High-performance thermal emitters based on laser-engineered metal surfaces

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Abstract: Effective thermal management is of paramount importance for all high-temperature systems operating under vacuum. Cooling of such systems relies mainly on radiative heat transfer requiring high spectral emissivity of surfaces, which is strongly affected by the surface condition. Pulsed laser structuring of stainless steel in air resulted in the spectral hemispherical emissivity values exceeding 0.95 in the 2.5–15 μm spectral region. The effects of surface oxidation and topography on spectral emissivity as well as high temperature stability of the surface structures were examined. High performance stability of the laser textured surfaces was confirmed after thermal aging studies at 320°C for 96 hours.

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1. Introduction

The development of new thermal management solutions is essential to enable future high energy, space and communication systems. Radiative heat transfer is the fastest energy transfer mechanism and becomes critically important in high-temperature systems due to the fourth-power temperature dependence of radiated heat energy according to the Stefan-Boltzmann law. Unlike conduction and convection, radiative energy transfer does not require the presence of an intervening medium, thus it suffers no attenuation in vacuum. For opaque materials such as metals, radiation is considered to be a surface phenomenon which exhibits wavelength and temperature dependent behavior. Emissivity is then a measure of how closely the surface approximates a blackbody, for which emissivity is unity (ε = 1). Absorption (α) and reflection (R) determine radiative properties of opaque surfaces, and are related to emissivity in thermal equilibrium state via Kirchhoff’s law:

$$\varepsilon(\lambda, \theta, T) = \alpha(\lambda, \theta, T) = 1 - R(\lambda, \theta, T)$$

where λ, θ, T indicate spectral, directional and temperature dependencies.

This fundamental relationship is the basis for the recently emerged topographical approaches to emissivity control [1] as well as for more traditional surface treatment techniques, such as oxidation and surface roughening [2]. Narrowband thermal emission control is achieved via periodic nano- and micropatterning which allows for the utility of photonic resonances for enhancement and suppression of thermal radiation in particular spectral regions. These selective thermal emitters [3–9] are desired for energy harvesting applications, such as in the field of solar thermophotovoltaics [10], and for gas sensing applications [11], requiring narrowband light sources. However, for effective radiative cooling, the broadband emissivity control is preferred. Passive radiative cooling solutions have been intensively investigated for space [12] and high energy applications [13,14] where severe mass and power consumption constraints as well as high operating temperatures are imposed. Textured metallic [12] and ceramic [15–17]
coatings have been shown as good material candidates exhibiting high emissivity ($\varepsilon \geq 0.8$), good temperature and corrosion resistance. However, adhesion, stress resistance and vacuum compatibility of coatings remain a significant concern for applications in high-energy physics and particle accelerators such as the Large Hadron Collider (LHC) at CERN [18–20].

Laser-assisted surface structuring approach has shown great potential for production of high-performance metal thermal emitters [21–24], addressing some intrinsic shortcoming of other fabrication techniques such as materials selection, area limitation and cost. A large variety of surface topographies can be accessed by varying laser treatment parameters (i.e. laser fluence and number of pulses per spot) and processing atmosphere (inert or reactive). Recent demonstrations have been dominated by application of femtosecond (fs) laser sources to direct nano- and microstructuring. High-emissivity performance ($\varepsilon > 0.9$) at 100°C in the spectral range from 4 to 16 µm was attained with a hierarchical surface structure [22], consisting of randomly positioned microcavities with sub-micrometer surface protrusions. High-temperature performance and structural stability up to 1000°C with a moderate emissivity performance (0.4 < $\varepsilon$ < 0.5) in the spectral range from 2 to 15 µm was shown for the microhole array arrangements [23]. An earlier report focused on the implementation of nanosecond pulse laser structuring [24] showed some evidence that high-emissivity performance at elevated temperatures (700 - 1100°C) can be achieved with the microcolumn array structures.

Here, nanosecond (ns) pulsed laser surface structuring of stainless-steel was investigated in order to establish optimal surface topography with high spectral emissivity in the region from 2.5 to 25 µm. The effects of surface oxidation and topography on spectral emissivity as well as high temperature stability of the surface structure were also examined.

2. Experimental methods

For this study, AISI 304L stainless steel foils (with the nominal composition in wt. %: (Balance) Fe, (18) Cr, (10) Ni, (2) Mn, (1) Si, (0.045) P, (0.03) C, (0.015) S, (0.1) N) were used for the laser treatment. The 1-mm thick steel sheets were cut in 20 × 20 mm squares and were used as received with no further surface preparation except cleaning and degreasing. The surface roughness of untreated samples was measured to be $R_a = 0.043$ and 0.082 µm for the surface profiles taken at 90° to each other using DektakXT stylus profiler (Bruker) equipped with a 2-µm stylus.

A self-assembled microstructuring with ns laser pulses, previously demonstrated in Refs. [24–26], was chosen as the most promising approach for the formation of a regular surface topography capable of withstanding the bake out process conducted in air at 320°C. A 1064-nm Nd:YVO$_4$ laser with a maximum average power of 20 W and a pulse length of 8 ns operating at 20 kHz was utilized for the laser treatment in air and under nitrogen. The laser beam with a Gaussian intensity profile ($M^2 \approx 1.1$) was focused onto the steel surface using a flat-field scanning lens system. The laser beam spot size at the focal plane was measured to be 70 µm at the $1/e^2$ intensity level. The energy fluences in the range from ~3.6 to 18.5 J/cm$^2$ were employed for the surface structuring. The laser beam was raster scanned over the surface at different speeds from 10 to 23 mm/s in a crossline manner using a computer-controlled two-axis scan head system. The distances between the adjacent scan lines (hatch distance) were adjusted from 50 to 107 µm with the increase in the incident laser fluence. The total number of pulses per spot delivered to the surface was varied from 140 to 1400 for one and ten passes, respectively.

A VERTEX 70 FT-IR spectrometer (Bruker) equipped with a 75-mm diameter gold-coated integrating sphere A562-G was used to determine the spectral hemispherical emissivity of the laser-treated surfaces in the spectral region from 2.5 to 25 µm. Spectra were recorded in direct mode at ~ 5 nm resolution. A beam-steering mirror in the sphere directed the incoming light from the FTIR spectrometer to either the sample port or reference point on the front wall of the sphere (see Fig. 6, Appendix A). With the mirror pointing towards the sample, the angle of incidence was 14.8°, fulfilling typical requirement of near normal light incidence for emissivity
analysis to reduce polarization effects. The measurement spot size was ~ 4 mm in diameter. A specular exclusion port allows measurements of the diffuse-only or the total (hemispherical) reflectance spectra, which is the sum of diffuse and specular components. In this work, the spectral hemispherical reflectance was determined as a ratio of total reflectance spectra of the sample to the reference point. The spectral hemispherical emissivity was then determined using Kirchhoff’s law (Eq. 1). All measurements were taken at room temperature. For each spectrum, 128 scans were averaged with the sample kept in the sample port for the sample and reference spectra to maintain a constant sphere albedo. The number of scans was further increased to 3096 for the best performing surface topography to improve signal-to-noise ratio. The measurements were taken under different sample orientations, for in-plane sample rotation, to establish the influence of the microstructure orientation on the emissivity response.

Chromium-nickel stainless steel acid pickling [27] of the laser processed sample was used in order to isolate individual contributions of oxidation during laser surface structuring in air. A mixture of 12% nitric (HNO₃) and 4% hydrofluoric (HF) acids, both by volume, in water was used for pickling at room temperature. HNO₃ is oxidizing in character, whereas HF is reducing. Therefore, in the mixture the oxide-removing feature and the base metal passivating action were combined, hence allowing for gentle removal of the oxide layer without significantly affecting the surface microstructure.

Controlled oxidation of the steel substrates processed in nitrogen was performed in air using Carbolite RWF1100 oven. The oxidation temperature was determined based on the temperature used during specific bake out operations in LHC. The lower oxidation boundary was attained after 7 h at 320°C. For the upper limit the temperature was increased to 600°C for 6-h oxidation treatment to speed up the process.

JEOL JSM-7400F scanning electron microscope (SEM) was used to obtain high magnification images of the steel surfaces.

### 3. Results and discussion

Figure 1(a) shows the spectral hemispherical emissivity responses of the untreated steel and the best performing laser-engineered surface, measured at 22°C, with corresponding surface topographies, see the SEM images in Figs. 1(b) and 1(c). The spectral emissivity performance of the as-received 304L steel substrate demonstrates a monotonic emissivity decay from ~0.3 at 2.5 µm to below 0.1 at longer wavelengths, Fig. 1(a) – dashed curve. This characteristically low emissivity behavior of untreated metal surfaces [2] represents a significant practical challenge, limiting the efficiency of temperature management systems. Markedly different behavior of the spectral emissivity was observed after the ns-laser structuring in air, Fig. 1(a) – solid curve. Dramatic emissivity increase to ~ 0.97 with almost flat response over a wide spectral range from 2.5 to 14 µm was attained after the laser structuring with a pulse fluence of ~ 3.6 J/cm² at a laser beam scanning speed of 10 mm/s, and a 75-µm hatch distance with a total number of pulses per spot equal to 1400. This resulted in the formation of highly organized conical structures with the deepest microcavity formed at the line crossing, see Fig. 1(c). The observed spectral emissivity increase is a result of combined action of the surface oxide layer, promoted by the laser processing in air, and the surface microstructure, formed as a result of the hydrodynamic instabilities of the melt produced on the surface during laser treatment [25,26].

To isolate individual contributions of the surface oxidation and microtopography effects, a set of laser-structured surfaces was produced in a nitrogen processing atmosphere, utilizing the laser structuring parameters resulted in the best performing surface topography. Nitrogen (N₂) is a known shielding gas that helps to exclude oxygen from the processing zone, preventing metal oxidation. Although it is reactive at elevated temperatures, it forms only small amount of lattice nitrides at low gas pressures [28,29]. The spectral response of the steel surfaces structured in nitrogen show noticeable reduction in the emissivity compared to the in-air treated surface, as
seen from Fig. 2(a). This change in the spectral emissivity behavior can be attributed largely to the microtopography change resulted from the processing in an oxygen-deficient atmosphere, Fig. 2(b). Formation of the highly regular conical structures produced in an air environment (Fig. 1(b)) can no longer be supported in the N₂ atmosphere, which promotes formation of a regular structure with a truncated cone microgeometry. This is due to differences in temperature within the processing zone as well as changes in properties of the molten pool. The latter is consistent with some earlier studies where it was shown that the presence of even small amounts of oxygen significantly reduces the surface tension of the liquid metal pool [30]. A similar drop in the spectral emissivity values was observed after the chemical removal of the oxide layer from the in-air processed sample which resulted in a comparable truncated cone microstructure, Fig. 2(c).

Controlled oxidation of the structures produced in the N₂ atmosphere was used to quantify the effect of surface oxidation on the emissivity response. The surface topographies before and after controlled oxidation show no visible change of the microstructure (Appendix A, Fig. 7). The differences in the spectral hemispherical emissivity between the reference (Fig. 2(a), N₂ atm) and the oxidized structures are relatively small occurring in the spectral region up to 10 µm for a heavily oxidized structure at 600 °C for 6 h. It should be noted that after a 50-h oxidation treatment the oxidation-dependent emissivity increase is no longer observed. This is consistent with a previous work on the emissivity of type 304 and 316 stainless steel [31], and is attributed to a limited oxide layer growth for austenitic alloys with high chromium (Cr) content.
The effect of microstructure on the hemispherical emissivity was studied with the structures produced in the \( N_2 \) atmosphere. The laser pulse fluence and processing speed were kept constant and identical to those used for the production of the best performing structure, with total number of pulses delivered per spot being the only variable parameter. This resulted in some alterations of the surface geometry (see Fig. A, Appendix A) accompanied by increase in the groove depth for larger number of pulses per spot. Figure 3(a) shows that a substantial increase in the spectral hemispherical emissivity response, compared to the untreated surface, can be achieved after as little as 140 pulses/spot, with the measured microcavity depth of \( \sim 160 \) \( \mu \)m, see Fig. 3(b). However further increase in the number of pulses to 1400, resulting in the microcavity depth of \( \sim 290 \) \( \mu \)m (Fig. 3(d)), does not yield any significant rise in the emissivity response, and is lower than the response achieved with the in-air processed surface. This can be attributed to the differences in the detailed microgeometry of the structures such as shape of microcones, microcavity apex angle and depth, Fig. 3(b) – 3(e). Earlier reports show that emissivity is highly sensitive to the detailed surface topography for surfaces with roughness exceeding the wavelength of light [32]. In this, so-called geometric region [32], geometrical optics principles are applied to analyze optical interactions and to predict emissivity response. It has been shown that periodical microgrooving not only increases specific surface area but also create favorable geometrical conditions for effective thermal dissipation, with V-shaped grooves performing better than rectangular or hemispherical microstructures by reducing the number of multiple radiation events between adjacent microchannels [33]. The apex angle of the groves also plays an important role in emissivity enhancement. A periodic V-shaped grooves with a 60° apex angle were shown to enhance normal emissivity by a factor of \( \sim 3.3 \). Further seven-fold increase in normal emissivity compared to a smooth surface was demonstrated with a groove angle of 30°, attributed to the increased surface roughness resulting in the increased number of radiation events for the identical measurement conditions, i.e. slit size [34]. On the other hand, presence of an oxide film on the surface affects its optical properties because of reduced interaction of the transmitted electromagnetic waves with electrons bounded to their nuclei in the dielectric oxide layer. Besides the compositional changes of the surface layer, oxidation generally leads to the increase of the surface roughness and interference effects that further enhance surface emissivity [14].

To quantify the effects of surface treatment on the emissivity performance, total hemispherical emissivity in the spectral region from 2.5 to 14 \( \mu \)m (\( \varepsilon_{2.5-14} \)) was calculated from the spectral
hemispherical emissivity data according to Eq. (2):

$$
\varepsilon_{\lambda_1 \rightarrow \lambda_2}(T) = \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda, T)E_b(\lambda, T)d\lambda}{\int_{\lambda_1}^{\lambda_2} E_b(\lambda, T)d\lambda}
$$

(2)

where \( \varepsilon(\lambda, T) \) is the spectral hemispherical emissivity, \( E_b(\lambda, T) \) is the Planck blackbody function.

The results summarized in Table 1 show that the observed emissivity increase is mostly due to the presence of the surface microstructure with less than 2% increase attributed to surface oxidation of AISI 304L stainless steel. Moreover, the laser-assisted microstructure engineering enables to achieve close to a blackbody performance, reaching a record high total emissivity value of 0.975 in the spectral region from 2.5 to 14 \( \mu \)m.

**Table 1. Total hemispherical emissivity performance of 304L steel surfaces in the spectral region from 2.5 to 14 \( \mu \)m.**

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>( \varepsilon_{2.5 \rightarrow 14} )</th>
<th>Laser Structuring Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>Acid pickling</td>
<td>0.704</td>
<td>Air, 1400 pl/s</td>
</tr>
<tr>
<td>( N_2 ) atmosphere</td>
<td>0.722</td>
<td>( N_2 ), 1400 pl/s</td>
</tr>
<tr>
<td>320°C, 7-h oxidation</td>
<td>0.711</td>
<td>( N_2 ), 1400 pl/s</td>
</tr>
<tr>
<td>320°C, 50-h oxidation</td>
<td>0.739</td>
<td>( N_2 ), 1400 pl/s</td>
</tr>
<tr>
<td>320°C, 100-h oxidation</td>
<td>0.738</td>
<td>( N_2 ), 1400 pl/s</td>
</tr>
<tr>
<td>600°C, 6-h oxidation</td>
<td>0.741</td>
<td>( N_2 ), 1400 pl/s</td>
</tr>
<tr>
<td>1 repetition</td>
<td>0.693</td>
<td>( N_2 ), 140 pl/s</td>
</tr>
<tr>
<td>5 repetitions</td>
<td>0.702</td>
<td>( N_2 ), 700 pl/s</td>
</tr>
<tr>
<td>Air atmosphere</td>
<td>0.975</td>
<td>Air, 1400 pl/s</td>
</tr>
</tbody>
</table>

The effect of temperature on total emissivity of the best performing structure, shown in Fig. 4, was evaluated taking into account temperature-induced shifts of the Planck distribution only. The potential discrepancies between the total emissivity and its estimated value, calculated for the experimental data measured in a finite spectral region from 2.5 to 25 \( \mu \)m, were accounted for by calculating the lower and upper theoretical limits Eqs. (3) and (4).

**Fig. 4.** Calculated temperature dependence of total hemispherical emissivity of 304L steel after laser structuring in air (laser fluence of \(~3.6 \text{ J/cm}^2\), scanning speed of 10 mm/s, hatch distance 75 \( \mu \)m, and 1400 pulses/spot). Dashed curves are the upper and lower theoretical limits of total emissivity.
The lower theoretical limit of total emissivity accounts for low spectral emissivity ($\varepsilon(\lambda, T) = 0$) in the unmeasured electromagnetic spectrum (i.e. from $0$ to $\lambda_1$ and from $\lambda_2$ to $\infty$):

$$
\varepsilon_l(T) = \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda, T)E_b(\lambda, T)d\lambda}{\int_{0}^{\infty} E_b(\lambda, T)d\lambda} = \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda, T)E_b(\lambda, T)d\lambda}{\sigma T^4}
$$

(3)

where $\sigma$ is the Stefan–Boltzmann constant, and $T$ is the absolute temperature.

The upper theoretical limit accounts for the blackbody-like spectral emissivity ($\varepsilon(\lambda, T) = 0$) in the unmeasured electromagnetic spectrum:

$$
\varepsilon_u(T) = \frac{\int_{0}^{\lambda_1} E_b(\lambda, T)d\lambda + \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda, T)E_b(\lambda, T)d\lambda + \int_{\lambda_2}^{\infty} E_b(\lambda, T)d\lambda}{\sigma T^4} = f_1 + \frac{\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda, T)E_b(\lambda, T)d\lambda}{\sigma T^4} + f_2
$$

(4)

where $f_1$ and $f_2$ are the blackbody radiation functions, representing the fraction of radiation emitted from blackbody in the wavelength region from 0 to $\lambda_1$ and from $\lambda_2$ to $\infty$ [2].

From Fig. 4, it can be seen that the total emissivity tends to increase with temperature. This accompanied by the decrease of the uncertainty range as the Planck distribution shifts towards shorter wavelengths.

To evaluate the microstructure stability, the in-air processed structure was subjected to thermal aging in air at 320°C for 96 hours. The spectral emissivity performance before and after the thermal aging remains almost identical in the spectral region from 2.5 to 14 µm, as shown in Fig. 5. The decrease of the spectral emissivity in the long-wavelength region can be attributed to minor changes in the surface nanotopography. Overall stability of the emissivity performance in the spectral region from 6 to 11 µm is attributed to the considerable size of microstructures making them less susceptible to surface diffusion at elevated temperatures.

![Fig. 5](image_url)  
**Fig. 5.** Room temperature spectral hemispherical emissivity responses of the laser-structured 304L steel in air before (solid black curve) and after (dotted red curve) thermal aging in air at 320°C for 96 hours.

4. Conclusions

In summary, we demonstrated that ns-laser structuring is an effective method for control and manipulation of the spectral emissivity in a wide spectral region, which can be tailored to a wide range of metal surfaces. Total hemispherical emissivity of 0.97 was achieved on laser-structured 304L steel surfaces. It was found that surface topography has dominant effect on the emissivity performance. Stability of the emissivity performance after thermal aging at 320°C for 96 hours was verified.
Appendix A. Supplementary material

This supplement provides details on the FT-IR spectroscopy, and the scanning electron microscopy of the laser structured surfaces.

Fig. 6. Schematic of the emissivity measurements.

Fig. 7. Surface topographies of the laser-structured surfaces in $N_2$ before and after air oxidation: (a) before oxidation, (b) after 7-h oxidation at 320°C, (c) after 50-h oxidation at 320°C, (d) after 100-h oxidation at 320°C, (e) after 6-h oxidation at 600°C.

Fig. 8. Surface topographies of the laser-structured surfaces in $N_2$: (a) 140 pulses/spot, (b) 700 pulses/spot, (c) 1400 pulses/spot.
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Disclosures

The authors declare no conflicts of interest.

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