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EVAPORATION MONITORING AND COMPOSITION CONTROL OF ALLOY SYSTEMS WITH WIDELY DIFFERING VAPOR PRESSURES

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Abstract

Lawrence Livermore National Laboratory is developing sensors and controls to improve and extend electron beam materials processing technology to alloy systems with constituents of widely varying vapor pressure. The approach under development involves using tunable lasers to measure the density and composition of the vapor plume. A laser based vaporizer control system for vaporization of a uranium-iron alloy has been previously demonstrated in multi-hundred hour, high rate vaporization experiments at LLNL. This paper reviews the design and performance of the uranium vaporization sensor and control system and discusses the extension of the technology to monitoring of titanium vaporization. Data is presented from an experiment in which titanium wire was fed into a molten niobium pool. Laser data is compared to deposited film composition and film cross sections. Finally, the potential for using this technique for composition control in melting applications is discussed.

1.0 Background

A primary limit to the full exploitation of electron beam processing of materials is preferential vaporization of volatile components. In melting applications, preferential loss of chromium and aluminum is a significant problem. In vaporization applications, control of vapor composition is difficult for alloys with constituents differing in vapor pressure by more than about 100x(1).

The authors first encountered these issues in the development of the Uranium Atomic Vapor Laser Isotope Separation (U-AVLIS) process at Lawrence Livermore National Laboratory(2). In the U-AVLIS process, an electron beam is used to co-vaporize uranium and iron. The uranium 235 isotope is selectively ionized by light from a set of tunable dye lasers. Ionized uranium 235 is then electrically stripped from the vapor stream, collected as a liquid and continuously cast into a form that can subsequently be used to manufacture fuel for light water nuclear reactors. Iron lowers the melting point of the

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collected liquid and so reduces the corrosive effects of the liquid metal on the collection surfaces. Iron and uranium form a eutectic, so to take full advantage of the reduced melting point, it is necessary to control the composition of the vaporized stream. The technical challenge is that the iron is roughly 350 times more volatile than the uranium. In addition, the process performance depends on the uranium density in the vapor so it is also necessary to control uranium vapor density.

We were unable to find existing, accurate, long-life evaporation rate and composition sensors that were suitable for high deposition rate environments. Thin film crystal devices and Sentinel monitors have inadequate life in a high deposition rate environment. Hollow cathode lamp monitors tend to saturate at high vapor densities and are susceptible to loss of calibration due to condensate buildup. Techniques such as emission spectroscopy are difficult because of extremely high background light levels and tend to provide only relative measures of density and composition.

As a result, we embarked on a long-term effort to develop a new class of vapor monitors based on laser absorption spectroscopy. These monitors, in conjunction with a model-based vaporizer controller also developed at LLNL, have been successfully used to control vaporizer operation for hundreds of hours in runs where tons of material have been evaporated. More recently we have been collaborating with US industry to extend this monitoring and control technology to other applications of commercial interest. In this paper we review the design and performance of the uranium-iron monitoring and control system, discuss recent work related to niobium and titanium evaporation and finally discuss the prospects for application of the laser monitor to the problem of composition control in remelting and refining systems.

2.0 Uranium-Iron Monitoring and Control System

Figure 1 schematically illustrates the method for density and composition monitoring. Light from a diode laser is frequency scanned over an atomic absorption line in the species to be monitored. The light is then acousto-optically modulated to improve noise rejection and to permit light from multiple lasers (each modulated at a different frequency) to be co-propagated along the same optical path. This permits simultaneous monitoring of multiple species. A portion of the light is split off from the beam and goes to a reference detector. This permits compensation for laser intensity fluctuations during the scan. The balance of the light enters the vapor, is partially absorbed and finally is detected at the exit from the vacuum chamber. The vapor density along the path of the laser is related to the attenuation of laser light by Beer's law,

$$I=I_0\exp(-n\sigma l)$$

where I and I_0 are input and output laser intensities, n is vapor atom density, σ is the absorption cross section for the selected transition and l is beam pathlength through the vapor.

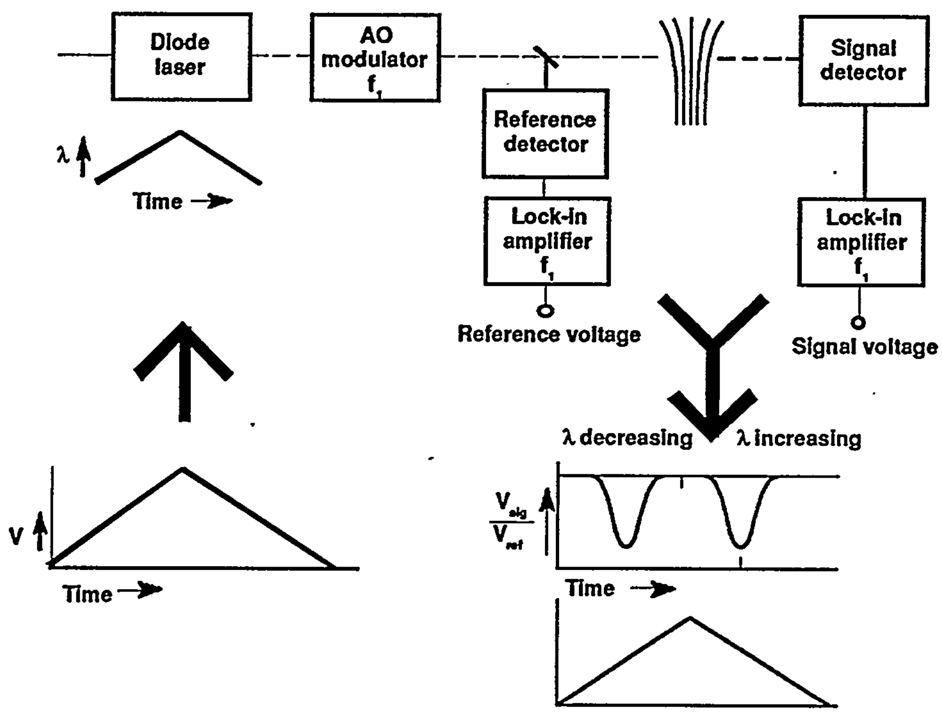

Figure 1 - Schematic illustration of vapor density monitoring technique.

A typical absorption waveform for iron is shown in Figure 2. The waveform is actually much broader than the natural linewidth of the iron transition. This is due to a Doppler broadening of the absorption line caused by the radial expansion of the vapor. An advantage of this technique is that the laser can be scanned over all the vapor present in the laser path, including that which is Doppler shifted. By scanning the laser past the absorption line, a new baseline for transmission is established for each scan. This reduces the sensitivity of the monitor to window darkening caused by vapor deposition.

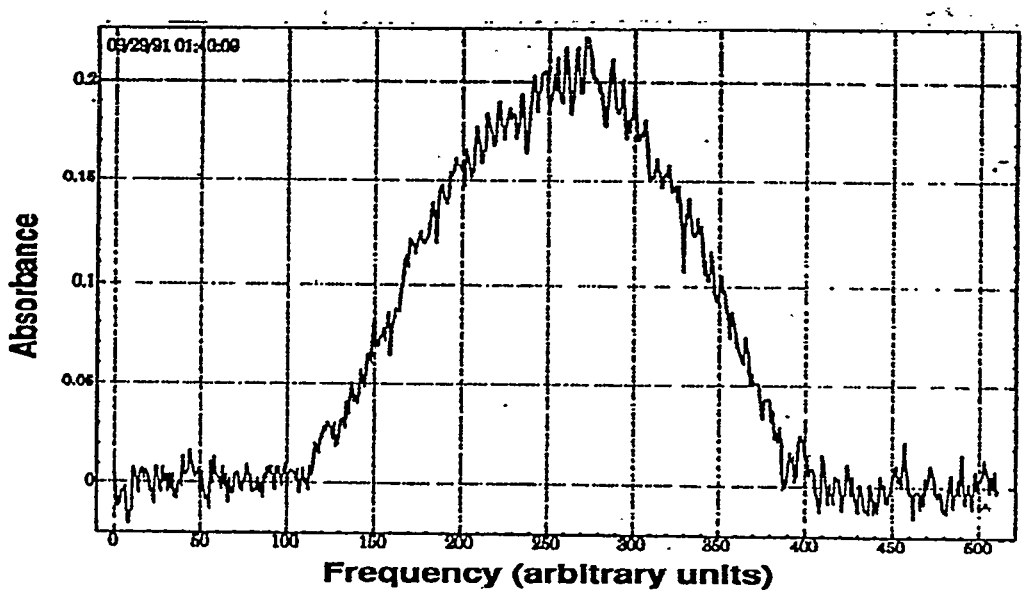

Figure 2 - Typical absorption waveform for the ground state of iron.

The sensor system is shown in Figure 3. The light source is a New Focus external cavity tunable diode laser. Processing of the waveforms is currently done on an IBM PC. Density sampling rates up to 4 Hz have been demonstrated. A major advantage of using a laser light source, as opposed to a hollow cathode lamp, is that the laser is a highly collimated light source permitting the laser and detector to be set back and protected from the vapor source. In our installation at LLNL, the diode laser is in a different room from the vaporizer. Light is carried to the vessel by fiber optics. All optical transport and detection hardware are outside of the vaporizer vacuum vessel. Optical windows on the vessel are protected from vapor deposition by proper placement and by gas scattering cells.

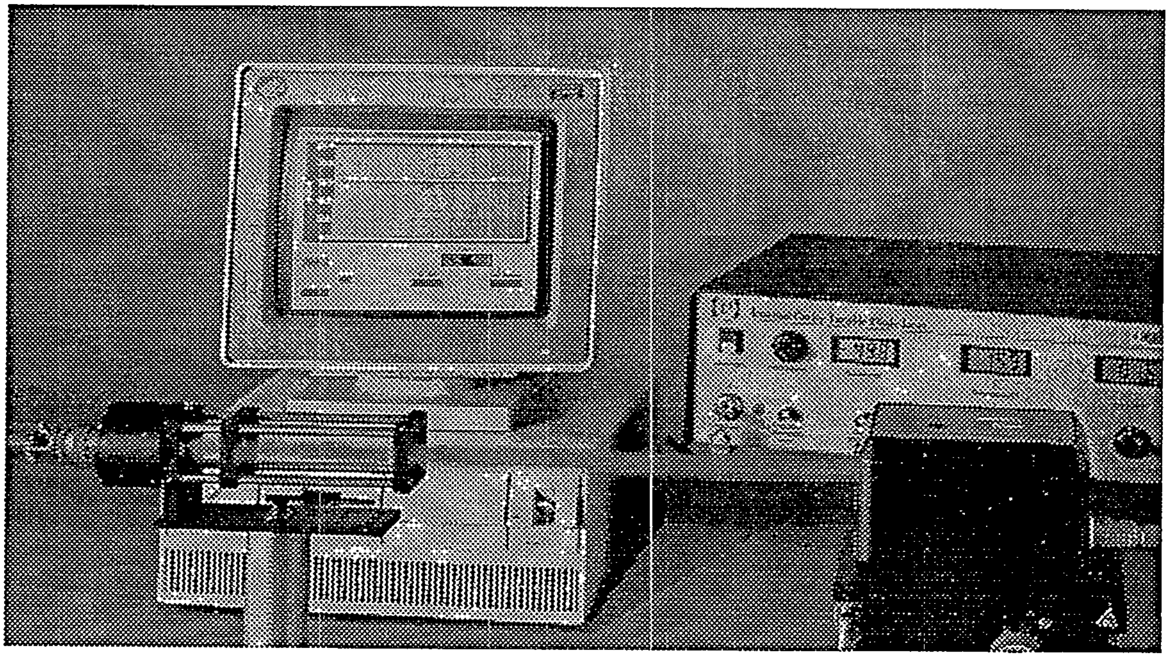

Figure 3 - Prototype of diode laser based vapor monitor.

Figure 4 shows the results of a sensor system verification run. An aperture was installed over the vapor source. Vapor which passed through the aperture was sampled by the diagnostic laser and then was collected as a solid on a specially designed collector plate. During the run, the laser monitor tracked the change in vapor density as the electron beam power was varied. A post-run comparison between the collected condensate weight and the vapor deposition predicted from the laser measured density agreed within about 1%. In uranium isotope separation demonstrations lasting hundreds of hours and where we are inferring deposition rate over a much larger volume than in the verification experiment, we find the laser monitor to be accurate within about 5%.

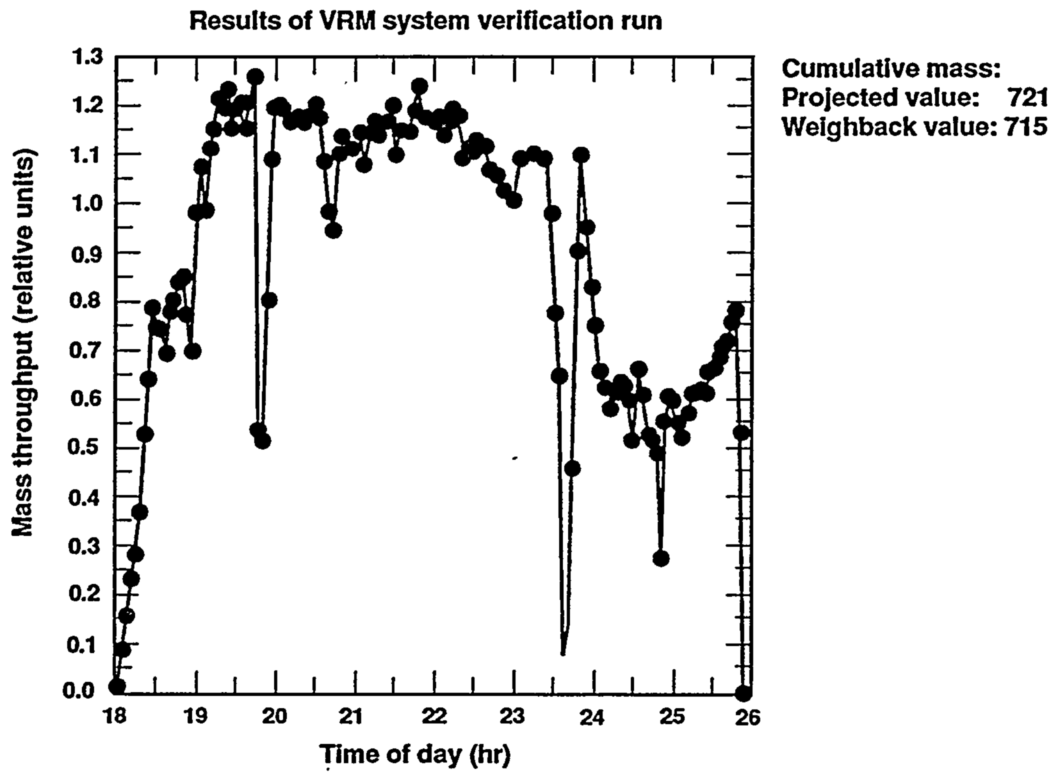

Figure 4 - Results of vapor monitor waveform.

Figure 5 shows data from an experiment designed to measure the transient characteristics of iron in the melt pool. When charges of iron were fed into the uranium pool, the laser monitor measured the rapid increase in iron density as the more volatile iron flashed out of the pool.

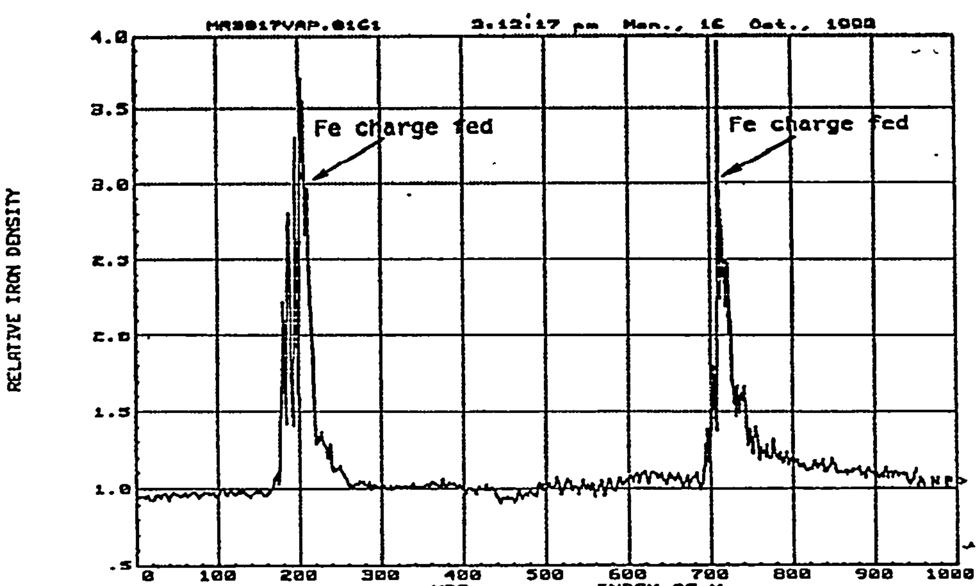

Figure 5 - Data from iron-uranium co-vaporization experiment.

The laser based monitoring system has been integrated with a model based controller for the U-AVLIS vaporizer. Figure 6 shows a block diagram of the integrated system. The density of the co-vaporized iron and uranium plume is monitored by the laser vapor monitor. A real time model converts line densities measured by the laser into evaporation rates for iron and uranium. The evaporation rate information is filtered and compared to setpoints. An internal model controller then varies the iron and uranium feed rates and the electron beam system power to maintain the desired operating conditions. Data from the vapor monitor is supplemented by video images which are processed to determine melt level and general status of the pool.

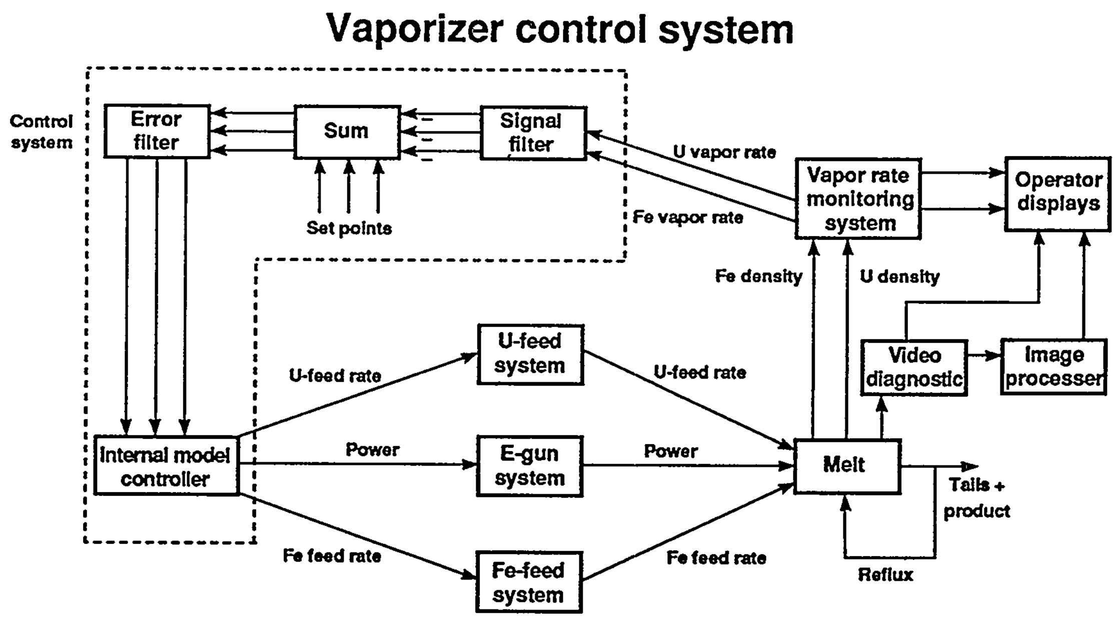

Figure 6 - Models based, closed loop vaporizer control system.

Figure 7 shows the performance of this system during a long duration isotope separation run. Vapor rate control is better than ±5%. Total duration of this run was 260 hr and several tons of uranium and iron were vaporized. The laser diagnostic and control system worked well throughout the entire run.

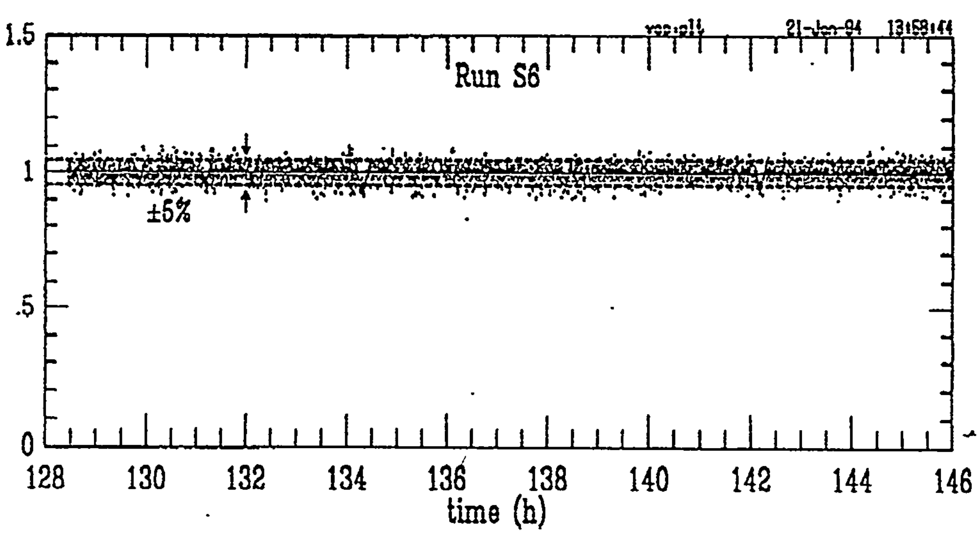

Figure 7 - Example of control system performance in uranium-iron system.

3.0 Extension to Other Vaporization Applications

Figure 8 summarizes the wavelength requirements needed to monitor the elements of the periodic table. In our previous work, we have tended to concentrate on the lanthanides and actinides because of their relevance to isotope separation missions. Most of these elements can be monitored with lasers that operate at wavelengths greater than 6500 A. This is significant because off-the-shelf diode lasers can be purchased that operate in this wavelength range. In addition to isotope separation, lasers in this wavelength range are applicable to the manufacture of high T_c superconductors where elements such as yttrium, barium and strontium are important.

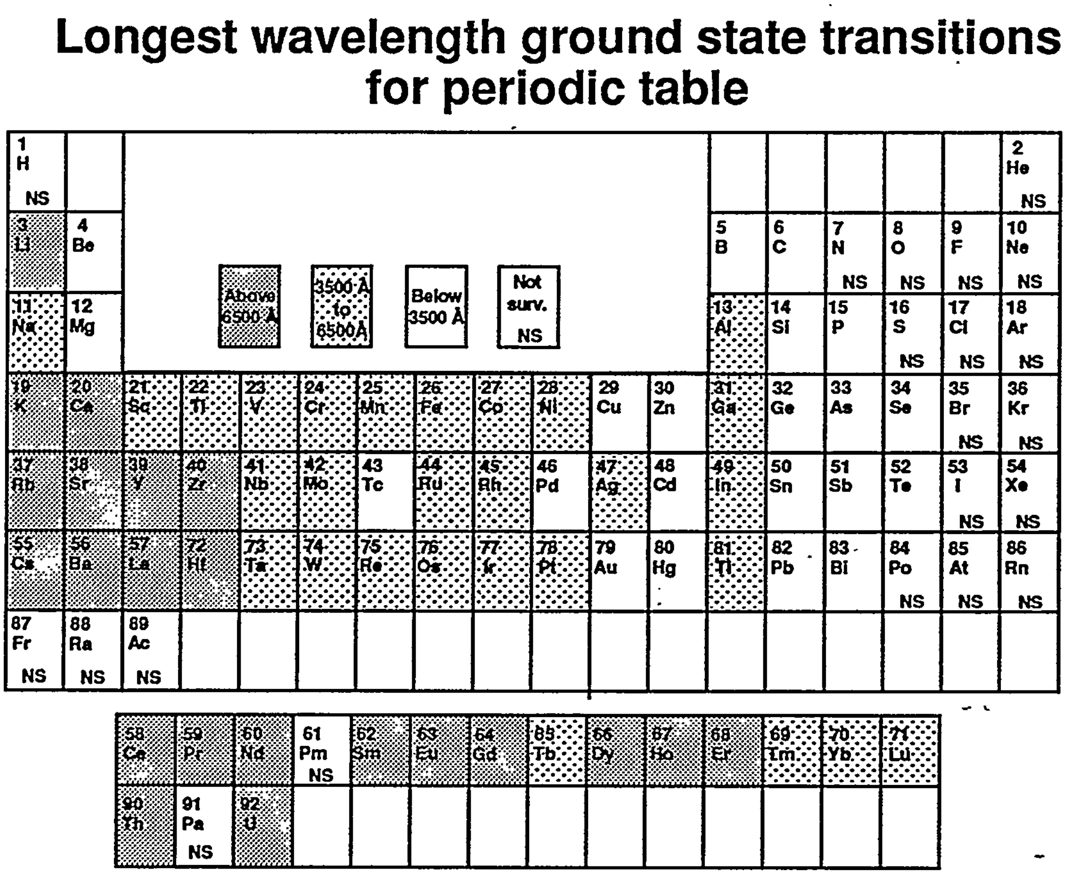

Figure 8 - Wavelength requirements for laser based vapor monitors.

Extending this monitoring technology to the transition elements, such as titanium and molybdenum, and other important elements such as aluminum and indium requires lasers that operate at shorter wavelengths than available from commercial tunable diode lasers. An important application that would benefit from this monitoring technology is the manufacture of advanced metal matrix composites.

The next generation of jet aircraft engines will rely on advanced titanium metal matrix composites in order to reach their performance goals. One of the leading approaches to manufacture of these materials is physical vapor deposition of metal on to ceramic fibers(3). The fibers are then consolidated into a monolayer tape, the tape is wound to the desired form and finally undergoes a hot isostatic press to consolidate the finished part. The advanced alloys generally contain titanium, aluminum and at least one refractory component such as niobium. Hence the problem of composition control in the evaporation process is important. Lawrence Livermore National Laboratory, 3M Corporation, New Focus Lasers Inc. and the Stanford University Center for Materials Research have formed an ARPA sponsored collaboration to develop the sensors and control technology needed for this application and to apply existing sensor technology to the manufacture of high T_c superconductors.

To reach the shorter wavelengths needed for the metal matrix application, New Focus Lasers is developing a frequency doubled tunable diode laser. This approach takes advantage of the large number of high power diodes that operate above 6500 A. Frequency doubling extends the wavelength range to below 4000 A and greatly increases the number of elements that can be monitored.

At LLNL, our early experimental work has concentrated on demonstrating the feasibility of monitoring the relevant elements, demonstrating the correlation between laser measurements and frozen film composition and on selecting appropriate atomic transitions to be accessed by the frequency-doubled diode lasers. Feasibility demonstrations at LLNL are performed using tunable light from argon ion pumped dye lasers and frequency doubled titanium sapphire lasers. These lasers provide the very broad wavelength range needed for exploratory studies, but are much larger and more expensive than diode lasers and thus are less suitable for use in an industrial monitoring system.

Figure 9 shows laser data from a recent experiment. In this experiment, titanium wire was fed into a niobium pool. Because the titanium vapor pressure is roughly four orders of magnitude greater than niobium, one would expect the titanium to flash evaporate from the niobium pool. A characteristic of such a system is that the evaporation rate of the more volatile component should closely track its feed rate. Storer has previously suggested this as an element in a scheme to control vapor composition(4). Figure 9 confirms the relatively tight coupling between the titanium wire feed rate and the titanium density in the vapor.

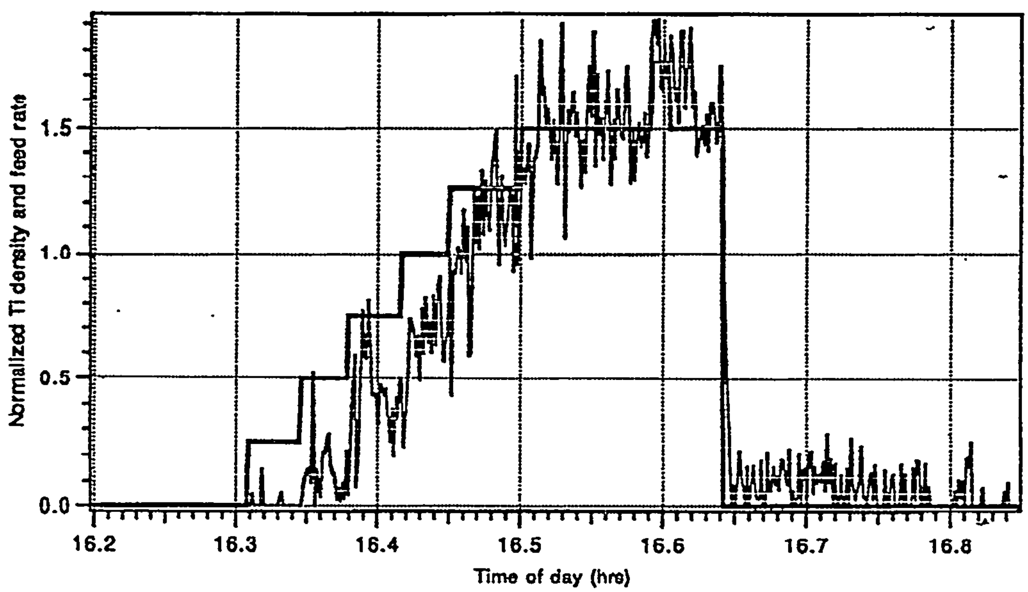

Figure 9 - Measured titanium vapor density compared to relative titanium feed rate.

After the experiment, frozen film samples were collected, etched and photographed. In addition, several of the samples were subjected to an Auger scan to illustrate the variations in niobium and titanium concentrations and to allow a comparison between laser density data and concentration profiles in the sample. Figure 10 summarizes the data for the sample taken directly above the center of the melt. Periods of time during which titanium wire was being fed are indicated by a black bar alongside the micrograph. The Ti wire feed is correlated with a banded structure in the etched micrograph. There are two bands in the cross section that are not correlated with wire feed. We assume that these bands correlate with Ti, which was held up somewhere in system, returning to the melt.

Figure 10 illustrates the correlation between the Auger scan over the indicated feature in the micrograph and the laser data taken during the corresponding time during the run. The peak Ti vapor density was scaled to match the peak in the Auger scan and the distance scale in the Auger scan is set to match the time scale of the Ti vapor density plot. Therefore it is the comparison of the shapes of the two curves which is significant not the absolute correspondence between the curves. Nonetheless the match is impressive and leaves little doubt that the diagnostic laser provides a good indication of the concentration profiles in the deposited film.

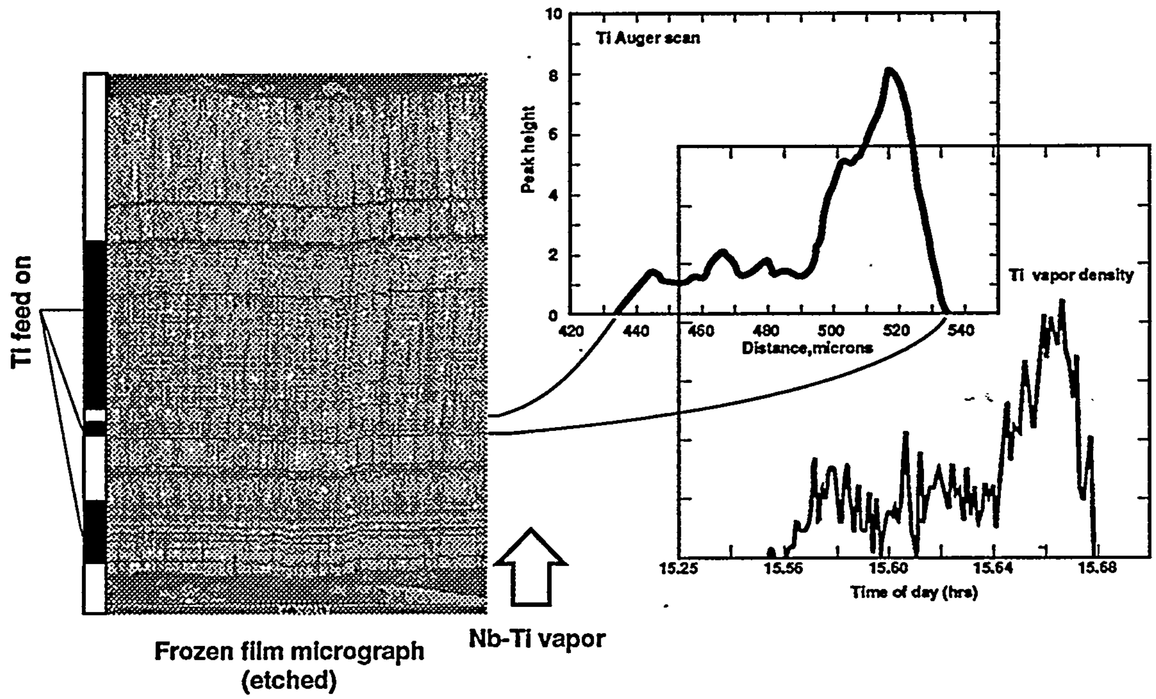

Figure 10 - Comparison of frozen film titanium concentration profile and titanium vapor density history.

Requirements for a titanium density monitor have been specified and development of a diode laser based system is underway. A demonstration on a coating furnace at 3M is planned for next year. Application of this sensor technology to a variety of other coating missions is being actively pursued. Examples include high rate production of high T_c superconductors and thermal barrier coatings for turbine engine components. Thermal barrier coatings are vaporized as molecular rather than atomic species and present new challenges in sensing and sensor interpretation.

4.0 Composition Control in Remelting and Refining Applications

Composition control is an important issue in the remelting and refining of alloys. In some systems, up to 20% of the melts are rejected because of out of specification chemistry. Based on our experience with other vaporization applications, it seems likely that a laser based sensor system can be designed to monitor the density and composition of the evaporated material. This was first suggested by McKoon in 1991 and documented in a paper by Berzins(5).

Compositional variability arises from a variety of sources. The feedstock is not perfectly homogeneous and its bulk composition can vary. Thermal contact resistance between the melting hearth and the melt ingot varies with time. This effect results in variations in pool temperature and hence vaporization losses. As feedstock is melted into the hearth, outgassing products are released. The electron gun differential pumping system must maintain a gun pressure low enough to prevent arc-down. If not, the melt rate must be reduced. Electron beam power is varied to control melt rate, hence evaporative losses will also vary with melt rate. Finally, the presence of dross on the melt surface can inhibit vaporization.

The design of the sensor system is dependent on the relative importance of the different sources of compositional variability. Consider the alloy Ti-6Al-4V where aluminum content control is the issue. If compositional variability arises primarily from changes in melt temperature or the amount of dross present on the surface, then a system which monitors only the aluminum vapor should be adequate for control.

The situation is somewhat more complex if compositional variations in the feed are also important. The reason is that an increase in the aluminum concentration of the feed results in an increase in the aluminum vaporization rate from Raoult's Law considerations. If only the aluminum vapor density is monitored, the control system cannot distinguish between an increase in pool temperature and an increase in feedstock assay. This is a problem because in the first case makeup feed should be added and in the latter case withheld. Monitoring of the titanium vapor allows discrimination between these two cases. If pool temperature increases then both the aluminum and titanium vaporization rates will increase, if on the other hand, aluminum content in the feedstock increases then aluminum rate increases but the titanium rate will decrease slightly.

Development of the integrated control system needs to address issues of where and how to introduce the makeup feed and a model to convert measured vapor density into an evaporation rate. However, none of these problems seem intractable. The development of a sensor and control system is probably more dependent on the level of interest and commitment of the industrial melting community and on acquiring the needed development funds.

5.0 Summary

LLNL has developed a laser absorption spectroscopy based vapor monitoring and control system for the Uranium AVLIS process. This system has been highly successful and demonstrated in long duration runs where many tons of metal have been evaporated.

The sensor system is accurate and robust. Vaporization rate control is within ±5%. This technology is currently being extended to the production of metal matrix composites using electron beam PVD. There do not appear to be any fundamental difficulties in applying laser based monitoring to the problem of composition control in electron beam melting applications.

Acknowledgement

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