Pyrometry of Materials With Changing, Spectrally-Dependent Emissivity – Solid & Liquid Metals

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Abstract. Spectropyrometers have been available for fifteen years and the large volume of data collected has confirmed that emissivity is best described as a property of a sample's condition rather than a property of a material; any conventional pyrometer that depends on assumed behavior or tabulated values of an emissivity is unlikely to be accurate. The advanced spectropyrometric technique in radiation thermometry discussed here uses hundreds of narrow wavebands over broad spectral bandwidths to accurately measure temperatures despite initially unknown and constantly changing emissivity. Metals and especially liquid metals are an extreme example; these exhibit substantial changes in both the magnitude and the spectral dependence of emissivity with time and processing. The spectropyrometer determines emissivity behavior from the data collected for every measurement, displaying and saving the thermal spectra as well as temperature, tolerance, and emissivity. Extensive testing carried out by third-party users comparing the results of multi-wavelength spectropyrometers with contact techniques on liquid metal targets shows that properly-used thermocouples agree with spectropyrometers to within a few tenths of a percent of the measured values.

Keywords: SpectroPyrometer, pyrometer, pyrometry, radiation thermometry, emissivity, temperature.

INTRODUCTION

A multi-wavelength spectropyrometer using a grating to disperse the spectrum into hundreds of narrow wavebands has been described elsewhere.[1,2,3] This spectropyrometer determines and reports the temperature without prior knowledge of the emissivity. In addition to temperature, the instrument reports a tolerance for each measurement and the emissivity as modified by the environment between pyrometer lens and target. The spectropyrometer saves the raw and corrected thermal spectra and the spectral emissivity for each measurement. The spectropyrometer has been commercially available since 1997, and a great deal of data has been generated and analyzed. These data confirm that emissivity is extremely variable, changing with composition, crystal structure, surface morphology, phase, and temperature; furthermore, metals usually exhibit a spectral dependence to emissivity that also changes with these characteristics. If the metal is liquid, turbulence and ever-changing target material produce additional variability. Samples of nominally the same material processed in nominally the same way have been observed to have very different emissivities. The unavoidable consequence of this variability in emissivity is that temperature measurements that depend on tabulated emissivity values have a high uncertainty. Results include poor product quality, reduced productivity, and wasted energy.

EMISSIVITY CHANGING WITH WAVELENGTH AND PHYSICAL ATTRIBUTES

Metals, the largest category of materials on the periodic table, are the most difficult for conventional pyrometry. The emissivities reported for metals overwhelmingly vary with wavelength. Almost all the published data for metallic emissivity is for the solid state. An example is shown Figure 1, which clearly shows that there is significant variation in the value of emissivity and that all the data have a spectral dependence.
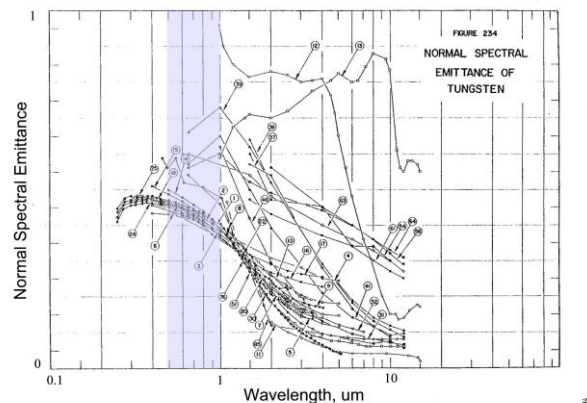

FIGURE 1. Emissivity of tungsten metal[4], a strong function of wavelength. The common pyrometry area is highlighted.

Surface, Crystal Structure, Temperature - Solids

Spectropyrometers were used to measure both the temperature as a function of current and the emissivity of new and old tungsten filament lamps. Figures 2 and 3 show results for one lamp at both ages. Temperature vs. current data falls on the same line for both ages (Figure 2), but the spectral dependence of emissivity changes with age (Figure 3). This variability in emissivity is attributable to changes in filament surface morphology due to the halogen cycle: tungsten that evaporates from the filament and deposits on the bulb is scavenged by the halogen gas and re-deposited on the filament. The bulk property resistivity governing temperature vs. current is unchanged.
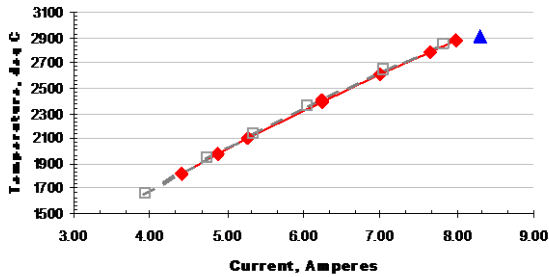

FIGURE 2. Same tungsten halogen lamp at different ages: new (filled diamonds), old (open squares). Nominal design temperature 2915°C (3300K color temperature) at 8.3A (100 W) is shown in a triangle.
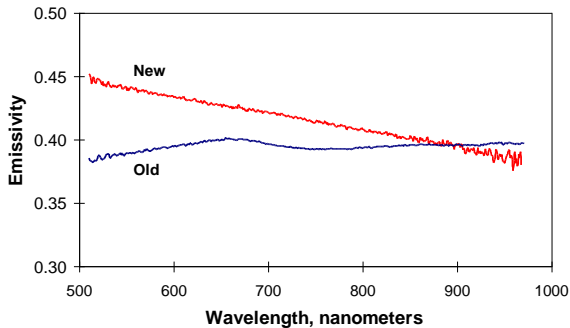

FIGURE 3. Spectral emissivity of a tungsten filament lamp when new and old. New emissivity is spectrally dependent; old is practically gray.

An example of emissivity changing with temperature and structure can be seen Figure 4. This material is a metallic substrate with a metallic anti-corrosion coating. The two metals alloy at the surface and adopt alternative crystal structures depending upon processing temperatures. The emissivity is relatively insensitive to temperature in the 465 - 490°C range, but shows increasing dependence as the temperature decreases. Below 440°C the crystal structure of the surface material abruptly changes and the emissivity drops sharply.
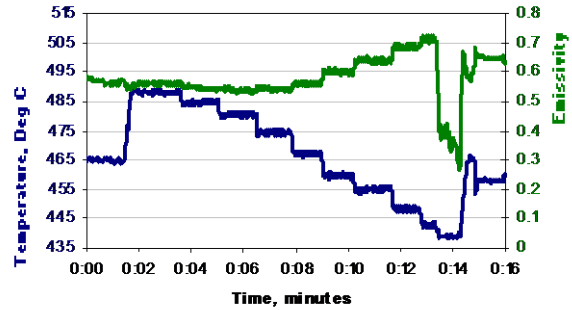

FIGURE 4. Upper trace is emissivity; lower trace is temperature.

Phase, Surface (Turbulence) - Liquids And Solids

Inductively heated investment casting operations are an excellent source of thermal data for liquid metals. The charge is loaded as a solid and is rapidly melted, heated to a setpoint and held briefly, then poured. Metals most commonly observed are nickel alloys, stainless steels, and titanium. Historically, the most common measurement technique is immersion thermocouples. Conventional pyrometers have also been applied, as in the following case.

Spectropyrometers and Conventional Pyrometers

A spectropyrometer was installed on an induction-heated vacuum investment casting furnace melting nickel superalloys. For a first effort, the operator in-creased and decreased the power settings manually several times, then allowed the sample to cool uninter-rupted. The spectropyrometer's log recording tem-perature and emissivity for this exercise is plotted in Figure 5. This shows the material is solid initially with an emissivity of around 0.58. At 0:30 hours it is melted rapidly; the emissivity decreases more than 60%, from 0.57 to 0.22 in the change from solid to liquid state. Several changes of power follow; at each power increase, there is a corresponding abrupt, transient increase in emissivity. These range from 5 to 65%, depending on the magnitude of the power in-crease. These spikes of emissivity result from to the violent stirring of the melt by the inductive electromagnetic pulse that accompanies the power increase. The surface of the melt is disturbed by the stirring and the resulting rough surface has a higher emissivity. After each power increase the melt returns to the previous behavior and the emissivity value
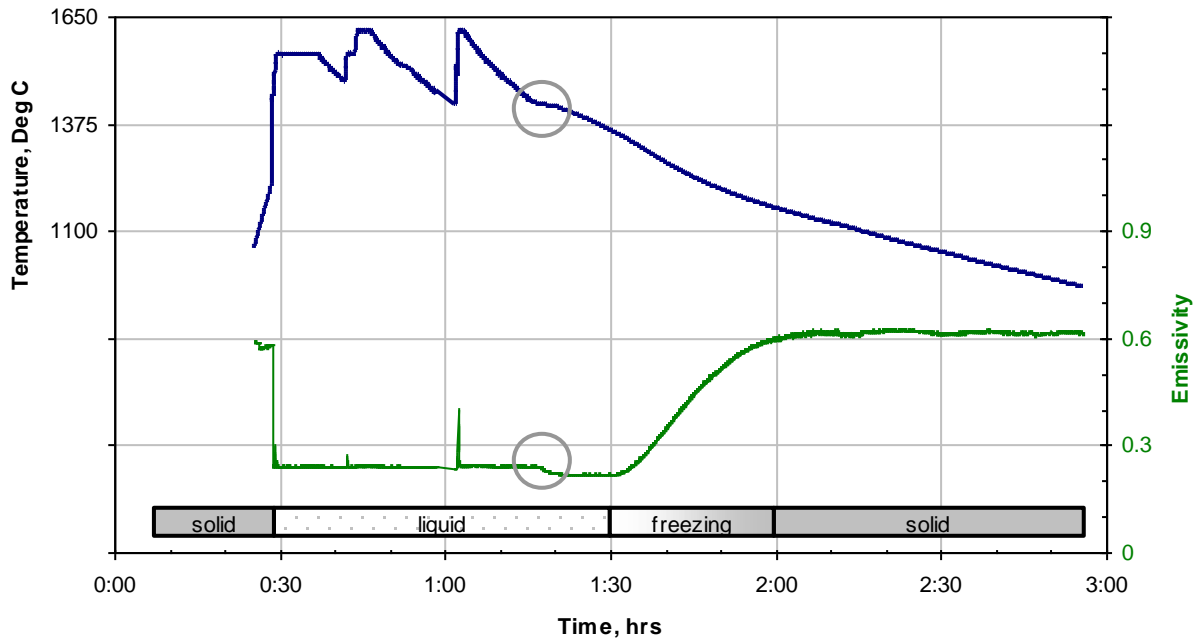
FIGURE 5. Emissivity changes with phase, turbulence, and composition. The top trace is temperature; lower is emissivity.

settles back. With no external influences at 1:18 hours a 10% decrease in emissivity is seen (circled in both traces). Temperature, which had been decreasing to this point, holds roughly steady for the duration of the emissivity change, and then continues its descent when emissivity reaches its new value. The operator suggested that this was a loss of alloying material due to evaporation, as it is known to this industry that keeping the melt at high temperature too long changes its composition. As the material cooled to 1337°C it began a slushy transition to a solid, which was completed around 1150°. The emissivity stabilized at about 0.61, an increase of 5% over the starting emissivity in the solid state.

The turbulence effect on emissivity is highlighted in Figure 6. This shows several melt cycles, four with a conventional pyrometer controlling and four with a spectropyrometer controlling. Each cycle consists of a controlled ramp to a setpoint followed by a hold there. Both sets of data were recorded by the spectropyrometer. The cycles controlled by a conventional pyrometer show a much higher ultimate temperature, although the setpoint was the same. This results from the emissivity variation between alloys; for nickel superalloys, liquid emissivities from about 0.15 to 0.40 have been observed but the conventional pyrometers are set to an average value.

Note the extreme spikiness of emissivity for the heating ramp of the cycles controlled by a

conventional pyrometer. This is due to the inductive electromagnetic pulse at each power increase. The pulse perturbs the melt violently, increasing the emissivity through surface roughness, which is interpreted by the conventional pyrometer as an over-temperature, and the controller in turn removes power. The melt quiets on power removal and the emissivity is reduced by the surface smoothing. The conventional pyrometer interprets this as an under-temperature, and attempts to catch up by applying power. This again perturbs the melt surface and the power on-off cycle repeats throughout the ramp. Even during the hold phase of the cycles there is enough turbulence for the high temperature to vary from cycle
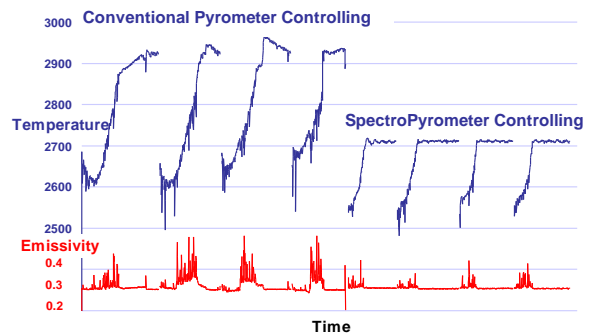

FIGURE 6. Four melt cycles controlled by a conventional pyrometer followed by four cycles controlled by a spectropyrometer. Emissivity is graphed on the lower traces; temperatures on the upper.

to cycle. Contrast this with the melt cycles under spectropyrometer control. There is much less turbulence during the heating ramp because there is no confusion between increased emissivity and increased temperature causing the power supply to turn off and on. The hold portions of these cycles show a repeatable temperature and constant emissivity.

Spectropyrometers and Thermocouples in Vacuum

The spectropyrometer's log for a single cycle from a different foundry illustrates that the melt is quite uniform in temperature (Figure 7). This is associated with inductively heated vacuum investment casting, where the power supply and load are very well matched. The graph below shows the instantaneous temperatures varying only ±3.0°C. The tolerance is 2.8°C throughout.
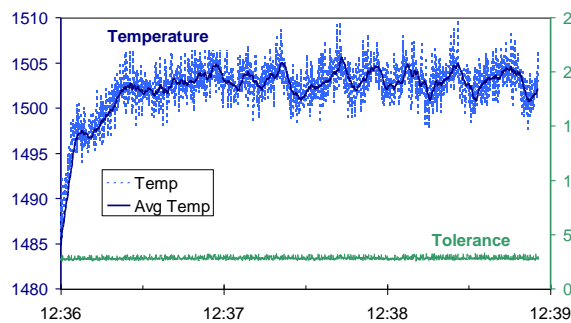

FIGURE 7. Instantaneous and average temperatures for an inductively-heated melt cycle on the left axis; tolerance on the right.

Before adopting spectropyrometers, the foundry of Figure 7 used thermocouples (t/c) for temperature measurement. Their technique for using the t/c was exemplary: t/cs were automatically (therefore reproducibly) immersed to 2/3 the sheath length in the melt for about two minutes, or 20% of a complete melt cycle of 10 minutes. In one month of careful comparison over 125 casting cycles, spectropyrometer and t/c measurements had an average difference of 2.2°C with a standard deviation of 2.8° at an average melt temperature of 1500°C[6]. This agreement is better than the combined uncertainty of the two measurements and is therefore considered exact agreement.

The liquid emissivity at a central wavelength (800 nm) was then tabulated for eleven different nickel superalloys; 99.8% of the values fell between 0.16 and 0.40. This large range would cause huge errors in conventional pyrometers as discussed for the ultimate temperatures in Figure 6. The emissivity of all liquid samples exhibited spectral dependence, which was itself seen to vary within each melt in random fashion: Figure 8 shows this in traces two minutes apart.
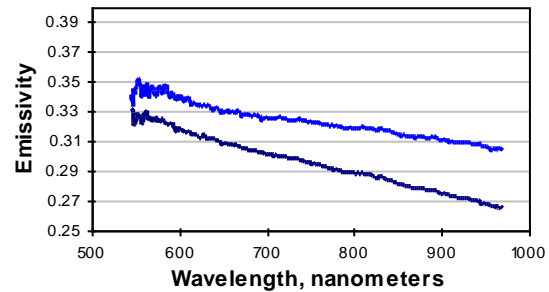

FIGURE 8. Two spectral emissivities measured 2 minutes apart within the same Ni superalloy melt. The temperature for the upper trace was 1468.8°C, for the lower 1475.4°C. Conventional ratio pyrometers uncorrected for the changing spectral emissivity would have returned 1501° and 1538°C, respectively.

This behavior, emissivity with different magnitudes and spectral dependency, is not limited to nickel superalloys. Data from a pour stream from a titanium vacuum arc remelting furnace showed two different emissivities only a few seconds apart (Figure 9).
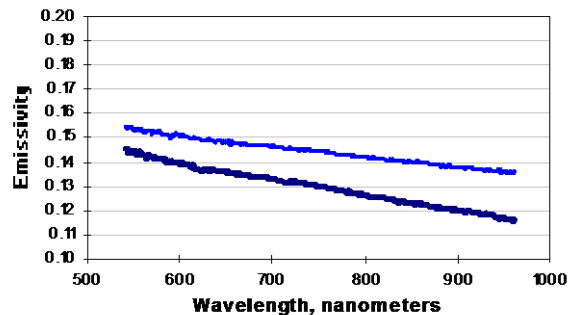

FIGURE 9. Spectral emissivity traces collected at 0.1 and 4.9 seconds from a Ti pour stream. Temperatures are 1659 and 1669°C; conventional ratio pyrometers would have returned 1700 and 1752°C, respectively.

When examining the spectropyrometer log from the pour, the operator spotted an anomaly in both temperature and emissivity, shown in Figure 10.
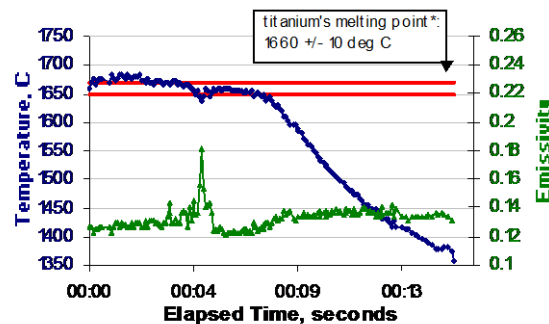

FIGURE 10. Titanium pour stream of six-second duration; remainder is cool-down of Ti frozen on the pour spout. The anomaly at 4.5 seconds was identified as a bolus of semi-solid material.

At 4.5 seconds: temperature decreased below the reported melting range and emissivity spiked. When the video for the event was examined, the operator identified a semi-solid bolus of material in the pour stream at that time stamp[7]. As has been seen in nickel, the solid phase exhibits a higher emissivity.

Not all foundries have such good thermocouple technique as the foundry whose data is shown in Figure 7. The data shown in Figure 11 was also collected in a foundry melting nickel superalloys in vacuum, but the practice there was to immerse the thermocouple only 25 mm, or about 25% of the length of the thermocouple sheath. The type B thermocouple was double-sheathed, with a metal-ceramic outer and alumina inner sheath, and immersed for one minute. This protocol was intended to maximize the life of the expensive thermocouples and sheaths. During initial testing a 40 - 45°C difference was seen between the t/c and the spectropyrometer, with the spectropyrometer reading higher. When the immersion depth and time were increased the difference between the two became smaller, until at 5 minutes the two agreed within their respective accuracies. Figure 11 shows this sequence. Afterwards, a sample of each of the two thermocouple sheaths was obtained and an expert was asked to calculate any temperature difference expected from the materials and protocols used. A 50°C offset was calculated, agreeing with observation[8].
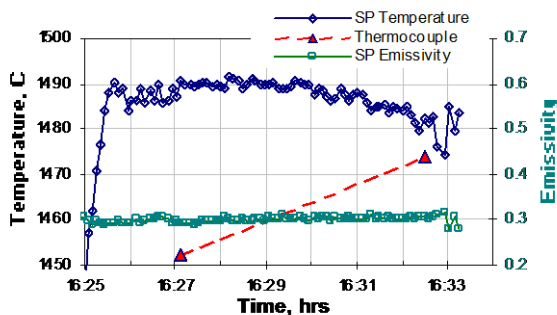

FIGURE 11. Thermocouple remained immersed between the two measurements contrary to prior practice of one-minute immersion at this foundry. Spectropyrometer tolerance was 2.9°C or 0.2%; t/c accuracy taken at 0.3% or 4.5°C. For the t/c measurement after five minutes of immersion the two methods agreed to within these limits.

Spectropyrometers and Thermocouples in Air

Vacuum foundries tend to immerse t/cs more reproducibly since they must have an automated immersing mechanism within the vacuum structure. Foundries that melt in air often use manual immersion which is problematic. Air melts are not as uniform as vacuum melts because there is less electromagnetic stirring. The reason is that the charges tend to vary more in weight and so the power supply and load are not as well matched. Reproducibility of the temperature measurement depends upon the positioning of the t/c. Some operators can achieve reproducible results and others cannot. Two operators were observed by a consultant with long experience in the investment casting industry. Figure 12 shows data from an air-melting foundry furnace controlled by Operator One. The consultant's analysis[9] was that this operator used good technique in both placing the thermocouple reproducibly and controlling the melt in general.
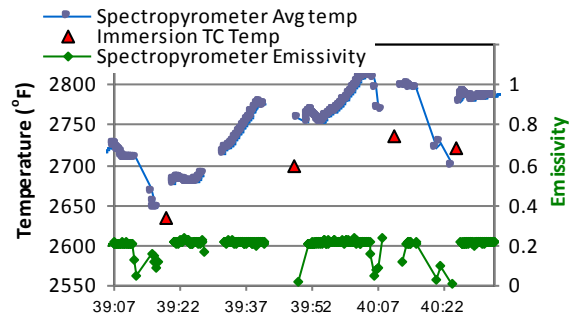

FIGURE 12. Operator One, spectropyrometer and t/c comparison for an induction heated air melt. Upper trace is temperature, lower is emissivity. The triangles show the t/c results.

Spectropyrometer data for this melt, and this operator in general, show a very constant emissivity magnitude and spectral dependence other than the times when the melt is disturbed for the t/c measurement. Temperatures change smoothly and achieve the casting point with little oscillation. From the time the operator began making t/c measurements to casting was just over a minute.

While the reproducibility of the t/c with respect to the spectropyrometer is good, there is the systematic offset, here 57°F, to consider. Inspection of the graph shows the entire interruption for thermocouple measurement is on the order of 8 − 10 seconds. The thermocouple measuring system incorporates a fast-read thermocouple head and integrated electronics which turn off the measuring function when some set of conditions is reached. It is not clear that the t/c equilibrates to the melt temperature. It has already been shown that long, deep immersion of the t/c is required for t/c measurements to agree with spectropyrometers (reference 8 &, Figure 11). Therefore it is not possible to determine whether failure of the t/c to equilibrate or a gradient in the melt with depth is the cause of the offset.

The reproducibility results were different for Operator Two, as can be seen in Figure 13. The consultant's analysis[9] was that this operator used poor technique. The temperature traces show rapid

variations; even the emissivity is affected as the melt is violently stirred by power changes and t/c manipulation. The offset and standard deviation are larger. In comparing the two operators, One achieves an average offset of -57°F/31°C with a standard deviation of 9°F/4°C; Two manages an offset of -67°F/42°C with a standard deviation of 27°F/15°C. Clearly the operator has a large effect on the t/c temperature measurement and its reproducibility.
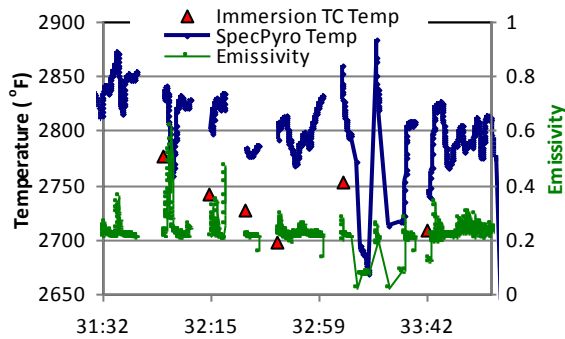

FIGURE 13. Operator Two, spectropyrometer and t/c comparison for an induction heated air melt. Upper trace is temperature, lower is emissivity; triangles are t/c results. The temperature shows much more variation than Figure 12.

Air melts with in-vessel refining present an added challenge to pyrometry. Refining additives are sprinkled as powders over the melt and either burn or form a slag. Despite deslagging, there is leftover slag on the melt surface. The emissivity of the metal has a spectral dependence; that of the slag does not. Because the slag is floating on an inductively-stirred surface, the target can change rapidly from metal to slag between one measurement and the next. Figure 14 shows the emissivity for two successive data points, one colorful, one gray, with temperatures within 2.4°C of each other: 1591 and 1593.4°C. If the colorful spectra had not been detected and corrected for by the spectropyrometer, the temperature returned for that point would have been 35° higher: 1629°C.
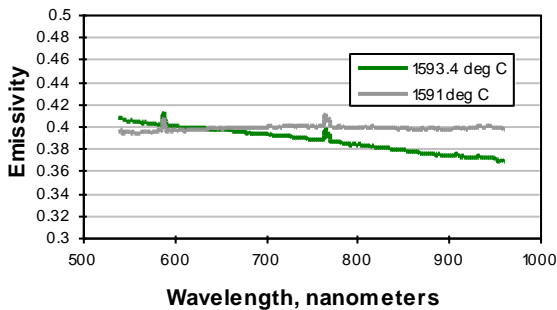

Figure 14. Emissivity for two successive measurements, one spectrally dependent, one gray.

SUMMARY

Emissivity is extremely variable; it varies with material composition, crystalline structure, phase, surface morphology, temperature, and wavelength. Metals add spectral dependence of emissivity, and liquid metals exhibit huge emissivity changes with surface structure due to turbulence. Further, all of these are a strong function of time, where successive measurements often encounter emissivities that are very different. Any technique that relies on previously measured values of emissivity for temperature measurement will be inaccurate. For radiation thermometry to measure temperature accurately, emissivity must be addressed during each measurement. Thermocouples are the de facto standard for liquid metal temperature measurements; it has been shown that where the temperature of the target is uniform and the thermocouple technique is good, thermocouples and spectropyrometers will agree exactly.

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