1 of 1

ergy

CONSUMPTION

**DOE/ID/13103-T1
(DE94007014)**

**MOLTEN METAL ANALYSIS BY LASER PRODUCED PLASMAS
Technical Progress Report**

**By
Yong W. Kim**

February 1994

Work Performed Under Contract No. FC07-91ID13103

**For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.**

**By
Lehigh University
Bethlehem, Pennsylvania**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the U.S. Department of Commerce, Technology Administration, National Technical Information Service, Springfield, VA 22161, (703) 487-4650.

MOLTEN METAL ANALYSIS BY LASER PRODUCED PLASMAS

Technical Progress Report

Work Performed Under Contract No. DE-FC07-91ID13103

**Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Sponsored by the Office of the Assistant Secretary
for Energy Efficiency and Renewable Energy
Office of Industrial Technologies
Washington, D.C.**

**Prepared by
Yong W. Kim
Lehigh University**

Executive Summary

A radically new methodology of molten metal analysis, consisting of time- and space-resolved spectroscopy of a laser produced plasma (LPP) plume off a molten metal surface, forms the basis of the research program. It has been implemented in the form of a prototype LPP sensor-probe, which permits in-situ elemental composition analysis of molten metallic alloys in less than a minute. A major patent has been issued for the concept and instrumentation of the LPP sensor-probe system. (U.S. Patent No. 4,986,658; additional foreign patents already issued or pending.) The DOE sponsorship under the Metals Initiative pertains to the final program phase of technology transfer, comprising deployment of two LPP sensor-probes in metals production shops and identification of a manufacturer(s) for mass production of the LPP sensor-probes.

The objective of the project is to develop and test two laser-produced plasma (LPP) sensor-probes in steel mills for rapid determination of the elemental composition of molten steel over a 42 month period. The project is divided into two overlapping phases, A and B. In Phase A, a new calibration protocol for the LPP sensor-probe was implemented to facilitate definitive assignment of elemental concentration to the spectral intensity of the LPP plume. Phase B tasks include design, installation and testing of two LPP sensor-probes at two steel plant sites, and identifying a future sensor-probe manufacturer(s).

The LPP sensor-probe system consists of a sensor-probe unit and a control console, connected by a hermetically sealed umbilical cord. The instrumentation is designed to function over an open-air furnace as well as inside a vacuum furnace. Normally, the sensor-probe penetrates the molten metal bath, and an intense laser pulse is delivered to the liquid metal surface. The spectral emission from the resultant plasma plume is measured during a sub-microsecond period some time after the laser pulse. A pattern recognition algorithm is used to obtain the elemental composition of the molten metal. The overall sequence resulting in elemental composition determination takes less than one minute.

During the past 12 month period, a new levitation-assisted molten metal source has been developed. By combined use of the molten metal source and the laboratory LPP sensor-probe we have confirmed the full calibration protocol. A set of five calibration curves, one each for Mn, C, Si, Al and S in a wide variety of molten steel alloys. In addition, the program of identifying the materials and design for the protective refractory sheath of the LPP sensor-probe was completed. The program of developing the statistics for repeated immersion of the sheath into a molten metal bath has been initiated and is continuing.

The intellectual property agreement has been negotiated, and signed, by the Department of Energy and Lehigh University. The budget for Phase B has also been submitted to the Department of Energy. Two host steel manufacturing facilities have been selected: they are Carpenter Technology and the Timken Company. The full 30% cost-sharing commitments for the expenditures associated with the first LPP sensor-probe installation have been finalized: they will be provided by the American Iron and Steel Institute, the Ben Franklin Fund and the CTU 5-2 consortium of Northamerican metals producers. The specific components of investigation are being pursued according to the schedule of the milestones.

The CarTech segment of the project will take place over a period of 24 months from the start of Phase B. The physics, technology development and engineering of the LPP sensor-probe system are described in the main text. Also described are the concept, laboratory implementation and analysis results, of the molten metal analysis protocol, as well as the progress with the selection of, and development of the immersion statistics for, the protective sheath material for the LPP sensor-probe. The plan for the deployment of the LPP sensor-probe systems and the current cost-sharing arrangements are presented.

Table of Contents

	page
Executive Summary	2
Table of Contents	4
List of Tables	5
List of Figures	6
1. Introduction	7
2. The Phase I and II Accomplishments of the Lehigh Program	9
3. Transient Spectroscopy of Laser Produced Plasmas	14
4. Description of the DOE Contract Milestone Tasks	19
5. Progress with the Phase III-A Milestone Tasks	26
6. Current Status of the Project Administration	40
Acknowledgement	41

List of Tables

	page
Table 1. <u>Milestone schedule - Revised.</u>	25
Table 2. <u>Comparative analysis of elemental composition of the original versus resolidified stainless steel specimens.</u>	30
Table 3. <u>Comparative analysis of elemental composition of the original versus resolidified low alloy steel specimens.</u>	31
Table 4. <u>The required concentration ranges by elements for steel alloy analysis.</u>	32
Table 5. <u>The required precision in weight percent and percent uncertainty for molten metal analysis according to concentration ranges.</u>	33
Table 6. <u>Summary of the molten metal calibration data.</u>	34

List of Figures

	page
Fig. 1. A schematic diagram of the series of events associated with each LPP analysis exercise.	11
Fig. 2. A schematic diagram of the experimental arrangement incorporating the levitation-assisted molten metal source and the optics for the laser and LPP spectroscopy.	28
Fig. 3. A schematic diagram of the 40 kW vacuum induction furnace with a motorized translation stage to which a water-cooled, simulated penetration tube is attached.	39

1. Introduction

The metal producing industry faces the major challenge of increasing productivity to reduce costs and maximize the benefits from existing equipment. In a detailed study of sensor needs within the steel industry, the American Iron and Steel Institute determined that rapid in-process analysis of molten metal was one of four sensors critically needed to reduce costs and increase productivity. It is quite apparent that development of a suitable sensor for steel would find broad applications with other metal producers.

Steelmaking involves the basic steps of charging the furnace, melting the charge, and refining. During refining, it is critical that the operating parameters be adjusted and controlled such that chemistry of the melt is within predetermined limits. To take a sample from an operating furnace and have it analyzed is time consuming and accounts for up to 20% of the overall time required to refine a heat of steel. Under the most ideal conditions, total sampling and analysis time takes up to 5 minutes.

According to the 1982 AISI report, development of equipment for the rapid in-process analysis of molten metal has the potential to provide over \$200 million annually in tangible benefits to the steel industry alone. The tangible benefits include reduction in heat time by up to 10%, with improved refractory life and reduced production costs, material costs, desulfurization costs, and variations in hot metal composition. In addition to the tangible benefits, the use of in-process

analysis of molten metal can provide intangible benefits by improving product quality and productivity, speeding up ladle metallurgy processes, eliminating major capital investments, and by improving the basic understanding of steelmaking process and reducing inventory by closer control of manufacturing.

There are numerous applications for such in-process analysis in steelmaking and some of them are to:

- provide iron composition continuously during furnace cast,
- provide rapid analysis of steel bath during refining,
- monitor sulfur removal during desulfurization,
- assure meeting ladle treatment requirements,
- optimize trim additions in the ladle,
- make ladle tests while ingot teeming,
- monitor metal composition in continuous caster, and to
- optimize alloy additions during vacuum degassing.

An updated assessment of the critical areas of need for a real-time, in-situ sensor for molten metal composition analysis, conducted by a task force of the AISI CTU 5-2 consortium in 1990, specifically identified the two primary areas of application: i) high-alloy steelmaking for high performance steel applications in existing manufacturing shops; ii) direct steelmaking for both low and high alloys in an integrated manufacturing environment. The first area of application is immediate and the second lies sometime in the future as several current initiatives for integration in the industry undergoes development.

The above considerations hold true for other metal industries

such as aluminum, copper, cast iron and refractory metals, and recognition of the needs has indeed been forthcoming within the respective industries in recent years.

The research project at Lehigh University on molten metal analysis by laser produced plasmas began in 1985, in direct response to the industrial needs. The broad objective of this research project has been to develop, and implement, instrumentation and equipment for rapid in-process analysis of molten metal in metals production shops by means of time-resolved spectroscopic analysis of a laser-produced plasma (LPP) from the molten metal surface. The research project has been structured in three major phases: Phase I. Laboratory verification of the basic concept; Phase II. Critical comparison of the new LPP method with the conventional analysis method for solid specimens and field trials of a prototype sensor-probe in small-scale metal shops; Phase III. Design, production and installation of two sensor-probes in metal production shops.

The 1987-1989 project period marked the successful conclusion of Phase II components; the program of solid specimen analysis by the LPP technique is complete. A prototype LPP sensor-probe, capable of applications to molten metal analysis, was constructed and put through field trials.

2. The Phase I and II Accomplishments of the Lehigh Program

The phase I and II investigations at Lehigh University established the rules for identifying the window of applicability

by exploring deeply into the underlying physical processes of laser-matter interaction, and formulated the workable strategy and hardware for real-time, in-situ analysis of molten metals under production conditions.

The LPP based analysis approach was shown to be manageable and superior to the conventional means in terms of its adaptability to different operational requirements, speed of execution, number of different elements that can be analyzed and the additional information it is able to generate for process control applications.

The concept has been implemented in the form of a prototype sensor-probe and a control console, with a hermetically sealed umbilical cord connecting the two. The instrumentation was designed to function over an open-air furnace as well as inside a vacuum furnace. The sensor-probe is introduced into the molten metal bath at a pre-selected speed. When a representative molten metal surface is detected at a pre-set distance from the sensor-probe, an intense laser pulse is triggered and the spectral emission from the resultant plasma plume is measured during a sub-microsecond period at a precise time after the laser pulse. The spectral data are then transferred to the control console for data reduction by a dedicated computer. A pattern recognition algorithm is used to obtain the elemental composition of the molten metal. The time required for a full measurement cycle is well less than a minute, as shown in the overall sequence of events in Fig. 1.

In order to make a connection between the new LPP methodology and the long-standing analysis methods, we have first directed attention to analysis of solid alloy specimens. The approach was to obtain emission spectra from the LPP plasma plume and compare the intensities of different elemental emission lines for a solid

Fig. 1. A schematic diagram of the series of events associated with each LPP analysis exercise. .

specimen with those of the solid alloy standards of known elemental composition. The resulting composition data were compared with the results for the same specimens analyzed by the conventional analytical techniques such as spark discharge emission spectroscopy and X-ray fluorescence.

Initially, twelve unidentified specimens were prepared by CarTech for our analysis by the LPP technique. The twelve

specimens represented twelve different grades of steel alloys which covered the full spectrum of the steel making activities of the industry. In a second follow-up analysis sequence, 28 unidentified specimens were provided by Bethlehem Steel for analysis by the LPP method, representing 28 different grades.

By using only six standards, in contrast to tens, if not hundreds, of standards used in the conventional analysis schemes, we obtained an initial set of the composition data for the unidentified specimens. (Remember that the LPP analysis entails firing of a single laser shot and making measurements on all elements of interest within that shot.) These were then compared with the results of the analyses at CarTech of the same specimens for the first set. Similar comparisons were made with those from Bethlehem Steel for the second set. After one iteration, the accuracy and long-term reproducibility of $\pm 2\%$ for individual elemental concentrations was attained. It was determined that, with some refinements in the operation of the sensor-probe, the uncertainty figure can be reduced to less than $\pm 0.5\%$ of any elemental concentration value. These undertakings not only provided a connection of the LPP technique to the conventional analysis methods but demonstrated its intrinsic power and requisite attributes as a one-shot method with minimal reliance on standards. This level of reproducibility is comparable to or better than that of the conventional analysis methods, and meets the accuracy and sensitivity requirements of composition analysis.

The focus was then shifted to molten metals. For this purpose

three different molten metal sources were used. One of the molten metal sources was that of a 1/2-ton induction furnace at the Homer Research Laboratory. Here, the prototype LPP sensor-probe was engaged for analysis and evaluation of its overall performance under production conditions. The two other sources were home-made vacuum furnaces for specific consideration of the response of molten metal to LPP excitation, dynamic range in concentration, reproducibility and detectability of the LPP sensor-probe. The response of metallic alloys to laser excitation when they are in solid state was contrasted to when they were in molten state. As will be discussed later, a fourth molten metal source was developed which is crucible-free and is being utilized for LPP analyses. This source is expected to be the center piece of the industry-wide protocol for molten metal calibration.

All aspects of the LPP analysis concepts have been verified and the entire measurement objectives have been achieved. It is significant to note that the investigations have been carried out both with a table top LPP sensor-probe and with a fully instrumented prototype LPP sensor-probe.

The success of the LPP methodology and the prototype sensor-probe is due to the rigorous understanding of both the fundamental mechanisms of laser-matter interaction leading to a plasma plume and the spatio-temporal properties of the plasma. In simple terms, a strictly defined regime of operation has been established for a number of parameters affecting the laser modes, power density, pulse shape, spatial resolution and timing for

emission intensity measurements. The result is that the cause and effect relationship between elemental composition and spectral intensities was predictably established at each given instant of measurement. In order to ascertain that the elemental composition of the plasma plume is same as that in the condensed-phase metal, an extremely important criterion has been developed and verified in the form of a new rule of thumb - namely, that the laser be operated in such a manner that the evaporation of the condensed-phase metal proceeds in pace with the propagation of the thermal conduction front into the bulk.

Following is a description of the underlying physical processes leading to transient spectroscopic determination of the elemental composition of molten metals by the LPP method.

3. Transient Spectroscopy of Laser Produced Plasmas

The interaction of a high power laser beam with a condensed phase target leads to a wide range of nonlinear phenomena. Of particular interest in the context of elemental composition analysis of condensed-phase specimens is the formation of a plasma plume which grows out of the surface when the incident laser power density exceeds a certain threshold value, typically in the neighborhood of 10^8 W/cm^2 . The high power lasers used for this purpose can be any one of the pulsed lasers operating in the ultraviolet to infrared range with pulse duration of 5 to 100 nsec. The threshold power density varies with the operating wavelength of a laser primarily because the absorptance of the

target surface depends on the wavelength of the incident light.

In the laser power density regime where a plasma plume can be produced from the target surface, the leading edge of the laser pulse is absorbed by the surface layer and heats it rapidly to vaporize the condensed-phase matter into gases. In a solid, power must be expended into the latent heat of fusion in addition to the latent heat of evaporation. The latent heat of fusion is not involved in the case of a liquid. Heating of the surface layer, of course, means a partial loss of the absorbed power into the bulk as a heat sink by the thermal conduction process. The early vapor-phase species interact with the incident laser pulse to be excited internally and ionized. For sufficiently short wavelength lasers, an ionization event may be a bound-free transition by single-photon absorption; for long wavelength lasers multi-photon absorption processes play a significant role. Similarly, free electrons are also released from the target surface by the single or multi-photon photo-electric effect. Collisions among these particles lead to a rise in temperature and pressure of the gas. Thermal ionization, however, remains a mechanism for production of charged species at all stages of laser heating.

The process of evaporation and heating continues until the electron density of the partially ionized gas becomes sufficient to heat the gas by the inverse Bremsstrahlung process. The weakly ionized plasma becomes gradually coupled to the middle segment of the laser pulse while remaining partially transparent to the laser

beam so that direct heating of the target surface continues. The inverse Bremsstrahlung process heats primarily the electrons in the presence of ions, resulting in free-to-free-state transitions, and the heated electrons increase the plasma temperature and, consequently, the electron density. At high laser powers the electron density of the plasma can attain a value sufficiently high that the core of the plasma becomes critical. In this case the frequency of plasma oscillation, as given by $(n_e e^2 / \pi m)^{1/2}$, is comparable to, or greater than, the laser frequency and the laser beam is no longer able to penetrate the critical region and reach the condensed-phase target surface. Here, n_e is the electron number density, e is the electronic charge and m is the electron mass. Heating of the target surface can continue only indirectly by thermal conduction from the plasma.

Laser heating of the plasma continues and the critical region advances toward the laser, thus resulting in a growth of the plasma plume towards the laser. The heating rate of the plasma, of course, increases sharply at high electron densities by both the linear process of inverse Bremsstrahlung and nonlinear processes that come into play. Multiply ionized, high-kinetic energy species are produced. These energetic particles escape the plasma essentially ballistically. Typically, a rapid expansion of the plasma due to the energetic particles is seen beginning at around the time corresponding to the peak intensity point of the laser pulse. The expansion velocity is in the neighborhood of 2×10^7 cm/s, quite independently of the ambient gas species.

Because of the above-mentioned mechanism by which the plasma plume develops towards the laser, the energetic particles become increasingly more energetic in time and more directional as the number of times a particle has been ionized increases. Consequently, the radial expansion of the plasma is characterized by greater concentration of neutral and singly ionized species than the axial expansion towards the laser which exhibits prominence of multiply ionized species.

The growth and heating of the plasma at high temperature and high density continues for the balance of the laser pulse. The plasma up to the end of the laser pulse is optically thick throughout the entire ultraviolet to infrared spectral range and, consequently, the observable spectrum is characterized by the surface temperature of the plasma, which is of the order of 10^4 to 10^5 K. The strong trapping and diffusion of radiation, together with the high density and temperature state of the plasma, make the plasma extremely high in energy density. This fuels the expansion and sustains the luminosity of the plasma for a long time after the expiration of the laser pulse. Depending on the density of the ambient gases the post-pulse plasma lifetime may be anywhere from about 300 nsec to more than 10 usec in length.

The high temperature and density of the laser produced plasma without any external confinement is a direct result of the extremely high rate of heating made possible by the high power laser pulse. The expansion of the main plasma becomes noticeable near the end of the laser pulse with launching of a shock wave

into the gas medium surrounding the plasma as a direct result of the expansion. The gas medium may be primarily the ambient gas which existed before the laser pulse or, in the case of vacuum, it may be the neutral gas species resulting from the escape of the fast ions. The region behind the shock wave consists of the shock heated ambient gas followed by the expanding plasma. The observed luminous core of the plasma decreases in size as a function of time because of the cooling associated with the expansion.

From the standpoint of elemental composition analysis of condensed-phase specimens, there are two particular segments of time in the full span of the evolution of a laser produced plasma that are of critical importance. The first segment is the very beginning of the interaction of the laser pulse with the target surface. The critical issue here is the kinetics of the formation of a plasma whose elemental composition is identical to that in the condensed-phase target. The second segment is the period after the incident laser pulse is extinguished, when the emission from the plasma undergoes a transition from a strong continuum emission to a line emission character as a result of a changing thermodynamic state of the plasma. It is here that quantitative determination of the elemental abundances is made.

The early spectrum is dominated by broadly peaked and continuous emissions from the plasma; these have little to do with the identities of the atomic or ionic species but rather result from the collective modes of the plasma as a collection of charged particles and from the interaction of the laser and the LPP

plasma. Therefore composition analysis cannot be made by arbitrarily time integrated measurement of emission line intensities. The afterglow spectrum, on the other hand, is determined by individual atomic and ionic emissions that are dependent on the exact atomic makeup of the plasma.

LPP analysis has been shown to be reproducible to an exceptionally high degree and sensitive to all elements of interest. This was achieved by rigorous application of the physics of the laser-matter interactions, strict control of the laser and intensity measurement timing and exploitation of new laser designs and detector instrumentation.

4. Description of the DOE Contract Milestone Tasks

The LPP sensor-probe consists of the following components: a Nd:glass laser; a range finder; high-dispersion spectrographs; gated photodetector arrays; a precision optics block; an actively cooled, hermetically sealed housing; a refractory-lined penetration tube; pressure controllers; local support electronics; an umbilical cord for connection to the control console.

The control console houses the laser power supply, laser trigger circuits including the Q-switch controller, time delay and gating circuits for the detectors, digitizer/signal processor, computer, gas and water supply and other supporting electronics.

A significant part of the LPP sensor-probe system is the sensor-probe control and signal processing software. The control software deals with issuing, and sensing, machine control

instructions, which are either pre-programmed or in response to a change of the status. The control software also handles preventive maintenance of the sensor-probe. The signal processing software handles data transmission, file management, wavelength calibration of spectral emission data, pattern recognition and decomposition of competing spectral lines, calibration of individual line intensities for determination of elemental composition. In addition, the signal processing software handles maintenance of the calibration by tracking the performance of the laser, timing electronics, optical alignment, and the detectors.

The Phase III tasks are individually described below. They are grouped into two sub-phases, A and B. Sub-phase A is essentially complete and Sub-phase B is about to start.

A-1) Standardization of the calibration procedure for molten metals. The interaction of a laser probe with molten metal is distinctly different from that with a solid specimen because the process of melting is absent and the transport properties and optical reflectance vary considerably between the two phases. The usual procedure of comparing the spectral response of a solid specimen with those of so-called "like" standards of solid form cannot be employed for molten metal because the chemical composition of a standard specimen undergoes rapid and significant changes in time during melting. This means that the certification of a standard alloy specimen of known chemical composition was lost during melting.

For solid specimen analysis, the calibration procedure

practiced by the metals industry developed slowly and deliberately through the process of multiple measurements by independent laboratories, the key ingredient being the use of certified "like" standards. It was therefore prudent to make a clear linkage between the LPP analysis of molten metals and the solid specimen standards. As discussed earlier, the LPP plasmas were reproducibly produced and the spectral responses were quantified in a consistent manner. The next step was to incorporate a rapid routine for sampling a small quantity of molten metal immediately after each LPP exposure. Such a solidified specimen was then analyzed by the LPP method in conjunction with the certified standards as well as by other conventional methods. This completed the calibration.

There was the matter of contamination by the interaction between a molten metal specimen and the container crucible. The degree of contamination is significantly influenced by the crucible size and mixing activity within the melt. In order to circumvent many potential ambiguities that could have arisen, the method of molten metal levitation was employed. Using this method, a solid metal alloy specimen could be rapidly heated to melting and the molten specimen could then be quickly resolidified and recovered after each exposure to a laser pulse for comparative analysis by conventional methods.

The main objective was to generate a large body of data for a wide range of specialty steel alloys by the procedure outlined above so that the calibration protocol could be firmly established

for molten metal analysis.

A-2) Performance statistics for sensor-probe immersion into molten metal. The immersed tip of the sensor-probe must penetrate deeply into a molten metal bath to expose an unadulterated molten metal surface for laser irradiation. The penetration is brief, minimizing the thermal load on the sensor-probe, but the probe must be capable of repeated immersions in a short time. The immersible tip of the sensor-probe must remain free from build-up of solidified slag and metal. Two strategies to accomplish this were identified. One was to use thermal shock resistant refractory skin layers on the leading end of the sensor-probe and allow the layers to achieve temperature equilibrium to prevent freezing slag or metal alloy. Another was to use a refractory lining which is alternately layered in such a way that after each immersion the outermost layer is ablated after each immersion. Considerable progress has been made on the first approach as presented Section 5.

B-1) Hardware integration. Earlier investigations established the basic principles of the LPP analysis of molten metal and developed several new instruments and devices. These were incorporated into the prototype sensor-probe. The remaining task is to streamline their implementations from the standpoint of maintenance and fabrication with emphasis on mass production. There are also new inventions pertaining to some of the above components and the plan is to implement these unique elements into the LPP sensor-probe systems for metals production shops.

B-2) Software integration. The entire sensor-probe system is operated under software control. The central software functions include spectral data collection, data transmission to a computer, signal processing for spectrally resolved intensity determination, interpretation of measured intensity by means of the calibration data base correlating intensities to elemental concentrations, and monitoring of drifts in instrument alignment and sensitivity. These functions are to be further implemented in software modules. The speed of execution is of great importance in the context of real-time analysis. The software modules meet the requirements individually but will be integrated and streamlined with a provision for flexibility in anticipation of two additional aspects of the sensor-probe operation: adaptation to each shop-specific environment, and self repair and adjustment capabilities.

B-3) Adaptation to shop-specific environment. Each metals production shop has its own particular mode of operation, and is specific in terms of the physical layout of the furnace and support facilities and in terms of the timing and use of elemental composition data. Consequently, a shop-specific site preparation must be completed in order to incorporate the sensor-probe system into the shop, and this site-specific preparation may prove to be quite extensive. Considerable preparatory interactions will have to take place with each of the two host shops so that a clear definition of the boundary conditions for the LPP sensor-probe can be attained in terms of its hardware configuration and software

requirements.

B-4) Self repair and adjustment capabilities. A high-density instrumentation package in the sensor-probe is envisioned with capabilities for self repair and adjustment. This is of particular importance given the fact that the applications will be a production shop(s) in contrast to a service facility. Furthermore, a certain level of programmability must be incorporated into the provision so that the sensor-probe can be utilized under conditions where a given shop may shift production from one class of alloys to a different class of alloys in a relatively short period of time.

B-5) Mechanical, thermal and electrical hardening. The constructed prototype sensor-probe was designed to be effective in a highly attentive environment. The two sensor-probes proposed for production shops, on the other hand, must be ruggedized to the point of being robust and self-reliant. These sensor-probes will have to endure considerable mechanical impact, intermittent exposure to intense heat and uncontrolled electrical noise in order to remain effective. The protective shell of the sensor-probe will need to be designed in such a manner that the needed hardening can be accomplished.

The schedule of the milestone tasks, as revised reflecting the effective start date of Sub-phase B, is shown in Table 1.

Milestone Schedule - Revised

<u>End Date</u>	<u>Milestone Tasks</u>
3 Dec '91	Kick-off meeting; Submit Phase A management plan.
3 Mar '92	Construct molten metal levitation facility; Complete intellectual property agreement; Form holding company.
3 Jun '92	Progress report on molten metal calibration protocol development; Submit Phase B budget.
3 Sep '92	Complete development of molten metal calibration protocol
3 Dec '92	Confirm molten metal calibration protocol for five elements.
3 Mar '93	Develop LPP sensor-probe sheath immersion facility; Complete selection of sheath material.
14 Jun'93	Submit technical report; Complete Phase B contract modification.
14 Sep'93	Submit Phase B management plan; Confirm molten metal calibration protocol for remaining elements; Develop LPP sensor-probe immersion statistics.
14 Dec'93	Quantify factory site parameters for first LPP sensor-probe to be installed.
14 Mar'94	Complete second generation designs for LPP sensor-probe hardware.
14 Jun'94	Complete installation of the first LPP sensor-probe; Complete selection of manufacturer(s).
14 Sep'94	Quantify factory site parameters for second LPP sensor-probe to be installed.
14 Dec'94	Complete development of second-generation software for control and calibration self maintenance.
14 Mar'95	Complete development of self repair and adjustment hardware.
14 Jun'95	Upgrade the first LPP sensor-probe for self repair and calibration self maintenance capabilities.
14 Sep'95	Complete installation of the second LPP sensor-probe.
14 Dec'95	Submit final technical report.

5. Progress with the Phase III-A Milestone Tasks

The objectives of the first sub-phase of Phase III-A was to develop a protocol for calibration of molten metal composition and to identify, and develop immersion statistics for, the LPP sensor-probe protective refractory sheaths. The progress in these two activities are as follows.

A. Development of the Molten Metal Calibration Protocol

At present, there are no calibration standards for molten metal alloys, as stated in the preceding section. In this effort, a protocol for calibration of molten metal composition analysis was developed. It consisted of the following steps: rapidly heating a metallic alloy specimen to a molten state in vacuum or in an inert gas medium (free of crucible contamination); executing LPP analysis; fast quenching, and recovering, of the specimen; and converting the resolidified specimen into a molten metal calibration standard for comparative analyses with conventional analysis methods.

The key to successful implementation of the protocol was ingenerating highly reproducible spectral responses to laser excitation of a molten specimen surface. The reproducible responses simultaneously required that a molten state identical in shape be created rapidly with identical temperature and composition, a laser pulse of a fixed power profile be delivered on a single pulse basis, and that temporally- and spatially-gated detection of spectral emission intensities from each laser-produced plasma be carried out consistently. To this end, a

new levitation-assisted molten metal source utilizing an RF generator was developed. The resolidified specimens were recovered in a form well suited for follow-up analyses. Each specimen took about 45 seconds to complete heating, full LPP analysis, and recovery. Less than five seconds were actually spent in a fully molten state, assuring reasonable preservation of its elemental composition.

A specimen in the form of a rod, two inches long and a quarter of an inch in diameter, was inserted into an RF induction coil with a single reversed turn at the top. A small volume of the top end of the specimen was heated and became molten, and was supported by electromagnetic levitation on top of the solid portion of the specimen. Upon termination of the RF power, the molten end rapidly resolidified into a hemispherical boss. The overall arrangement of the levitation-assisted molten metal source is shown schematically in Fig. 2. The RF coil consists of three turn conical coil and a single reverse turn above it, and is connected to the RF generator through a coaxial transmission line as a vacuum feedthrough. This technique required considerable experimentation and computational analysis to achieve perfection, but was successfully applied to a number of different alloys ranging from low alloy steel to specialty steel.

The ability to handle different alloys without changing the RF induction coil was a particularly significant achievement. Full levitation of a molten metal drop was limited to a single

Fig. 2. A schematic diagram of the experimental arrangement incorporating the levitation-assisted molten metal source and the optics for the laser and LPP spectroscopy.

alloy composition for a given RF coil configuration because of the intrinsic characteristic of the alloy. Furthermore, the feature that the molten metal specimen was supported by the solid body of the same alloy is extremely important: i) it is free of any complication by contamination from foreign matters; ii) resolidification is rapid by virtue of the available heat sink provided by the supporting solid portion underneath, increasing the likelihood of preserving the elemental composition of the molten state; iii) the final shape of the resolidified specimen was most well suited for subsequent handling and preparation for analysis as a solid specimen; and iv) comparison of the resolidified specimen with the original could be made unambiguously, allowing clear assessment of the effect of melting on composition. This technique of preparing a molten state of metallic alloy has wide ranging applications elsewhere as well.

The tested materials that differed widely in elemental composition were provided, in assorted shapes and sizes, by the Sparrows Point plant of Bethlehem Steel Corporation, Carpenter Technology Corporation, Armco, Inc., Lukens Steel Company and other commercial distributors. All were machined into a standard rod shape, 1/4" diameter and 2" long, in the Physics machine shop at Lehigh University. Altogether, approximately 1,500 specimens were used for development of the levitation-assisted molten metal source and confirmation of the molten metal calibration protocol in a statistically significant manner.

Tables 2 and 3 show comparisons of the elemental composition

of an original specimen with that of a resolidified specimen for two different groups of alloys. The analyses were performed by the conventional methods (spark discharge spectroscopy and wet chemical analysis) at Carpenter Technology and Armco. Each specimen was analyzed at both ends, one being in the original solid form and the other being in a resolidified form of hemispherical shape. The resolidified end was first ground off by 1/32" before analysis.

The results summarized in the two tables show quite clearly that melting changes the elemental composition of the alloy from that of the solid form. The change is selective in that some elements undergo a large change in concentration while others do

Table 2. Comparative analysis of elemental composition of the original versus resolidified stainless steel specimens.

Element	Weight Percent							
	<u>SS-303</u>		<u>PH13-8MO</u>		<u>SS-316</u>		<u>SS-440C</u>	
	Resolid	Solid	Resolid	Solid	Resolid	Solid	Resolid	Solid
C	0.066	0.084				0.048	0.99	0.99
Mn	1.52	1.84	0.020	0.025	1.20	1.51		0.36
Si	0.53	0.57			0.43	0.45	0.93	0.93
S	0.39	0.37				0.22	<0.001	0.001
Cr	17.3	17.4	12.7	12.4	16.8	16.8	16.6	17.0
Ni	8.95	9.05	7.9	8.3	10.2	10.4	0.21	0.21
Mo	0.46	0.48	2.16	2.22	2.22	2.20	0.43	0.44
Cu	0.36	0.36	0.035	0.038	0.50	0.50	0.047	0.042
Co	0.20	0.20	<0.01	<0.01	0.16	0.16	0.023	0.023
V	0.07	0.08			0.02	0.05	0.047	0.048
Al	<0.003	<0.003	1.00	1.04			0.019	0.014
Ti	<0.002	<0.002	0.013	0.014				
Cb	0.022	0.021	<0.002	<0.002				
P	0.036	0.036	0.008	<0.003				

Table 3. Comparative analysis of elemental composition of the original versus resolidified low alloy steel specimens.

Element	Weight Percent							
	AISI-1002		AISI-1022		AISI-1060		AISI-1086	
	Resolid	Solid	Resolid	Solid	Resolid	Solid	Resolid	Solid
C	0.016	0.018	0.21	0.23	0.54	0.56	0.81	0.84
Mn	0.20	0.24	0.68	0.98	0.43	0.67	0.30	0.39
Si	<0.05	<0.05	0.19	0.20	0.25	0.26	0.20	0.22
S	0.017	0.018	0.007	0.008	0.013	0.013	0.010	0.012
Cr	0.019	0.023	0.020	0.020	0.062	0.064	0.029	0.029
Ni	0.044	0.046	0.013	0.014	0.036	0.036	0.012	0.011
Mo	0.01	0.01	<0.002	<0.002	0.007	0.007	0.003	0.003
Cu	0.083	0.092	0.008	0.008	0.065	0.076	0.017	0.019
Co	0.006	0.006	0.005	0.005	0.005	0.005	0.003	0.003
V	<0.001	<0.001	0.001	0.001	0.002	0.002	0.001	0.001
Al	0.022	0.030	0.029	0.046	0.029	0.032	<0.002	<0.002
Ti	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.002
Cb	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
P	0.004	<0.003	0.012	0.013	0.021	0.015	0.024	0.009

not. The case in point is the behavior of manganese; in a time period of three to five seconds the manganese concentration decreased by one third. There is some evidence that copper and aluminum undergo noticeable changes, although not by quite as large a fraction as that for manganese. There is also a hint of a slight decrease for carbon. Most other elements remain unchanged within the inherent measurement uncertainties. This comparison provides a clear demonstration of the need for the molten metal calibration protocol, distinct and separate from the protocol used for solid specimen analysis calibration. The elemental composition of the recovered resolidified specimens provided the molten metal composition standards.

A high level of reproducibility and sensitivity in terms of produced LPP emission spectrums with the levitation-assisted molten metal source as the target of laser exposure for various elements of interest to steel industry was achieved. This means that molten metal calibration standards were established by means of the protocol as defined above. The spectral intensities, which relate to elemental abundances in an alloy specimen, were assigned the numerical values of elemental concentrations according to the data derived from the conventional solid specimen analyses of the resolidified specimens. Thus, a calibration curve was established for each of the five elements: Mn, C, Si, Al and S. A wide range of steel alloys were used to provide a range of concentrations currently practiced in the steel industry.

The industry, as represented by the AISI CTU 5-2 Committee, prepared the guidelines for the sensitivity and precision to be achieved by the LPP sensor-probe system for these five elements; concentration are shown in Table 4.

Table 4. The required concentration ranges by elements for steel alloys analysis.

<u>Element</u>	<u>Concentration Range in W%</u>
Carbon	0.01-2.0 W%
Manganese	0.05-1.0
Sulfur	0.001-0.50
Silicon	0.01-3.5
Aluminum	0.01-1.0

In the metals industry, the required precisions are usually presented in units of weight percent (W%), which vary from one concentration range category to another. These values are tabulated in Table 5; in addition, the required precisions are reexpressed in terms of percent uncertainty for each given concentration (W%), expressed as a percentage of the concentration.

The corresponding experimental sensitivity and precision were obtained using the molten metal calibration protocol as described earlier. An assortment of alloys as marked by the steel industry, rather than alloys custom made for this particular calibration procedure, were used to assess this wide range of concentrations

Table 5. The required precision in weight percent and percent uncertainty for molten metal analysis according to concentration ranges.

<u>Concentration Range in W%</u>	<u>Required Precision in W%</u>	<u>Percent Uncertainty as Percentage of W%</u>
0.001-0.02W%	$\pm 0.003W\%$	$\pm 300\%$ to 15%
0.02-0.10	± 0.01	$\pm 50\%$ to 10%
0.11-0.40	± 0.02	$\pm 18\%$ to 5%
0.41-1.0	± 0.03	$\pm 7\%$ to 3%
1.0-5.0	± 0.05	$\pm 5\%$ to 1%

for each of the five elements. The conventional analyses of the resolidified specimens were used to assign the concentration values to each of the emission spectral intensities. The results are shown in Table 6.

The experimental percent uncertainty (Table 6) represents the mean variation in concentration expected from one specimen to

another, rather than successive measurements on one specimen. The percentage uncertainty was calculated for a set of measured spectral intensities from multiple single-LPP-shot analyses.

Table 6. Summary of the molten metal calibration data.

<u>Element</u>	<u>Concentration in W%</u>	<u>Percent Uncertainty as Percentage of W%</u>
Carbon	0.01	± 150
	0.02	± 75
	0.10	± 40
	0.50	± 24
	1.0	± 15
Manganese	0.3	± 13
	1.0	± 5
	1.4	± 6
Sulfur	0.05	± 120
	0.2	± 33
	0.4	± 16
Silicon	0.05	± 100
	0.3	± 17
	0.5	± 10
	1.0	± 5
Aluminum	0.01	± 50
	0.02	± 25
	0.05	± 10

(Remember that only one measurement is made of each alloy rod by heating it into a molten metal specimen.) In contrast, the required precision data from the AISI CTU 5-2 Committee are based on the statistical fluctuation of the concentration values obtained for the same solid specimen by subjecting it to analysis repetitively. This means that the above experimental uncertainties shown in Table 6 contains significantly large error

contributions which stem from material property inhomogeneities and the variabilities in handling of specimens, such as aligning of the specimens with respect to the optics and RF heating coil and melting history variation. It is estimated that at least two thirds of the total uncertainty are of extrinsic origins as mentioned above. Detailed theoretical modeling of the RF heating process, by numerical simulation, compared to the results of extensive measurements of the heating and melting times of different alloy specimens, is complete. Excellent agreement has been attained. The numerical code has then been executed to establish the nature of the anticipated variations between individual specimen rods undergoing the heating and melting. These analysis supports the estimate of the extrinsic contributions to the overall uncertainties.

Such extrinsic uncertainties can be eliminated quite readily, in due course, as the overall procedure for the molten metal calibration protocol is further refined. Confirmation during the planned calibration activities with the levitation-assisted molten metal source is anticipated.

The remaining uncertainty, namely, the last third of the experimental uncertainty data shown above, is intrinsic in the sense that the signal to noise ratio of the LPP sensor-probe system could become the limiting factor. This could be further reduced when the second generation design of the LPP sensor-probe system is implemented as part of Phase III-B. It is anticipated that the intrinsic uncertainty will be reduced by a factor of

three to four. The total reduction of the experimental uncertainty will be then by a factor of ten or more better than the data shown above, making the uncertainty significantly better than the stated target values for in-situ molten metal analyses by the LPP sensor-probe system. This also means that the current industry benchmark for solid specimen analysis will be exceeded.

Assembly of a wide selection of commercial alloy specimens that will provide the necessary range of concentrations for each of the remaining elements of interest is in process. This assembly has proven to be an extremely taxing task. Once the specimens are prepared in the form and composition suitable for the molten metal calibration (presumably numbered in thousands) the calibration as well as the statistics can be completed.

As an integral part of the molten metal calibration, a database combining atomic and ionic structure data with spectral emission data for more than 27 elements of interest is being developed. The latest measured and computed values for the energy levels, degeneracies and radiative lifetimes as well as the spectral wavelengths, intensities and transition probabilities are combined into the database, in the form of diagrams and computerized data files. This activity is approximately 75% complete.

B. Development of Protective Refractory Sheaths

Significant progress with the selection of the protective sheath material for the LPP sensor-probe and its performance

evaluation has been made. A particular type of refractory was selected. The material is currently available, possesses excellent machinability, is highly thermal shock resistant, and is non-wetting to molten steel alloys and non-dissolving in molten alloys.

The design and fabrication issues associated with constructing an integrated protective sheath assembly for the entire lower end of the LPP sensor-probe, including the immersion tip is complete. The questions are: i) how well does the selected material perform under repetitive exposures to the molten steel alloys?; and ii) how well does a multi-component assembly perform as an integrated structure under such multiple exposures? For the expressed purpose of evaluating, and developing immersion statistics for, the protective sheath, a 40 kW induction furnace was constructed to provide a medium-sized molten metal source under controlled atmospheric conditions. The volume of molten metal can be as large as 150 cm^3 . The crucibles for the molten metal were also machined out of the selected material such that long term wear by flaking or dissolution could be evaluated.

To evaluate repetitive immersions into the molten metal bath, a vertical translation stage was installed above the vacuum induction furnace. A simulated penetration tube was constructed of stainless tubing and mounted on the translation stage. The tube was actively cooled by a bidirectional, annular flow of water, and connected to the furnace through a mechanical motion feedthrough flange. The flange is part of a transparent pyrex

dome such that the immersion process can be monitored visually. The penetration tube is threaded on one end and a vacuum/gas supply manifold is connected to the other end. The protective sheath assembly is screwed onto the threaded end of the penetration tube.

The overall arrangement of the molten metal source within the vacuum induction furnace and the translation stage, with the mounted penetration tube, is shown in Fig. 3. The translation stage facilitates vertical movement of the penetration tube, the tube acting as a vacuum mechanical feedthrough. The refractory sheath assembly is screwed on the front end of the penetration tube, which is then repeatedly immersed into the molten metal bath with a slag covering. The atmosphere of the furnace can be changed from vacuum to inert gas to synthetic air, in order to simulate the likely furnace atmosphere which in turn affects the nature of the slag.

The penetration tube is lowered and raised repetitively by the motorized translation stage. The protective sheath is allowed to achieve thermal equilibrium with the bath on the immersed end and remains in contact with the water-cooled end of the penetration tube. It has been established that this extreme thermal gradient can be maintained indefinitely in the sheath assembly, which consists of three machined parts. The tested assemblies have remained intact in the sense that the sheath has remained free of frozen slag or steel alloy layers, fractures and cracks, peeling of the skin, erosion by dissolution or any other

Fig. 3. A schematic diagram of the 40 kW vacuum induction furnace with a motorized translation stage to which a water-cooled, simulated penetration tube is attached.

general signs of failure for in excess of 100 immersions. The threaded parts can still be separated after such extended exposures to high temperature gradients and high number of immersions.

Repeated immersions will continue to accumulate a significant body of statistics for the selected material under varying configurations of the assembly, size, and number of exposure cycles, with and without aggressive slags.

6. Current Status of the Project Administration

The intellectual property agreement, a draft of which was first submitted to the DOE's legal office in Chicago back in February 1992, has been fully negotiated between Lehigh University and the Department of Energy, and signed.

The total Phase A budget for the project of \$575,084 contained \$179,879 in cost sharing. The full amount of this cost share was secured through cash contributions: \$100,000 from the American Iron and Steel Institute; \$50,000 from the Center for Materials Production of the Electric Power Research Institute; \$29,897 from the CTU 5-2 Consortium of North American metals producers.

The Phase-B budget was submitted to the contracting office at the DOE's Idaho National Engineering Laboratory and has been approved. This budget is based on deployment of two LPP sensor-probes, one at CarTech and the other at The Timken Company. The 30% cost sharing commitments for the first unit are complete.

Funding will be provided by cash and in-kind contributions from the American Iron and Steel Institute, the Ben Franklin Fund, the CTU 5-2 consortium of Northamerican metals producers and Lehigh University.

Project progress has remained on schedule and in keeping with the statement of work. The Phase-B objective is to install two LPP sensor-probes at two steel production shops, the first in 1994 and the second in 1995.

Acknowledgement

The research and investigations described in this report contain valuable contributions from the author's colleagues, students and technical staff of the Physics Department: Sook Kim, Chung Park, and Dan Xie; Paul Bashus, Thomas Daugherty, Robert DeSipio, Joseph Hanley, Jeffrey Laub, Conrad Lloyd-Knight, and Kelly Kriebble; John Gregoris, Robert Wolfinger, and Joseph Zelinski; Stacy Behrens, Alex Marcus, and Jeffery Spirko. Technical expertise shared, and critiques provided, by the CTU 5-2 Committee members are gratefully acknowledged; in particular, the assistance in procuring numerous steel alloy specimens by Bethlehem Steel-Sparrows Point, CarTech and Lukens Steel, and the assistance of CarTech and Armco through provision of the resolidified steel alloy specimen analyses by the conventional means has been most helpful. This project has been supported jointly by the U.S. Department of Energy, American Iron and Steel Institute, EPRI Center for Materials Production, Northeast Tier

Ben Franklin Advanced Technology Center, the CTU 5-2 Consortium of North American Metals Producers and Lehigh University. The author expresses his appreciation for the able support and cooperation provided by the DOE Office of Industrial Technologies, DOE-Idaho, EG&G-Idaho, DOE-Chicago and the Office of Research and Sponsored Programs of Lehigh University.

DATE

FILMED

4 / 13 / 94

END