Temperature-dependent reflectance of copper with different surface conditions measured at 1064 nm

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Abstract

In order to fully understand and eventually overcome the instabilities in laser welding of copper using 1064 nm wavelength lasers, it is important to get a deeper understanding about the interaction of the incident beam with the copper surface during the process. One of the main parameters determining this behavior is the temperature-dependent absorptance. However, the existing datasets only show little consistency between the different sources, do often not include the important absorptance step at melt temperature, or they are only calculated. This article thus presents our experimental approach to measure the reflectance of electro tough pitch copper (Cu-ETP) from room temperature until beyond the melting point with an integrating sphere setup. The setup was developed with particular attention to measurement accuracy up to high temperatures. We measured the reflectance using a 1064 nm laser under an incident angle of 12° for four different sample groups, which are untreated copper as received from the supplier, mechanically polished copper, copper that we annealed in a nitrogen atmosphere for oxide reduction and copper that had resolidified after melting in nitrogen atmosphere. The measurement results reveal significant differences in the temperature-dependent reflectance between the sample types and, for some types, also between the samples of the same type. This study investigates the origins of the most significant features in the reflectance curves and their potential impact on laser copper processes like laser welding.

1. Introduction

Copper is the second best metallic conductor for electricity and heat, only outperformed by silver (Ref 1). Since it is significantly less expensive than silver, its high conductivities make it the preferred material for many electrical and thermal applications. However, copper is known to be a challenging material when it comes to laser-based processing applications such as laser welding. While the availability of green and blue lasers has significantly facilitated reproducible laser welding of copper, the same process remains challenging when using NIR lasers, which are widely used in the industry. The main difference is the absorption. While the absorptance of copper for green and blue lasers decreases upon melting, the absorptance for near infrared lasers increases abruptly (Ref 2), leading to a sudden increase of the absorbed laser power and thus a narrow process window if predetermined process parameters are applied. A small process window alone does not necessarily lead to instabilities, but while the absorptance of copper for green and blue lasers at room temperature is in the region of 40 % or even more (Ref 2), the absorptance of copper is usually only 5 % or even less. Oxides or other surface impurities with their substantially higher absorptance thus have a significantly larger impact on the absorbed power of near infrared lasers and lead to substantial shifts of the already narrow process window. The constant shifts of the narrow process window make it difficult to control the welding process. In order to achieve a more stable process, it is hence important to investigate which process strategies can increase the width or reduce the shifts of the process window. This can be done by simulation studies that focus on the exact relation between the temperature-dependent absorption and the process behavior.
But reliable data for the absorptance of copper for 1064 nm over a wide temperature range are still difficult to obtain from literature. Values for the absorptance can either be measured directly, or they can be derived from reflectance values, since copper is not transmitting any light except for the case of ultra-thin coatings. A significant proportion of the literature on laser copper interactions focuses on reflectivity, which is, however, only of limited use for the simulation of welding processes. Different from reflectance values, reflectivity values only represent the reflected fraction of light from a single interface. This might not be problematic as long as perfectly pure and smooth copper surfaces are regarded, since they indeed only reflect once from a single interface. But copper materials for industrial processing applications, however, are usually not perfect and involve a combination of oxide layers, other surface impurities, surface roughness and other defects. The light is thus no longer reflected only once at a single interface and the amount of reflected light is no longer equal to the reflectivity. Instead, reflectance or absorptance values are required then.

In the following we give a brief overview of publications that present reflectance or absorptance data for copper at room temperature in the wavelength range from 1000 to 1100 nm, including those who report on reflectivity or absorptivity. Duley (Ref 3) for example calculated the reflectance for copper at room temperature over the range from 300 nm to 1100 nm from measured literature values of $n$ and $k$.

Several authors report on calorimetric measurements at room temperature, such as Quimby, Bass et al. (Ref 4), who performed calorimetric measurements at vacuum conditions to determine the absorptance of diamond turned or mechanically polished samples of OFHC copper at 1.08 µm wavelength. Engler, Ramsayer et al. (Ref 5) conducted calorimetric absorption measurements, in which they irradiated an untreated and thus slightly oxidized SE-Cu58 sheet with a 1064 nm processing laser. The laser was defocused during these measurements to avoid surface melting. Moalem, Witzendorff et al. (Ref 6) performed calorimetric absorption measurements at 1064 nm for freshly polished copper samples according to ISO 11551:2003. Zhu, Lu et al. (Ref 7) determined the absorptance of bare, unpolished copper wires at a wavelength of 1064 nm via the temperature increase in response to millisecond laser pulses of 5 joules and 9 joules. They determined this temperature increase of up to more than 100 kelvins by optical diffraction measurements.

Other authors performed reflective measurements at room temperature. For example, Hass (Ref 8) presented measurement results for the reflectance at room temperature for a freshly evaporated coating of copper for wavelengths from 0.22 to 10 µm. Lehman, Livigny et al. (Ref 9) measured the reflectance of a copper mirror under 45° by shifting it into or out of a 1064 nm laser beam of either p- or s-polarization and measuring the power of the reflected and the direct laser beam with two identical detectors. Lee, Watkins et al. (Ref 10) presented the reflectance of laser cleaned copper samples from 500 nm to 1100 nm, which they measured with an unspecified reflectance spectrometer that was calibrated by reflecting a white light source on a silver glass mirror. Helm, Schulz et al. (Ref 11) measured the reflectance of untreated and laser structured copper samples at room temperature from 400 to 1100 nm with a Lambda 1050 spectrometer from PerkinElmer. Hummel, Schöler et al. (Ref 12) determined the absorptance spectrum for Cu-ETP, also by the help of a Lambda 1050 Spectrophotometer from PerkinElmer. Bergström
et al. (Ref 13) used an integrating sphere of 150 mm diameter in a double beam setup to determine the absorptance of commercially pure copper (99.8 % purity) with a surface roughness $S_a$ of 0.16 µm for a wavelength of 1064 nm and at an incident angle of 8°. Their study also included other nonferrous alloys and they found that the measured values for engineering grade surfaces have considerably higher absorptances than published values for pure, polished surfaces.

Some authors also investigated the temperature-dependence of the interactions of light with copper. Ujihara (Ref 14) calculated the reflectivity of solid copper over temperature up to the melting point for the wavelengths 0.69 µm, 1.06 µm and 10.6 µm, based on the Drude theory and the theory of electron-phonon collision. Siegel (Ref 15) extended the calculations of Ujihara for the liquid metal, by using the Drude theory and the Percus-Yevick collective coordinate theory of simple liquids. He presents discrete reflectivity values for the solid copper at melting temperature and for the liquid copper at 1.0, 1.5 and 2.0 times the melting temperature. Walter (Ref 16) used the electron-phonon collision frequency, the plasma frequency and the temperature-dependent resistance to calculate the reflectance of liquid copper at its melting temperature. He further demonstrated that the results of Ujihara (Ref 14) deviate significantly from experimental values. Xie, Kar et al. (Ref 17) used the Hagen-Ruben relationship and the temperature-dependent d.c. resistivity to calculate the temperature-dependent absorptivity for copper at 1064 nm from 300 to 1900 kelvins. Quimby, Bass et al. (Ref 4) also presented their results for a calorimetric measurement on a diamond turned copper sample, that they conducted under high vacuum conditions within the quartz glass tube of a furnace for room temperature and temperatures of 473, 673, 873 and 1073 kelvins. After the temperature cycle, the measured absorptance of the sample at room temperature was increased with respect to before heating. Kohl, Kaufmann et al. (Ref 2) calculated the absorptivity over wavelength for solid copper at 293 kelvins and for liquid copper at 1873 kelvins from literature values for the optical properties at the respective temperatures. Blom, Dunias et al. (Ref 18) presented the temperature dependent absorptance of copper for 1064 nm from about 250 to 2000 kelvins.

Already for polished copper samples at room temperature, the absorbed respectively reflected fraction of light in the given literature differs by more than 1 percentage points, sometimes even within a single study. A difference of the absorptance from 1.00 % to 2.04 %, as reported within a single study, would lead to an increase of the absorbed laser power by more than 100 %. The results for the untreated copper samples with their inherent imperfections such as slight oxidation layers even differ by up to several percentage points between the studies. Here, the absorbed laser power would even increase by more than 200 %, if the highest reported absorptance of more than 6 % is compared to the lowest one of 2 %. Only two of the studies in our literature survey present absorptance data that rely on measurements, in one of the two on calorimetry, in the other the absorptance is calculated from measured temperature-dependent optical properties that are reported in literature. Both studies do not provide any information on the height of the absorptance step due to the phase change at melting temperature, which is known to be crucial for the stability of a welding process. The other studies on the temperature-dependent development are either based on calculations or the method is not provided. Also, they again show big differences, especially if regarded from the perspective of the absorbed power. The step size in the absorbed laser power, if provided, differs from about 50 % to 100 % increase with respect to the lower value of the step.
Reliable information for copper on the absorbed or reflected fraction of laser light at 1064 nm, that covers the temperature range from room temperature up to the liquid copper at melting temperature, is evidently missing. We therefore considered it important to conduct our own measurements. Since the overall absorptance of copper is so low, reflectance measurements would need to be conducted with a particularly high precision to avoid extreme relative errors for the resulting absorptance. Calorimetric measurements thus seem to be a good solution at first glance, since they measure the absorptance directly. This means that the error of the measurement is equal to the error for the absorbed laser power. But calorimetric measurements face the problem that they require an irradiation induced temperature increase, which in turn leads to a manipulation of the absorptance. Therefore, a precise calorimetric measurement requires that the irradiated power or energy is high enough to provide a sufficient measurement resolution but at the same time stays low enough to not excessively influence the measured absorptance. At elevated temperatures, especially when the sample temperature approaches the melting point, this might become a problem that even leads to unintended melting of the sample. Precise calorimetric measurements additionally require a thermal equilibrium, what means that not only the sample, but its environment has to be heated to the temperature of interest. Additionally, according to ISO 11551:2019, the interval to measure the temperature drift before the irradiation shall be at least 30 seconds and the cooling interval after the irradiation shall be at least 200 seconds. This means that the temperature of the environment for the sample would need to stay constant for about 4 minutes for each measured absorptance value. A more or less continuous measurement of the absorption over a large temperature range would thus take very long and allow even slow processes to have significant effects on the surface characteristics.

The previous paragraph indicates the difficulties associated with the direct measurement of the absorption, especially when aiming for a precise determination of the absorptance over a wide temperature range. In our study, we therefore measured the reflectance over temperature of copper with an integrating sphere. According to the literature, the expected values for the reflectance are 95 % or even higher. Hence, even small relative deviations in the measured reflectance can lead to a strong relative uncertainty in the absorptance, which governs the welding process. It is therefore important to measure the reflectance as precisely as possible. To achieve this objective and to make our results thus useful for process simulations, we carefully examined possible error sources and implemented a set of different measures to minimize their impact on our measurement values. We conducted our measurements with a 1064 nm laser source on electro tough-pitch copper (Cu-ETP or CW004A), which is widely used in electrical applications, from room temperature to above the melting point. To not completely oxidize our samples during the measurements, we conducted them in a nitrogen atmosphere, which is also advantageous for the production of high-quality welds. Since industrial applications usually do not use freshly polished copper with a perfect surface, our study includes copper samples with different surface conditions, namely untreated, reduced, mechanically polished and resolidified surfaces. After pointing out the key features in our measurement results, we analyze their potential origins as well as their significance for welding applications in our discussion. We conclude our discussion by assessing the quality of our measurements and give suggestions for their successful usage in simulation models.
2. Experimental setups and methods

We conducted the temperature-dependent reflectance measurements in a specially equipped integrating sphere, that allows to heat the sample and to freely adjust the incident angle of the measurement laser on the sample. In the following sections, we provide detailed descriptions of the optical measurement system and the temperature control system for the sample. We then present the experimental procedures followed by an explanation of our signal processing routine.

2.1 Measurement Setup

2.1.1 Optical measurement system

Figure 1 shows a sectional view of the experimental setup. The central element is an integrating sphere (short: sphere), which is mounted rotatable around the axis of the sample holder to allow any desired incident angle of the laser on the sample. The sphere has an inner diameter of about 500 mm, which allows a small ratio of openings to the overall inner surface. The inner surface of the sphere is coated with barium sulfate (BaSO$_4$) to improve the light integration behavior. The sphere has 6 ports: A sample port for sample delivery, a reference beam port, a sample beam port, a viewport for process observation with a camera, a gas port for the supply with shielding gas and a measurement port. A continuous wave fiber laser (not depicted) delivers the 1064 nm radiation through an optical fiber to the collimation optics at the top of the optical power. When leaving the collimation optics, the linearly polarized laser beam has a power of less than 0.4 watts, which is low enough to not significantly heat the sample. The laser beam is then linearly polarized by a linear polarizer with a guaranteed extinction ratio higher $10^5$ in order to stabilize the polarization and to prevent reflectance fluctuations due to uncontrolled polarization shifts. The polarization stabilized beam then arrives at the optical chopper wheel, which rotates at a fixed frequency of 6.5 Hertz. The chopper wheel features 2 cutouts, one mirror and a counterweight (not depicted) that is displaced by 180° to avoid vibrations due to imbalance. The chopper wheel constantly switches through the three different phases of measurement:

1. Background signal measurement, twice per rotation: The chopper wheel blocks sample beam path and reference beam path to enable the background signal measurement.

2. Reference signal measurement, once per rotation: Mirror 1 on the chopper wheel reflects the laser beam into the reference beam path to enable tracking of changes in the incident laser power or in the behavior of other setup components.

3. Sample signal measurement, twice per rotation: One of the two cutouts in the copper blade allows the laser beam to pass straight through the sample beam port to the sample in the sphere.

During the sample signal measurement, the s-polarized sample beam hits the sample at an incident angle of 12°. The reflected fraction of the beam is collected by the sphere coating, which integrates the light flux by multiple reflections within the sphere. In the case of unpolished samples, we aligned the samples such
that the surface structure from the sheet rolling process is parallel to the incident plane of the laser and thus the main directions of the reflections do not include any ports of the sphere.

During the reference signal measurement, the reference beam is reflected by mirror 1 on the chopper wheel to mirror 2, which reflects the beam through one of the two cutouts in the chopper wheel to mirror 3. Mirror 3 reflects the beam through the reference beam port onto mirror 4 in the sphere, which reflects the beam onto to coating of the sphere, in proximity of the position to which the sample reflects the main proportion of the sample beam. The similar position reduces shifts between the reference signal measurement and the sample signal measurement that do not result from changes of the sample surface but from changes of the setup. These can be, for example, a location-dependent temperature development of the sphere coating during the sample heating or different effective sizes of the heating element from the perspective of the positions of the first scatterings.

During the sample signal measurements as well as the reference signal measurements, a proportion of the integrated light flux arrives at the measurement port below the baffle. The baffle has an optimized geometry that only allows light from the bottom region of the sphere to reach the measurement port directly and thus blocks direct illumination from all positions on the sphere coating to which the sample can reflect or scatter to. This reduces the measurable signal amplitude and thus the signal to noise ratio, but results in an improved independence of the measured signal from the angle under which the sample beam is reflected or scattered. Light that arrives at the measurement port is scattered by a ground glass diffusor into a black anodized extension tube. The tube serves as a spatial filter by absorbing light that would leave the tube at angles larger 3°. This helps to reduce blue shifts of the transmission window of the bandpass filter behind the tube. The transmission window has a central wavelength of 1064 nm and a full width half maximum of 8 nm. It blocks most of the heat radiation, which else would exceed the laser signals by factors up to larger 10 and thus decrease the available measurement resolution. Finally, the transmitted light arrives at the photodiode just behind the bandpass filter. This photodiode measures the sample signal, the reference signal and the background signal. A transimpedance amplier converts the diode current into a voltage, which gets by a measurement card at a sampling rate of 50 kHz.

During the background signal measurement, no laser light is entering the integrating sphere. This is essential for a precise measurement because the heat radiation emitted by the sample and the heating element also includes the wavelength of the laser. This means bandpass filters cannot filter the heat radiation completely without impeding the measurement. While the bandpass filter reduces the background radiation and thus increases the selectable signal amplification for the measurement, the regularly updated background measurement makes it possible to completely subtract all background signals from the measured sample signal and reference signal during evaluation.

### 2.1.2. Temperature control system

The sample rests on the heating element, which is made from silicon nitride (Si$_3$N$_4$). The sample and also the maximum temperature position of the heating element are aligned with the position of the sample
beam. The sample has a length of 49 mm, a width of 30 mm, and for the melting experiments a thickness of 1 mm, while the heating element has a length of 75 mm, a width of 14.7 mm and a thickness of 4.4 mm. The sample is wider than the heating element to prevent the edges of the specimen from melting, which allows a solid frame to persist when the center of the sample is melting. Without the frame, the low wettability of silicon nitride for copper resulted in the formation of a small melt bullet, which does not allow reflectance measurements under a defined incident angle, and which might even form outside of the laser spot. In pre-experiments, we placed the sample on a steel plate, which helped to keep the sample flat. But heavy oxidation only within the melt area and the results of EDX-measurements indicated that several elements from the solid steel had dissolved into the molten copper. The remaining copper frame, however, keeps the melt in the sample plane even when it is lying directly on the cuprophobic heating element. It thus allows measurements with a defined incident angle and without contaminations of the melt.

Preliminary tests with a ratio pyrometer and our copper samples showed changes for the measured fusion temperature of up to 600 kelvins, which is why we employed a type S thermocouple for the temperature measurement instead. The high electrical conductivity of the sample allows a measurement configuration in which the two wires of the thermocouple are only connected by the sample surface, as illustrated in Fig. 1. This configuration brings the material transition, which is the actual measurement position, right to the surface of the sample. The agreement between the measured temperature and the actual temperature of the sample surface is therefore substantially better than in the standard configuration, in which a weld bead directly interconnects the thermowires. Also, the surface contacting problem is reduced to either measuring the correct temperature or measuring no temperature at all. The distance between the thermowires and the laser spot is 9 mm, what leads to a reduction of the measured temperature but is necessary to avoid any relevant interference of the wires with the reflectance measurement.

In all our experiments, a microcontroller realized the closed-loop temperature control of the sample. Depending on the current sample temperature, which it receives from the thermometer once per second, it commands a solid state relay which adjusts the input power for the heating element through a phase-angle control. The phase-angle control operates synchronized with the power grid and cuts each 50 Hz 230 VAC half-phase. In combination with the heat inertia of the heating element, this cutting-frequency of 100 Hz is high enough to keep the temperature of the sample sufficiently stable at any preset temperature.

2.2. Experimental procedures

To prevent measurement errors due to changes in environmental variables or due to possible degradations of the setup, we determined the initial reflectance of each sample individually. To do so, we conducted a 60 seconds measurement on the sample without thermowires and related the average value to the combined average of a pre- and a succeeding 60 seconds measurement on the reference mirror in the sample position. The reference mirror was an ion beam sputtering low loss laser mirror (short: IBS-
mirror) with a theoretical reflectivity of 99.999837% for s-polarized light at the wavelength of 1064 nm (guaranteed 99.98%). The maximum error due to the mirror specification is therefore < 0.02%.

For the temperature-dependent reflectance measurement, we placed the referenced sample, contacted the thermowires to the sample surface and drove the sample holder into the sphere. To prevent oxidation during heating, we then flushed the sphere with nitrogen (N5.0) for at least one hour before the heating experiments. We continued flushing throughout the experiments until the sample was back at room temperature, since the sphere could not be hermetically sealed and thus needed a slight overpressure to prevent gas contamination. The measurements started with a segment of at least one minute at room temperature, which is used in the later evaluation to refer a stable average signal to the predetermined starting reflectance. In the second segment, the temperature control heated the sample up to the predefined sample temperature, kept the temperature for a predefined duration and then shut down the power supply. In some measurements we manually shut down the power supply to prevent the sample from collapsing due to complete melting. We conducted several repetitions of the reflectance measurements with the four different sample types from Table 1.

### Table 1
Description of sample types

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated sample</td>
<td>• cut from 100 µm thick sheet of Cu-ETP&lt;br&gt;• used as delivered</td>
</tr>
<tr>
<td>polished sample</td>
<td>• cut from 1 mm thick sheet of Cu-ETP R290&lt;br&gt;• first grinded samples up to 2400 grit, then polished up to 3 µm&lt;br&gt;• cleaned with isopropanol in ultrasonic bath after polishing&lt;br&gt;• blown dry with a hair dryer</td>
</tr>
<tr>
<td>reduced sample</td>
<td>• cut from 100 µm thick sheet of Cu-ETP&lt;br&gt;• heated to 1073 Kelvin in pure nitrogen (oven 3 times evacuated, 3 times refilled)&lt;br&gt;• cooled down to around 300 Kelvin in pure nitrogen</td>
</tr>
<tr>
<td>resolidified sample</td>
<td>• based on our 1 mm thick polished sample of Cu-ETP R290&lt;br&gt;• sample was melted and resolidified in nitrogen between 1 and 3 times&lt;br&gt;• no additional treatments after resolidification&lt;br&gt;• thickness about 1 mm</td>
</tr>
</tbody>
</table>

In addition to these regular measurements, we also carried out supplementary measurements to gain a better understanding of the processes on the sample surface, notably regarding the reversibility of reflectance changes in a specific temperature window. For this purpose, we conducted a cyclic
experiment, in which the temperature control heated an untreated sample to about 1073 kelvins, kept the
temperature for a specified duration, then let the sample cool down to 853 kelvins and kept the
temperature again for a specified duration. From there the temperature control heated the sample and let
it cool down two more times to the respective temperatures with the respective holding times and then let
the sample cool down back to room temperature.

We further conducted or had externally conducted the following spectroscopic measurements on selected
samples to get additional information on possible chemical changes of the sample surface as a result of
our reflectance measurements:

- Energy-Dispersive X-ray spectroscopy (EDX)
- Nuclear Reaction Analysis (NRA), measurement conducted externally
- Rutherford Backscattering Spectroscopy (RBS), measurement conducted externally
- Raman Spectroscopy

2.3. Signal processing

Figure 2a) shows a raw signal segment of 50,000 data points, equal to one second, as it was recorded by
the measurement card. Three levels are clearly distinguishable: The background signal at about 0.11
volts, the reference signal at about 1.24 volts and the measurement signal at about 1.76 volts. Since the
chopper wheel has two openings but only one mirror, the reference signal only appears half as often as
the other two signal types.

In the first step, the processing routine suppresses all negative edges from the sample signal to the
background signal. Then, in predefined distances from the beginning of each remaining data block, the
routine selects a predefined number of consecutive data points as background data (orange), reference
data (yellow) and sample data (purple), as displayed in Fig. 2b), and transfers each data type to the
Corresponding columns of a data matrix. The distance of selected data to slopes or to the bump in the
background signal is sufficient to exclude any undesired influence on the results. The bump results from
the counterweight position of the chopper wheel when the reference beam path is already cleared. Since
the first grey data block in Fig. 2b) is incomplete, a shift from suppressed to unsuppressed data is
missing within the 1 seconds segment and the whole data block is ignored to avoid any error potential.
The occasional omission of single data blocks is less critical for the results than accidental inclusions of
slopes due to shifted starting points.

In the next step, the routine summarizes the data points of every 0.5 seconds interval (equals 25,000 data
points) by one mean value per data type. This helps to reduce the noise and the required data processing
capacity for the following steps significantly, while the remaining update rate is still double as high as the
1 Hz from the thermometer. Then the routine calculates the corrected reference signal \( U_{\text{ref}}(t) \) from the
reference raw signal \( U_{\text{ref,raw}}(t) \) and the concurrent background signal \( U_{\text{backgr,raw}}(t) \), leading to
\[ U_{\text{ref}}(t) = U_{\text{ref,raw}}(t) - U_{\text{backgr,raw}}(t). \]

The routine calculates the corrected reference signal \( U_{\text{ref}}(t) \) from the sample raw signal \( U_{\text{sample,raw}}(t) \) likewise, which results in

\[ U_{\text{sample}}(t) = U_{\text{sample,raw}}(t) - U_{\text{backgr,raw}}(t). \]

The ratio of the two results

\[ Q_{\text{sample2ref}}(t) = \frac{U_{\text{sample,raw}}(t)}{U_{\text{ref}}(t)} \]

represents the uncalibrated equivalent to the reflectance of the sample \( R(t) \). The resulting curves are shown in Fig. 2c). Finally, the routine calculates the calibrated reflectance of the sample

\[ R(t) = Q_{\text{sample2ref}}(t) \]

with \( Q_{\text{mirror,avg}} \) being the averaged ratio of the cleaned signals for the IBS mirror and \( R_{\text{mirror}} \) being the known reflectance of the mirror. The routine can plot the resulting reflectance of the sample over the corresponding temperature of the same time stamp to show the temperature-dependent reflectance of the sample \( R(T) \).

### 3. Results and discussion

#### 3.1. Results

Figure 3a) shows the measurement results for 3 untreated copper samples, which we cut from the same copper sheet of 100 µm thickness. Two of the untreated samples were placed on a polished sample to increase the overall copper thickness and thus avoid rupture of the melt. The specifications of all sample types are summarized in Table 1. All three samples show a similar behavior with two substantial reflectance increases. The measurements start with a reflectance between 94.74% and 94.94%. After a short initial decrease, the reflectance rises to between 95.60% and 95.77% at a temperature of about 670 kelvins. From there it decreases again, until the second substantial increase takes place from values between 94.95% and 95.21% at about 860 kelvins to values between 96.76% and 96.91% at about 1050 kelvins. From there, the measured values do not show a clear trend until the reflectance drops due to melting. The plot only shows two reflectance drops, because the sample without support of a polished sample was not sufficiently heated for melting. Only one of the reflectance drops leads to available reflectance values for liquid copper, since the melt film ruptured for one of the samples despite the
support of a polished sample. The two reflectance drops happen at a measured temperature of 1190 respectively 1220 Kelvin. The available values for the liquid copper show an average reflectance of 93.66% at a temperature of 1349 kelvins.

Figure 3b) shows the measurement results for 6 polished samples, like they are described in Table 1. They originate from a 1 mm thick sheet of Cu-ETP to avoid rupture during polishing and to avoid rupture of the melt during the measurements as it happened amongst the untreated samples. The measurements show one substantial reflectance increase up to temperatures of around 600 kelvins, which is followed by an approximately linear decrease up to the melting temperature. The measurements start with an initial reflectance between 96.57% and 97.70%. After a short initial decrease, the reflectance rises to values between 97.96% and 98.27% at about 600 kelvins. From there, the reflectance decreases approximately linear until reaching values between 96.60% and 96.95% at the melting point, with measured temperatures between 1270 and 1320 kelvins. The reflectance in the liquid melt lies between 93.40% and 93.94% at measured temperatures between 1251 and 1376 kelvins, depending on the sample.

Figure 3c) shows the measurement results for 3 reduced samples, like they are described in Table 1. These samples were only heated to shortly below their melting temperature to avoid rupture of the samples. Their reflectance principally shows an approximately linear decrease from the initial temperature to the maximum temperature, with a temporary but significant drop followed by a rebound back to the initial linear decrease. For an unknown reason, the reflectance values of one measurement start to deviate persistently by approximately +0.13 percentage points above 620 kelvins and later by up to about +0.35 percentage points at temperatures above 1000 kelvins. The values of the other two measurements, however, are generally in good agreement with each other. The measurements start with an initial reflectance between 98.90% and 98.96%. The reflectance drop starts between 740 and 800 kelvins and reaches its minimum value of 96.13–96.88% at temperatures between 950 to 1050 kelvins. After the rebound, the reflectance continues to decrease until it reaches a final reflectance of 97.13% at 1077 kelvins respectively 96.94% at 1189 kelvins for the two agreeing measurements. The deviating measurement has a final reflectance of 97.36% at 1130 kelvins.

Figure 3d) shows the measurement results for the resolidified samples, like they are described in Table 1. We conducted between 1 and 3 subsequent measurements on the same resolidified sample, depending on how many measurements the melt film allowed without bursting. As result, we conducted 7 measurements that distribute on 4 different samples. The initial reflectance of the resolidified samples is not directly related to the initial reflectance of the polished sample or the number of conducted resolidificaton cycles, for example, the initial reflectance of the 3 times resolidified sample is equal to the initial reflectance of another sample that has been resolidified only once at that time. The general course of the reflectance is an approximately linear decrease, followed by a dip with rebound and then a tendentially decreasing reflectance until the reflectance drop due to melting. The measurements start with an initial reflectance between 97.41% and 98.70%. Despite the different starting values, the reflectance in all 7 measurements decreases at a similar gradient, ranging between −2.92 and −3.68 percentage points per 1000 kelvins, with a tendency of steeper gradients for lower initial reflectance levels. The reflectance
dip starts at above 800 kelvins and reaches a minimum of between 93.37% and 96.49% at around 1000 kelvins. At the end of the following rebound, the reflectance has a more uniform reflectance of 96.80–97.15% at temperatures around 1200 kelvins. All samples show reflectance values between 96.60% and 96.97% when they melt at temperatures between 1302 and 1344 kelvins. The reflectance values for the melt lie between approximately 93.4% and 93.8% at measured temperatures of above 1305 kelvins for one of the measurements and between 1340 and 1355 kelvins for the 6 other measurements.

Figure 4a) shows an overlay plot of the measured temperature over time for all samples, while Fig. 4b) shows an overlay plot of the measured reflectance over temperature for all sample types. Most of the samples were heated at the maximum power of the heating element. However, the untreated sample, which was not supposed to melt, was heated at a lower and defined heating rate of 8 kelvins per second. This leads to a significantly increased number of data points for the reflectance over temperature during heating but does obviously not affect the course of the curve in a significant extent. An even lower heating rate of 2 kelvins per second applies to all reduced samples. Their data points in the plot of the reflectance over temperature are therefore that close to each other that the individual data points can only hardly be distinguished.

When we compare the different sample types, the average initial reflectance is the highest for the reduced samples with an average value of 98.93%, followed by 98.12% for the resolidified samples, 97.01% for the polished samples and 94.85% for the untreated samples. The spread for the initial reflectance is the lowest for the reduced samples with 0.06 percentage points, followed by the untreated samples with 0.20 percentage points, the polished samples with 1.13 percentage points and the resolidified samples with the greatest spread of 1.29 percentage points. We identified the most similar behavior for the reflectance over temperature between the reduced and the resolidified samples. Both types start with a reflectance decrease of comparable slope over a wider temperature range, followed by a reflectance dip with rebound within the range of 800 to 1200 kelvins. Unlike for the reduced samples, the rebound for the resolidified samples typically results in a significantly increased reflectance compared to the values before the dip had started. On the other side the polished and the untreated samples all show, after a rather short initial decrease over some tens of kelvins, a substantial increase of reflectance up to a temperature in the region of 600 kelvins. From there, the polished and the untreated samples show a reflectance decrease of a similar gradient as also the other sample types do. The main difference in the general behavior between the polished and the untreated samples is that the untreated samples show another substantial reflectance increase in the temperature range of 860 to 1050 kelvins, while the polished samples follow the same linear decrease function as the reduced samples, only without the reflectance dip and the following rebound. Despite the often significant differences of the initial reflectance, all measurements in Fig. 4b) end in the same corridor of reflectance over temperature after reaching a temperature of about 1200 kelvins, except for the single deviating measurement on reduced copper. The reflectance after the reflectance drop at melting temperature is comparable for all measurements that melted during our measurements, but scattering for the reflectance values of molten copper is high even within the single measurements. To receive a more representative value for the reflectance of molten copper, we therefore calculated the combined mean value of all measured reflectance values after the reflectance drop and
before the not depicted rise of the reflectance upon resolidification. It is important to mention that the sample does not melt all at once, but that the melt pool starts from the position of the highest temperature in the center of the sample and then extends gradually until it eventually exceeds the unsharp and thus not clearly visible boundaries of the laser spot. Only then the measured reflectance value fully corresponds to the reflectance value of the melted copper. The calculated mean value for the reflectance of liquid copper just above melting temperature is 93.68%. Summarized, except for the dips in the cases of the reduced and the resolidified samples, the negative slope sections for all samples show a comparable reflectance gradient. The main difference between the different samples appears to be the occurrence and magnitude of reflectance increases at specific temperatures.

Figure 5 shows the measurement results for the cyclic experiment in which we heated an untreated copper sample to 1073 kelvins, let it cool back to 853 kelvins and repeated heating respectively cooling to these two temperatures 2 more times, before letting the sample cool back down to room temperature. We kept each of the target temperatures constant for a specific duration, before proceeding to the next target temperature. We conducted the measurements with a previous version of the measurement setup, which we calibrated with a gold mirror instead of the more accurate IBS mirror and which had less advanced features to compensate transverse effects due to heating of the measurement setup. Also, the sample material had a different aging condition. The exact measurement values are therefore not directly comparable with the ones for the other samples in the latest setup configuration. The experiment is nevertheless suitable to analyze the basic effect that leads to the reflectance increase above 800 kelvins for the untreated sample type. The reflectance starts from its initial value with a short decrease, followed by a reflectance increase at about 670 kelvins. After a decrease between about 600 to 800 kelvins, the reflectance increase of interest is clearly visible. From about 900 kelvins, the reflectance starts to decrease again until the temperature is kept constant at 1073 kelvins. Despite the constant temperature, the reflectance rises and continues to rise still when the temperature is decreasing, until the measured temperature falls below about 950 kelvins. Then the reflectance decreases and continues to decrease even when the temperature stays constant at 853 kelvins, until the temperature exceeds a measured temperature of about 1000 kelvins again. From where it rises again and continues to rise until the measured temperature falls below 950 kelvins again. By choosing temperature holding times of 1 minute at 853 kelvins and 10 minutes at 1073 kelvins, we were able to realize the repetitions in Fig. 5c) in which the reflectance over temperature follows exactly the path of the previous cycles. After the third holding time at 853 kelvins, the reflectance increases again during final cooling. Figure 5a) and b) show the corresponding reference respective sample beam signals over temperature. They demonstrate that the reflectance decrease at 853 kelvins is not due to a cooling of the setup but due to the sample surface, since the reference signal continues to rise.

Our spectroscopic measurements with Energy-dispersive X-ray spectroscopy (EDX) and Raman spectroscopy did not reveal any significant differences between an untreated sample that we did not heat and an untreated sample that we heated in nitrogen to 1073 kelvins within the integrating sphere previously. The results of the nuclear reaction analysis (NRA) for carbon, nitrogen and oxygen showed a substantial decrease of carbon from 7.56e15 atoms/cm² to 9.85e15 atoms/cm² and of nitrogen from
7.33e15 atoms/cm² to 0.21e15 atoms/cm². However, the presence of oxygen stayed nearly unchanged with 23.15e15 atoms/cm² for the untreated sample and 22.29e15 atoms/cm² for the heated sample. The Rutherford Backscattering Spectrometry (RBS) did not show any significant difference between the samples.

3.2. Discussion

3.2.1. Interpretation of reflectance measurements

Our results show that a universally applicable reflectance over temperature, that applies to all types of copper samples, does not exist. Instead, not only the initial value at room temperature but also the development of the reflectance during heating is strongly related to the specific sample conditions. The measured reflectance values for samples of the same type all show the same trends at comparable temperatures, but their exact reflectance at a given temperature depends on their exact initial conditions and may differ significantly up to a temperature of about 1200 kelvins, above which no significant differences between our samples were noticeable anymore. Therefore, our goal is not to find a generalized equation for the temperature-dependent reflectance, but to discuss the general trends that we observed for the different sample types, identify important features and try to find the reasons for them.

Since we conducted all reflectance measurements in nitrogen atmosphere, we generally did not expect strong oxidation effects. However, for already reduced samples and for polished samples, which are both nearly oxide free, no significant reduction should happen either. This means that the reduced and the polished samples should show a behavior that is close to that of pure copper within the purity of Cu-ETP. Resolidified copper should show a similar behavior, since it is formed from the melt of Cu-ETP in the nitrogen atmosphere. The measured initial reflectance for the reduced samples is highly uniform, with a spread of only 0.06% over all 3 samples. The reflectance develops almost linearly from the beginning, at least up to 700 kelvins, and continues in the direct extension of this path after the reflectance dip with rebound. The reflectance of the polished samples joins the same path over temperature after reaching 600 kelvins. From 1200 Kelvin at the latest, the reflections of all sample types run, within small limits, along this line. We therefore consider this the baseline for the reflectance of pure copper. As can be expected after a uniform reflectance just before the melting point, the reflectance for the liquid copper after the reflectance drop does not show any dependency from the initial surface conditions, at least within the scope of our samples. The fluctuations of the value might be resulting from dynamics in the melt surface.

The reflectance measurements of all our samples deviate from the baseline in certain temperature ranges at solid state, which are specific to the initial surface condition under the existing ambient conditions. Unexpectedly, the polished samples do not start with the same initial reflectance as the reduced samples but at lower values, that also show a significantly larger spread. These are both indicators of surface imperfections. The reflectance of all polished samples increases from shortly above room temperature until it homogenizes among all polished samples and aligns with the discussed baseline of copper. A similar effect can be observed at similar temperatures for the untreated copper. The reflectance of the
untreated sample starts with the lowest initial reflectance and shows a similar behavior until about 650 kelvins, only at a generally lower level of reflectance. It is still too low to join the baseline at this temperature, but it starts to decrease parallel to it. According to the manufacturer, our untreated copper was treated with the organic compound benzotriazole as an oxidation inhibitor. We cannot finally confirm that the first reflectance peak of the untreated copper results from the evaporation of benzotriazole, but at least the temperature of the reflectance increase in our measurements is in good agreement with the evaporation temperature of benzotriazole at 623 kelvins. Also, the decrease of carbon in the results of the nuclear reaction analysis (NRA) from 75.76e15 atoms/cm² to 9.85e15 atoms/cm² and the decrease of nitrogen from 7.33e15 atoms/cm² to 0.21e15 atoms/cm² rather support than contradict this assumption. The polished samples were not treated with benzotriazole during nor after polishing, but although we cleaned the polished samples in an ultrasonic bath with isopropanol, rinsed them thereafter with fresh isopropanol and dried them with a hairdryer thereafter, we cannot guarantee that absolutely no remains for example from the diamond suspension somehow remained on the surface. A reasonable explanation for the increase of the reflectance until shortly above 600 kelvins for the polished samples could therefore also be the evaporation of organics, although we do not have a final proof for this.

The curves for the polished samples do not exhibit any further indications for changes of the surface constitution until the melting point. But the reduced, the resolidified and the untreated samples all show a significant reflectance increase that starts at temperatures between 850 and 1050 kelvins. In the case of the untreated sample and the resolidified sample, the difference in the starting temperature is similar to the difference between the temperatures where the two sample types melt. Since the melting temperature of copper is a physical constant, this indicates that the recorded difference for the temperatures of the reflectance increase is only a consequence of a different measurement error for the temperature and that therefore the same temperature applies. In the case of the reduced and the solidified sample, the reflectance increase is also preceded by a reflectance dip that is significantly more pronounced than the decrease of the baseline of copper. Our spectroscopic measurements, including the nuclear reaction analysis (NRA), did not reveal significant changes of the oxygen content. But the threshold temperature between the reversible reflectance decrease and the reversible reflectance increase in the reflectance cycle in Fig. 5 agrees well with the threshold temperature at which the reflectance drop continues into the rebound for the other samples. The evident reversibility of the increase and decrease in the experiment with holding times at 853 and 1073 kelvins, together with the knowledge that the only available reaction partners are the sample and the surrounding gas, only allows the conclusion that the increase and decrease of the reflectance result from reduction and oxidation of the sample. According to the Ellingham diagram for copper and its oxides (Ref 19), the oxygen partial pressure for the equilibrium of

$$4Cu + O_2 = 2Cu_2O$$  \hspace{1cm} (5)$$

at a temperature of 1050 kelvins is between 10^{-8} and 10^{-9} bar. Due to the position of the thermowires, the actual threshold temperature in the laser spot is most likely even higher than the measured temperature, what further increases the derived oxygen partial pressure. The setup of the integrating
sphere was not equipped to measure the concentration of the remaining oxygen content but these values for the oxygen partial pressure seem to be reasonable if we consider the nominal purity of the delivered gas. The results strongly suggest that the intensified decrease of the reflectance for the reduced and the resolidified sample before 1000 kelvins is caused by oxidation and that the following increase for all samples but the polished one are caused by the reduction of oxides. The oxidation below the equilibrium temperature might also be the reason why the resolidified copper starts with lower and less uniform initial reflectance values than the reduced copper: While the reduced copper was heat treated in a specialized oven that provides a feature for quick cooling within the sealed volume, the resolidified sample cooled down on the heating element in the constantly flushed but not sealed integrating sphere. Therefore, it is possible that it was subject to oxidation, similar to the sample in Fig. 5.

In the end, the reflectance of all samples basically follows the baseline of copper, but this behavior is in some cases superposed by other effects. With regards to the process stability in laser welding, the reduced copper seems to be the best option at first look, since it has the most uniform starting values for the reflectance. It also follows the baseline of copper without any indications of chemical reactions, except for the reflectance dip with rebound, which is likely to be less pronounced if the sample is heated quickly enough. However, for most processing applications the absorptance is of interest, for which the initial value of the reduced copper is the lowest among all our samples. Relative to the derived absorptance value of 1.04–1.10%, the spread of 0.06 percentage points already scales to about 5.6%. The spread of the initial values of the untreated copper might appear larger when looking at the reflectance, but if the 0.2 percentage points are related to the derived absorptance of 5.26–5.06% this spread is only 3.9%. This clearly demonstrates that the suitability of the highly reflective copper materials for processes like laser welding can only be reasonably estimated from the absorptance point of view. Also, while the differences between the samples seem to be small when looking at their reflectance values, the average initial absorptance of 5.15% for the untreated samples is 4.81 times as high as the average initial absorptance for the reduced samples of 1.07%.

### 3.2.2. Data quality and transfer to simulations

Our measured reflectance values at room temperature lie within the range that could be expected from the values for similar surfaces from our literature overview. Regarding our temperature-dependent measurements in the solid phase, we see the best agreement with the values of the diamond turned copper sample from Quimby, Bass et al. (Ref 4), who used an calorimetric approach. While their value at room temperature corresponds to 99.19 %, our reduced samples have a reflectance of 98.93 % on average. At the highest temperature in Quimby, Bass et al. (Ref 4), their value corresponds to about 97.5 %, while ours is on average about 97.0 %. Our deviation from their values is thus −0.26 percentage points at room temperature and about −0.5 percentage points at 1070 kelvins. Regarding the absorbed power, our absorptance is 132 % of their value at room temperature and 120 % of their value at 1070 kelvins, which is a good agreement compared to how the results of the other studies deviate from each other. Quimby, Bass et al. do not present any values for liquid copper. Our average reflectance value for liquid copper of 93.68 % shows the best agreement with the calculated value of about 93.9 % for liquid copper at 1873
kelvins from Kohl, Kaufmann et al. (Ref 2). Transferred to the absorption, our value is 101.37 percent of
their value and thus approximately equal. In a previous study (Ref 20), we incorporated the absorptance
from Blom, Dunias et al. (Ref 18) into our simulation model and found that the laser power to melt the
sample in our simulations was 1.7 times lower than in our corresponding welding experiments. Since the
absorptance values from Quimby, Bass et al. (Ref 4) are lower than the ones in Blom, Dunias et al. (Ref
18), the best agreement with Quimby, Bass et al. is a promising indication that our measurement results
come close to the actual temperature-dependent absorptance of copper.

Before using the results of this study for simulations, some aspects regarding the setup and the
experimental procedure should be taken into consideration. In general, our measurement results have
demonstrated a good reproducibility with respect to the reflectance; at the temperature of 1200 kelvins,
the maximum spread for the reflectance between all measurements is less than 0.6 percentage points.
Also, our results did not show a relevant dependence of, for example, noise from the current value.
However, the remaining absorptance decreases with increasing reflectance, which means that relative
errors with respect to the absorptance value tend to grow substantially as the reflectance increases.
Therefore, our measurement results for the reduced and polished samples have, on average over the
whole temperature range, a lower reliability to predict the exact absorbed laser power compared to our
measurement results for the untreated samples.

We were further able to identify 2 effects that might lead to deviations of our reflectance measurements
from the actual reflectance during, for example, a welding process. One of these effects is a thermal drift
of the reflectance values, which is not related to the actual reflectance but to an unintended temperature
increase of the setup. The other one is the time-dependence of the reflectance decrease or increase due to
oxidation respectively reduction of the sample surface.

Figure 6a) demonstrates the effect of the thermal drift on the example of a polished sample. When the
sample cools down, the reflectance generally increases with decreasing temperature, what can also be
expected from literature. But when the temperature has almost returned to room temperature, the trend
changes and the reflectance decreases by another 0.2 to 0.4%, although the concurrent temperature
decrease is nearly negligible in comparison to the previous decrease. Figure 6b) shows the same
measurement over time, with the increase in reflectance turning into an exponential decrease typical of
cooling processes. This indicates that our measurement setup shifts the reflectance to higher values with
increasing temperature of the setup or some of its components, and the shift reduces again when the
setup cools down. As a consequence, our recorded reflectance values at higher temperatures should
actually be considered lower than measured.

The other effect of time-dependence for the reflectance decrease or increase due to oxidation or reduction
can be observed in the experiment in Fig. 5. The longer the sample stayed in the respective temperature
region, the stronger was the total increase or decrease of the reflectance. This means that the velocity, at
which the sample is heated, can have a substantial effect on the extent to which the sample surface is
oxidized or reduced until a specific temperature is reached. In our measurements, the sample was heated
relatively slowly, at heating rates of only some kelvins per second. If the sample surface is, however, heated to the melting point within milliseconds or even faster, the effect of oxidation or reduction when arriving at the same temperature might be significantly less pronounced than in our measurements. In some cases, like for the already reduced sample, oxidation might even be negligible and the following reduction thus may not happen as well. This would mean that the dip and rebound of the reflectance between 800 and 1000 kelvins might not be present at all, even for the same atmospheric conditions as in our integrating sphere.

Besides the forementioned effects on the reflectance data, the temperature measurement has two regimes, which we refer to by the unmolten regime and the molten regime. When heating in the unmolten regime, the temperature measurement always shows temperatures that are lower than in the laser spot, since the thermowires cannot be placed in the center of the laser spot, where the temperature of the sample is at its highest. This usually leads to the effect that the sample melts at measured temperatures below the theoretical melting temperature. This temperature deviation can be used to recalibrate the temperature for the solid sample, providing a good approximation with respect to the position of the reflectance measurement. However, as the sample melts, the melt pool will usually grow quickly and reach the thermowires, which is when the diagrams of reflectance over temperature tend to show a shift to the direction of the theoretical melting temperature. This shift happens because the thermowires are now no longer measuring in the unmolten but in the molten regime. This includes a permanent change of the contact conditions between the sample and the heating element in the whole molten area, leads to a more homogenous temperature distribution and is also the reason why the deviation of the measured temperature upon melting from the theoretical melting temperature is the lowest for the resolidified samples.

Different processes can lead to slightly different reflectance curves of the reflectance over temperature, even if the same surface conditions apply. We therefore decided to present the results of our measurements in their original version. However, our above discussion of the effects can be used to adjust our results with respect to the process to be simulated.

4. Conclusions

In this study we were able to experimentally measure the reflectance over temperature for untreated as well as for reduced or polished or resolidified samples of electro tough pitch copper in nitrogen atmosphere over the whole temperature range from solid copper at room temperature to liquid copper just above the melting point. The detailed measurement results revealed significant differences of the reflectance over temperature for the different sample types but also typical features for the temperature-dependent reflectance of each specific group. We were able to explain most of the striking features and also discussed their significance for processes like laser welding. However, we also identified a reflectance drift of the integrating sphere setup as an error source that could not be eliminated completely, and we found that the effect of redox reactions on the reflectance depends on the heating rate, what should be considered when the data shall be applied in simulation models that involve
significantly faster heating. Simulations that implement the measurement results in combination with accompanying experiments for comparison might help to characterize these error sources more in detail and to develop compensation strategies.

Declarations

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Conflict of interests:

The authors declare no competing interests.

References


Figures

Figure 1

Section view of the integrating sphere setup
Figure 2

a) 1-seconds raw signal as recorded, b) separation of background, reference and sample signal, c) corrected and averaged reference and sample signal with the resulting ratio $Q_{\text{sample2ref}}$
Figure 3

Recorded reflectance over temperature for a) 3 measurements on separate untreated copper samples, b) 6 measurements on separate polished copper samples, c) 3 measurements on separate reduced samples, d) 7 measurements on resolidified copper, some of them conducted consecutively on the sample
Figure 4

a) Overlay of temperature curves for all sample types, b) overlay reflectance measurements for all sample types

Figure 5

Threefold heating and cooling cycle with a) reference signal, b) sample signal and c) reflectance, with arrows indicating process direction
Figure 6

a) Measured reflectance over temperature for a polished sample from before heating until cooled back to room temperature and b) the same process, but plotted over time