Abnormally strong decrease in reflectance of molten copper due to possible generation of levitating sub-micron melt droplets

Vladimir Ya. Mendeleyev, Vladimir V. Kachalov, Andrey V. Kurilovich, Leonid A. Dombrovsky

Abstract

A strong decrease in reflection of a probe laser radiation at wavelength 0.66 \( \mu \text{m} \) from the surface of molten copper in argon atmosphere is observed in laboratory experiments for the first time. Theoretical estimates based on the Mie theory indicated that this effect can be qualitatively explained by a condensation of copper vapor leading to formation of sub-micron droplets levitating above the sample. This physical model is supported by the observed diffuse scattering of incident radiation and also by a regular structure of small crystals on solid sample surface after its cooling. This structure is similar to a solidified cluster of melt droplets after the crystallization of single droplets of copper melt and subsequent growth of the crystals.

1. Introduction

Combined physical effects accompanying the surface melting of various materials have attracted permanent interest of researchers during many years not only because of practical applications but also due to specific combination of various physical properties accompanying the phase change [1–7]. A relatively simple case of melting of pure copper considered in the present paper appeared to be also interesting because of unexpected strong scattering of a probe laser radiation and abnormally decrease in the normal reflection of laser beam from the sample surface. To the best of our knowledge, this effect was observed for the first time.

The objective of the present study is twofold: (1) to study experimentally the time variation of the melt reflectance and (2) to suggest a preliminary physical model for the observed scattering of probe radiation from the molten sample surface.

2. Laboratory set-up and experimental procedure

The schematic of the laboratory installation is presented in Fig. 1, where 1 is the degassing volume, 2 is the optical window, 3 is the electric heater, 4 is the thermal insulation, 5 is the platinum-platinum rhodium thermocouple, 6 is the copper sample clamped around the edge by nickel substrate, 7, 8 is the probe laser (\( \lambda = 0.66 \mu\text{m} \)), 9 and 10 are the semi-transparent mirrors, 11 and 12 are the sensors, 13 is the interference filter, 14 is the screen, 15 is the digital camcorder LightWay-Systems, and 16 is the electrical connector for both the heater and thermocouple. The heating was controlled by thermocouple with a bead separated from the lower surface of the sample by nickel layer of thickness 100 \( \mu\text{m} \). The divergence angle and power of probe laser beam were equal to 0.3 mrad and 40 mW, respectively. The beam incidence angle (measured from the normal) was about 5°. The fluctuations of laser power were measured by sensor 11, whereas the sensor 12 was used to measure the radiation intensity reflected from the sample in the specular direction. This intensity is proportional to the normal (narrow-cone) reflectance of the sample. For simplicity, the corresponding normalized values will be hereafter called as the normalized reflectance. Both the screen 13 and camcorder 14 were used to observe the patterns of the probe light scattered by the sample. The thermo-emf of thermocouple, the data of both sensors and the scattering patterns on the screen were registered by a computer with time interval of 1 s.

3. Copper sample and experimental results

The copper sample (99.9% Cu) was placed in a volume filled by argon at pressure about 10 kPa. The horizontal upper surface of a
cylindrical sample of diameter 10 mm and height of 2.2 mm was ground in one direction. The grooves of roughness about 70 nm on the original surface (Fig. 2a) were made to make evident the melting of a surface layer with the use of scattering patterns. At low temperatures, the pattern looks as a bright central spot and the narrow strip in the direction perpendicular to the grooves. Obviously, the melt surface is smooth, and the melting can be well identified by a disappearing the strip as was suggested in recent papers [8,9].

After the experiment, the central part of the sample surface is covered by a several groups of small crystals (Fig. 2b). This picture is qualitatively associated with the self-assembled levitating clusters of water droplets over the locally heated water surface. The latter phenomenon was observed for the first time by Fedorets [10] and then studied in detail during several years. Some of the most interesting results have been reported in recent papers [11–14]. Note that a formation of copper nanoparticles and their clusters in a gas phase is also studied in recent papers [15,16].

We have no sufficient information to be sure that sub-micron melt droplets form a regular cluster above the sample surface. At the same time, the observed partial regularity of small crystals on the sample surface after the experiment (Fig. 2b) can be treated as an indirect confirmation of such a possibility.

It is interesting to compare the images of the screen taken in the beginning of experiment and at the stage when the scattering of probe light was observed (Fig. 3a and b). It is quite obvious that light scattering in a “mist” of fine particles above the melt surface is significant.

The main results of measurements during the melting experiment are presented in Fig. 4. The time dependence of thermo-emf follows the sample temperature. The almost constant temperature measured at \( t > 8810 \) s corresponds approximately to the final stage of copper melting. The long “plateau” in time dependence of the thermo-emf (and temperature) is explained by a considerable value of the latent heat of copper melting.

The normalized spectral reflectance increases a little at \( t > 8660 \) s, and the increase appeared about three time less at \( 8660 < t < 8805 \) s. The maximum reflectance is reached at \( t = 8817 \) s. According to the observed disappearing the strip, this corresponds to the complete melting of the sample surface.

It is interesting that there is a subsequent strong decrease in the reflectance of the copper sample accompanied by the observed diffuse scattering (Fig. 3) which increases almost monotonically with time. Unfortunately, a quantitative registration of this diffuse scattering appeared to be problematic because insufficient sensitivity of the camcorder. The upgrade of the equipment and conducting a series of experiments at various key parameters using the modified set-up will take time. Therefore, we prefer to present this technical note without an additional time delay.

4. Possible explanation of the experimental data

A qualitative physical model considered in this section is based on the assumption of a partial homogeneous condensation of copper vapor and formation of a plane cluster of small melt droplets levitating over the molten sample. The calculations based of the data reported in [17] showed that mass flow rate of copper vapor in vacuum is rather large at temperatures greater than the melting point and it is well described by the Arrhenius kinetic law:

\[
\dot{m} = A \exp\left(-\frac{E_a}{T}\right)
\]

\[
E_a = 35628 \text{ K} \quad A = 1.9215 \times 10^7 \text{ kg m}^{-2} \text{ s}^{-1}
\]

\[
\text{(1)}
\]

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( a )</td>
<td>droplet radius</td>
</tr>
<tr>
<td>( A )</td>
<td>pre-exponential factor</td>
</tr>
<tr>
<td>( d )</td>
<td>distance between droplets</td>
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<td>( E )</td>
<td>activation energy</td>
</tr>
<tr>
<td>( m )</td>
<td>mass flow rate</td>
</tr>
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<td>( n )</td>
<td>index of refraction</td>
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<tr>
<td>( Q )</td>
<td>dimensionless efficiency factor</td>
</tr>
<tr>
<td>( R )</td>
<td>reflectance</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( s )</td>
<td>surface fraction of droplets</td>
</tr>
<tr>
<td>( u )</td>
<td>thermo-emf</td>
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Greek symbols

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<th>Symbol</th>
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<tr>
<td>( \kappa )</td>
<td>index of absorption</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>form-factor</td>
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<tr>
<td>( \rho )</td>
<td>density</td>
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Subscripts and superscripts

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<td>( a )</td>
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<tr>
<td>( A )</td>
<td>Arrhenius</td>
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<tr>
<td>( m )</td>
<td>melting</td>
</tr>
<tr>
<td>( n )</td>
<td>normal</td>
</tr>
<tr>
<td>( t )</td>
<td>total (extinction)</td>
</tr>
<tr>
<td>( 0 )</td>
<td>referenced value</td>
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Fig. 1. The schematic of laboratory installation.
This simple relation is true only at very low pressure of ambient argon and the general calculations at an arbitrary pressure are much more complicated [18,19]. It is assumed that condensation process in the upcoming argon-vapor flow over the sample of melted copper may lead to homogeneous nucleation and formation of submicron droplets of the melt. To simplify the estimates, the melt droplets are assumed to be spherical with the same radius $a$ and invariable distance $d$ between the centers of neighboring droplets. These assumptions are based on the observations of clusters of water droplets levitating above the locally heated water surface [13,14]. In subsequent estimates, we will use the variable surface fraction of melt droplets defined as:

$$s = \frac{\zeta (a/d)^2}{n}$$

where the form-factor $\zeta$ depends on the cluster pattern and the total number of droplets. To obtain an estimate of time variation of parameter $s$, one can assume the exponential decrease in the net mass rate of condensation:

$$m = m_0 \exp(-t/t_0) \quad m_0 = A \exp(-E_A/T_m)$$

where $t_0$ is the characteristic time of the droplet growth and $T_m = 1358$ K is the melting temperature of copper. The exponential time decrease of mass condensation rate should be considered as a qualitative description of its asymptotic behavior. Of course, this approximation does not pretend for the correct quantitative results. The mass balance equation leads to the following initial-value problem for the droplet radius:

$$a = \frac{m}{\rho_m} \quad a(0) = a_0$$
and the resulting analytical relation:

\[ a = a_0 + \frac{m_0 t_0}{\rho_m} [1 - \exp(-t/t_0)] \]  

where \( t \) is the time measured from the conventional nucleation moment. It is assumed in subsequent calculations that the initial droplet radius is equal to \( a_0 = 5 \) nm. Note that this is not a strong parameter of the problem.

Generally speaking, the rigorous modeling of radiation scattering by a cluster of closely spaced and partially ordered small particles is a very complicated problem because the wave effects of the so-called dependent scattering should be taken into account. It would be not realistic to solve this problem as applied to the present experiment because there is no data for a hypothetical cloud of melt droplets. The relatively simple theoretical estimates are based on the Mie theory for single spherical droplets and the simplest theoretical model of independent scattering. According to this widely used approach, each droplet is assumed to absorb and scatter the radiation in exactly the same manner as if other droplets did not exist. In addition, there is no systematic phase relation between partial waves scattered by individual particles, so that the intensities of the partial waves can be added without regard to phase. In other words, each particle is in the far-field zones of all other particles, and scattering by individual particles is incoherent.

The single scattering of radiation by independent droplets of copper melt seems to be an acceptable physical model. It is known that light scattered by sub-micron droplets has no narrow peaks in both the forward and backward directions. It means that both the absorbed and scattered radiation do not contribute to the normal reflectance of the sample. The resulting relation for the relative normal reflectance is as follows:

\[ \bar{R}_n = \frac{R_{0n}}{R_{abs}} = 1 - 3Q_t \]  

where \( R_{0n} \) is the normal spectral reflectance of the melt (without partial shielding by levitating melt droplets) and \( Q_t \) is the dimensionless efficiency factor of extinction to be calculated using Mie theory. Obviously, the minimum value of \( R_{0n} \) should be positive even in the case when the theory gives the value of \( Q_t > 1 \).

According to the Mie solution, this value depends on diffraction (size) parameter \( x = 2\pi a/\lambda \) and also on complex index of refraction \( m = n - i\kappa \), where \( n \) is the index of refraction and \( \kappa \) is the index of absorption. The spectral values of \( m \) for pure copper in the visible range are well studied at room temperature starting from the early papers, but the value of \( m \) changes with temperature. The measurements of spectral emittance of copper at wavelength \( \lambda = 0.656 \) \( \mu \)m in [30] showed that the effect of temperature is relatively small for solid copper, whereas the normal emittance decreases sharply from 0.16 for solid copper to 0.12 at the melting. Similar results have been obtained more recently at \( \lambda = 0.6845 \) \( \mu \)m in [31,32].

The calculated spectral values of both extinction factors of absorption and extinction using the Mie theory code published in early book [33] (see also [22]) are presented in Fig. 5. The optical constants of solid copper from papers [27,28] were used in these calculations. One can see that a contribution of scattering increases strongly with droplet radius and the maximum value of \( Q_t \) (Fig. 5b) is reached at the wavelength about 0.6 \( \mu \)m. The latter means that our choice of the probe laser wavelength appeared to be close to the best one. The value of \( Q_t \) increases strongly from \( Q_t = 0.2 \) at \( a = 45 \) nm (this point is not shown in Fig. 5a) to the maximum value of \( Q_t \approx 3.8 \) at the droplet radius about 100 nm.

It is clear from Mie calculations (Fig. 5a) that an additional increase in radius of the melt droplet at \( a > 100 \) nm could lead to a decrease of \( Q_t \) and the resulting increase in the sample reflectance. The latter has not been observed in the experiment. Therefore, it seems natural to conclude that the radius of levitating melt droplets is less than about 100 nm.

The computational data obtained using approximate Eqs. (2)–(6) at two different values of \( t_0 \) according to the experimental data of Fig. 4 are presented in Fig. 6b. The realistic values of \( d = 1.5 \) \( \mu \)m and \( \xi = 2.5 \) were used in the calculations. A comparison of the theoretically predicted decrease in normal spectral reflectance of the copper sample (see Fig. 6b) and the experimental data (Figs. 3 and 4) enable us to say that the qualitative physical model suggested gives a satisfactory explanation of the effect observed in the laboratory experiments and confirms the condensation growing of the levitating nanodroplets up to the radius about 100 nm.

![Fig. 5](https://example.com/fig5.png)

**Fig. 5.** Spectral dependences of efficiency factors of (a) absorption and (b) extinction for copper melt droplets: 1 - 40 nm, 2 - 50 nm, 3 - 100 nm.
5. Conclusions

The strong decrease in reflection of a probe laser radiation at wavelength 0.66 μm from the surface of molten copper accompanied by scattering of radiation observed in laboratory experiments was qualitatively explained by a partial condensation of copper vapor and formation of numerous growing melt droplets levitating above the sample surface. It is expected that the radius of these droplets increases from few nanometers and may reach the maximum value about 100 nm. The last estimate was obtained using the Mie theory. The physical model suggested is supported not only by observations of the scattered light of a probe laser but also by a specific regular structure of small crystals on the sample surface after its cooling.

Conflict of interest

None declared.

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References


