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L. V. Berzins
M. A. McClelland
T. M. Anklam
S. Galanti
C. A. Haynam
T. C. Meier
Lawrence Livermore National Laboratory
Livermore, California

J. Storer
3M Company
Mendota Heights, Minnesota

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# DEVELOPMENT OF A SENSOR AND CONTROL SYSTEM FOR THE PRODUCTION OF TITANIUM MATRIX COMPOSITES

L. V. Berzins, M. A. McClelland, T. M. Anklam, S. Galanti, C. A. Haynam, T. C. Meier
Lawrence Livermore National Laboratory
P. O. Box 808, L-470
Livermore, CA 94550
Phone (510) 423-2671 Fax (510) 422-3165

J. Storer
3M Company
2465 Lexington Avenue South
Mendota Heights, MN 55120

## ABSTRACT

Titanium matrix composites promise to dramatically increase the thrust-to-weight ratio of gas turbine engines[1]. Electron Beam Physical Vapor Deposition (EB-PVD) is ideal for coating fibers if issues with composition control can be worked out. LLNL is developing a control system based on Diode Laser Absorption Spectroscopy (DLAS) for the deposition of titanium orthorhombic alloys[2]. In this paper, the important features and components of a DLAS control system are reviewed and a methodology for selecting the appropriate atomic transitions is described. Data characterizing the diagnostic performance as well as information on potential control strategies is presented. Finally, applications of this diagnostic to other alloy systems are discussed.

## INTRODUCTION

At present aircraft engine performance is limited by the high temperature material properties of engine components. The aft compressor and turbine stages of modern engines employ nickel-based superalloys. These provide adequate strength and environmental resistance but at the penalty of high rotating weight. Greater performance will be achieved through the use of titanium matrix composites[1]. In the near term Ti-6Al-4V will be used as the matrix but greater operating temperature can be tolerated through the use of advanced intermetallic matrix materials. Some examples are: $Ti_2AlNb$, $Ti_3Al$, TiAl, NiAl, or $MoSi_2$.

The orthorhomic composition, $Ti_2AlNb$, is particularly attractive because of its higher specific strength, low temperature ductility, and low temperature fracture toughness as compared to $\alpha_2$ alloys. In addition composites of this alloy do not exhibit the thermal fatigue problem observed for some $\alpha_2$ composites[3,4]. Alloy development based on this composition is ongoing, but clearly this class of alloys offers tremendous potential for high temperature applications.

High rate production of composites based on $Ti_2AlNb$ is challenging. One approach with significant promise is electron beam physical vapor deposition (EB-PVD)[5]. EB-PVD is a well established method for high rate vapor deposition. Traditionally, single source EB-PVD is limited to alloys whose constituents have vapor pressures within a factor of approximately 100. Large differences in vapor pressure oleads to unsteady vaporization which results in significant variations.Active correction for these variations is possible if the vapor composition is known.

Diode laser absorption spectroscopy is an ideal technique for measuring the absolute vapor composition and providing a feedback signal to a composition control system. Laser absorption spectroscopy is a highly specific and non-intrusive technique for monitoring vapor composition.

The development of diode lasers appropriate for monitoring high rate vaporization makes this technique highly reliable and robust. The reliability and low maintenance of a diode laser absorption spectroscopy diagnostic changes this technique from a research tool into an industrial instrument. Below we describe the important features and components of a rugged control system based on diode laser absorption spectroscopy. The performance for this diagnostic depends critically on the choice of atomic transitions being monitored. We review the methodology for selecting an atomic transition. Experiments demonstrating the performance of this technique for monitoring the vaporization of titanium and niobium have been carried out. DLAS is seen to provide an accurate measure of the deposited film composition.

## LASER ABSORPTION SPECTROSCOPY

Lawrence Livermore National Laboratory (LLNL) has been using laser absorption spectroscopy (LAS) to monitor electron-beam generated vapor plumes for almost 20 years. LAS has proven itself to be an accurate and reliable method to monitor both density and composition. During this time the diagnostic has moved from a research tool to being a robust component in a process control system.

In laser absorption spectroscopy, laser light is scanned in wavelength through an atomic transition. The light absorbed by the vapor is a measure of the vapor density. By scanning the laser wavelength through the atomic transition and establishing the zero absorption baseline, absolute calibration is maintained for every scan. The narrow line width of the laser, together with the large separation of atomic transitions compared to the transition line width, insures no interference from other elements. This feature insures that the density measurement is element specific and in some cases isotope specific. This high degree of selectivity while maintaining absolute calibration makes LAS a highly reliable method for measuring vapor densities.

Fig. 1 illustrates the components in an industrial diode-based LAS diagnostic. The diode laser makes this system economical, highly reliable, and capable of high vaporization rate operation. Past LAS systems used argon ion pumped ring dye laser systems to generate light of the necessary wavelength. While very flexible, these systems are expensive and difficult to maintain. Diode lasers eliminate the necessity for high voltage and toxic chemicals while providing the reliability of solid state systems. Diode lasers also avoid the disadvantages of incoherent light sources. Incoherent light is difficult to transport or absolutely calibrate. Incoherent systems rely on strong resonant lines and short vapor pathlengths. This reliance leads to a measurement that is either intrusive or useable only at low vaporization rates. With laser absorption spectroscopy the laser light is easily delivered using fiber optics and transported through large vacuum vessels. In addition proper selection of the atomic transition permits optimizing the diagnostic to the density range of interest.

Another feature of the system depicted in Fig. 1 is synchronous detection of the amplitude modulated laser light. Chopping the light, together with synchronous detection using lock-in amplifiers, minimizes the effects of power fluctuations in the laser and external noise sources. Modulating each laser system at a different frequency allows several lasers to be multiplexed into one transport and detection system. Therefore multiple species can be measured simultaneously at the same location.

External to the vessel a portion of the light is focused on to a reference detector. The remainder of the light is launched through the vapor plume and detected by the signal detector. The ratio of the signal to the reference yields the transmission as a function of frequency. The transmission is then turned into a density by application of Beer's Law[6]. This density is then delivered to a model-based vaporizer control system.

## TRANSITION SELECTION METHODOLOGY

A LAS sensor system must be designed to match the process of interest. For EB-PVD the vaporization rate, relative vapor pressures, electronic temperature, isotopic frequency shifts, and hyperfine structure all affect the selection of the appropriate atomic transitions. The methodology of designing a vapor composition diagnostic (see Fig. 2) is illustrated below for the alloy $Ti_2AlNb$.

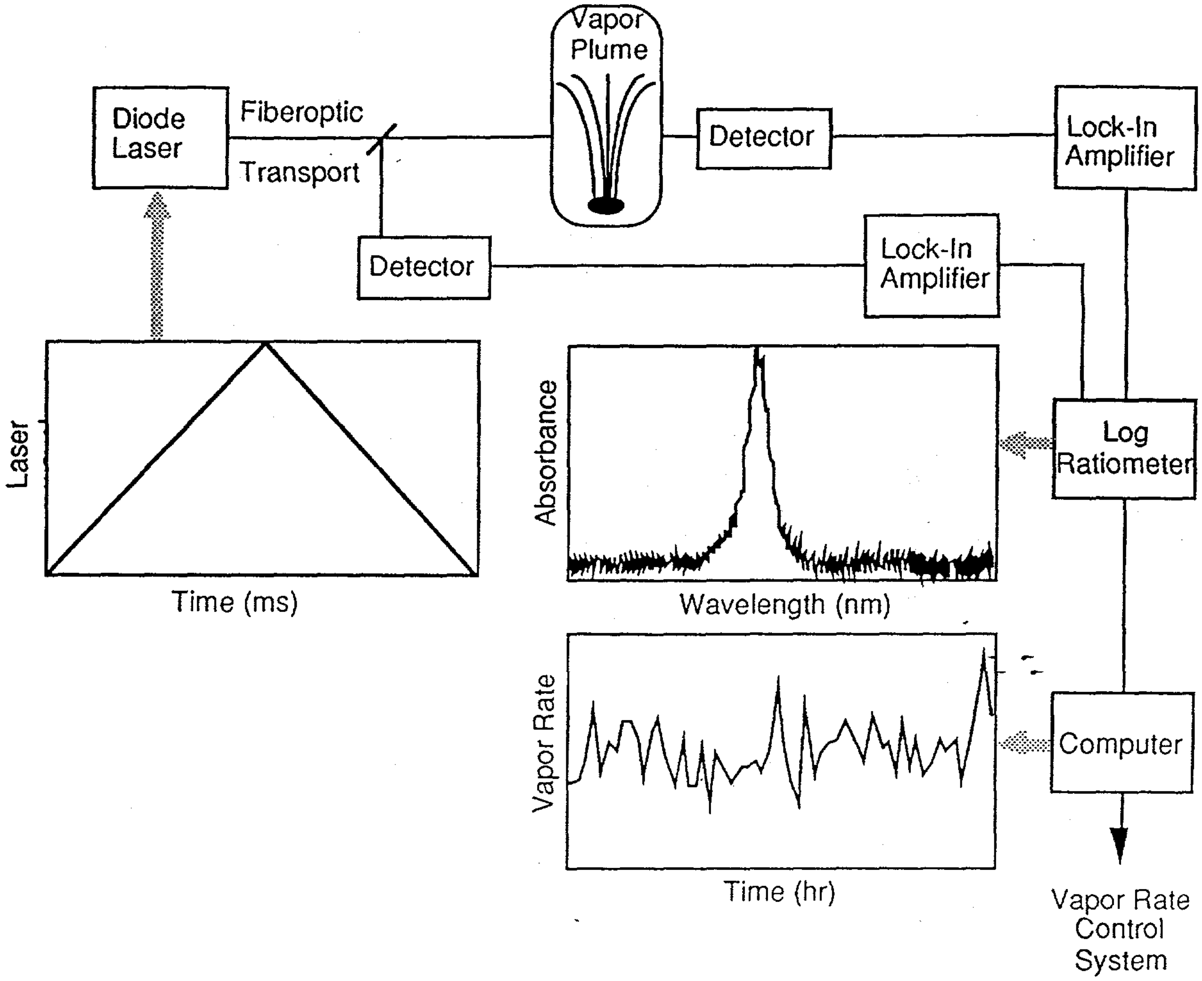


Figure 1. Components of an industrial vapor composition diagnostic.

Simultaneous vaporization of titanium and niobium at approximately equal rates, consistent with the production of $Ti_2AlNb$, is limited by the attainable niobium vaporization rate. Experimentally, niobium vaporization rates of 1-2 kg/hr are easily achievable. Under these conditions the titanium and niobium vapor pressures differ by a factor of approximately 10,000[7]. This large difference in vapor pressures makes steady vaporization of titanium and niobium from a single source and at a fixed ratio extremely difficult without a vapor composition monitor. In this case monitoring both titanium and niobium is necessary in order to control vapor composition. Using a standard $\cos^3\theta/r^2$ vapor distribution[7] where $\theta$ is the angle from vertical, and r is the radial distance from the source, the titanium and niobium densities at any measurement location can be calculated. In addition the role of electronic temperature on the fraction of the atoms in the state being measured must be taken into account. Fig. 3 shows the dependence of the titanium ground and low lying metastable densities on the electronic temperature. For the anticipated range of electronic temperatures, the fractional population in the titanium 170 $cm^{-1}$ state is seen to be independent of electronic temperature. Therefore monitoring just the first metastable state of titanium is sufficient for calculating the total density. Niobium is not as simple. The fractional populations for the niobium ground and metastable levels are a more sensitive function of the electronic temperature.

For this reason it is necessary to monitor two levels in niobium in order to calculate the total niobium density.

Using the information developed above, it is now possible to survey potential transitions for monitoring titanium and niobium. Titanium is used as an example to illustrate the process of selecting an optimal atomic transition. There are 78 titanium transitions from ground and low lying metastable levels with wavelengths longer than 385 nm. Of these transitions approximately 38% lack cross section information. For those transitions with cross section information[8], nine are appropriate for monitoring titanium. Table 1 shows the atomic transitions appropriate for monitoring titanium at vaporization rates of up to 2 kg/hr.

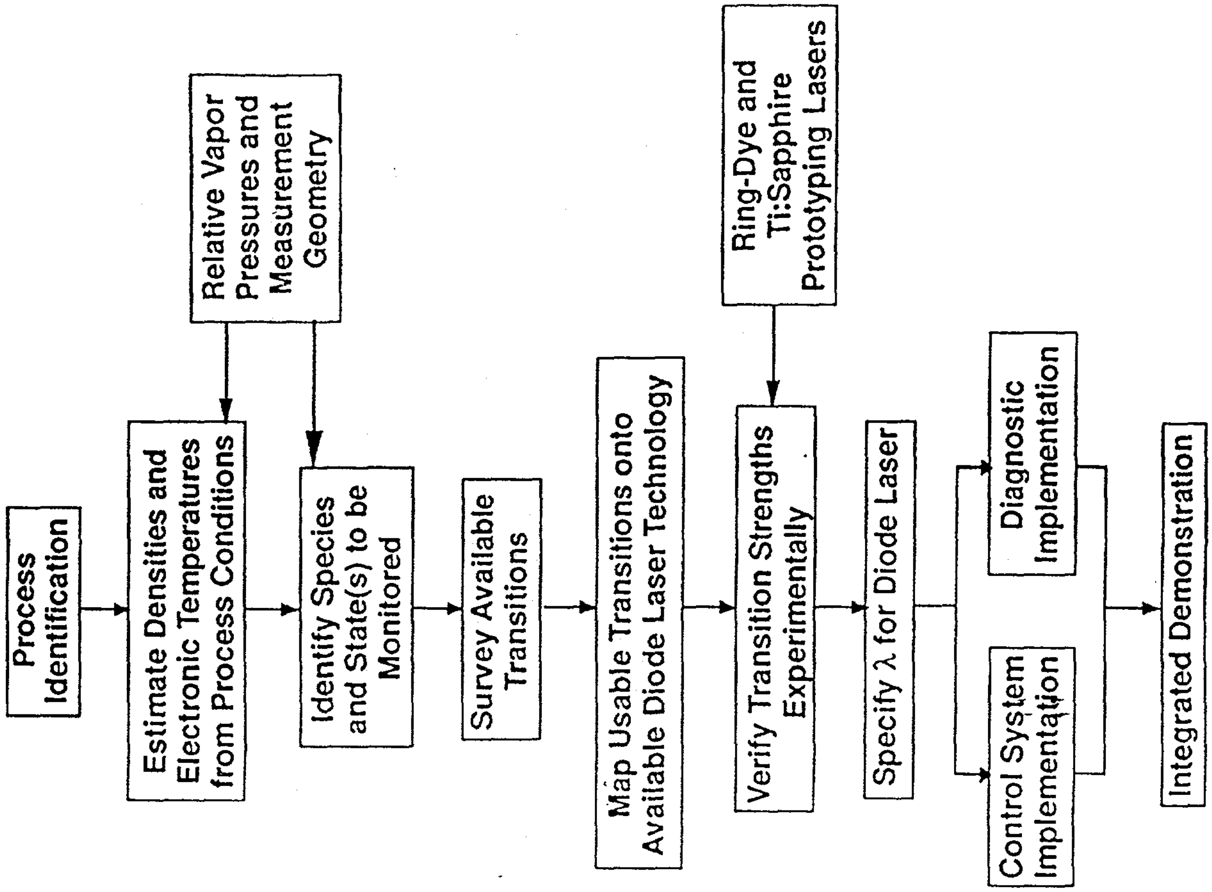


Figure 2. Methodology for selecting and implementing a vapor composition diagnostic.

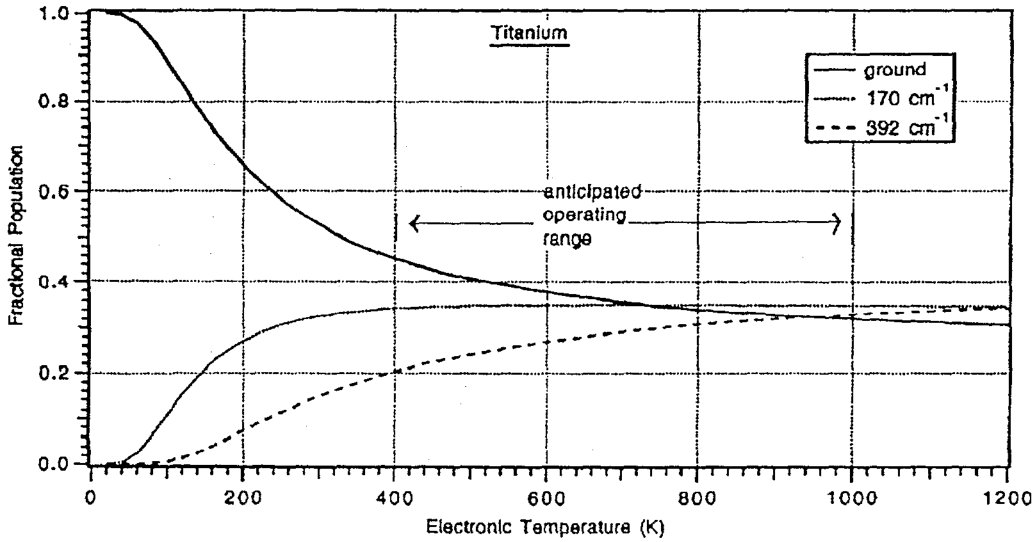


Figure 3. Fractional populations of titanium metastables as a function of electronic temperature.

Having identified atomic transitions of the appropriate strength is not sufficient. The selected atomic transition must match available diode laser technology. Since the diode laser wavelength is set by the band gap energy of the lasing material, diode lasers are available only in discrete wavelength regions. In addition, for spectroscopic measurements the diode laser should operate continuously in a single longitudinal mode and be scannable in frequency. Fig. 4 shows the commercially available diode lasers as well as wavelengths where frequency doubled diodes are expected to be available soon. Frequency doubled diodes require around 100 mW of single longitudinal mode output at the fundamental wavelength in order to produce usable levels of blue to ultraviolet light. Waveguide doubler technology using periodically poled lithium niobate[9,10] is being commercialized for these wavelengths. Table 1 shows the overlap between titanium transitions useful at high vaporization rates together with available diode technology. Clearly the titanium 170 cm-1 transitions at 391.588 nm and 388.139 nm offer the best match between available transitions and available technology. Unfortunately the same laser cannot reach both transitions. Therefore before specifying the laser wavelength it is useful to experimentally verify the performance of these transitions. Another reason to experimentally verify the performance of the chosen atomic transition is that published cross sections for weak transitions have 30% random errors and different sources differ by factors of two or more[8,11]. Using this approach, we have identified titanium and niobium transitions appropriate to high vaporization rate processes. Cross sections for these transitions have been experimentally verified. Experiments demonstrating the performance of these transitions and this technique are discussed below.

Table 1. Titanium transitions appropriate for monitoring high rate vaporization (near 2 kg/hr).

| State ($cm^{-1}$) | Wavelength (nm) | Cross Section [5] ($x10^{-15}$ $cm^2$) | Matching Diode Laser Technology |
|---|---|---|---|
| 0 | 446.210 | 1.24 | No |
| 170 | 544.661 | 0.774 | Maybe |
| | 542.624 | 1.37 | Maybe |
| | 521.970 | 6.81 | No |
| | 469.365 | 2.36 | No |
| | 456.264 | 2.57 | No |
| | 449.624 | 2.68 | No |
| | 391.588 | ~1.0 | Yes |
| | 388.139 | 6.05 | Yes |

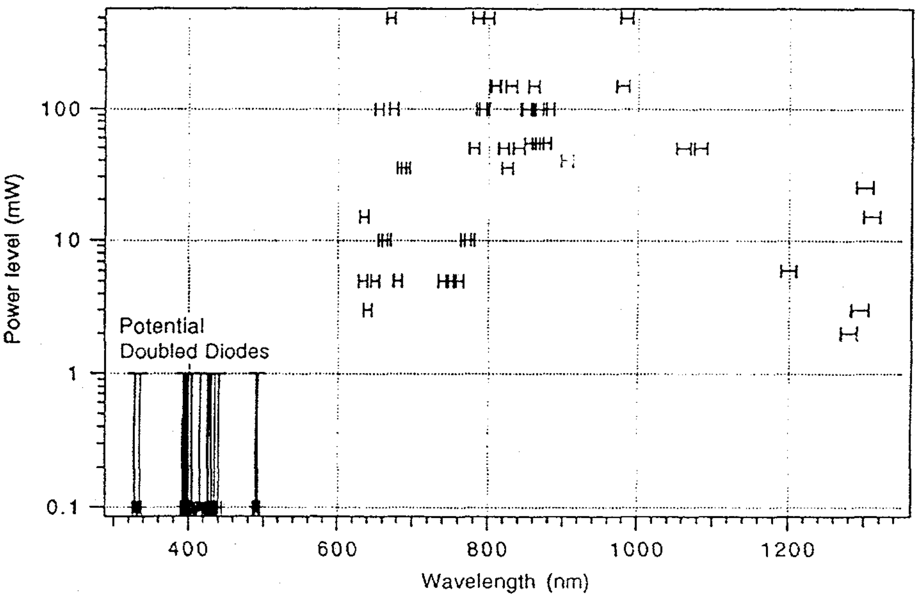


Figure 4. Wavelength regions where diode lasers are available.

## DIAGNOSTIC PERFORMANCE

In order for this approach to be useful in a control system, the vapor measurement must mimic the composition of the deposited film. A series of experiments were undertaken to demonstrate diagnostic performance. In the first experiment titanium wire was fed into a niobium pool at various rates. The titanium flash vaporizes off the niobium pool because of its much larger vapor pressure. Fig. 5 shows the time history of the feed rate as well as the titanium vapor density. The titanium vapor density tracks the changes in titanium wire feed rates. This experiment demonstrates the rapid time response of the titanium density signal.

In a related experiment involving titanium wire feed into a niobium pool, a foil was collected after the run and analyzed via scanning Auger. Fig. 6 shows an Auger line scan of titanium in the foil together with the titanium density measured during the run. For this comparison multiple titanium density points were averaged together to simulate the effects of the finite sample size of the Auger scan and titanium diffusion during deposition. The titanium vapor density mirrors that seen in the deposited foil. In making the foil, two different titanium wire feed rates were used. These show up clearly in both the Auger line scan and the titanium vapor density. This data shows a direct relationship between the vapor density and the deposited foil.

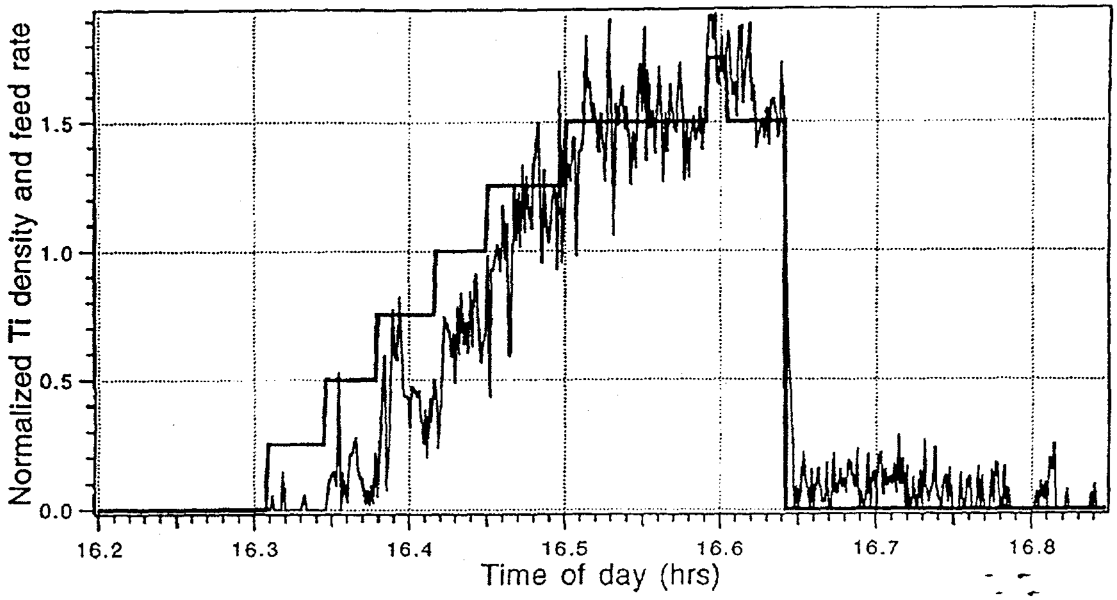
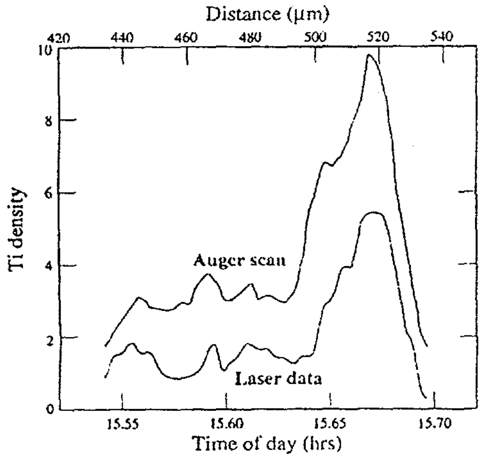


Figure 5. Comparison of titanium wire feed rate to measured vapor density.



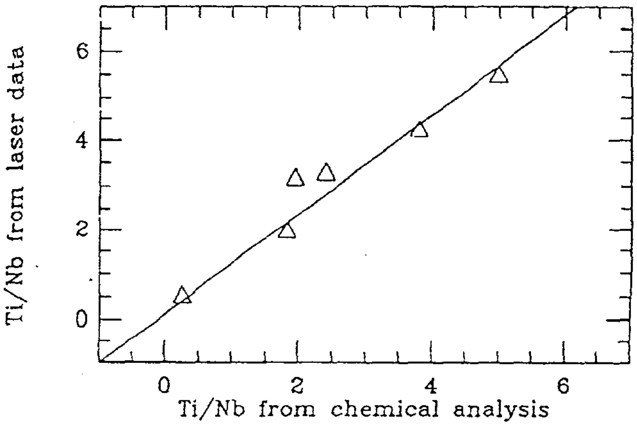


Figure 6. Comparison of titanium vapor density to post-run Auguer line scan of deposited film.

Figure 7. Composition measured during deposition versus chemical analysis of deposited film.

In a final experiment the vapor composition was measured in real time and compared to the composition determined from post-run chemical analysis. For this experiment separate vaporization sources for the titanium and niobium were used. This configuration was used to provide greater flexibility and more stable operation. A sample was created for each operating condition by placing a sample wheel above an aperture. Each time the operating conditions were changed the sample wheel was indexed to a new location. This procedure permits direct comparison of the chemical analysis to the measured vapor composition. Fig. 7 shows that the vapor composition is linearly related to the chemical composition over a wide range of operating conditions. Differences between film and laser compositions are due to either errors in the cross sections or experimental geometry effects. These errors can be eliminated by using a calibration curve.

The above data demonstrates the utility of laser absorption spectroscopy for monitoring composition in electron beam vaporization processes. Further experiments are underway to demonstrate reproducibility. The diagnostic responds to rapid changes in vapor composition and tracks the deposited film composition. The dynamic range of the measurement is significantly larger than is needed for the production of $Ti_2AlNb$. These features make this diagnostic ideal for providing a composition signal to a control system.

## CONTROL SYSTEM DEVELOPMENT

The diagnostic verification experiments also provided insight into potential control strategies. When the pool is fed with the volatile component from above the surface, vaporization rates are highest at the feed entry point. For sufficiently high concentrations of the volatile species, the thrust generated by the vapor can propel liquid "spits" to the surroundings. If feed material is introduced from below as is done with a "bottom feed" system, the volatile species are transported by convection from the lower pool boundary to the pool surface. With this approach spitting is less likely and the vaporization of volatile species is better distributed over the surface of the pool. However, alloy feed bars must be fabricated that include both the volatile and refractory species.

An alternative approach is to evaporate species of greatly differing vapor pressure from separate pools. However, the vapor plumes now originate from different sources which yields a more complex vapor deposition profile. In addition, at high vaporization rates it is possible for the collision rates to be large enough for the vapor streams to interact. These interactions could be avoided by isolating the plumes and depositing the metal as a laminate. The substrate would be transported from one plume to the other, and the alloy would be formed by diffusion at elevated temperatures.

This experience must then be folded into the objectives for the control system. The first objective is to maintain a specified deposition flux for each species over a region of interest. The second objective is to keep the pool level in each vapor source at a specified value. In addition to insuring the availability of material for vaporization, achieving this second objective helps keep the vapor sources stationary and the pools at constant composition.

We consider a control system for the simultaneous deposition of two species from separate sources, see Fig. 8. Laser absorption measurements are processed to obtain deposition fluxes for each species. The important relationship between absorption measurements and fluxes is established using models and the results of the diagnostic verification experiments. Measurements of pool level are obtained by processing images from a camera view. The measured vapor deposition fluxes and pool levels are passed through filters and compared with set point values. Based on the four error signals, a controller using the Internal Model Control (IMC) strategy makes adjustments in the gun power and feed rates for each source[12]. The model includes the steady-state relationships between gun power and deposition fluxes, feed rate and pool level, and the response characteristics of the measurement, electron-gun, and feed systems. An initial approach would be to employ four single-input-single-output loops in which e-gun powers are paired with vapor fluxes and feed rates with pool levels. If the interaction between the vapor fluxes is strong, a multi-variable control strategy could be employed for the two vapor flux loops. Experiments in this area are ongoing at 3M and LLNL.

## SUMMARY

A diode laser based absorption spectroscopy diagnostic has been developed for monitoring the composition of titanium-niobium vapor plumes. Diagnostic performance is critically dependent on the appropriate choice of atomic transitions. We have developed a methodology for selecting the optimal transitions which is based on process conditions, transition line shape, and available laser technology. Using transitions selected with this approach, we have demonstrated the unambiguous relationship between vapor composition and film composition. Efforts are now underway to develop the composition control system consistent with the production of orthorhombic titanium alloy coated SiC fibers.

While this system was developed for monitoring titanium and niobium, the technique is generalizable to composition or rate control for most alloy systems. The most difficult step is matching an atomic transition of the appropriate strength to available diode laser technology. But even this is becoming less of an issue as shorter wavelength diode lasers become available. As an example, the waveguide-doubled diode laser system being developed by New Focus, Inc. has an initial tuning range of ±1nm around 391.5 nm. While designed specifically for monitoring titanium, this laser should be able to monitor a number of elements, depending on exact process conditions. A cursory survey shows that at least 13 elements have potentially useful transitions within the tuning range of the first prototype device. Elements of special interest to metal matrix composites in this wavelength range include molybdenum, cobalt, iron, niobium, and vanadium. Future development efforts at LLNL involve applying this technology to the vaporization of aluminum and copper alloys as well as ceramics.

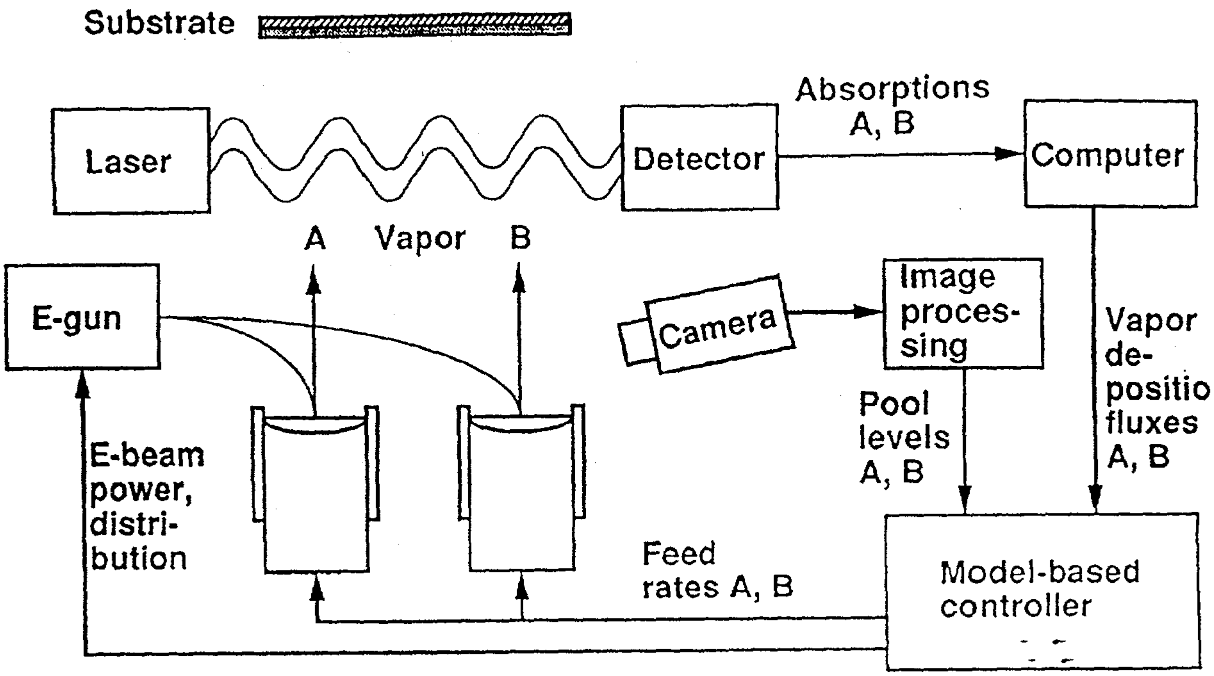


Figure 8. Components in a composition control system.

## ACKNOWLEDGEMENTS

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