

**N 9 3 - 2 6 9 3 6**

# **Laser Diagnostics for NTP Fuel Corrosion Studies**

*Paul J. Wantuck*

**Chemical and Laser Sciences Division  
Los Alamos, NM 87545**

**Contributors: *D.P. Butt*  
*A.D. Sappey***

**Nuclear Propulsion Technical Interchange Meeting  
NASA-Lewis Research Center, Plum Brook Station**

***October 20-23, 1992***

## Issues Associated with NTP Fuels

- Reactor operates at temperatures approaching 3000 K
- Fuel is susceptible to corrosion
- Need to quantify corrosion products / rates to assess fuel performance
- Severe environment during test: limits methods of measurement

Laser-based diagnostics offer means of probing environment about fuel

Advantages: non-intrusive  
unaffected by harsh local conditions

CLS-92-1582

In order to generate the necessary propulsive performance, the nuclear reactor will operate at temperatures approaching 3000 K. Such temperatures, in combination with the high-pressure hydrogen propellant flowing through the core, provide a very hostile operating environment for the fuel material, particularly with respect to hydrogen-induced corrosion. Identifying the corrosion products as well as experimentally quantifying the corrosion rates of these fuels under a variety of conditions is critical to assess the expected lifetime of the reactor. The severe environment surrounding a fuel material under test is not conducive to probing by standard instrumentation. Thus alternative diagnostic techniques are required to provide real-time monitoring of corrosion products. Laser diagnostics offer a means of non-intrusively probing the high-temperature environment above the surface of the fuel to identify and establish spatial distributions and local concentrations of many of the anticipated corrosion species.

## U-Zr-C system corrosion products

- $(U_x Zr_{1-x}) C_y$  solid solution or  $(U_x Zr_{1-x}) C_y + C$  composite fuel material serious candidate for NTP reactor fuels
  - High melting temperature
  - Good resistance to  $H_2$  corrosion
- Calculations indicate that for  $H_2$  temperatures  $>2800$  K, acetylene,  $U(g)$ , and  $Zr(g)$  are primary vapor constituents
- Zr selected as species to probe
  - Major corrosion product
  - Corrosion of  $(U_x Zr_{1-x}) C_y$  may be rate limited by transport of Zr away from fuel surfaces
  - Obviates need for testing in  $H_2$  environments or with uranium-containing samples

CLS-92-1957

Solid solution refractory carbide fuel materials, such as  $U_x Zr_{1-x} C_y$ , are being seriously considered as candidate NTP reactor fuels because of their high melting point and resistance to corrosion by hydrogen.<sup>1</sup> Butt<sup>2</sup> has calculated the equilibrium partial pressures above the surface of  $U_{0.05}Zr_{0.95}C_{1.07}$  during exposure to 1 atm of hydrogen over a temperature range of 2000 to 3200 K. The results show that in high temperature hydrogen,  $U(g)$ ,  $Zr(g)$ , and various hydrocarbon species dominate the gas-phase products. Above approximately 2800K, acetylene and gas phase uranium and zirconium are predicted to be the primary vapor constituents. Confirmation of such predictions through experimental measurements is critical to the development of accurate corrosion kinetics models.

In the current study, Zr atoms were selected as the species to probe using laser techniques. This selection was influenced by several factors. First, the zirconium atom is predicted to be a major corrosion product. Second, the corrosion of  $U_x Zr_{1-x} C_y$  in hydrogen may be rate limited by the transport of gas phase Zr away from the surface.<sup>2</sup> Third, testing a laser diagnostic for zirconium obviates the need to perform experiments in a hydrogen environment or with uranium-containing fuel samples.

1. S. K. Bhattacharyya, R. H. Cooper, R. B. Matthews, C. S. Olsen, R. H. Titran, and C. E. Walter, "Fuels and Materials for Space Nuclear Propulsion," AIP Proceedings of the 9th Symposium on Space Nuclear Power Systems, Albuquerque, New Mexico, Vol. 2. pp 681-691 (1992).
2. D. P. Butt, "Corrosion of  $U_x Zr_{1-x} C_y$  Nuclear Fuel Materials in Hydrogen Gas at High Pressures and Temperatures," IAF Paper No. 92-0570, 43rd Congress of the International Astronautical Federation, Washington DC (1992).

## Planar Laser-Induced Fluorescence (PLIF)

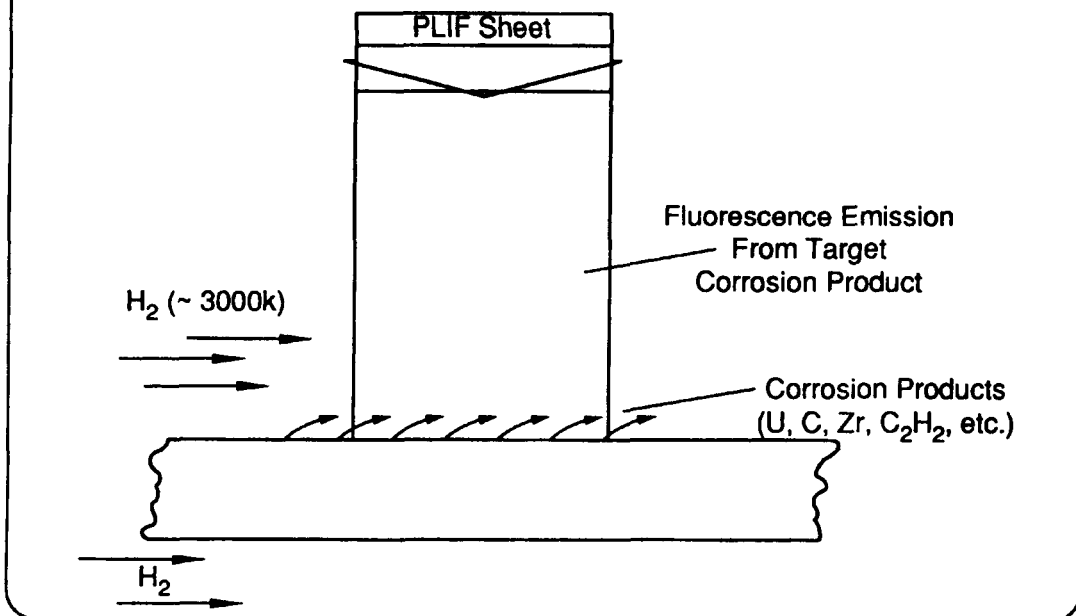
- Highly sensitive technique
- Absorption of laser light by atomic or molecular species followed after some finite time by emission from the excited state
- Intensity of emission can be related to concentration, temperature, velocity, etc.
- PLIF represents extension from point or line diagnostic to 2D or field measurement technique

CLS-92-1583

Laser-induced fluorescence (LIF) offers a highly sensitive technique for monitoring many of the NTP fuel corrosion products (including Zr) as well as for determining properties of the NTP exhaust. Quite simply, LIF can be viewed as an absorption of laser light, at a specific frequency, by an atomic or molecular species followed after some finite time by an emission from the excited state. This emission or fluorescence is, in general, at a different (typically longer) wavelength than the exciting laser light's wavelength. By viewing this off-resonance fluorescence, it is possible to avoid interference from scattered laser light.

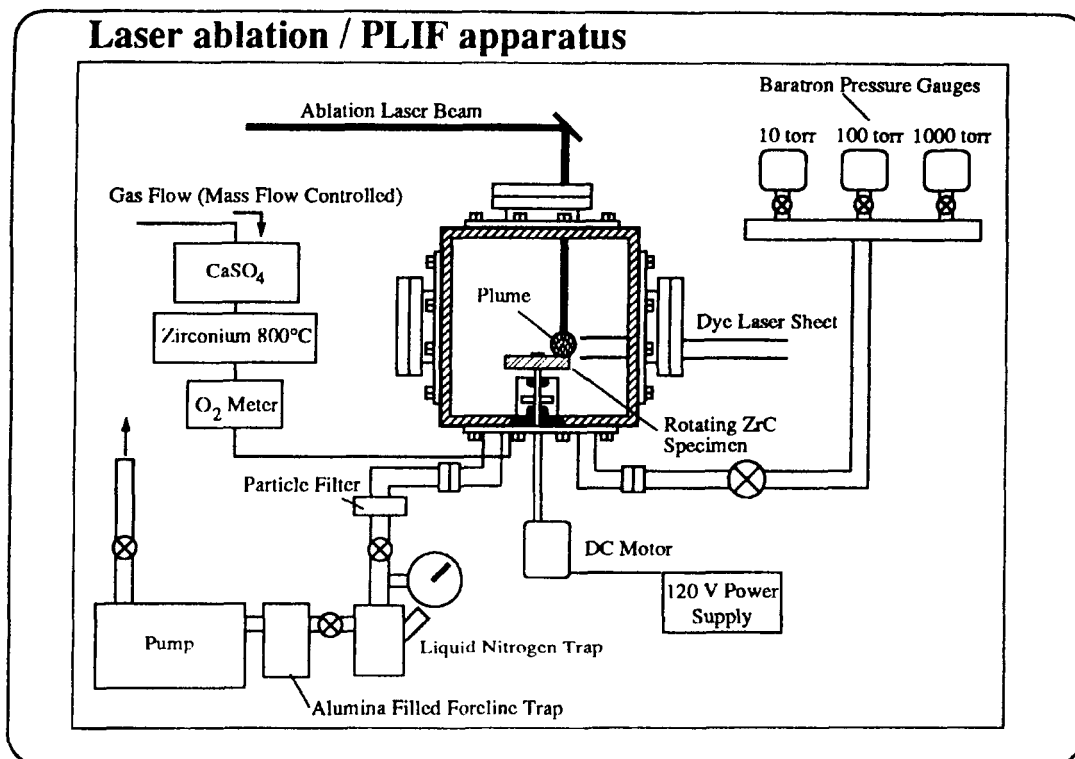
Planar LIF or PLIF represents an extension of the LIF technique from a point or line diagnostic to a 2D or field measurement method. In general, the species-exciting laser beam is transformed into a thin sheet by the placement of cylindrical lenses into the optical train. A camera is typically used to collect the resulting fluorescence emission, perpendicular to the species-exciting laser sheet. The local intensity of the collected light can then be related to the concentration, temperature, or velocity of the target species. The non-intrusive nature of this technique, as well as its good spatial and temporal resolution, make it particularly well suited for application as a diagnostic in the high temperature NTP operating environment.

### Utilization of PLIF for Corrosion Product Characterization of Nuclear Thermal Rocket (NTR) Fuel Elements Under Test



CLS-92-

A PLIF scheme for measurement of corrosion species evolving during the test of an NTP fuel sample/element could take the above configuration. The laser sheet is passed through the high temperature hydrogen stream, which contains the various corrosion products, and contacts the surface of the fuel. Fluorescence emission from the chosen target species is then imaged producing a two-dimensional distribution map.



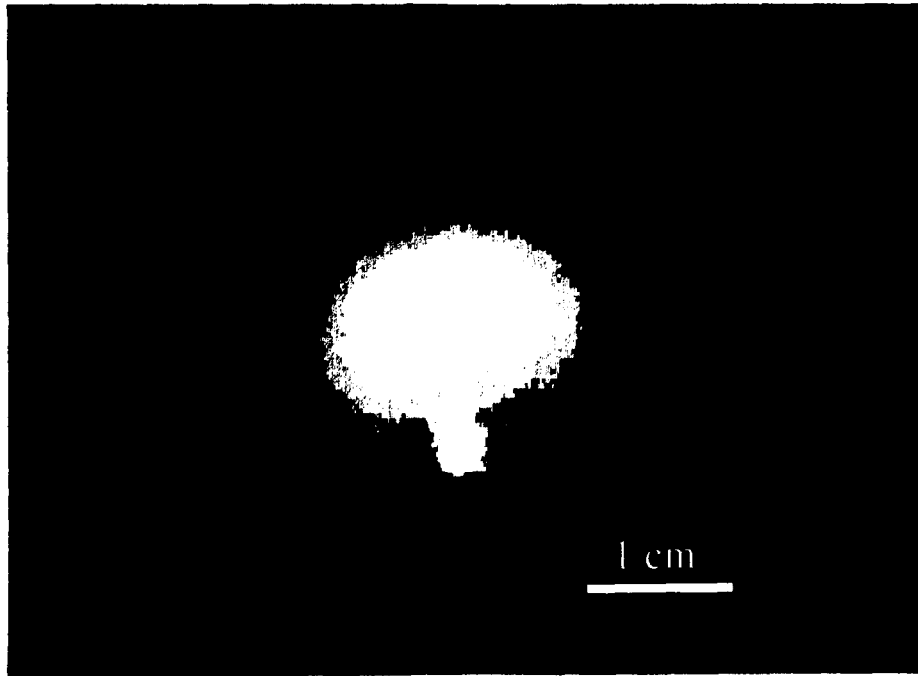
CLS-92-829

Production of zirconium vapor for subsequent illumination by a PLIF diagnostic, is accomplished by focusing a pulsed laser onto a ZrC target. This technique, known as laser ablation, represents a relatively simple method for producing gas phase samples of refractory materials.

The apparatus utilized for these experiments is displayed above. The cubical (~30 cm) ablation chamber contains five, window ports which allows optical access to its interior. The chamber is evacuated by a standard mechanical pump through both a liquid nitrogen and alumina-filled trap. The chamber can be backfilled with a variety of gases through a separate, flow regulated feed line. During each experiment, a slow flow of argon is maintained through this line and the chamber to minimize the buildup of particulate. A series of capacitance type manometers and thermocouple gauges are available to monitor chamber pressure. The base pressure for the chamber is 20 mtorr. Typical operating pressures are between 7 to 10 torr. The ZrC target specimen is positioned on a rotating table which is externally driven by a variable speed DC motor. Rotation of the target prevents the formation of a pit in the ZrC disk by action of the ablation laser.

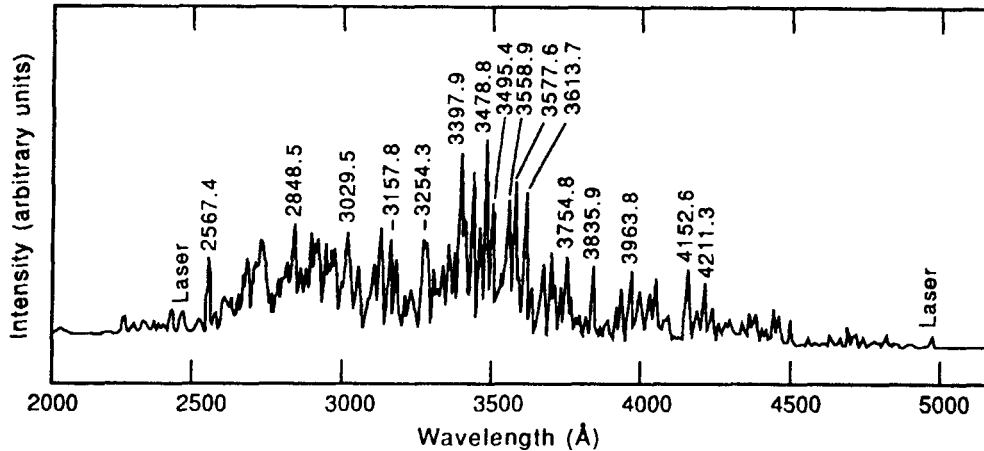
A Lumonics model TE-860-4 excimer laser operating at 248 nm is used to produce the ablation pulse. Beam energies are on the order of 100 mJ/pulse and the laser is operated with a 5-10 Hz repetition frequency. The beam is brought to the ablation chamber by several high reflectance mirrors and focused at normal incidence onto the target using a 18.3-cm focal length quartz lens. The ablation spot size is approximately 1 mm<sup>2</sup> and the corresponding laser fluence at the target is ~670 MW/cm<sup>2</sup>. The PLIF sheet is passed, at right angles, through the plume.

## ZrC Plume Emission



Plume emission images were recorded at different delay times. One representative ZrC plume emission image is displayed above. The ability to acquire such images represents a necessary step in the application of the PLIF technique. An intensified, gated uv camera (Xybion model ISG-250-U) with a 105 mm, f/4.5 quartz focusing lens was interfaced with an EPIX Silicon MUX RGB frame grabber board with a programmable trigger option. The timing of the camera intensifier, frame grabber board, and excimer laser was controlled using a Stanford Research System model DG535 programmable delay/pulse generator. The above image was captured 50  $\mu$ s after the excimer laser pulse. The ablation chamber's argon background pressure was held constant at 7.5 torr and the camera gate width set at 20  $\mu$ s. In these expanding plasmas, atom velocities can exceed  $10^6$  cm/s at low background pressures (tens of mtorr) with neutral gas temperatures near the target surface approaching 15,000 K.

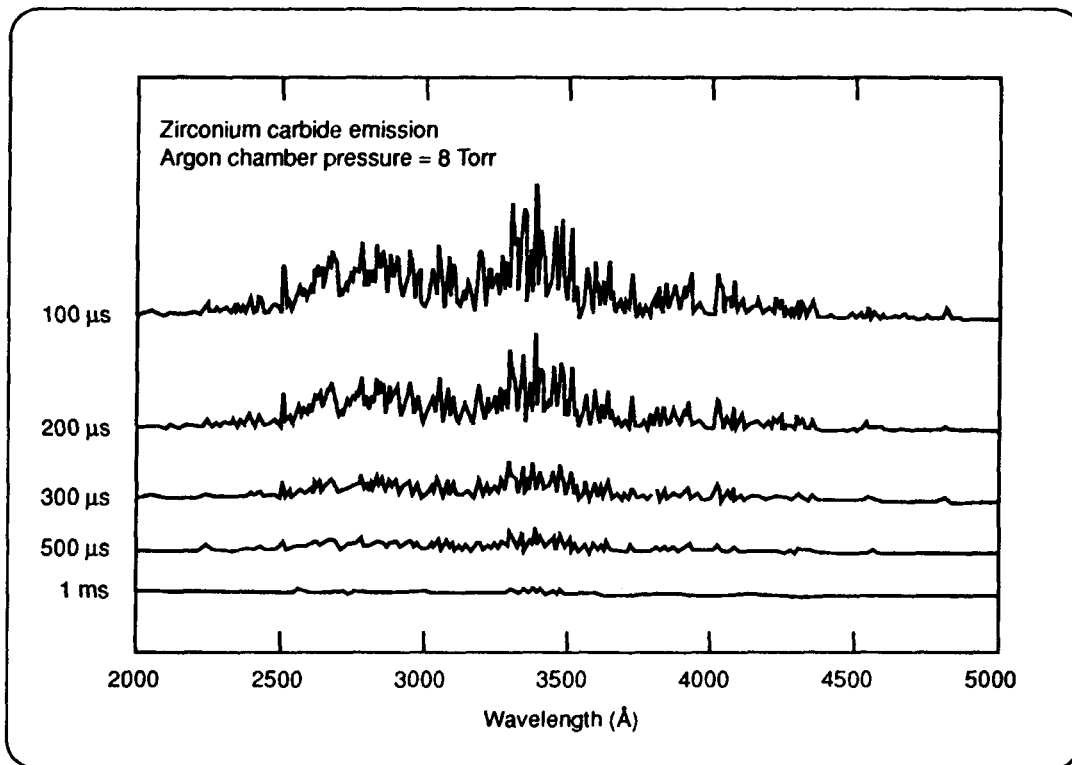
## ZrC Emission Spectrum



CLS-92-794

Temporally resolved ZrC plume emission spectra were recorded for regions near the target surface. The chamber pressure was maintained at 8 torr. A representative ZrC plume emission spectrum, recorded 10  $\mu$ s after the excimer laser pulse, is shown above. This emission spectrum, which covers a wavelength range from 200.0 to 500.0 nm, is dominated by the presence of zirconium atom emission (several of the many Zr(I) lines are identified in the figure). No emission lines from other species, such as carbon atoms are identified in the emission traces.





CLS-92-1590

By adjusting the delay time, it is possible to establish emission spectra at specific times during the plume expansion event. For example, ZrC emission spectra recorded for increasing delay times indicate that the plume emission intensity has reduced to essentially undetectable levels at approximately 1 ms (for a background pressure of 8 torr). Such a reduction is due to expansion cooling and quenching through radiative and collisional processes. Quantifying the temporal behavior of plume emission intensity is important for establishing the proper delay times to acquire PLIF images of the expanding zirconium vapor as it reduces interference from background emission.

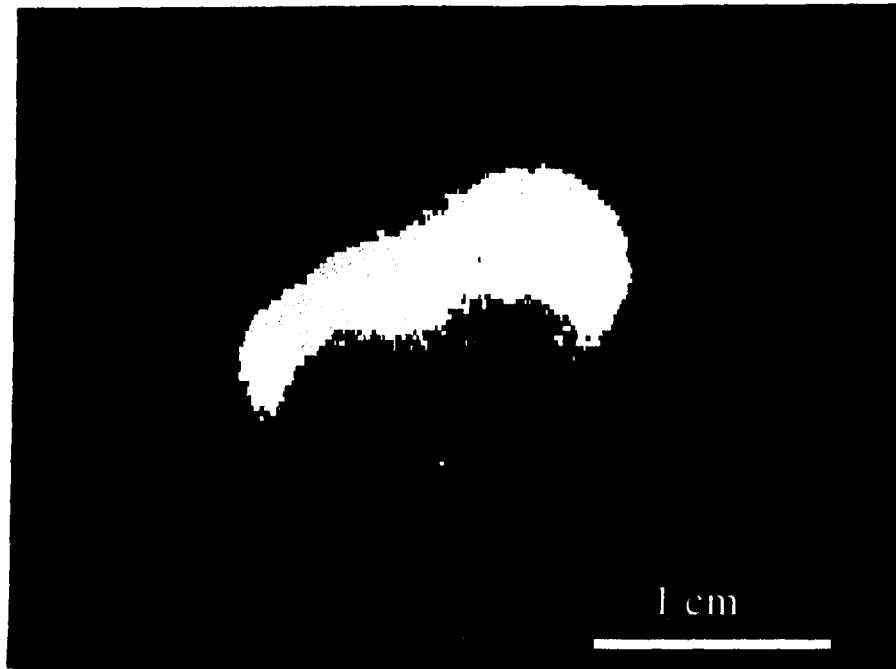
## PLIF Imaging of ZrC Plume

- **Zr(I) ground state to excited state transition at  $35515\text{ cm}^{-1}$  pumped using Nd:YAG laser-pumped dye laser (R590 dye)**
- **Fluorescence emission monitored at  $418.76\text{ nm}$  using filtered, gated, uv-intensified CCD camera coupled to frame-grabber board**
- **Image capture at different times after excimer pulse**
- **PLIF sheet  $30.0\text{ mm} \times <0.5\text{ mm}$**

CLS-92-1584

PLIF images of the spatial distribution of the zirconium atom in the ZrC plume have been acquired. To capture these images, the Zr(I) ground state to the excited state ( $t^3F^0_2$ ,  $J=2$ ) transition at  $35,515.4\text{ cm}^{-1}$  ( $281.5\text{ nm}$ ) was pumped using the frequency doubled output of a Nd:YAG laser-pumped dye laser operating on Rhodamine 590 dye. Fluorescence emission at  $418.76\text{ nm}$ , corresponding to the transition from the  $t^3F^0_2$  excited state to the  $b^3F_2$  ( $J=2$ ) intermediate state at  $11640.7\text{ cm}^{-1}$ , was captured with the uv-intensified CCD camera. A dye laser sheet approximately  $30.0\text{ mm}$  by  $0.5\text{ mm}$  was formed for passage through the plume by a lens combination consisting of a  $+100\text{ mm}$  (converging) lens and a  $-100\text{ mm}$  (diverging) focal length cylindrical lens and a  $150\text{ mm}$  focal length spherical lens.

### PLIF Image of Zr in Ablated Plume



A PLIF image showing the spatial distribution of ground state zirconium atoms in the ZrC plume is shown above. The fluorescence emission was filtered using a GG395 filter. The image was recorded 625  $\mu\text{s}$  after the ablation laser pulse with the camera gate width set at 20  $\mu\text{s}$ . The spots observed in this image are pieces of hot (radiating) sputtered material from the target.

## Summary

- Utilized a focused excimer laser to ablate material from ZrC targets
- Zr prevalent in plumes
- Temporally resolved CCD image of plume emission generated

$$\tau_{\text{plume}} \sim 1 \text{ ms } (P_{\text{Background}} = 8 \text{ torr}); T_{\text{exc}} \cong 12,000 \text{ K}$$

- PLIF utilized to successfully image Zr atom distribution in plume
- PLIF technique should be able to monitor Zr about fuel element under test

CLS-92-1585

We have utilized a focused excimer laser to ablate material from ZrC targets for the purpose of developing appropriate laser-based diagnostics for gas-phase, corrosion products from hydrogen-exposed  $U_xZr_{1-x}C_y$  fuel elements proposed for NTP application. Temporally and spatially resolved emission spectra from the produced vapor plumes show the dominating presence of zirconium atoms. Temporally and spatially resolved images of the ZrC plume emission have also been recorded. The PLIF technique has been successfully used to image Zr atom distributions in the ablated ZrC vapor plume and thus could potentially be utilized to monitor Zr about fuel elements under test.

## Future Activities

- **Investigate other fluorescence excitation wavelengths for Zr**
- **Expose samples to rf-heated, hydrogen containing flow and probe flowfield around and downstream of sample with PLIF diagnostic**
- **Investigate other NTP fuel materials; (U-Nb-C) system**
- **Quantify Zr, Nb, etc. concentration in terms of fluorescence emission**

CLS-92-1586

Potential future activities include investigating other zirconium atom excitation wavelengths to ascertain the optimal transition for obtaining PLIF images in the ZrC ablation plumes. Following such determination, ZrC samples will be exposed to radio-frequency (rf) heated, hydrogen-containing flows and the PLIF diagnostic will be used to measure Zr atom distributions in the region surrounding the samples or in the nozzle exhaust flow.

For this study, a radio frequency discharge driven flow system will be used to produce a continuous, high temperature, chemically-clean gas stream. The unique feature of this system, which has been described by Wantuck,<sup>1,2</sup> is the use of an inductively coupled plasma tube as a high enthalpy gas source. A 50 kW rf generator is used to supply power to the tube where the gas is heated to between 5000 to 10,000 K. The system configuration will allow two different modes of ZrC sample heating, namely, placement of the sample within the plasma tube for direct inductive/plasma heating or positioning downstream of the nozzle exit for heating by the gas stream. The first configuration approximates corrosion species distribution in an NTP exhaust flowfield. The second configuration best simulates propellant flow over a fuel element. In both cases, a dye laser beam, operating at the same wavelength employed for the plume PLIF illumination studies, will be used to probe the nozzle exit flowfield or the region surrounding the gas-stream heated ZrC sample.

1. P. Wantuck and H. Watanabe, "Radio Frequency (RF) Heated Supersonic Flow Laboratory," AIAA Paper No. 90-2469, 1990.
2. P. J. Wantuck, R. A. Tennant, H. H. Watanabe, "Supersonic Combustion of a Transverse-Injected H<sub>2</sub> Jet in a Radio Frequency Heated Flow," AIAA Paper No. 91-2393, 1991.