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Technical Note

Spectral emissivity of oxidized and roughened metal surfaces

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ABSTRACT

The effects of materials' surface oxidation and roughness on spectral emissivity have been investigated for design improvement and effective thermal management of energy systems. Experiments confirm that both surface oxidation and surface roughness affect spectral emissivity with surface oxidation having a more dominant effect. The surface oxidation layer effect is substantial at low wavelengths, and the affected wavelength range widens as oxidation temperature and time are increased. Increasing surface roughness increases spectral emissivity independent of wavelength. To describe the experimental results, a computational model based on Kirchhoff's Law is used. The dependence of optical constants on oxidation conditions were measured, and included in the computational model. Surface morphological characteristics for the roughened surfaces are described by multiple superimposed cosine function Fourier series. There is good agreement between computational predictions and experimental results.

1. Introduction

In high temperature systems, radiative heat transfer becomes significant because of the fourth power temperature dependence of radiated energy. The key material parameter in radiation heat transfer is emissivity which is defined as the ratio of emissive power of the materials' surface (grey body) to that of an ideal black body. In terms of designing advanced high temperature energy systems, predicting emissivity is important because emissivity is the only variant parameter at given operating conditions and it is strongly affected by surface conditions [1–4]. Understanding emissivity aids not only in design improvement of high temperature systems, but also in effective thermal management of energy systems via noncontact in-situ measurement techniques which use the known or correlated relationships between emittance and physical properties such as oxide layer thickness and temperature [5–8].

Emissivity is a surface phenomenon but depends on physical parameters such as surface temperature and wavelength. So, connecting surface characteristics with physical parameters is required to predict emissivity. In previous study, the parameter defining emissivity modeling has been surface roughness, with surfaces defined as optically smooth or rough based on the ratio of surface roughness to wavelength (R/λ) [9]. For optically smooth surfaces, the characteristics of light propagation should be included with the indices of refraction in Fresnel's equation and Kirchhoff's law [10]. For a sufficiently thick and/or lossy material where transmission is negligible, Kirchhoff's law can be written as follows,

$$\varepsilon(\lambda,\theta,T) = 1 - R(\lambda,\theta,T) \tag{1}$$

where ε is emissivity, R is reflectivity. $\lambda, \theta,$ and T indicate wavelength, incident angle and temperature, respectively. So emissivity can readily be described in terms of optics and reflectivity. As surface roughness becomes larger than the wavelength of light, optical interactions may be conveniently represented using geometric optics.[9,11,12]. On a roughened metal surface, the contact area of incident light reflected on the cavity of the surface will have a major impact on the emissivity value of the roughened surface.

Due to the physical nature of light, emissivity analysis can be approached differently depending on medium characteristics. For instance, metal and metal oxides may be treated differently [10,13–22]. Incident light (electromagnetic waves) consisting of a continuous range of wavelengths will be reflected, transmitted or absorbed at the boundary surface or within the interior of the solid medium. Practically many shiny metals can be approximated to have perfect reflection [11], and most metals have very high absorption coefficients due to unbound electrons within the conductive medium. Theoretically, Drude free-electron theory [23], and the Hagen-Rubens relation [24] developed for long wave length ranges are applied for describing optical phenomena in a metal medium. For metal oxidation, on the other hand, dielectric characteristics of the oxide layer have to be considered. In the oxide layer, transmitted electromagnetic waves will have less

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interaction with electrons bounded to their nuclei, thereby affecting optical properties.

Surface oxide films that form on the metals at high temperature have emissivities different from the original metal surface because of the oxides' dielectric characteristics. Furthermore, oxidation changes not only the composition of the surface but also its structure since oxidation generally leads to rougher surfaces. As discussed previously, a roughened surface induces greater interface contact with incident light which results in less reflection, greater transmission and greater absorption. Therefore, emissivity increases according to Eq. (1).

There has been a number of studies demonstrating the dependency of emissivity on oxidation kinetics [3,5,19–21,25,26]. Brannon and Goldstein [25] described the variation of total normal emittance as a function of oxide thickness on Al-Al_2O_3 and Cu-CuO surfaces and showed that the measured normal emissivity increases as the oxide thickness increases. Greene et al. [26] found that oxidized samples show a significant increase in emissivity over un-oxidized samples but they did not report an explicit pattern in the change of emissivity as a function of oxidation time. Interference due to multiple reflections has been observed for heat-resistant alloys where the oxide layer is very thin [19]. Other studies have also investigated the influence of surface oxide layer on spectral emissivity as a function of wavelength [3,16,21]. Although these previous studies provide a background for the development of new models and correlations for specific materials, fundamental and practical approach is still required to fully explain emissivity changes due to metal oxidation.

In this study, spectral emissivities of metal oxidation of iron-based alloys are described with a computational simulation based on Kirchhoff's law and measured optical constants. In the computational model, the effects of surface roughness and oxidation are included. The results are expected to improve the predictive capabilities of emissivity of surfaces with various roughnesses and with surface oxide layers that would be expected in energy applications, while also enhancing the fundamental understanding of emissivity and radiation heat transfer.

2. Materials and method

In this study, experimentally measured spectral emissivities of SA508 steel are analyzed to observe the effect of oxide layer

Table 1
Sample matrix.

Surface condition		Sample No.	Roughness, R_a (μm)
Mirror polished	–	S1	0.011
Mirror polished + air oxidation	350 °C, 10 h exposed	S2	0.008
	350 °C, 100 h exposed	S3	0.016
	350 °C, 200 h exposed	S4	0.016
	300 C, 100 h exposed	S5	0.011
	600 °C, 5 h exposed	S6	0.6
Roughened surface	320-grit finished	S7	0.01
	Shot-peening finished	S8	1.86

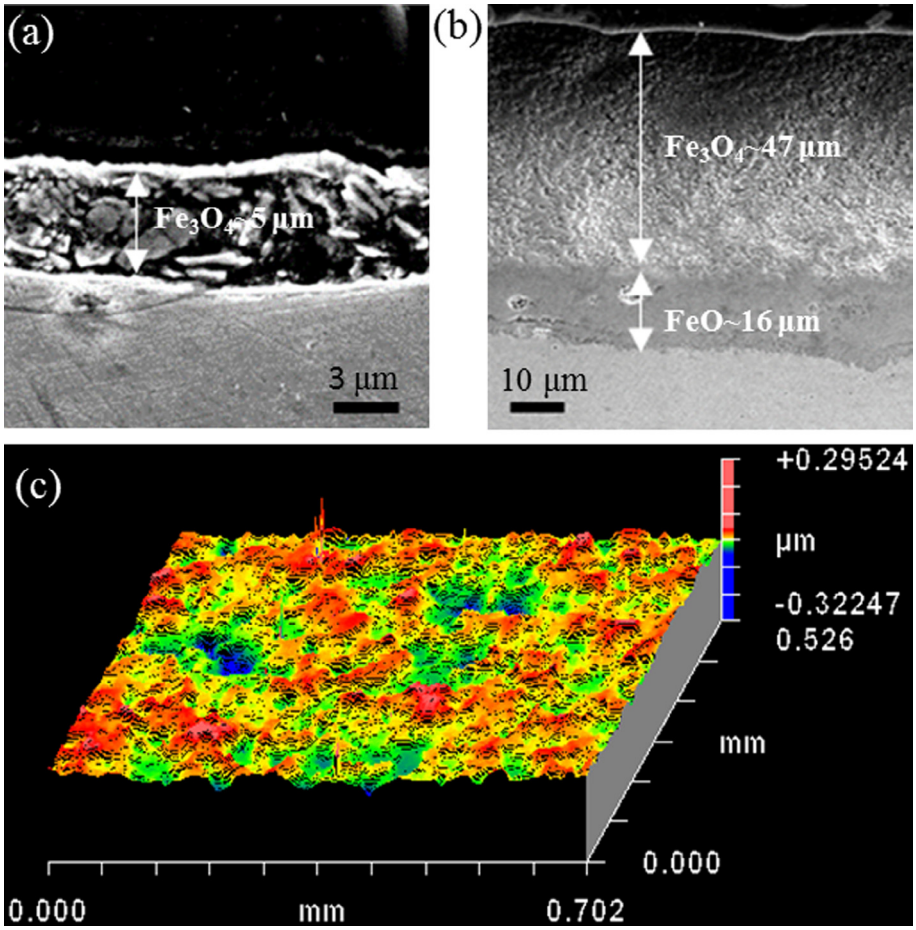

Fig. 1. The characterized samples used in this study: SEM cross section images of SA508 oxidized samples (a) for 10 h at 350 °C, and (b) for 5 h at 600 °C, and (c) Profilometer image of the mirror-polished SA508 surface.

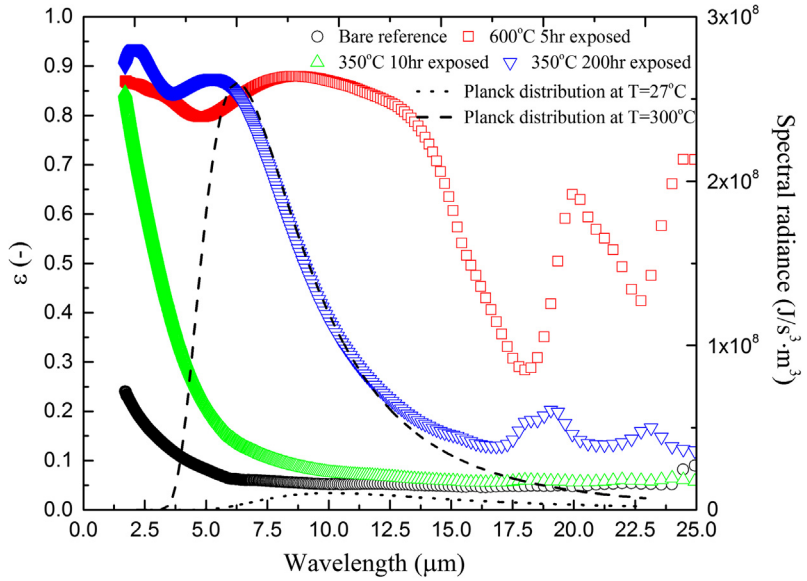

Fig. 2. Measured spectral emittance and Planck distribution at room temperature and 300 °C.

growth on the emissivity of SA508 steel samples. The samples (25.4-mm wide squares of 1.5-mm thickness) were mirror-polished as initial reference samples before being subjected to either air oxidation or roughening. To explore the effect of oxidation, some SA508 samples were exposed to high temperature air (300, 350, and 600 °C) in a preheated General Signal Lindberg Box Furnace set to ambient pressure for different exposure times and temperatures (10–200 h). The oxidation temperatures were determined based on application of SA508 in power plants [27] and heat treatment temperatures for iron [28]. SEM examination confirmed that the thicker oxide layer is formed on the sample exposed at 600 °C for 5 h compared to the sample exposed at 350 °C for 10 h, as shown in Fig. 1. On the mildly oxidized sample (350 °C for 10 h) a magnetite oxide layer (Fe_3O_4) ~5 μm in thickness formed, whereas for the heavily oxidized sample (600 °C for 5 h), the oxide layer consisted of ~47 μm thick outer magnetite oxide layer and ~16 μm thick inner wüstite (FeO) oxide layer. For the study of surface roughness, shot peening and 320-grit SiC papers were used to increase roughness, resulting in an average roughness of 1.86 μm on the shot-peened surface which is substantially larger than the roughness (0.01 μm) of mirror-polished reference and 320-grit finished samples. The formation of an oxide layer by thermal exposure increased surface roughness, and the roughness (0.6 μm) of the heavily oxidized case (600 °C for 5 h) was between that of the shot-peened surface and the mirror polished surface. Table 1 summarizes the roughness of samples used in this study.

Spectral emissivity was measured with a SOC-100 Hemispherical Directional Reflectometer (HDR) with Fourier Transform Infrared Spectroscopy (FTIR) managed by the Concentrated Solar Power Group at the National Renewable Energy Laboratory in Golden, CO. Measurements could be taken at several separate angles and, if desired, at two light polarizations. For this study, incident angle was fixed at 10°, near normal incidence. Based on Section 3.2.1.3 of Howell's text [29] where normal emissivity is compared to hemispherical emissivity, we assumed that near-normal emissivity should reasonably resemble hemispherical emissivity. The measurement spot size of this device was approx-

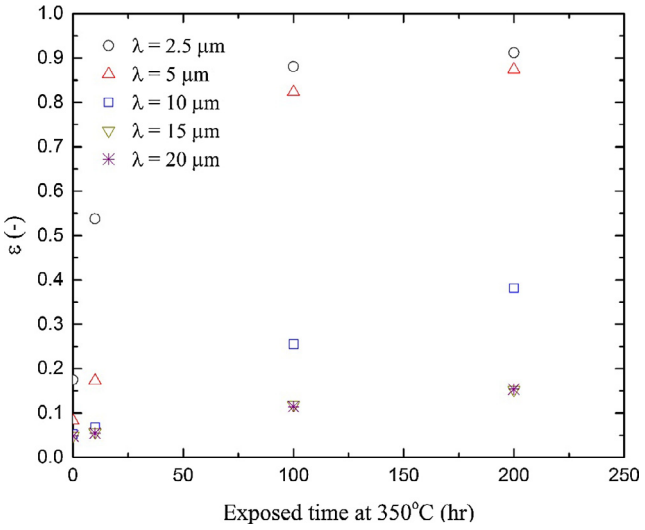

Fig. 3. Measured spectral emittance of oxidized SA508 at 350 °C for different exposed time as a function of exposed time.

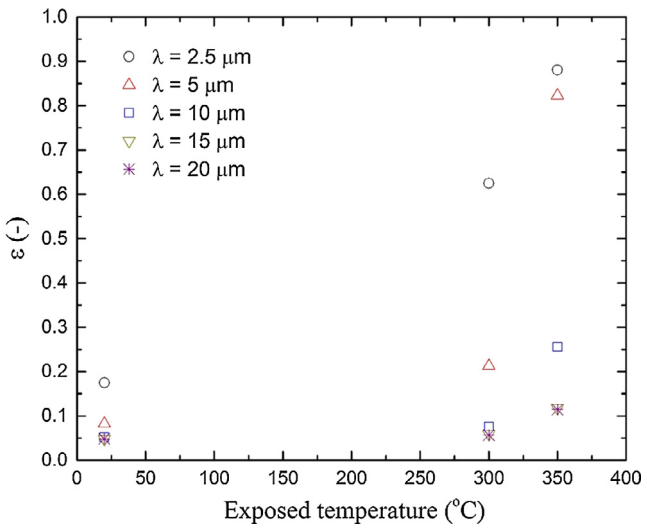

Fig. 4. Measured spectral emittance of oxidized SA508 at different temperature for 100 h as a function of temperature.

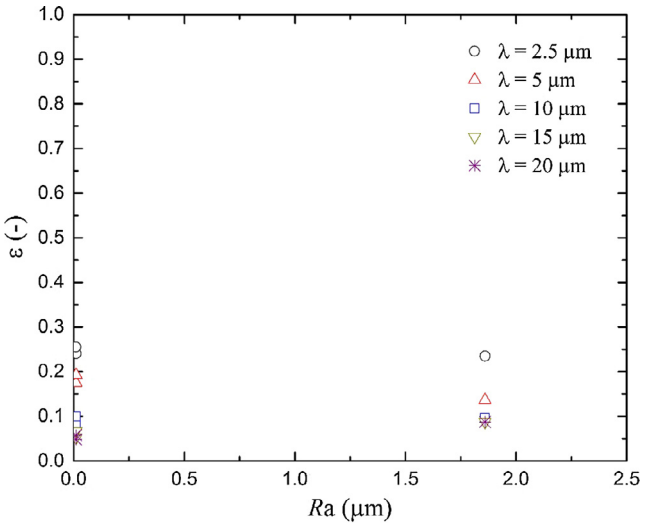

Fig. 5. Measured spectral emittance of differently finished SA508 as a function of surface roughness.

imately 15 mm in diameter. The spectral range of the device ranged from 1.7 to 25.4 μm, which well-represents the domain of interest based on the Planck spectral energy distribution (Fig. 2). A detailed description of the procedure for this experiment is included in King [30], which reported the spectral emissivities used in this study for predicting total directional and hemispherical emissivities of each samples. In this study, we analyzed the spectral characteristics of the experimental data with the surface effects.

3. Results

Figs. 3and 4 shows a comparison between spectral emissivity of SA508 oxidized at different oxidation times and temperatures. Spectral emissivity of oxidized SA508 is higher than the unoxidized reference sample, particularly at low wavelengths. This wavelength range affected by oxidation gradually widens as exposure time increases. This indicates that the influence of the oxide layer on the spectral emissivity of the material spans longer wavelengths as the oxide layer grows thicker. The substantial change at shorter wavelengths, when the wavelength range is on the order of oxide layer thickness, has been reported on other metals and oxide layers [17]. The sample oxidized at 600 °C for 5 h (sample S6) is the most affected by oxidation layer in terms of spectral emissivity (Fig. 2). At shorter wavelengths, the spectral emissivity of sample (denoted by S6) is higher than the unoxidized sample, and even in the higher wavelength range there is higher spectral emissivity than that of the unoxidized sample. The roughness effect on spectral emissivity was explored by comparing the values for a mirror polished reference and other surface roughnesses as shown in Fig. 5. The 320-grit finished sample shows similar emissivity as mirror polished samples due to the similarities in surface roughness. The shot peened sample shows slight increases in spectral emissivity but the roughness effect is not significant compared to the oxidation layer effect.

We believe that the roughness effect is mainly attributed to more interface area on the roughened surface with the same optical constants but the oxidation effect is associated with different optical constants from the oxide layer. In this study, to describe the spectral emissivity on oxidized surfaces, we measured the optical constants for each surface condition, and these constants are implemented in our code.

4. Analysis and discussion

4.1. Surface characterization with optical properties

Refractive index (n) and extinction coefficient (k) were measured by a J. A. Woollham Mark II IR-VASE Ellipsometer. During measurements, the incident light separates into rays of different path lengths, which reflect from top and bottom interfaces of the film. The resulting phase differences produce constructive or destructive interference. Although the ellipsometer does have limitations for very rough surfaces and thick films, the roughness and film thickness of all samples evaluated within this study were within the acceptable range of the measurement method.

As shown in Fig. 6, surface oxidation affects both refractive index and extinction coefficient. It was found that the oxidized surfaces had decreased refractive indices compared to those of the unoxidized surfaces. This is supported by the conceptual behaviour of electromagnetic waves propagating through media having bound electrons versus propagation through media having unbound electrons. It can be seen that of the real and imaginary components of the refractive index, the real component is the most sensitive to surface oxidation. Even for the sample of shortest

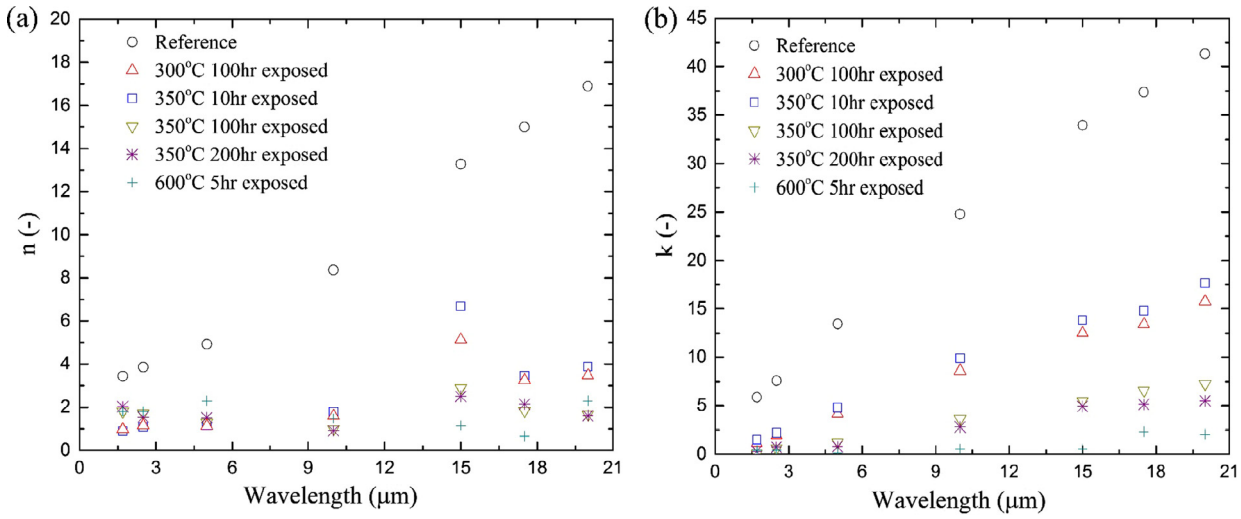

Fig. 6. Measured spectral optical constants: (a) refractive index and (b) distinction coefficient.

exposure time (10 h), there is sharp decrease in refractive index, and the difference between the 10-h exposure case and 200-h exposure case at 350 °C is not significant. In other words, even a thin oxide layer can affect refractive index, and the refractive indices on oxidized SA508 samples will be similar whether the oxidation layer is thick or thin in the range examined in this study. There is a decrease in extinction coefficient on oxidized samples as well. On the contrary, the extinction coefficient shows gradual change as oxidation time and temperature increase. While n remained relatively constant after initial oxidation, k continued to vary for different exposure conditions. We believe that the gradual change in extinction coefficient would explain the difference of spectral emissivity on samples oxidized under different conditions. The effect of oxidation on optical constants is included in our computational model.

4.2. Computational model for spectral emissivity

Here, we predict spectral emissivity using a geometric optics approximation model developed in our previous work [31]. Fig. 7 provides a basic schematic of the model. The required inputs of the model are the optical constants (n, k) of the surface and an artificial roughness parameter, Ψ. The optical constants used in the model were obtained by ellipsometry measurements for each sample while the Ψ value was selected by interpolating the Ψ using our profilometry data and previously observed relationships between Ψ and roughness. This procedure follows the approach proposed by Iuchi et al. [10] where effective optical constants are taken from ellipsometry measurements and used as inputs in a physical model to predict emissivity.

The model was also used to quickly check the relationship between directional emissivity and the expected hemispherical emissivity. According to our model, across all pairs of optical constants that were measured in this study where n > 1, emissivity at 10° incidence is expected to be within 20% of the hemispherical emissivity. This accounts for over 90% of the optical constant pairs measured in this study and so measurement at 10° incidence should provide good resemblance to hemispherical emissivity.

4.3. Discussion

The comparison shown in Fig. 8 indicates good agreement between experimental and simulation results. The results indicate that the computational model based on Kirchhoff's law can effectively describe spectral emissivity on sufficiently oxidized surfaces with appropriate optical constant inputs. The model effectively mimics the experimentally measured spectral emissivity. In metals (electrically conducting material), the free electrons of the metal can move freely, which induces large extinction coefficients and phase velocity reduction of wave propagated in the metal. In the Lorentz model, for metals, electrons and their nuclei may be treated as simple harmonic oscillators with zero restoring force [23,24]. However, in oxide layers (dielectric material), the binding force between electrons and their respective nuclei, should be considered as a restoring force, which results in a smaller refractive index and extinction coefficient than the un-oxidized metal sur-

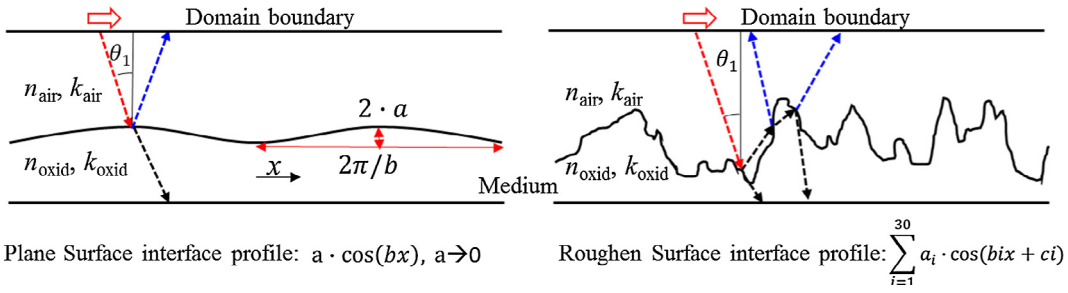

Fig. 7. Schematic of computational refractive model used in this study for different surface roughness.

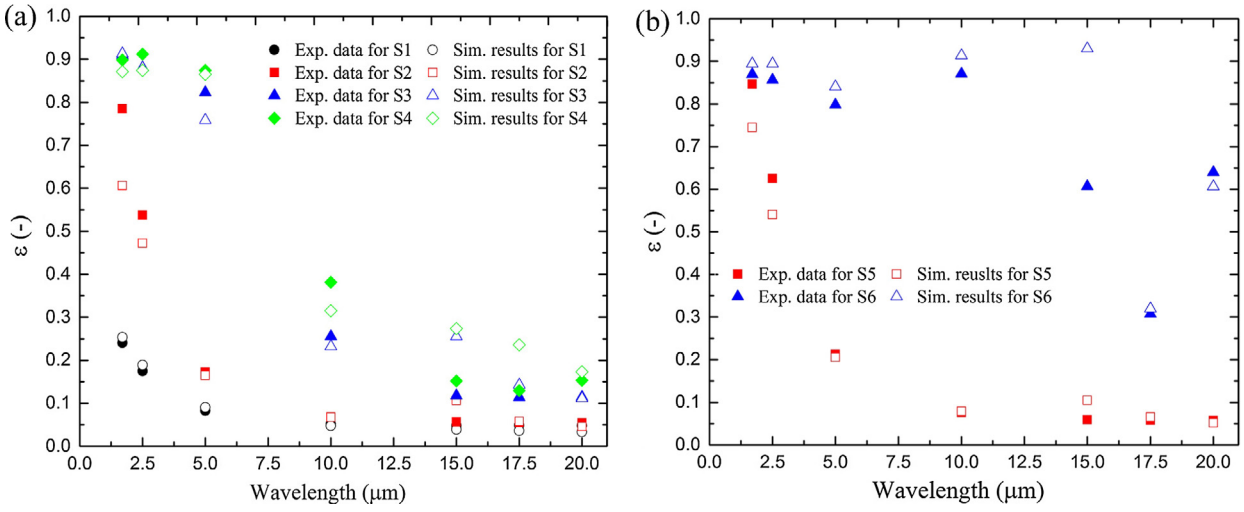

Fig. 8. Comparison of experimentally measured spectral emissivity and predicted emissivity by the computational model for (a) mirror polished reference and oxidized samples at 350 °C and (b) oxidized samples at 300 °C and 600 °C.

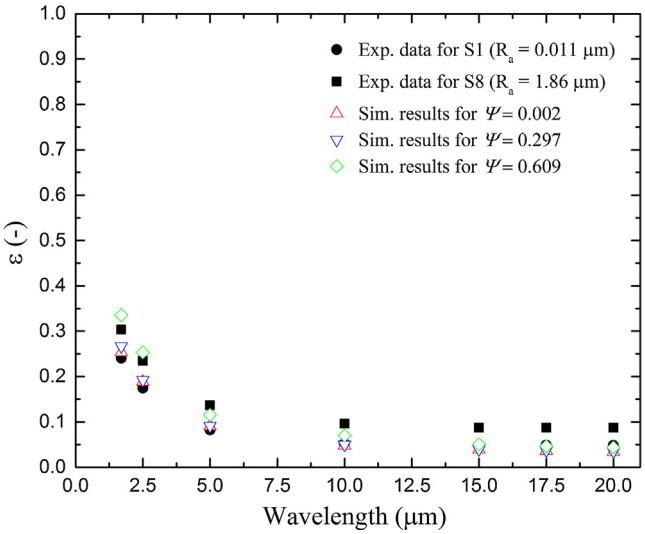

Fig. 9. Comparison of experimentally measured spectral emissivity and predicted emissivity by the computational model for roughened surfaces.

face. In our computational model, optical constants are represented by the experimentally measured optical constants for the oxidized surfaces. The bare reference SA508 surface is expected to have an exceedingly thin native oxide layer due to exposure to air environment even at room temperature. Therefore, the optical characteristics of the bare reference are mainly attributed to the pure metal substrate. However, as the oxide layer thickness increases due to thermal exposure, the proportion of free electrons decreases, consequently reducing optical constant values. The range of wavelength in which emissivity is affected by oxidation is expected to be related to the effective penetration length scale of the wave on the oxidation layer. Even for the heavily oxidized sample (exposed at 600 °C for 5 h) where a multi-layered oxide formed, our simulation model could effectively predict experimentally measured spectral emissivity.

On roughened surfaces, no optical constant change occurs, but the roughened surfaces lead to more contact of incident light reflected on the surface in the model, which can explain spectral emissivity increases on the roughened surfaces (Fig. 9). In the model, the surface profile is superimposed by using Fourier series with selected cosine functions for target roughness which could reproduce trends in emittance phenomena on the roughened surfaces. In the simulation, we can confirm that the roughness effect on spectral emissivity is not significant compared to the effect of oxidation in the range investigated in this study.

5. Conclusions

Experimental and theoretical investigations were conducted to better understand emittance phenomena on oxidized and roughened surfaces. Emissivity was observed to strongly depend on the thickness of the oxide layer. This effect is significant at shorter wavelengths, even under mild oxidation conditions, and the affected wavelength range widens as the oxide layer thickness increases. This effect is attributed to the vastly different optical constants of the oxide layer compared to the base metal. The effect of surface roughness on emissivity was lower than the effect of surface oxidation on spectral emissivities. There was excellent agreement between experimental values and those predicted by our computational model based on Kirchhoff's law. In the computational model, refraction, reflection and absorption of radiant energy in the oxide layer were simulated with measured spectral optical constants. The emissivity of roughened surfaces is effectively described using random surface profile generation via a Fourier series having multiple cosine functions. Consequently, the model predicts the emittance phenomena on surfaces roughened by oxidation.

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Conflict of interest

The authors declare that they have no conflict of interests for financial.

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