de Ciencia de Materiales de Aragón (ICMA – Universidad de Zaragoza), María de Luna 3, E-50018 Zaragoza, Spain

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ABSTRACT

The use of laser technology in the ceramic industry is undergoing an increasing trend, as it improves surface properties. The present work aimed to assess ultrafine and nanoparticle emissions from two different types of laser treatments (tile sintering and ablation) applied to two types of tiles. New particle formation mechanisms were identified, as well as primary nanoparticle emissions, with concentrations reaching up to 6.7×10^6 particles cm^{-3} and a mean diameter of 18 nm. Nanoparticle emission patterns were strongly dependent on temperature and raw tile chemical composition. Nucleation events were detected during the thermal treatment independently of the laser application. TEM images evidenced spherical ultrafine particles, originating from the tile melting processes. When transported across the indoor environment, particles increased in size (up to 38 nm) with concentrations remaining high (2.3×10^6 particles cm^{-3}). Concentrations of metals such as Zn, Pb, Cu, Cr, As and Tl were found in particles <250 nm.

1. Introduction

Laser irradiation of ceramic material is a novel technique with numerous advantages regarding the sintering process such as speed, temperature and enhanced durability and surface properties of structural materials (Schmatjko, Endres, Schmidt, & Banz, 1988; Toenshoff & Gedrat, 1991; Jervis, Nastasi, Hubbard, & Hirvonen, 1993; de Francisco et al., 2011; Lahoz, de la Fuente, Pedra, & Carda, 2011). The use of high powered CO_2 lasers for industrial ceramic materials processing was studied in the framework of LIFE projects and is currently being assessed for two different industrial processes: (i) tile sintering in a high-temperature furnace and, (ii) ablation of ceramic materials. A recently developed "in-situ" melting method (tile sintering) makes use of a CO_2 laser scanner combined with simultaneous external heating of the substrate (in a conventional furnace) and uniform movement (Estepa & de la Fuente, 2006; de Francisco et al., 2011). This innovative technology allows to obtain coatings of practically any oxide material on an alumina substrate (Estepa & de la Fuente, 2006; de Francisco et al., 2011). In addition, this novel tool can also make use of CO_2 lasers in pulsed mode (induced laser ablation) to perform engravings on the surface of ceramics (Lahoz et al., 2011).

* Corresponding author at: Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Jordi Girona 18, 08034 Barcelona, Spain. Tel.: +34 934006100; fax: +34 932045904.
E-mail address: ana.godinho@idaea.csic.es (A.S. Fonseca).

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The high-energy nature of these laser processes implies a significant potential for the generation and emission of particles in the ultrafine and nanoparticle size range. However, nanoparticle emissions have so far never been evaluated for these industrial processes, mainly due to the novelty of this technology. The high temperatures applied in the furnace (up to 1195 °C) may cause chemical transformations in the raw tiles and the emission of particulate and/or gaseous pollutants into indoor air, which could be enhanced by the addition of the laser treatment.

Nanoparticle emissions from industrial processes are receiving increasing attention in the literature in recent years (Demou, Peter, & Hellweg, 2008; Pfefferkorn et al., 2010; Curwin & Bertke, 2011; Gandra, Miranda, Vilaça, Velhinho, & Teixeira, 2011; Koivisto et al., 2012; Van Broekhuizen, 2012; Gómez, Irusta, Balas, & Santamaria, 2013; Fonseca et al., 2014; Gomez et al., 2014; Voliotis et al., 2014; Koivisto et al., 2014). These works focus on different types of processes, and reveal that nanoparticle emissions and subsequent exposures may reach up to particle number concentrations of 1×10^6 parts cm^{-3} such as the cases of firing processes where the painting and glazing of ceramics occur (Voliotis et al., 2014), as well as during and welding/soldering (Gómez et al., 2013). However, because of the vast number of industrial processes with potential for nanoparticle emissions, the assessment of nanoparticle emissions under real-world scenarios should be encouraged. The present work addresses the emissions from a highly innovative process with a large potential for global-scale implementation in the ceramic industry, which has so far not been evaluated regarding nanoparticle emissions.

This work aimed to identify and characterize nanoparticle formation and emission mechanisms during tile sintering and laser ablation processes in a pilot plant-scale furnace (3 m long). Special attention was paid to new particle formation processes and their dependence on process variables such as temperature or raw tile chemical composition. Finally, nanoparticle transformations through transport in indoor air are also described.

2. Materials and methods

2.1. Materials and experimental procedure

Nanoparticle monitoring and sampling was conducted over three consecutive days (from 23rd October to 25th October 2013), in a research laboratory at the Instituto de Ciencia de Materiales de Aragón (ICMA) located in Zaragoza, Spain. The experiments were not extended over a longer period of time due to two main reasons: (a) particle emissions detected (see next section) were significantly above background concentrations, and thus the data obtained were considered statistically representative of the processes under study, and (b) the availability of the pilot-plant scale furnace was limited. The laser used included a Rofin-Sinar 350 W SLAB-type CO_2 laser resonator and an optical beam steering system (Estepa & de la Fuente, 2006). Two types of laser-based processes were assessed:

a) *Tile sintering*

Industrial ceramic tiles were sintered by laser irradiation in a high-temperature furnace. The tile sintering process was performed using a CO_2 laser emitting at a wavelength $\lambda = 10.6$ μm. The tiles were introduced in the furnace at a constant speed (1.5 m h^{-1}) in an orthogonal direction to the laser focus. The samples were gradually externally heated with a resistance furnace in a temperature range from ambient temperature up to 850 °C. Afterwards, the tiles followed the standard thermal cycles used at industrial-scale, with gradually increasing temperatures which reached peak values of about 1195 °C and 1115 °C for porcelain and red clay tiles, respectively.

Six conventional industrial tiles were selected: raw porcelain (#1), porcelain with frit (#2), porcelain with frit and colored decoration (#3), raw red clay (#4), red clay with frit (#5) and red clay with frit and colored decoration (#6). These are six of the most frequently used types of tiles in the industry.

b) *Laser ablation*

Laser ablation is the process by which material is expelled from a surface by irradiating it with a pulsed laser (Bäuerle, 1996; Rubahn, 1999; Lahoz et al., 2011). Fig. S1 in the supplementary information presents an illustration of these effects. It illustrates the presence of a melted layer at the surface of the porcelain tiles where the laser is irradiating. Particle emissions during laser ablation were only assessed for one type of material (raw porcelain; #7).

2.2. Sampling locations

The laboratory under study had a surface of 29 m^2. The particle monitors and samplers were placed simultaneously at the emission source, directly above the furnace, at a second location indoors to assess the influence of transport (referred to as the breathing zone), and in outdoor air. Measurements at the emission source were performed between the furnace and the extraction system, and were therefore only influenced by emissions generated in the furnace (no contamination from background air was possible). Fig. S2 of the supplementary information shows the layout of the indoor area under study and sampling locations.

The height of the furnace from the floor is 1.1 m. At the source, instrument inlets were placed inside a 15 cm diameter tube (2.05 m above ground level), which acted as ventilation system for the furnace. In addition, measurements were made in the worker area, located at approximately 2 m from the furnace. Inlets were placed at breathing zone height (~1.6 m).