

# Laser-Produced Plasma Measurement of Thermal Diffusivity of Molten Metals<sup>1</sup>

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We have shown that a laser-produced plasma plume which is representative in elemental composition of the condensed phase target can be reproducibly generated if the movement of the surface due to evaporation is kept in pace with the thermal diffusion front propagating into the bulk. The resulting mass loss is then strongly controlled by the thermal diffusivity of the target matter, and this relationship has been exploited to measure the thermal diffusivity of metallic alloys. We have developed a novel RF levitator-heater as a contamination-free molten metal source to be used as a target for LPP plume generation. In order to determine the mass loss due to LPP excitation, a new high-sensitivity transducer has been constructed for measurement of the resulting impulse imparted on the specimen. The impulse transducer is built onto the specimen holder within the levitation-assisted molten metal source. The LPP method has been fully exercised for measurement of the thermal diffusivity of a molten specimen relative to the value for its room temperature solid. The results for SS304 and SS316 are presented, together with a critique of the results. A numerical modeling of the specimen heating in the molten metal source and the physical basis of the new method are also presented.

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**KEY WORDS:** impulse transducer; laser-produced plasmas; levitation-assisted molten metal source; molten metals; RF heating; SS304; SS316; thermal diffusivity.

## 1. INTRODUCTION

When a material surface is excited by a high-power laser pulse of carefully selected time profile and power density, a plasma plume can be reproducibly generated which has the same elemental composition as that of the

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condensed phase target. The movement of the target surface due to ensuing evaporation is kept in pace with the thermal diffusion moving into the bulk when such a representative laser-produced plasma (LPP) is generated. This presents two fundamentally new opportunities: (a) any condensed-phase materials can be characterized for elemental composition and thermo-physical and mechanical properties [1–4], and (b) vapor plumes of arbitrary composition can be created from designer-blend targets for nanoscale deposition on a substrate [3, 5, 6].

We have developed a general rule for producing such representative plasma plumes through rigorous basic research. A novel analysis methodology and instrumentation facilitating real-time *in situ* composition determination of molten metallic alloys have been implemented [7, 8]. The mass loss per LPP excitation is highly correlated with the thermal diffusivity of the target matter [3]. This relationship has been exploited to measure thermal diffusivity [4]. Potentially, the strategy of measurement by laser produced plasmas can be extended to many other thermophysical and mechanical properties of any condensed matter over a wide range of temperature.

## 2. REPRESENTATIVE LPP PLUME PRODUCTION

When a metallic surface undergoes a sustained excitation by a pulsed laser at  $1.06\ \mu\text{m}$  at power densities in the range of  $10^9$  to  $10^{11}\ \text{W}\cdot\text{cm}^{-2}$ , it is possible to produce supercritical plasma plumes whose plasma frequency exceeds the laser frequency. The electron density can exceed  $10^{21}\ \text{cm}^{-3}$  and the temperature may rise beyond several hundred electron volts in the core at its peak [2, 3, 9]. The plume becomes optically thick so that the conventional plasma diagnostic methods often become inadequate. Instead, the plasma properties are determined from the second harmonic generation, measurement of ion acoustic wave frequency, plasma spectroscopy, and numerical simulation [3].

Streak photography shows two distinct stages of the plasma plume development: a “fast ion” plasma, with the radial expansion velocity reaching  $2.5 \times 10^7\ \text{cm}\cdot\text{s}^{-1}$ , and a plasma core, which evolves over a longer period of time. A strong shock wave emerges due to the expansion of the plasma core into the remnant gaseous atmosphere of the fast ion plasma (or the pre-existing background gas). The shock speed may be as high as  $5 \times 10^6\ \text{cm}\cdot\text{s}^{-1}$ .

Once a weakly ionized plasma is formed at the surface, direct heating of the vapor plume by the laser beam is initiated through the inverse Bremsstrahlung process. At sufficiently high laser power densities, the plasma enters into the supercritical state some time during the laser pulse, which then prevents the laser from reaching and heating the target surface directly.

Production of an LPP plume whose composition is the same as that of a multielement target is necessary for both types of measurements mentioned above. If the velocity of the surface movement is small compared with the thermal diffusion velocity, the evaporation takes place preferentially for those species of high evaporation rates. The result would be an LPP plume whose elemental composition is different from that of the bulk. As the surface heating rate is raised and the movement of the bulk surface is sharply increased, the elemental dependence of the evaporation rate basically disappears. If the laser heating rate is further increased, the laser beam becomes eventually disconnected from the surface due to its direct coupling to the plasma as stated earlier. The plasma emission spectrum becomes dominated by continuum emissions due to the plasma processes, in contrast to the atomic excitations.

The criterion is then to choose the laser pulse power profile in such a way that the movement due to evaporation of the bulk surface is kept in pace with the thermal diffusion front advancing into the interior of the target. The LPP plume becomes representative of the bulk in elemental composition. We have found that such a representative plasma is always spectroscopically productive and robust.

The physics of LPP plume production discussed above have been established through a critical comparison of theoretical predictions by numerical simulation [2, 9] with detailed laboratory measurements [3, 9]. An important conclusion which can be constructed from the numerical code so verified is the general rule for production of representative LPP plumes. The rule highlights the importance of the rate of mass removal from the surface.

### 3. BASIS FOR THERMAL DIFFUSIVITY DETERMINATION

Given that the conditions of the general rule are met, the rate of mass removal scales as the thermal diffusivity of the target matter, subject to the energy cost of evaporation and the LPP plume's ability to disperse away from the target surface so that the evaporation process can continue. This means that the thickness of surface ablation grows inversely with the heat of formation and decreases with increasing molecular weight. The scaling of the experimentally measured thickness of ablation for four pure solid targets—namely, aluminum, copper, manganese, and lead, as correlated with the known elemental and thermophysical properties, is given by Eq. (1) [4]:

$$\theta = CD_T^\alpha M^\beta H_f^\gamma \quad (1)$$

Here  $\theta$  denotes the thickness in cm,  $D_T$  the thermal diffusivity in units of  $\text{cm}^2 \cdot \text{s}^{-1}$ ,  $M$  the molar weight, and  $H_f$  the heat of formation in  $\text{J} \cdot \text{g}^{-1}$ .  $C = 11.07 \pm 0.45$ ,  $\alpha = 0.91 \pm 0.01$ ,  $\beta = -\alpha$ , and  $\gamma = -1$ .

The existence of the scaling relationship of Eq. (1) is remarkable in that it is empirical but its existence was anticipated as a result of the extensive numerical simulation study. The four pure elemental specimens span a range of the values of respective thermophysical properties, wide enough to cover typical metallic alloys. We intend to track the validity regime of Eq. (1) as the basic data on alloys accumulate.

Given the density, heat of formation, and molar weight, determination of the thermal diffusivity of a molten metal in a given thermal state reduces to measuring the ablative mass loss per laser excitation. The mass loss can be obtained by measuring the impulse on the molten metal target.

It is now possible to extend this as a general method of thermal diffusivity measurement for arbitrary materials. The specimen may be an alloy composed of many elemental species. Here, its elemental composition is determined by time- and space-resolved spectroscopy of the LPP plume, while the ablative mass loss is determined by measuring the impulse imparted on the target by an LPP plume. The analysis is not restricted to metallic substances.

#### 4. NUMERICAL MODELING OF LEVITATION-ASSISTED MOLTEN METAL SOURCE

*In situ* molten metal analysis requires a new calibration protocol for two reasons: (i) the interaction of a laser pulse with molten metal is distinctly different from that with a solid specimen because of the absence of energy expenditures for melting in the liquid phase and the differences in transport properties and optical reflectance between the two phases; and (ii) the conventional analysis procedure of comparing the spectral response of a solid specimen to excitation by spark discharges with those of so-called "like" standards of solid form cannot be applied to molten metal analysis because upon melting the certified elemental composition of a standard specimen is quickly lost in time due to evaporation, contamination from crucibles, or gas-phase reactions at the surfaces.

For solid specimen analysis, on the other hand, the calibration procedure had evolved over several decades through the process of multiple measurements by independent laboratories, the key ingredient being the use of certified "like" standards. It is therefore prudent to maintain a clear linkage between the LPP analysis of molten metals and the solid specimen standards. The new calibration protocol which we have developed for molten metal analysis is to capture a solidified specimen of molten metal

immediately after each LPP excitation. Such a solidified specimen is then analyzed by the conventional methods to close out the calibration loop.

We have thus developed a crucible-free molten metal source, which consists of an RF levitator-heater for momentary generation of molten metallic specimens [3, 4]. The levitation-assisted molten metal source, described previously [3], is powered by a 15-kW RF power generator, operating at frequencies from 70 to 200 kHz. The RF coil has the basic levitator-heater design with three turns and a fourth turn in reverse at the top. The diameter of the levitator-heater coil is about 3.0 cm at its maximum. A metallic rod specimen is placed vertically just below the minimum-B point. The top end is heated to melting while supported by the levitation field; this prevents the molten metal from spilling over. A 5.0-cm-long solid rod specimen 6 to 9 mm in diameter is first mounted on a specimen holder in order to begin the process of momentary creation of a molten metal specimen.

The heating history depends sensitively on the dimensions of the specimen as well as its thermophysical properties. Under a fixed set of

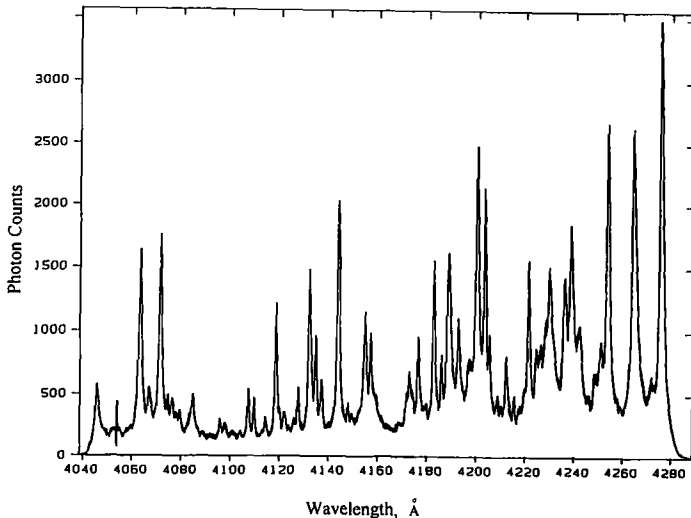
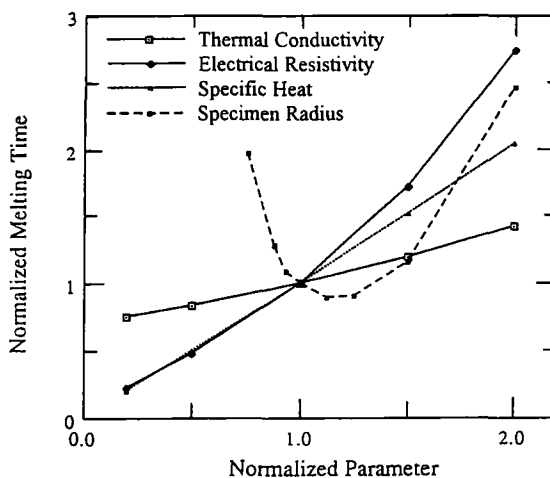


Fig. 1. The measured LPP spectrum from a molten AISI 1018 target. Five successive runs are superimposed without any rescaling. Each of the five specimen rods used was heated to melting, starting from room temperature, in the RF levitator-heater in a helium atmosphere. A 6.88-J laser pulse of 65-ns full-width-at-half-maximum was incident on the molten metal surface, and the time-resolved, gated spectrum was taken after a fixed delay time.

operating conditions, heating of a specimen of given elemental composition is highly reproducible, provided that the placement of the specimen within the heater is strictly controlled. This reproducibility is essential to both the molten metal calibration and the thermophysical property measurement. The degree to which a measurement sequence is reproduced is well demonstrated in Fig. 1, where a segment of the emission spectrum from an LPP plume off the molten metal surface is shown for five successive runs. The high degree of reproducibility is particularly significant when one notes the fact that each of the five runs starts with positioning a fresh rod specimen within the RF levitator-heater, heating it to the fluid molten state where a thin crust covering the molten top end of the specimen first breaks open, exciting the surface with a laser pulse and taking the time-resolved emission spectrum from the LPP plume. Despite the numerous steps involved in each run the overall reproducibility is excellent as demonstrated by the small spread in the emission intensities across the entire spectrum.

The temporal history of a specimen heating in the levitation-assisted molten metal source has been modeled by means of a numerical simulation code we have developed. The result is summarized in Fig. 2 in the form of



**Fig. 2.** The normalized time of melting as a function of four normalized thermophysical properties: thermal conductivity, electrical resistivity, specific heat, and specimen rod radius. The reference metal is SS316, whose normalized thermophysical properties are taken to be unity. In the computations, only one parameter was changed at one time while keeping others at the reference values. The temperature dependences of the parameters were taken to be those of SS316. The reference radius was set at 3.2 mm.

the dependence of the heating time to reach the molten state at a fixed RF power level on thermophysical properties of the specimen material. The objective here is to minimize the changes in the elemental composition of the specimen material by minimizing the heating time, and this modeling by numerical simulation provides the road map for optimal preparation of the molten specimen so as to maximize the reproducibility. Four parameters have been systematically varied: thermal conductivity, electrical resistivity, specific heat, and specimen radius. The temperature dependence of each parameter is modeled according to the particular thermophysical property of steel alloys: carbon steel alloys of AISI 1002 through 1086 and stainless steel of the 303, 304, and 316 series. All specimens are assumed to be 5.0 cm in length, and the reference diameter is 6.4 mm. The specimen holder plays a role as a heat sink, and this has been kept fixed in this simulation.

We note that the code prediction of the heating time has been checked against the measurement with different alloy materials. Excellent agreements have been obtained. A full detail of the modeling of the heating process in the levitation-assisted molten metal source will be presented in a separate paper [10].

## **5. DETERMINATION OF LPP MASS LOSS BY IMPULSE MEASUREMENT**

The key step here is to determine the total mass of the laser ablated target material through measurement of the impulse imparted on the target in the process. The impulse measurement capability is built into the specimen holder by spring-loading a piezoelectric force gauge at the base [4]. The impulse from the LPP plume drives the specimen into motion, and this displacement is detected by the piezoelectric force gauge after a characteristic time delay. For absolute determination of the impulse, the transducer is calibrated by dropping a steel bearing ball from a known distance above. The time of flight over a fixed distance interval is measured before, and after, each impact so that the coefficient of restitution can be determined and the impulse calculated. The distance of fall and the size of the ball are varied in order to change the impulse. A calibration curve is generated by measuring the maximum value of the transducer output.

The output of the impulse transducer from a molten metal specimen contains a large background signal at the frequency of the RF generator. We have developed a robust signal recovery method by which this background signal is deleted self-consistently from the total transducer output, thus obtaining the true impulse data. The method has been described elsewhere, together with sample data taken for solid as well as molten metal

specimens [4]. The impulse on the molten metal surface is transmitted to the transducer, which is located at the bottom of the specimen holder. A measure of the impulse is defined by the first maximum of the transducer output following the laser pulse excitation. The experimental arrangement is the same as that given in Ref. 4.

We have thus far accomplished  $\pm 2\%$  uncertainty in maximum impulse measurement for solid specimens and  $\pm 4\%$  for molten metal specimens. By means of the calibration curves, the result can be converted into the impulse at the surface. The total mass loss per laser pulse can be found from the measured impulse once the elemental composition of the LPP plume and their mean velocity normal to the target surface are determined. From Ref. 4, the impulse on the target specimen due to LPP ablation may be written out as follows:

$$\text{Impulse} = \sum_{i=\text{species}} \int_0^{\infty} dt \int_0^{\infty} dv_{\perp} M_i(t) f_i(\mathbf{r}, \mathbf{v}, t) A v_{\perp}^2 \quad (2)$$

$$= \sum_{i=\text{species}} \frac{1}{2} A k_B \int_0^{\infty} dt n_i(t) T_i(t) \quad (3)$$

Here  $M_i$  and  $f_i(\mathbf{r}, \mathbf{v}, t)$  denote the particle velocity distribution function and the mass of the  $i$ th species, respectively. The component of the particle velocity normal to the target surface is indicated by  $v_{\perp}$ .  $A$  is the area of the surface exposed to the laser excitation and  $k_B$  is the Boltzmann constant.  $n_i(t)$  denotes the number density and  $T_i(t)$  the temperature of the  $i$ th species in the LPP plume at time  $t$ . The second step [Eq. (3)] follows from the equipartition theorem. Notice that the collision time in the plume is of the order of 1 fs, while the relevant dynamics in the system develop in the nanosecond time regime, and therefore the plasma remains in thermal equilibrium throughout its evolution. In other words, the temperature becomes common for all species,

The composition is obtained from the time-resolved spectroscopy of the LPP plume by the method we have already developed. The mean velocity of the escaping plume species may be measured from the Doppler shifts of the elemental emission lines at the peak of the plasma temperature and density. Or this could be a matter of obtaining the temperature of the LPP plume as a function of time, as Eq. (3) indicates. The reduction of the thermal diffusivity of the molten metal then follows from Eq. (1)

## 6. DETERMINATION OF RELATIVE THERMAL DIFFUSIVITY

Alternatively, the thermal diffusivity of a molten metal may be determined relative to that of the same specimen in its solid phase. This has



**Table I.** Measured LPP Impulses for SS304 and SS316 in Solid and Liquid Phases

Specimen	Impulse (mV)
SS304	
Solid	$3.071 \pm 0.060$
Molten	$1.164 \pm 0.070$
SS316	
Solid	$3.206 \pm 0.060$
Molten	$1.053 \pm 0.040$

considerable utility given the complexity associated with defining the standard materials over the extremely wide range of metal alloys that are manufactured industrywide. The levitation-assisted molten metal source facilitates the change of phase and temperature with a high degree of reproducibility. According to the basic physics contained in Eq. (3), we simply need to compare the impulses of the specimen in two different phases. Table I summarizes two sets of measurements, one with SS304 specimens and another with SS316 specimens.

The exact surface temperature to which the molten metal was heated remains somewhat uncertain. No attempt has been made to independently measure the surface temperature to date. On the basis of the heating rate, we estimate that it was approximately 50 K above the melting point. The melting point is approximately known to be in the range of 1648 to 1723 K. In view of the fact that we operate slightly above the melting point, we put the temperature of the molten metal to be at  $1720 \pm 50$  K.

By taking the ratio of the LPP impulses, we have found that the thermal diffusivity of the molten SS304 specimen relative to that of the same specimen in solid form at room temperature is  $0.38 \pm 8\%$ . We also obtain a corresponding value for SS316 of  $0.33 \pm 6\%$ . The differences in the absolute as well as the relative thermal diffusivity for these two stainless alloy specimens are greater than the margins of experimental uncertainties and are, therefore, of a significant indicator of their different thermophysical properties.

We have found no other measurements in the literature that can be directly compared with the present results. Some inferences, however, may be made by piecing together a number of thermophysical data available in the literature. For aluminum, copper, and zinc, the thermal conductivity decreases by a factor of 2 to 2.3 in going from a room-temperature solid to a molten state [11, 12]. The specific heat for aluminum, copper, iron,

chromium, and nickel increases by a factor of 1.21 to 2.04 in going from a room temperature solid to a molten metal [11–13]. The mass density for aluminum, copper, zinc, and iron, on the other hand, decreases by a factor of 1.08 to 1.18 when they undergo transformation from a room temperature solid to a molten metal [14]. Combining these general trends into a scaling for the thermal diffusivity, the measured liquid-to-solid thermal diffusivity ratios for SS304 and SS3 16 appear very reasonable.

The primary sources of experimental uncertainties in the LPP impulse measurement are (i) the variability of specimen placement within the RF levitator-heater, which affects the history of specimen heating; and (ii) the composition inhomogeneity from one specimen to another. As far as the rigorousness of the methodology is concerned, the relative thermal diffusivity measurement is on an exceptionally sound footing. The measurement in a solid and molten state can be performed back to back on the same specimen. The compositions in the two phases are nearly identical except for the element-specific evaporative loss, which is subject to the length of heating time. Maintenance of a short, consistent heating time is very important here, and the facilities and numerical modeling we have developed for this investigation help meet the requirements.

## 7. CONCLUDING REMARKS

Laser-produced plasmas can be realized in many ways. Generating a representative LPP plume, however, requires a rigorous adherence to the general rule for production of representative LPP plumes. This opens up fundamentally new opportunities in materials characterization and synthesis. The plasma emissions, acoustic emissions, and mechanical events, all generated from a single LPP excitation, can provide unlimited views into a thin slice of the target surface, ranging from elemental composition to transport properties to strength and wear characteristics.

The LPP method of measuring the thermal diffusivity of molten metals as presented is a powerful one in its simplicity and versatility. The fact that simultaneous determination of the thermal diffusivity can be made for both a solid and a liquid state on a single specimen may provide a unique opportunity for rigorous first-principle studies of thermophysical properties of metallic alloys. A large body of thermal diffusivity data can be generated in the thermodynamic regimes where relevant data simply do not exist at present. For instance, by incorporating a pyrometric thermometer into the levitation-assisted molten metal source, the measurement may be extended into higher temperatures well above the melting point of a specimen material.

We note that it is, in principle, possible to determine the LPP mass loss spectroscopically. This notion is derived from our established LPP method of elemental composition determination. The emission intensities by elements must be integrated over time so that a measure of the total mass loss can be obtained during a single LPP excitation of the target. This means that the thermal diffusivity measurement can, in principle, be achieved without any physical contact with the target specimen because use of the impulse transducer may be avoided. We are currently engaged in implementing such an approach.

It is conceivable that when such an alternative, noncontact method is perfected, and the database for molten metallic alloys is extensively developed, a new set of experiments can be carried out with molten alloy specimens, instead of solids, in order to refine the exponents in the scaling relationship of Eq. (1) for molten alloys.

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