Studies of Metal Combustion

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ABSTRACT

A CO_2 laser heating technique has been developed for studying the ignition and combustion of metals. Luminosity-time records, the principal output of the technique, provide valuable semi-quantitative information about these high temperature processes.

From the records produced during the heating of titanium, zirconium and the alloy, Zr_3Al, in both oxygen and nitrogen and from examination of the reaction products recovered after solidification, we conclude tentatively that: (a) the melting temperature of a metal may not necessarily play a governing role in its ignition; (b) neither zirconium nor the alloy Zr_3Al will provide a good substitute for DU in a fire environment; and (c) at present, titanium seems the best candidate for the proxy metal.

The technique has a serious shortcoming, however–that these records cannot be converted reliably to temperature-time traces, the desired end product of the studies. Although we hoped to make these conversions on the basis of luminosities emitted during the melting and solidification of the metals and their oxidation products, and standard substances such as aluminum oxide (solidifies at 2054 ^{o}C), we have concluded that a high-speed pyrometer is needed before studies of depleted uranium (DU) can continue.

Experiments are ready to start with DU but must remain on hold until accurate temperature calibrations of the ignition and combustion of the metals can be achieved.

ACKNOWLEDGEMENT

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INTRODUCTION

This is the final report that describes experimental studies of metal combustion performed in the Department of Engineering Physics, University of Wisconsin-Madison, during the period June 1, 2001, through March 15, 2002. Earlier portions of this work have been summarized in two informal letter reports submitted to Sandia National Laboratories on October 1, 2001 and December 31, 2001 (Nelson et al., 2001 a, b).

The objectives of this work stated in the contract between the University and the sponsor, Sandia National Laboratories, Albuquerque, NM, are:

1. Investigate the combustion chemistry and material physical behavior that govern the ignition of DU in gases typical of a fire environment.

2. Select a substitute material to simulate DU in nitrogen and gases typical of a fire environment.

3. Consider the suitability of using zirconium as the simulant.

We have based our experiments on the technique devised by Runyan, Clark and Moulder (1974), in which a sample of metal in a flowing gas is heated with the focused radiation from a CO_2 laser. Our diagnostics include photographic and video imaging of the metal samples during heating, ignition and combustion, measurements of emitted luminosity vs. time, and examination of the samples recovered after the experiments.

During this program, we have:

- Developed a reliable experimental apparatus and procedures for heating, ignition and combustion of metals in various gaseous atmospheres.

- Recorded luminosity-time traces during the CO_2 laser heating of titanium, zirconium and the alloy, Zr_3Al, in both oxygen and nitrogen.

- Performed preliminary investigations of the effects of melting temperature of a metal on its heating, ignition and combustion.

- Attempted to determine the temperature of a metal as it ignites by comparing its luminosity with that of molten aluminum oxide as it solidifies at 2054 ^{o}C.

- Photographed the solid products of the interactions.

- Prepared for studies of the ignition and combustion of DU.

EXPERIMENTAL

CO_2 Laser

The Model 41 CO_2 laser was manufactured by Coherent Inc., Santa Clara, CA. It emits a beam ~10 mm in diameter at a wavelength of 10.6 micrometers.

For safety, the laser has been mounted on an elevated platform with the beam directed horizontally 1.88 m above the laboratory floor. After leaving the laser, the beam passes through a heavy metal tube for ~150 mm, is directed downward with a 90^o mirror, travels for ~250 mm through a second heavy metal tube and is focused with a 250 mm effective focal length zinc selenide lens. The focal point is located ~300 mm above a workbench. The lens is protected from splatter and smoke by covering it with a disk of potassium chloride (a "lens saver").

The focal point is centered within a roughly cubical safety enclosure 750 mm on a side made of hinged 6 mm-thick transparent acrylic sheets that extend well above the head heights of the operators. The open top of the enclosure is fitted with a flexible 100 mm-diameter tube to exhaust fumes and aerosols generated by the laser heating.

During heating in the focus of the laser, the metal sample rested in a small depression in a graphite block as recommended by Runyan, Clark and Moulder (1974). The graphite we used was POCO EDM-3. The block is 117 mm in the direction viewed by the camera (front-to-back) x 130 mm perpendicular to direction viewed by the camera (side-to-side) x 66 mm tall. The block is mounted on a three-dimensional positioner to allow the sample to be moved into the focus of the laser. During heating, the samples were bathed in flowing oxygen or nitrogen at local atmospheric pressure obtained from a commercial high pressure cylinder. In a few early experiments, the flowing gas was directed across the surface of the graphite from a tube with a 2 mm-diameter orifice; in all later experiments, the orifice diameter was 6 mm.

A photograph of the experimental arrangement is shown in Figure 1.

Measurement of Laser Beam Power

Before each experiment, the power of the CO_2 laser beam is measured with a hand-held digital probe obtained from Macken Instruments, Inc., Santa Rosa, CA. The probe is a metal block calorimeter that is inserted in the beam for a measured time (usually 20 s). The block has an internal thermocouple to measure its temperature rise that is then converted into beam power with a digital readout system. We use one of two blocks to measure beam powers: the smaller H1 head for the range 10 to 100 W and the larger H2 head for the range 100 W and 1000 W. Accuracies are better than ±1%. A photograph of the digital readout system with both heads is shown in Figure 2.

The beam powers obtained from the laser ranged between a minimum of ~60 W, below which the discharge through the lasering gas mixture becomes unstable, to the maximum achievable of ~180 W with the current alignment.

Materials

The titanium and zirconium were obtained from Alfa Aesar Co., Ward Hill, MA, as follows:

- Zirconium slug, 3.175 mm diameter x 3.175 mm long, 99.5% (metals basis excluding Hf), Hf nominal 3% (Stock No. 42511) and

- Titanium rod, 3.175 mm diameter, 99.99% (metals basis) (Stock No. 14000).

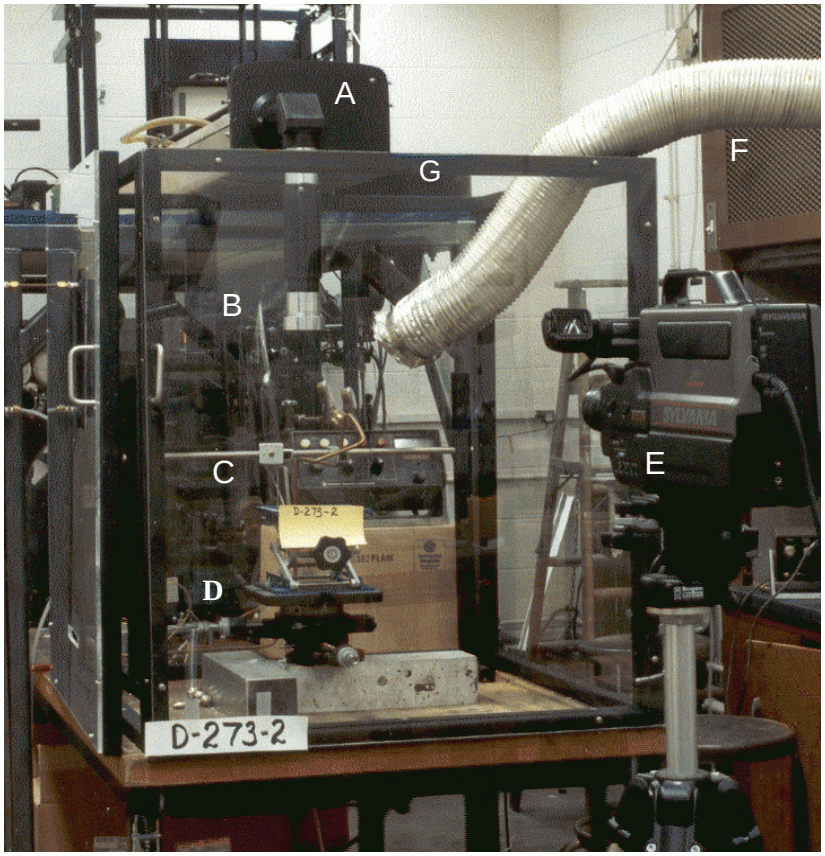


Figure 1. Photograph of the CO_2 Laser Heating Apparatus. (D-273-2). A. CO_2 Laser. B. Zinc Selenide Lens. C. Graphite Block. D. 3-D Positioner. E. Video Camera. F. Exhaust Duct. G. Safety Enclosure.

Figure 2. Photograph of the Macken digital laser beam probe. The larger H2 head for the range 100 W and 1000 W is at the left, while the smaller H1 head for the range 10 to 100 W is at the right.

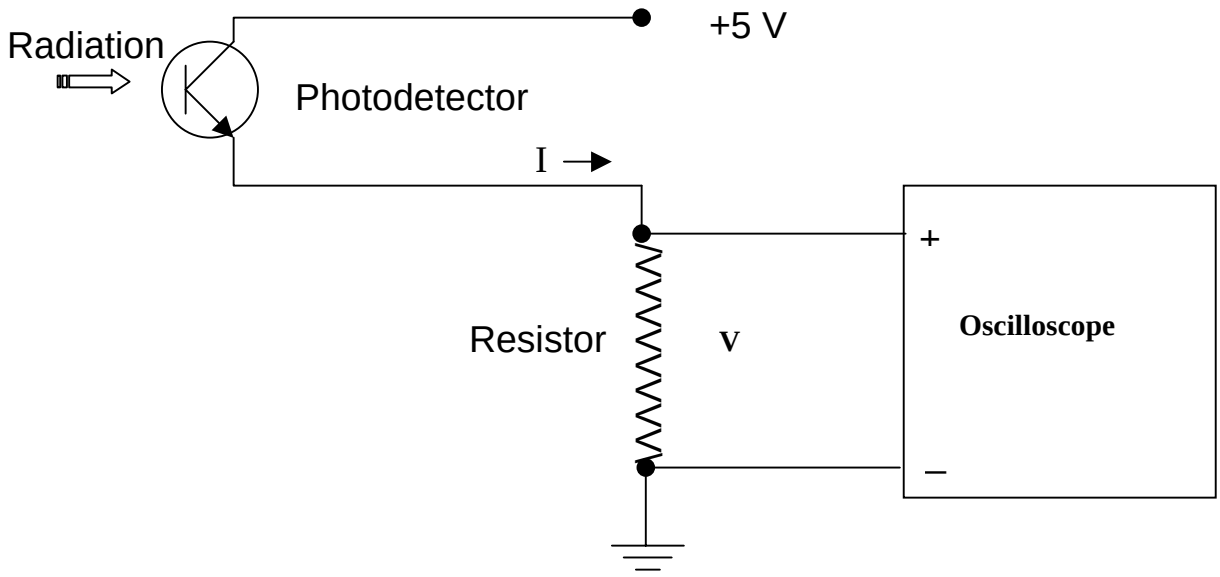


Figure 3. Circuit used to record the output voltage of the silicon diode photodetector as a function of time. The value of the resistor determines the sensitivity of the reading (volts per unit of light, V = I x R, where R is proportional to light intensity).

Samples of the alloy, Zr_3Al, were obtained from Dr. Doug Rodgers, Manager of the Materials and Mechanics Branch, Chalk River Nuclear Laboratories, Atomic Energy Commission of Canada. This material was originally prepared for E. Schulson (Causey et al., 1977).

The flowing gases, both oxygen and nitrogen, were commercial grade obtained in high pressure cylinders and used without further purification.

Luminosities

Our primary diagnostics for this program involved recording the luminous behavior during heating and subsequent reactions of the samples. We used:

Video Imaging

Video imaging provides a general overview of the experiment and is used to time and correlate various occurrences such as the durations of laser heating and sparking . An entire experiment, several minutes long, was imaged by a continuously operating video camcorder (Sylvania Model HQ-VHS) that records on standard VHS tape. Afterward, the tape could be viewed continuously or frame-by-fame with a time resolution of 30 frames/second (0.033 s per frame).

Photodetector Measurements

Luminous intensity vs. time was recorded with a silicon diode photodetector (Model P33001 obtained from Clarostat Controls, Richardson, TX) attenuated as needed with neutral density filters. The output voltage of the photodetector is recorded as a function of time with a Hewlett Packard Infinium 500 MHz / 1 GSa/s oscilloscope, Model 54815A, using the circuit shown in Figure 3. The digital data (32,768 voltage-time points) for each experiment are downloaded onto a floppy disk for further manipulation on a personal computer via Excel plots.

Photography

Several 35 mm photographs were exposed at important times during the experiments. We used a Minolta X-370N camera with a 50 mm, 1:1.7 lens, ISO 200 film, automatic exposure, and lens apertures of f/8 to f/22. In many experiments, a synchronized flashgun, directed toward the video camera, was fired when the camera operated. The sharp pulse of light marks the time of the photographic exposure on both the video record and on the luminosity-time trace. Moreover, the very intense pulse of light from the photoflash usually indicates the voltage at which the photodetector saturates.

Sometimes, we used the camera (f/8, automatic exposure) to photograph the monitor during projection of single video frames.

(Note: A Hycam high speed 16 mm camera with 500 f/s to 10,000 f/s capability and several rolls of color film were available but not used during this program.)

Examination of the Samples

Before the experiments, the samples of metal were weighed with a balance that has a sensitivity of 0.00001 g.

Photographs of the samples before and after the experiments were taken with a 35 mm camera equipped with +7 close-up lens (Minolta X-370N camera with a 50 mm, 1:1.7 lens, ISO 200 film, automatic exposure, ambient room lighting and a lens aperture of f/22).

The solidified samples recovered after each experiment were also archived for future analyses, for example, by scanning electron microscopy, electron microprobe or X-ray diffraction.

RESULTS

During this program, we performed 62 experiments in which samples in either flowing oxygen or nitrogen were heated with focused radiation from the CO_2 laser. In Table 1, these experiments are summarized in the order in which they were performed.

Standard Optical Conditions (SOC)

We began luminosity-time measurements with the photodetector in mid-August, 2001 (experiment D-265-1). As we performed these experiments, we frequently adjusted the position and aiming of the photodetector and inserted and removed neutral density filters in the optical path. Because of the strong light emitted by the heated samples, many adjustments were required to obtain output voltages that did not saturate the oscilloscope. Thus traces from the various experiments usually had different light intensity-voltage relationships and could not be compared directly with each other.

Finally, in early October, 2001, beginning with experiment D-290-2, we achieved a combination of (a) positioning of the photodetector 145 mm behind and approximately in the same horizontal plane as the laser focus, (b) three 4X neutral density filters ("4X" designates four photographic stops or a 16-fold reduction of intensity by each filter, with a total reduction by the three filters of 48-fold) and (c) aiming that remained unchanged for the last 2½ weeks of experiments. This produced traces from the final 23 experiments that could be compared quantitatively with each other. We call this combination of filtering and aiming "Standard Optical Conditions" (SOC). Our discussions of luminosity-time traces below, therefore, will concentrate mostly on these final 23 experiments.

Titanium Heated in Oxygen

During the program, we performed 21 experiments in which nominally 115 mg samples of titanium in flowing oxygen were heated with the CO_2 laser. The experimental conditions are summarized in Table 2. Only the last three of these experiments were performed with the standard optical conditions (SOC). In these three experiments, heating times were about 20 s and the laser power was between 60 W and 70 W. These three luminosity-time traces are plotted in Figure 4. In this figure, we have adjusted the maximum vertical scale value of each plot to 3 volts.

The samples recovered after the last three experiments were slightly flattened glossy black beads, each with a small pit.

Zirconium Heated in Oxygen

We also heated 13 nominally 160 mg samples of zirconium in flowing oxygen with the CO_2 laser. Again, only the last three experiments were performed with the standard optical conditions (SOC). Heating times for these last three experiments again were about 20 s and the laser power was in the same range used for the titanium samples, namely, 60 W to 70 W. The experimental conditions for the 13 experiments are summarized in Table 3, while the luminosity-time traces for the last three experiments performed with SOC are shown in Figure 5. In this figure, as in Figure 4, we have adjusted the maximum vertical scale value of each plot to 3 volts.

The samples recovered after the last three experiments had a yellowish or white cap of solidified material on top of a cylinder of partially melted metal. Each cap had a pit formed by the focused laser beam.

Table 1. Heating of Materials with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-252-1	Ti	0.1510	O_2	NM	~24	No sparks	Metal crawled out of laser focus. Completely melted. Metallic worm with white oxide coating.
D-253-1	Ti	0.1265	O_2	NM	~103	16-27	A few sparks. First experiment with hole in graphite. Completely melted. Glossy black coat, dimple.
D-255-1	Ti	0.1142	O_2	162	~70	38-59	Many sparks. Completely melted. Glossy black coat, dimple. Smaller than D-253-1.
D-255-2	Ti	0.1215	O_2	179	~63	37-51	Many sparks Completely melted. Glossy black coat, dimple. Smaller than D-253-1.
D-257-1	Zr	0.1609	O_2	182	~98	14-98	Sessile drop shape coated with glossy white oxide. Bottom is black. Perhaps unmelted metal inside.
D-257-2	Zr	0.1613	O_2	184	~28	26-28	Laser turned off when first sparks appeared. Unmelted metallic cylinder with dab of grey oxide on top.
D-257-3	Zr	0.1603	O_2	185	NM	NM	Laser on about half as long. No video. Unmelted metallic cylinder with dab of glossy white oxide on top. Less unmelted metal and more oxide than in D-257-2.
D-261-1	Ti	0.1140	O_2	172	~40	37-41	Strong sparks. White worn-like specimen. Metallic blob shows through white oxide.
D-261-2	Ti	0.1121	O_2	173	~36 s	25-35	Strong sparks. Almost spherical white specimen with open bottom.
D-261-3	Ti	0.1124	O_2	168	NM	NM	Uneven globby oxide, yellow top, dark metal glob shows through white oxide. Specimen slid to side. No video.
D-261-4	Ti	0.1167	O_2	171	~38	27-38	Strong sparks. Almost spherical white specimen with open bottom.Glob of metal shows through oxide.
D-265-1	Ti	0.1141	O_2	173	~37	8-15	1st photodetector experiment; scope didn't trigger. Black shiny bead. Strong sparks; 2 photos.
D-265-2	Ti	0.1098	O_2	176	~18	8-14	Photodetector experiment; scope triggered, pegged. Black shiny bead; conical bottom, pit off-center. Strong sparks.

Table 1 (Continued). Heating of Materials with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-269-1	Ti	0.1142	N_2	177	~13	No sparks	Sample crawled out. Irregular white worm.
							No scope trace.
D-269-2	Ti	0.1135	N_2	163	~114	37-46	Creamy white sessile drop not in hole.
							No scope trace.
D-269-3	Ti	0.1111	N_2	177	~46	No sparks	No sparks, no photos. Sample crawled out. Irregular
							rectangular white glob. No scope trace.
D-272-1	Zr	0.1596	N_2	175	~160 s	24-96	Sparks 24-96 s, then decrease and restart 105-142 s; 4 photos.
						105-142	Completely melted white glob with probosci. No scope trace.
D-272-2	Zr	0.1579	N_2	170	~166	26-97	Sparks 26-97 s, pause, then restart 105-146 s. Completely melted
						105-146	white half-cylindrical glob. No scope trace.
D-272-3	Zr	0.1626	N_2	167	~39	28-39	Very stong sparking; one very long track. Grey metallic
							rod with grey glob of frozen melt on top. No scope trace.
D-273-1	Ti	0.1118	O_2	100	37	10-34	1st viewing of control box turnoff. Many sparks, 1 photo.
							Black shiny dome with white shawl-like patches.No scope trace.
D-273-2	Ti	0.1148	O_2	103	26	10-16	Very long spark tracks on 1st photo at f/22. Black shiny dome
							with white patch on top; pits on sideand bottom. No scope trace.
D-275-1	Ti	0.1116	O_2	101	13	11-13	Demo. Laser turned off during sparking; poor photo. Flat black
							button with fried egg bottom. No scope trace.
D-275-2	Zr	0.1569	O_2	104	14	8-15	Demo. Laser turned off during sparking; photo OK. Grey metallic
							globule, white oxide coat, deep pit on top. No photodetector trace.
D-278-1	Ti	0.1148	O_2	104	15	9-15	Photo at 10s. Laser off ASAP. Photodetector trace was pegged.
							Glossy black button, indented top, fried egg bottom.
D-278-2	Ti	0.1116	O_2	103	15	9-15	Two 4X ND filters. Late trigger but PD not pegged. Flash at 10s
							not recorded. Glossy black button, indented top, fried egg bottom.
D-278-3	Ti	0.1142	O_2	104	17	10-17	Same filters. Good trace w. flash at 11 s; not pegged. Hit by laser
							accidentally. Glossy black button, indented top, fried egg bottom.
D-278-4	Ti	0.1175	O_2	66	27	13-19	Lowered laser power. Same filters. Good trace with flash at 18 s.
							Photodetector not pegged. Glossy black bowl, dull black bottom.

Table 1 (Continued). Heating of Materials with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-282-1	Ti	0.1177	O_2	66	28	10-28	Same filters. Good trace w. flash at 12 s; not pegged.Many sparks
							on photo. Glossy black button, indented top, fried egg bottom.
D-282-2	Zr	0.1614	O_2	62	54	7-34	Same filters. Good trace w. late flash at 24 s; not pegged. Grey-
							white dome, yellowish on top, metallic globule inside.
D-282-3	Zr	0.1570	O_2	69	22	7-22	Same filters. Good trace w. early flash at 5 s; not pegged. Sample
							almost identical to D-282-2. Very tiny sparks up to laser turnoff.
D-285-1	Ti	0.1153	N_2	68	91	43-45; 64	Two 49 mm 4X filters; moved photodetector. Unmelted
						81-96	rod w. dab of black on top. Scope trigg'd on one flash.
D-285-2	Ti	0.1153	N_2	97	47	25-28	Same ND filters. Reaimed PD. Billowy white solid. No
							photos.
D-285-3	Ti	0.1177	N_2	95	65	27-33	Same filters. Photos at 30 s (good), 43s (NG). Larger
							dab of black on unmelted rod than D-285-1. Strange trace
D-285-4	Zr	0.1598	N_2	100	52	21-52	Same ND filters. Scope overdriven immediately.Long sparks.
							Photo at 24 s (good); 2nd (?). Sample unmelted w. white coating.
D-288-1	Zr	0.1586	O_2	66.2	21	5-21	Two 4X filters.Scope overdriven. Good photo of sparks with flash at
							6 s. Unmelted rod and yellowish cap with depression on top.
D-288-2	Zr	0.1602	O_2	66.5	28	9-28	Two 4X filters.Scope overdriven. No photo of sparks. Unmelted rod
							and billowy white cap with deep pit.
D-288-3	Zr	0.1580	O_2	66.7	31	9-31	Tilted PD, two 4X filters. Good trace but low. Fair photo of sparks
							with flash at 10 s. Sample similar to D-288-2.
D-288-4	Zr_3Al	0.1745	O_2	68.3	27	No sparks	Scope didn't trigger @ 100mV. Square intact, tiny pit
							within small ring of melt. Three 4X ND ilters.
D-290-1	Zr	0.1594	O_2	66.1	22	7-9	Three 4X ND ilters.Scope didn't trigger @ 100mV. Photo with flash
							at 8 s. Unmelted rod and yellowish cap with depression on top.
D-290-2	Zr	0.1576	O_2	68.3	27	8-23	First at SOC. Manual trigger'g; good trace. Photo with flash at 9 s.
SOC							Unmelted rod and yellowish cap with depression on top.
D-290-3	Zr_3Al	0.1890	O_2	66.3	29	No sparks	Same ilters. Manual triggering. Square intact, very tiny pit within
SOC							small ring of melt. Some frozen melt on bottom.Photo, flash at 9s.

Table 1 (Continued). Heating of Materials with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-292-3	Ti	0.1167	O_2	65.4	24	11-18	Manual triggering. Good ignition.and trace.
SOC							One photo with flash at 12 s, one without .Black, glossy bead.
D-293-1	Zr_3Al	0.1863	O_2	80.5	16	No sparks	Manual triggering. Square intact, pit within ring
SOC							of melt. Some frozen melt on bottom. Photo with flash at 12 s.
D-293-2	Zr_3Al	0.1743	O_2	136	18	No sparks	Manual triggering. Square intact with groove cut by beam. Metal
SOC							vaporized a lot at 8 s. Photo with flash at 13 s.
D--294-1	Al_2O_3	NM	O_2	110	10	No sparks	Manual triggering. Short halt during solidification, not during
SOC							melting. Sphere diameter = 3.11 mm.
D-294-2	Al_2O_3	NM	O_2	154	11	No sparks	Manual triggering. Subcooling and longer halt at higher
SOC							luminosity during solidification. Sphere diameter = 3.11 mm.
D-294-3	Al_2O_3	NM	O_2	143	13	No sparks	Manual triggering. Subcooling and longer halt at higher
SOC							luminosity during solidification. Sphere diameter = 3.11 mm.
D-295-1	Al_2O_3	NM	O_2	113	10	No sparks	Normal triggering. No subcooling, very short halt during
SOC							solidification. Spherediameter = 3.11 mm.
D-295-2	Al_2O_3	NM	O_2	180	12	No sparks	Normal triggering. Subcooling and longer halt at higher
SOC							luminosity during solidification. Sphere diameter = 3.11 mm.
D-295-3	Al_2O_3	NM	O_2	176	17	No sparks	Normal triggering. Subcooling and longer halt at higher
SOC							luminosity during solidification. Sphere diameter = 3.11 mm.
D-295-4	Al_2O_3	NM	O_2	177	18	No sparks	Normal triggering. No subcooling, very short halt during
SOC							solidification. Sphere diameter = 4.76mm.
D-295-5	Al_2O_3	NM	O_2	176	13	No sparks	Normal triggering. No subcooling, very short halt during
SOC							solidification. Sphere diameter = 4.76mm.
D-296-1	Ti	0.1152	N_2	69.4	16	13-14	Scope didn't trigger. Tiny spot of frozen melt on top of
SOC							unmelted rod. Flash not seen on VCR. Tiny sparks.
D-296-2	Ti	0.1166	N_2	104.9	20	No sparks	Normal triggering, good trace. Complete melting, billowy
SOC							yellowish-white solidified globule. Photo with flash at 10 s.

Table 1 (Continued). Heating of Materials with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-296-3	Zr	0.1579	N_2	102.6	22	20-21	Normal triggering; good trace. Photo w. flash at 16 s. Tiny sparks.
SOC							Dab of frozen melt on top of unmelted metal.
D-296-4	Zr	0.1621	N_2	146	23	No sparks	Normal triggering; good trace. Photo w. flash at 15 s. No sparks.
SOC							Dab of frozen melt on top of unmelted metal.
D-296-5	Zr_3Al	0.2156	N_2	144	26	No sparks	Normal triggering. Photo w.flash at 18 s. Good trace. Melt ran out
SOC							of partially melted solid. Black bottom.
D-296-6	Zr_3Al	0.2360	N_2	172	21	No sparks	Normal triggering. Photo w. flash at 11 s. Very brilliant luminous
SOC							surge at ~18 s. Complete melting; melt flowed from small volcano.
D-298-1	Ti	0.1171	O_2	63.8	18	10-17	Normal triggering. Photo at f/22 w. flash at 15 s. Good trace.
SOC							Shiny black bead with pit.
D-298-2	Ti	0.1161	O_2	71.5	22	14-20	Normal triggering. Beautiful photo at f/22 w. flash at 16 s. Good
SOC							trace. Shiny black bead with pit.
D-298-3	Zr	0.1581	O_2	66.3	27	14-24	Normal triggering. Photo at f/22 w. flash at 11 s. Trace pegged.
SOC							Unmelted rod and light grey cap with depression on top.
D-298-4	Zr	0.1597	O_2	71.6	20	6-19	Normal triggering. Photo at f/22 w. flash at 8 s. Trace pegged.
SOC							Unmelted rod and yellowish cap with depression on top.

Table 2. Heating of Titanium with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-252-1	Ti	0.1510	O_2	NM	~24	No sparks	Metal crawled out of laser focus. Completely melted. Metallic worm with white oxide coating.
D-253-1	Ti	0.1265	O_2	NM	~103	16-27	A few sparks. First experiment with hole in graphite. Completely melted. Glossy black coat, dimple.
D-255-1	Ti	0.1142	O_2	162	~70	38-59	Many sparks. Completely melted. Glossy black coat, dimple. Smaller than D-253-1.
D-255-2	Ti	0.1215	O_2	179	~63	37-51	Many sparks Completely melted. Glossy black coat, dimple. Smaller than D-253-1.
D-261-1	Ti	0.1140	O_2	172	~40	37-41	Strong sparks. White worn-like specimen. Metallic blob shows through white oxide.
D-261-2	Ti	0.1121	O_2	173	~36 s	25-35	Strong sparks. Almost spherical white specimen with open bottom.
D-261-3	Ti	0.1124	O_2	168	NM	NM	Uneven globby oxide, yellow top, dark metal glob shows through white oxide. Specimen slid to side. No video.
D-261-4	Ti	0.1167	O_2	171	~38	27-38	Strong sparks. Almost spherical white specimen with open bottom.Glob of metal shows through oxide.
D-265-1	Ti	0.1141	O_2	173	~37	8-15	1st photodetector experiment; scope didn't trigger. Black shiny bead. Strong sparks; 2 photos.
D-265-2	Ti	0.1098	O_2	176	~18	8-14	Photodetector experiment; scope triggered, pegged. Black shiny bead; conical bottom, pit off-center. Strong sparks.
D-273-1	Ti	0.1118	O_2	100	37	10-34	1st viewing of control box turnoff. Many sparks, 1 photo. Black shiny dome with white shawl-like patches.No scope trace.
D-273-2	Ti	0.1148	O_2	103	26	10-16	Very long spark tracks on 1st photo at f/22. Black shiny dome with white patch on top; pits on sideand bottom. No scope trace.
D-275-1	Ti	0.1116	O_2	101	13	11-13	Demo. Laser turned off during sparking; poor photo. Flat black button with fried egg bottom. No scope trace.
D-278-1	Ti	0.1148	O_2	104	15	9-15	Photo at 10s. Laser off ASAP. Photodetector trace was pegged. Glossy black button, indented top, fried egg bottom.

Table 2 (Continued). Heating of Titanium with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-278-2	Ti	0.1116	O_2	103	15	9-15	Two 4X ND filters. Late trigger but PD not pegged. Flash at 10s
							not recorded. Glossy black button, indented top, fried egg bottom.
D-278-3	Ti	0.1142	O_2	104	17	10-17	Same filters. Good trace w. flash at 11 s; not pegged. Hit by laser
							accidentally. Glossy black button, indented top, fried egg bottom.
D-278-4	Ti	0.1175	O_2	66	27	13-19	Lowered laser power. Same filters. Good trace with flash at 18 s.
							Photodetector not pegged. Glossy black bowl, dull black bottom.
D-282-1	Ti	0.1177	O_2	66	28	10-28	Same filters. Good trace w. flash at 12 s; not pegged.Many sparks
							on photo. Glossy black button, indented top, fried egg bottom.
D-292-3	Ti	0.1167	O_2	65.4	24	11-18	Manual triggering. Good ignition.and trace.
SOC							One photo with flash at 12 s, one without .Black, glossy bead.
D-298-1	Ti	0.1171	O_2	63.8	18	10-17	Normal triggering. Photo at f/22 w. flash at 15 s. Good trace.
SOC							Shiny black bead with pit.
D-298-2	Ti	0.1161	O_2	71.5	22	14-20	Normal triggering. Beautiful photo at f/22 w. flash at 16 s. Good
SOC							trace. Shiny black bead with pit.

Table 3. Heating of Zirconium with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-257-1	Zr	0.1609	O_2	182	~98	14-98	Sessile drop shape coated with glossy white oxide.
							Bottom is black. Perhaps unmelted metal inside.
D-257-2	Zr	0.1613	O_2	184	~28	26-28	Laser turned off when first sparks appeared.
							Unmelted metallic cylinder with dab of grey oxide on top.
D-257-3	Zr	0.1603	O_2	185	NM	NM	Laser on about half as long. No video. Unmelted
							metallic cylinder with dab of glossy white oxide on top.
							Less unmelted metal and more oxide than in D-257-2.
D-275-2	Zr	0.1569	O_2	104	14	8-15	Demo. Laser turned off during sparking; photo OK. Grey metallic
							globule, white oxide coat, deep pit on top. No photodetector trace.
D-282-2	Zr	0.1614	O_2	62	54	7-34	Same filters. Good trace w. late flash at 24 s; not pegged. Grey-
							white dome, yellowish on top, metallic globule inside.
D-282-3	Zr	0.1570	O_2	69	22	7-22	Same filters. Good trace w. early flash at 5 s; not pegged. Sample
							almost identical to D-282-2. Very tiny sparks up to laser turnoff.
D-288-1	Zr	0.1586	O_2	66.2	21	5-21	Two 4X filters.Scope overdriven. Good photo of sparks with flash at
							6 s. Unmelted rod and yellowish cap with depression on top.
D-288-2	Zr	0.1602	O_2	66.5	28	9-28	Two 4X filters.Scope overdriven. No photo of sparks. Unmelted rod
							and billowy white cap with deep pit.
D-288-3	Zr	0.1580	O_2	66.7	31	9-31	Tilted PD, two 4X filters. Good trace but low. Fair photo of sparks
							with flash at 10 s. Sample similar to D-288-2.
D-290-1	Zr	0.1594	O_2	66.1	22	7-9	Three 4X ND ilters.Scope didn't trigger @ 100mV. Photo with flash
							at 8 s. Unmelted rod and yellowish cap with depression on top.
D-290-2	Zr	0.1576	O_2	68.3	27	8-23	First at SOC. Manual trigger'g; good trace. Photo with flash at 9 s.
SOC							Unmelted rod and yellowish cap with depression on top.
D-298-3	Zr	0.1581	O_2	66.3	27	14-24	Normal triggering. Photo at f/22 w. flash at 11 s. Trace pegged.
SOC							Unmelted rod and light grey cap with depression on top.
D-298-4	Zr	0.1597	O_2	71.6	20	6-19	Normal triggering. Photo at f/22 w. flash at 8 s. Trace pegged.
SOC							Unmelted rod and yellowish cap with depression on top.

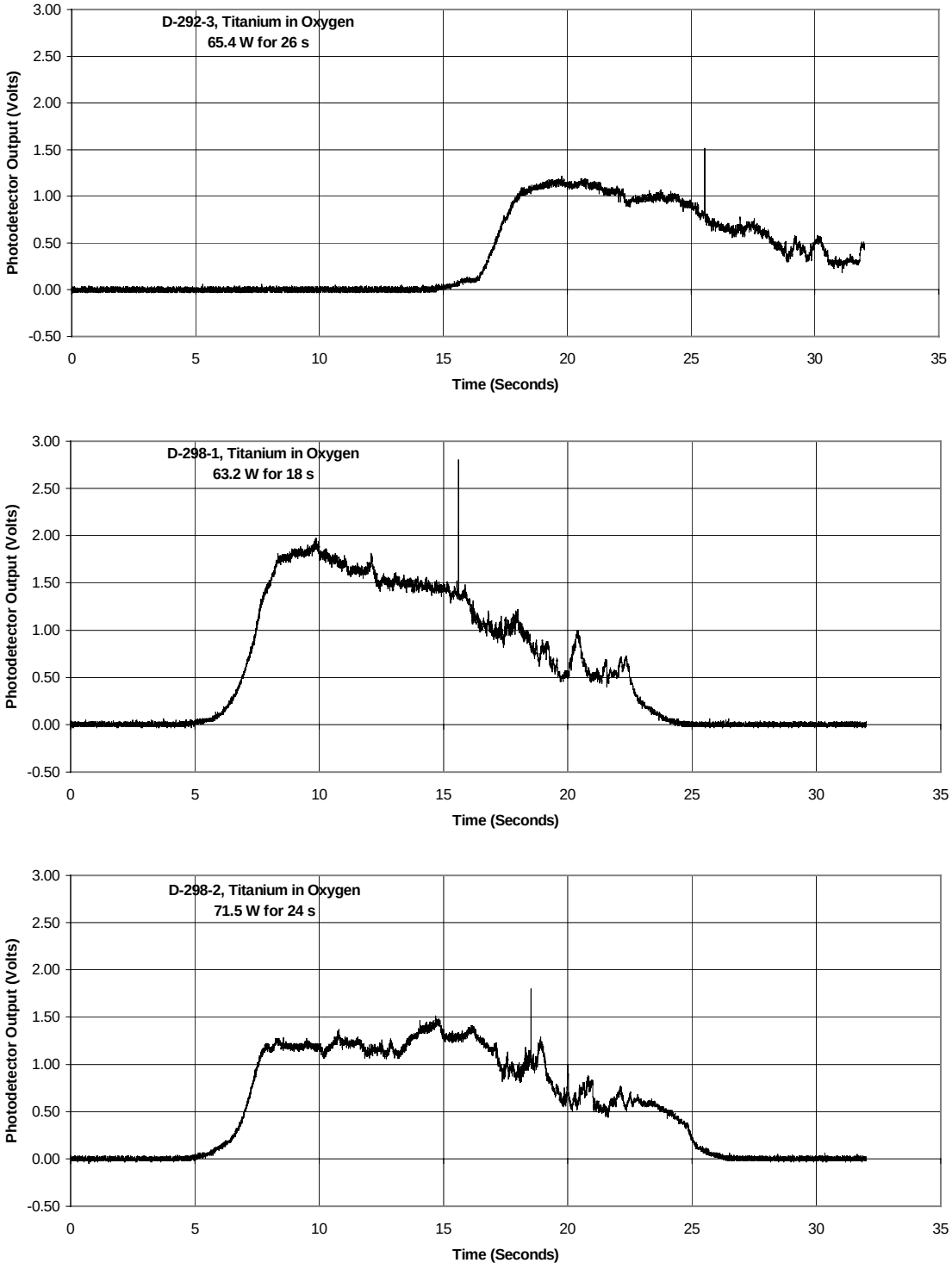


Figure 4. Luminosity-time traces recorded during three experiments in which nominally 115 mg samples of titanium in flowing oxygen were heated with the CO_2 laser. Each experiment was performed with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 3 volts.

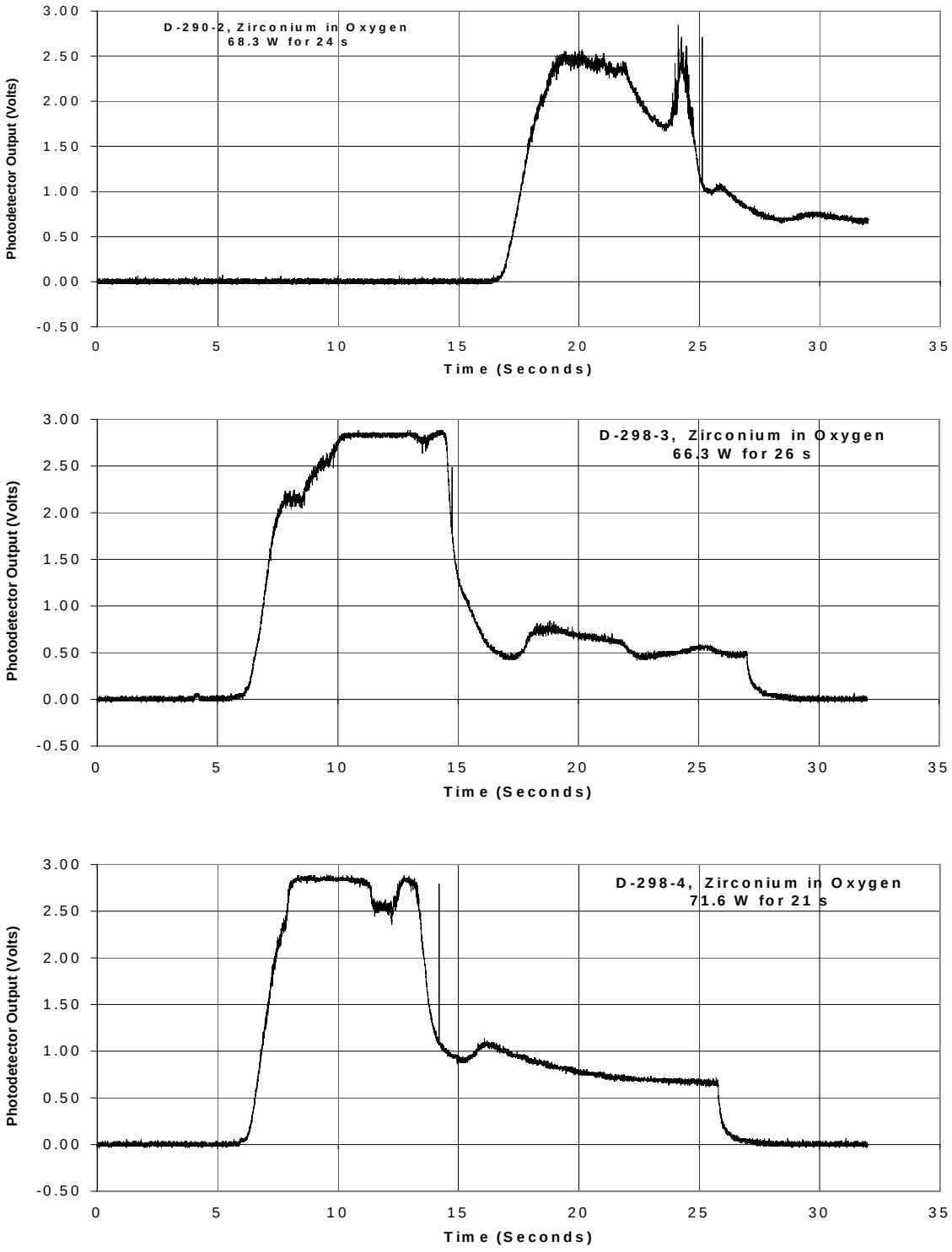


Figure 5. Luminosity-time traces recorded during three experiments in which nominally 160 mg samples of zirconium in flowing oxygen were heated with the CO_2 laser. Each experiment was performed with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 3 volts.

Zirconium-Aluminum Alloy Heated in Oxygen

We also performed four experiments in which nominally 180 mg samples of the zirconium-aluminum alloy, Zr_3Al, in flowing oxygen were heated with the CO_2 laser. The last three experiments were performed with the standard optical conditions (SOC). Heating times again were about 20 s and the laser power was increased from 66 W to 81 W to 136 W in the attempt to achieve ignition. The experimental conditions for the four experiments are summarized in Table 4 and the luminosity-time traces for the three experiments performed with SOC are shown in Figure 6. In this figure, as in Figures 4 and 5, we have adjusted the maximum vertical scale value of each plot to 3 volts.

The samples recovered after each experiment were white unmelted cubes with progressively deeper pits on top as the laser power increased. Also, the bottom of each cube had a small amount of frozen material.

Titanium Heated in Nitrogen

We also performed eight experiments in which nominally 115 mg samples of titanium in flowing nitrogen were heated with the CO_2 laser. Heating times were as short as about 13 s to as long as about 114 s: beam powers ranged from 68 W to our current maximum, ~177 W.

Only the last two experiments were performed with the standard optical conditions (SOC) but the oscilloscope did not trigger in the first experiment. Because very little interaction or melting (or luminosity) occurred in the first experiment, where the laser power was 69.4 W, the power was increased to 104.9 W for the next experiment. In this second (the last) experiment, there was melting, good ignition and strong luminosity that triggered the oscilloscope. The experimental conditions for the eight experiments are summarized in Table 5 and the single luminosity-time trace generated with SOC during the second experiment is shown in Figure 7. In this figure, as in Figures 4, 5 and 6, we have adjusted the maximum vertical scale value of each plot to 3 volts.

The first experiment produced a sample that was an unmelted cylinder of metal with a small bead of frozen material in a shallow depression on top. The second experiment produced an irregular piece of solidified billowy white material.

Zirconium Heated in Nitrogen

Six experiments were performed in which samples of zirconium in flowing nitrogen were heated with the CO_2 laser. Only the last two were performed with the standard optical conditions (SOC). Heating times were as short as 22 s and as long as ~160 s, and laser beam powers ranged from 100 to 175 W.

The first experiment with SOC was performed with a laser power of 102.6 W and produced little reaction. Therefore, we increased the power to 145 W for the last experiment. There was not much more reaction at the higher laser power, however. The experimental conditions for the six experiments are summarized in Table 6 and the luminosity-time traces for the last two experiments are shown in Figure 8. In this figure, as in Figures 4 through 7, we have adjusted the maximum vertical scale value of each plot to 3 volts.

The samples recovered from the last four experiments (D-272-3 through D-296-4, including the two performed with SOC) were unmelted cylinders of metal with beads of frozen material on top–smaller beads at the lower laser powers and somewhat larger beads at the higher laser powers. Only the first two experiments, D-272-1 and D-272-2, performed at our maximum power (170 W to 175 W) and longest heating times (160 s to 166 s) showed complete melting and reaction.

Table 4. Heating of the Alloy Zr_3Al with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-288-4	Zr_3Al	0.1745	O_2	68.3	27	No sparks	Scope didn't trigger @ 100mV. Square intact, tiny pit within small ring of melt. Three 4X ND ilters.
D-290-3	Zr_3Al	0.1890	O_2	66.3	29	No sparks	Same ilters. Manual triggering. Square intact, very tiny pit within small ring of melt. Some frozen melt on bottom.Photo, flash at 9s.
SOC							
D-293-1	Zr_3Al	0.1863	O_2	80.5	16	No sparks	Manual triggering. Square intact, pit within ring of melt. Some frozen melt on bottom. Photo with flash at 12 s.
SOC							
D-293-2	Zr_3Al	0.1743	O_2	136	18	No sparks	Manual triggering. Square intact with groove cut by beam. Metal vaporized a lot at 8 s. Photo with flash at 13 s.
SOC							

Table 5. Heating of Titanium with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-269-1	Ti	0.1142	N_2	177	~13	No sparks	Sample crawled out. Irregular white worm.
							No scope trace.
D-269-2	Ti	0.1135	N_2	163	~114	37-46	Creamy white sessile drop not in hole.
							No scope trace.
D-269-3	Ti	0.1111	N_2	177	~46	No sparks	No sparks, no photos. Sample crawled out. Irregular
							rectangular white glob. No scope trace.
D-285-1	Ti	0.1153	N_2	68	91	43-45; 64	Two 49 mm 4X filters; moved photodetector. Unmelted
						81-96	rod w. dab of black on top. Scope trigg'd on one flash.
D-285-2	Ti	0.1153	N_2	97	47	25-28	Same ND filters. Reaimed PD. Billowy white solid. No
							photos.
D-285-3	Ti	0.1177	N_2	95	65	27-33	Same filters. Photos at 30 s (good), 43s (NG). Larger
							dab of black on unmelted rod than D-285-1. Strange trace
D-296-1	Ti	0.1152	N_2	69.4	16	13-14	Scope didn't trigger. Tiny spot of frozen melt on top of
SOC							unmelted rod. Flash not seen on VCR. Tiny sparks.
D-296-2	Ti	0.1166	N_2	104.9	20	No sparks	Normal triggering, good trace. Complete melting, billowy
SOC							yellowish-white solidified globule. Photo with flash at 10 s.

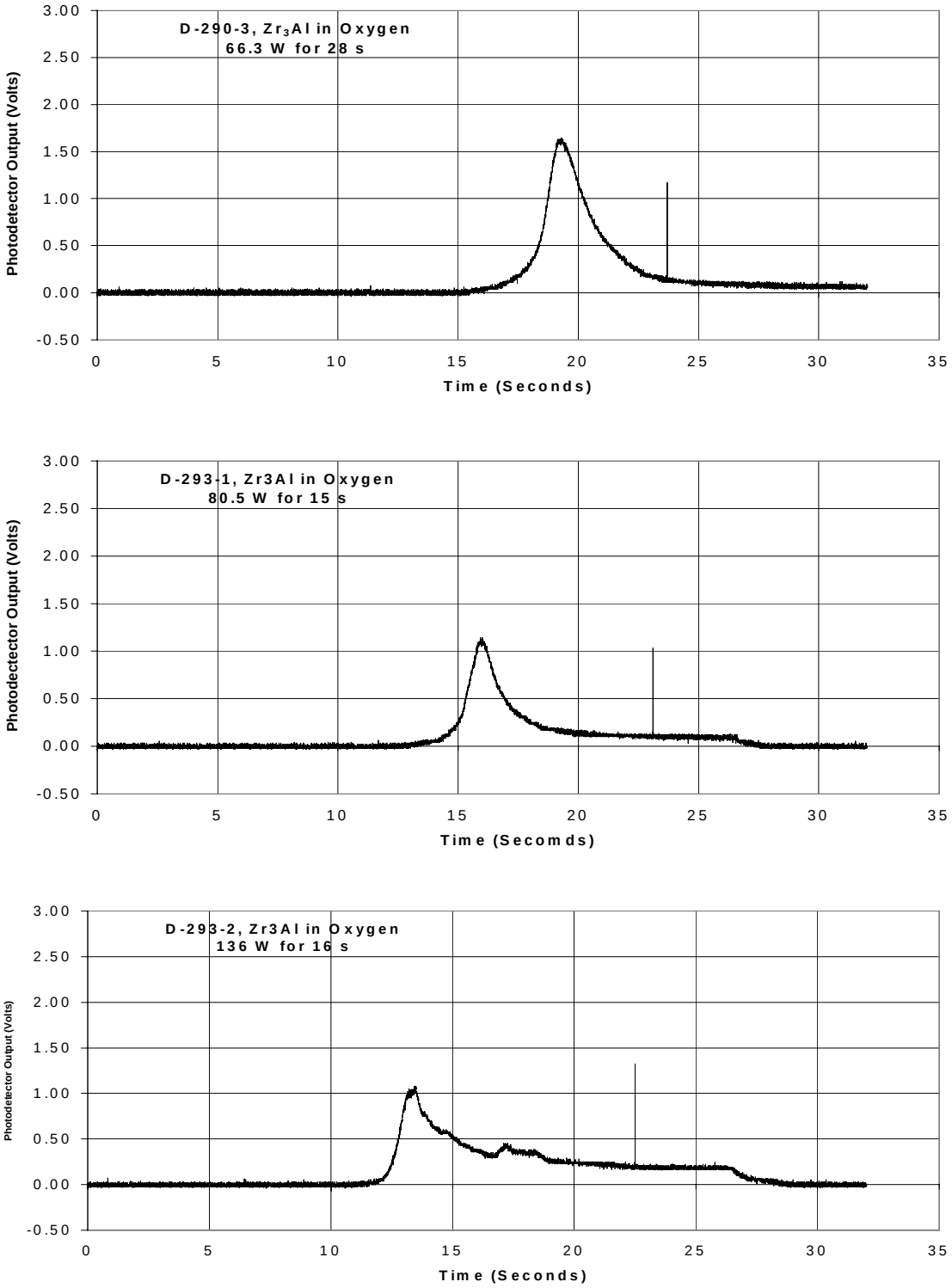


Figure 6. Luminosity-time traces recorded during three experiments in which nominally 180 mg samples of the zirconium-aluminum alloy, Zr_3Al, in flowing oxygen were heated with the CO_2 laser. Each experiment was performed with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 3 volts.

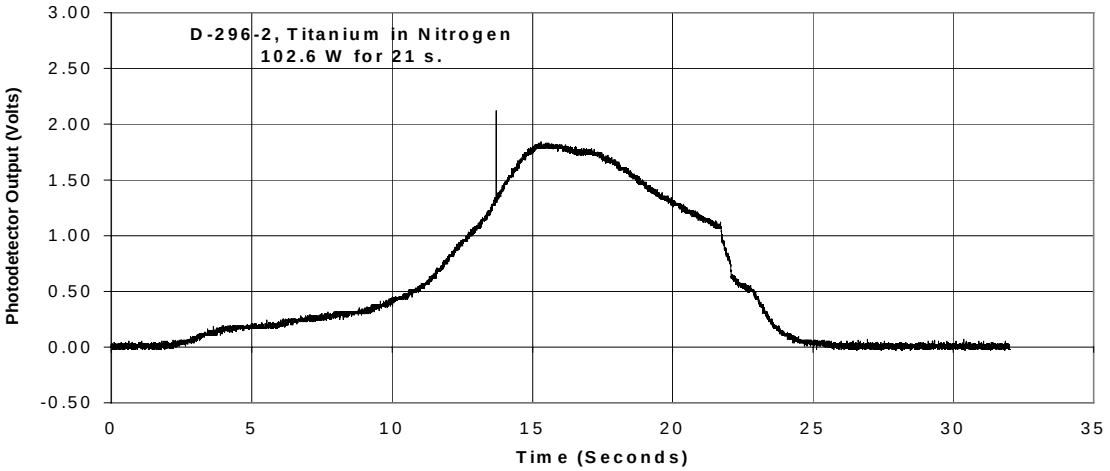


Figure 7. Luminosity-time trace recorded during an experiment in which a nominally 115 mg sample of titanium in flowing nitrogen was heated with the CO_2 laser. The experiment was performed with standard optical conditions (SOC). The maximum ordinate of the plot has been adjusted to 3 volts.

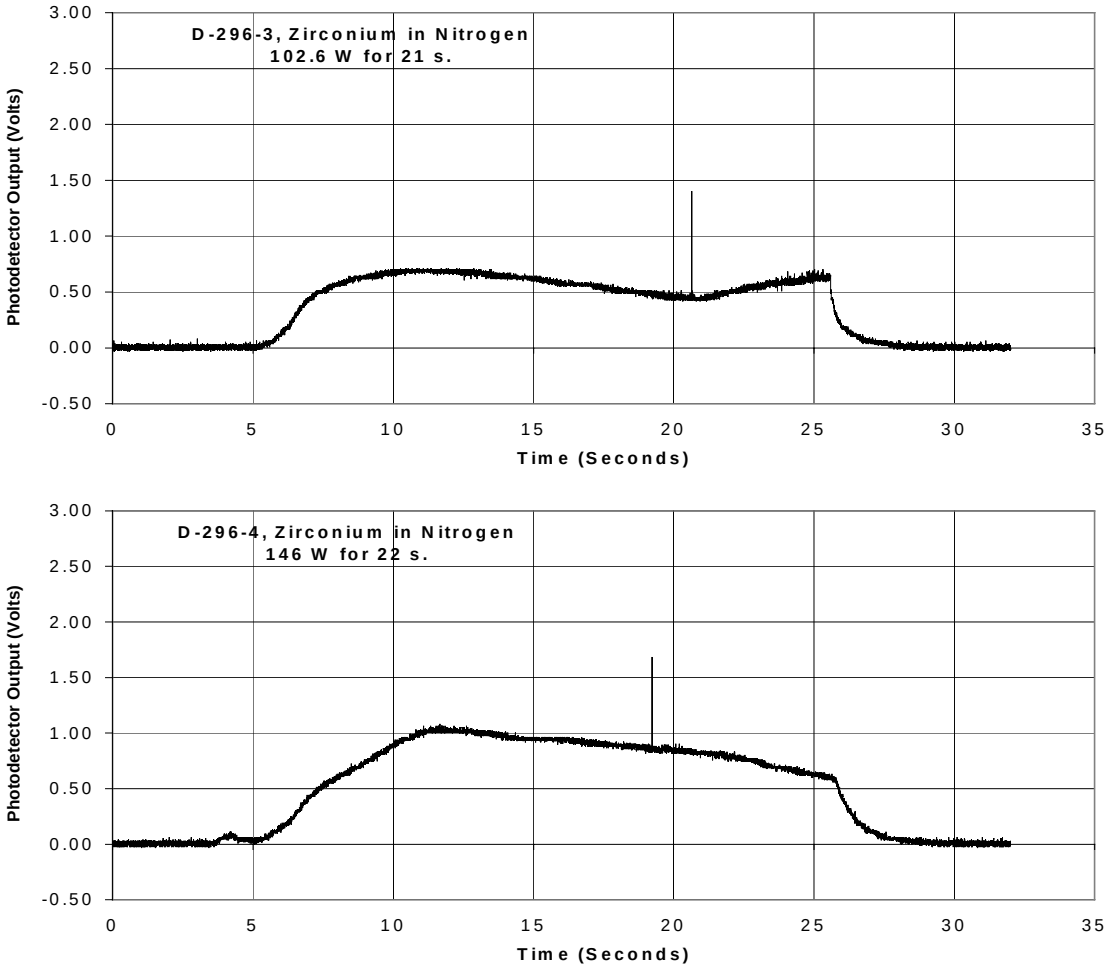


Figure 8. Luminosity-time traces recorded during two experiments in which nominally 160 mg samples of zirconium in flowing nitrogen were heated with the CO_2 laser. Each experiment was performed with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 3 volts.

Table 6. Heating of Zirconium with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-272-1	Zr	0.1596	N_2	175	~160 s	24-96	Sparks 24-96 s, then decrease and restart 105-142 s; 4 photos.
						105-142	Completely melted white glob with probosci. No scope trace.
D-272-2	Zr	0.1579	N_2	170	~166	26-97	Sparks 26-97 s, pause, then restart 105-146 s. Completely melted
						105-146	white half-cylindrical glob. No scope trace.
D-272-3	Zr	0.1626	N_2	167	~39	28-39	Very stong sparking; one very long track. Grey metallic
							rod with grey glob of frozen melt on top. No scope trace.
D-285-4	Zr	0.1598	N_2	100	52	21-52	Same ND filters. Scope overdriven immediately.Long sparks.
							Photo at 24 s (good); 2nd (?). Sample unmelted w. white coating.
D-296-3	Zr	0.1579	N_2	102.6	22	20-21	Normal triggering; good trace. Photo w. flash at 16 s. Tiny sparks.
SOC							Dab of frozen melt on top of unmelted metal.
D-296-4	Zr	0.1621	N_2	146	23	No sparks	Normal triggering; good trace. Photo w. flash at 15 s. No sparks.
SOC							Dab of frozen melt on top of unmelted metal.

Table 7. Heating of the Alloy Zr_3Al with a Carbon Dioxide Laser

Expt. No.	Material	Weight (g)	Flowing Gas	Laser Power(W)	Heating Time (s)	Sparking Time (s)	Remarks
D-296-5	Zr_3Al	0.2156	N_2	144	26	No sparks	Normal triggering. Photo w.flash at 18 s. Good trace. Melt ran out
SOC							of partially melted solid. Black bottom.
D-296-6	Zr_3Al	0.2360	N_2	172	21	No sparks	Normal triggering. Photo w. flash at 11 s. Very brilliant luminous
SOC							surge at ~18 s. Complete melting; melt flowed from small volcano.

Zirconium-Aluminum Alloy Heated in Nitrogen

We performed two experiments in which samples of the zirconium-aluminum alloy, Zr_3Al, in flowing nitrogen were heated with the CO_2 laser. Both experiments were performed with the standard optical conditions (SOC). Heating times were in the range 21 s to 26 s. We performed the first experiment with a laser power of 143 W. Because there was incomplete reaction, we increased the power for the second experiment to the maximum available from the laser–171 W. The experimental conditions are summarized in Table 7 and the luminosity-time traces are shown in Figure 9. In this figure, as in Figures 4 through 8, we have adjusted the maximum vertical scale value of each plot to 3 volts.

During the second experiment, D-296-6, the sample emitted an unexpected burst of brilliant white radiation that saturated the photodetector for approximately the last 4 seconds of the laser heating. This emission was the most intense observed during the program.

The sample recovered from the first experiment was a partially melted cube with some material that seemed to have run from the cube as melt before freezing. The sample recovered from the second experiment was bell-shaped, as if much melt had run from small volcano and froze. The first sample had a pit on top, while the second had a hole that extended vertically through the entire sample.

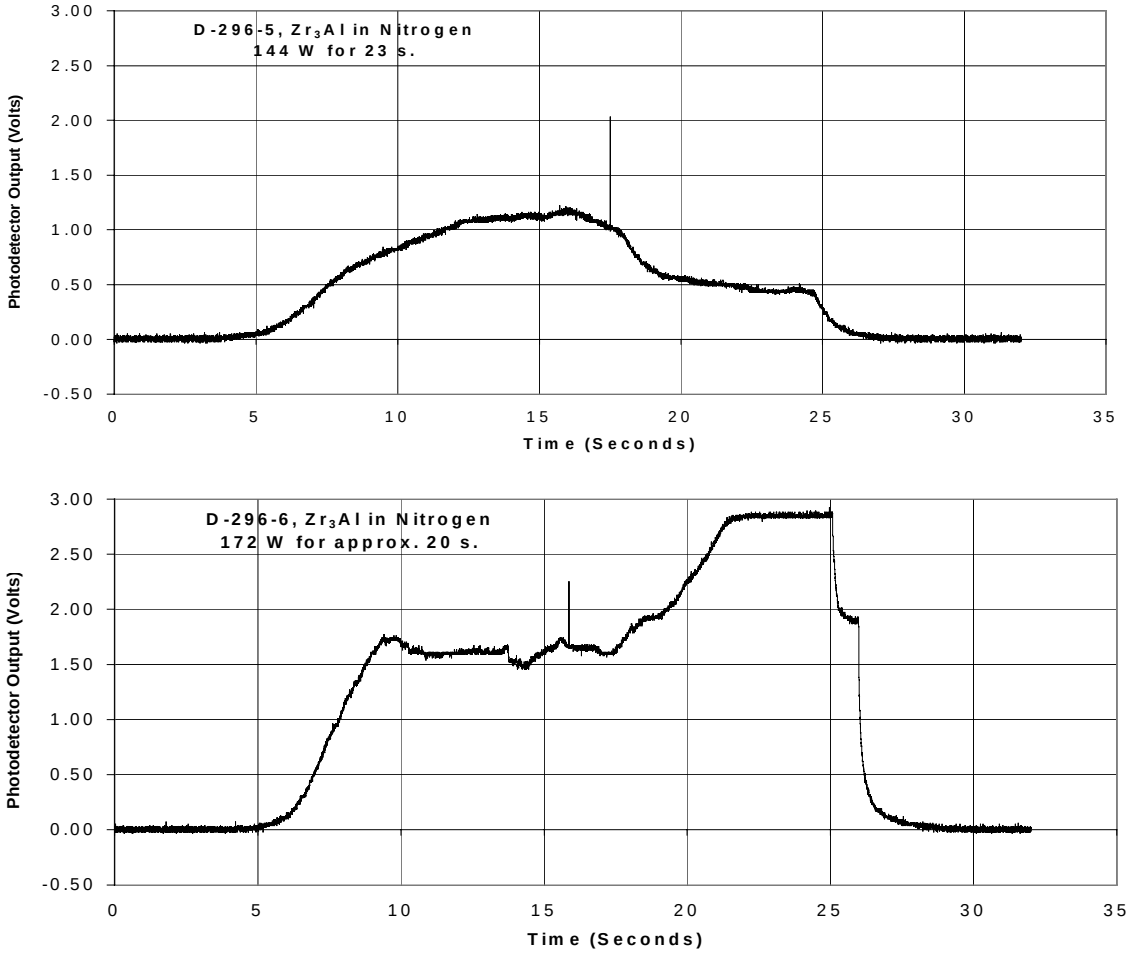


Figure 9. Luminosity-time traces recorded during two experiments in which nominally 180 mg samples of the zirconium-aluminum alloy, Zr_3Al, in flowing nitrogen were heated with the CO_2 laser. Each experiment was performed with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 3 volts.

Generation of Sparks

When titanium and zirconium were heated in either oxygen or nitrogen with the CO_2 laser, showers of luminous sparks were often observed visually and in the photographic and video images. Typical images of such a shower generated during the heating of Ti in flowing oxygen with 104 W for 15 s are shown in Figure 10 for experiment D-278-1. As indicated in Tables 1 and 2, the shower of sparks occurred between 9 and 15 s after heating began and one photograph was taken at 10 s. This photograph is shown as the upper image in Figure 10, while the lower was photographed as a single frame captured at approximately the same time from the continuous 30 f/s video record. (Note that even though these two images seem similar, they were taken from two different directions, 90^o apart.)

The images often show fragmentation and explosions of the sparks and in some instances "spearpoints" (recalescence) caused by the freezing of droplets that had strongly supercooled (Nelson, 1965). The sparks from both metals fell onto the graphite block as microspheres and are presumed to have been tiny droplets of molten material that cooled and froze in flight.

As indicated in Tables 4 and 7, sparks were never generated when samples of the zirconium-aluminum alloy, Zr_3Al, were heated in flowing oxygen or nitrogen with the CO_2 laser.

Recovered Solid Products

The solid products recovered after the experiments should shed light on the processes that occur when samples of metal are heated in an oxidizing gas with radiation from a CO_2 laser. Although we have not analyzed these specimens in any systematic fashion, we have archived them for future studies.

In this section, we present enlarged photographs of samples of the three metals, titanium, zirconium and the alloy, Zr_3Al, recovered after they were heated in oxygen and nitrogen. These photographs have been arranged approximately in order of increasing laser power and/or heating time–that is, in order of increasing energy deposited in the specimens.

Some qualitative observations follow.

Metals Heated in Oxygen

In Figure 11 we show specimens pf titanium heated in flowing oxygen when exposed to three laser beam powers that span our entire range from 64 W to the maximum of 176 W, each with exposure times of about 20 s.

Complete melting and reaction apparently occurred at all energy depositions. Each specimen is a shiny black bead with a small pit, and all seem essentially identical. (In our earliest experiments, several specimens showed patches of white on basically black beads. We attributed these patches to reaction with nitrogen in the air in the experiments before D-261-4 where a 2 mm tube was used to direct the oxygen over the graphite. In experiment D-261-4, the diameter of this tube was increased to 6 mm for the remainder of the program: all specimens of titanium recovered after this change were entirely black.)

Figure 12 is a similar set of photographs for specimens of zirconium heated in flowing oxygen. These specimens had been exposed to our lowest powers of 66 W to 72 W for ~20 s and to our maximum of 182 W to 184 W for ~28 s and ~98 s. There was incomplete melting and reaction at the lowest powers (66 to 72 W), somewhat more at the highest power for the shortest time (184 W for ~28 s) and essentially complete melting and reaction at the highest power and longest time (182 W for ~98 s).

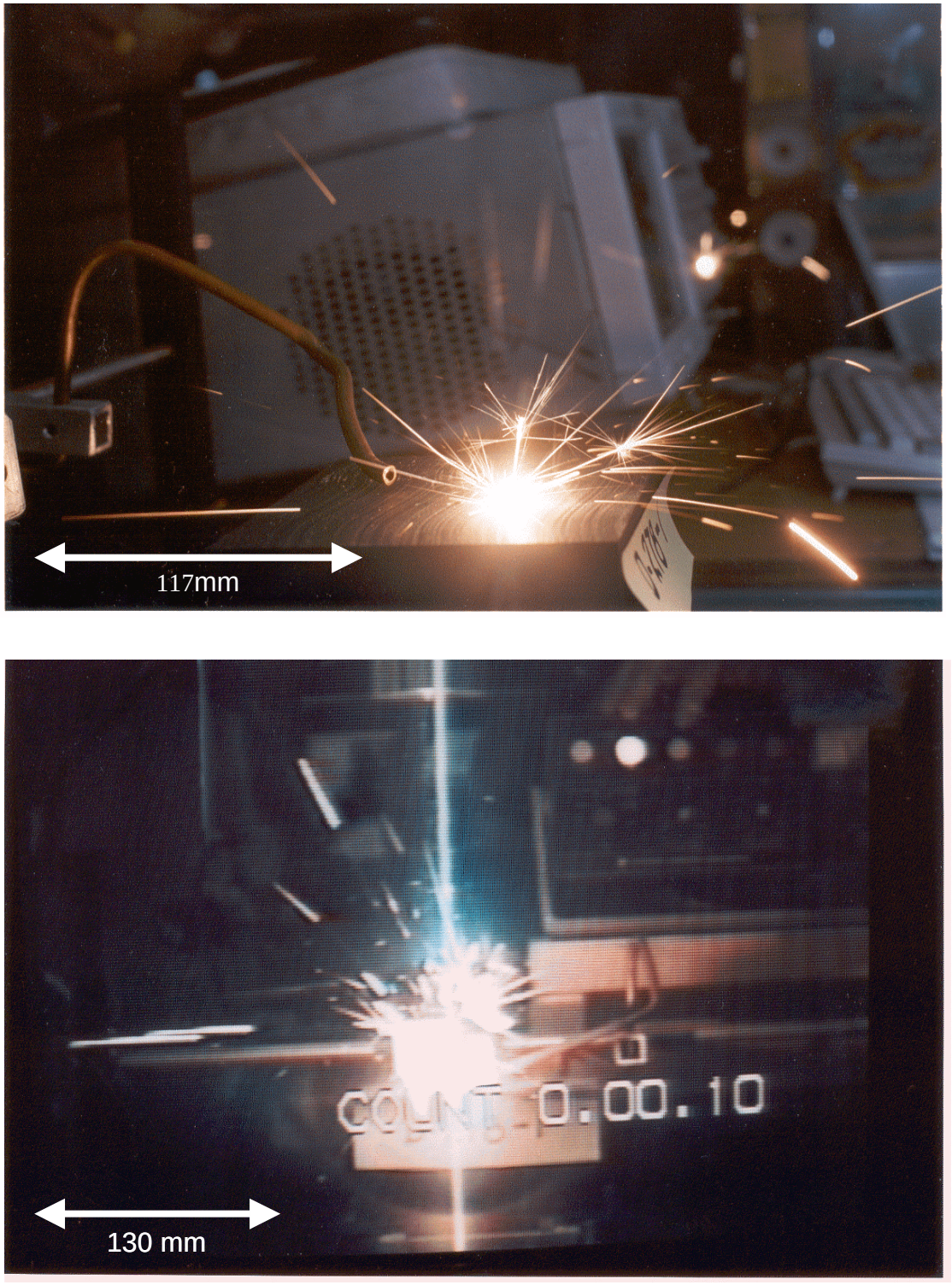


Figure 10. Sparks generated when a specimen of titanium is heated in oxygen with CO_2 laser radiation at 104 W for 15 s. Comparison of images recorded at ~10 s: film (above) and video (below). D-278-1.

The specimens of the alloy, Zr_3Al, heated in oxygen for about 20 s, shown in Figure 13, indicate incomplete melting and reaction at three powers between 63.8 W and 136 W. There was somewhat more reaction with each increase in power, but none of the specimens seemed to have reacted completely.

From Figures 11, 12 and 13, it seems that, in oxygen, titanium melts and reacts almost completely, even at the lowest laser powers. Zirconium certainly seems less reactive in oxygen than titanium, and the alloy, Zr_3Al, is the least reactive.

Metals Heated in Nitrogen

Figure 14 shows photographs of samples of the three metals, titanium, zirconium and the alloy, Zr_3Al, recovered after heating in nitrogen. In this figure, photographs of the specimens heated with higher powers are placed above those heated with lower powers. Each sample was heated for about 20 s at the powers shown below the photographs.

The first sample of titanium, shown at the lower left in Figure 14, D-296-1, was heated in nitrogen with 69.4 W for 16 s, approximately the same conditions used when titanium was heated in oxygen (see Figure 11, experiments D-298-1 and D-298-2). The sample heated in nitrogen showed only a tiny spot of frozen melt on top of unmelted rod, while those samples heated similarly in oxygen showed complete melting and reaction. But in experiment D-296-2, when the laser power was increased by about 50% to heat the second sample of titanium in nitrogen at 104.9 W for 20 s, there was complete melting and reaction, producing the billowy yellowish-white solidified globule shown at the upper left of Figure 14.

The two samples of zirconium shown in Figure 14, D-296-3 and D-296-4, were heated in nitrogen with moderate laser powers (106.2 W and 146 W) for similarly short times (22 s and 23 s). The melting and reaction of both samples were incomplete with both recovered samples showing only a dab of frozen melt on top of unmelted metal.

In experiment D-272-3, when a sample of zirconium was heated in nitrogen at the highest laser power (167 W) for a somewhat longer time (~39 s), the melting and reaction increased somewhat, but were still incomplete; the recovered sample was a gray metallic rod with a larger glob of frozen melt on top. This specimen is shown at the left in Figure 15. In experiments D-272-1 and D-272-2, however, when our highest laser powers (170 w to 175 w) were used to heat the zirconium in nitrogen for considerably longer times (~160 s to ~166 s), there was essentially complete melting and extensive reaction. Photographs of these specimens are shown at the center and right in Figure 15.

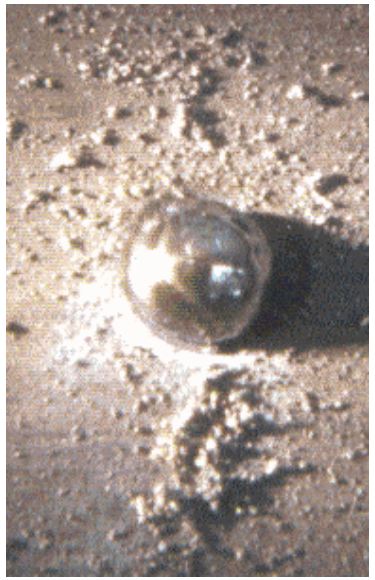
In experiment D-296-5, when we heated a sample of the alloy, Zr_3Al, in nitrogen at 144 W for 26 s, melt ran out of partially melted cube of solid. But in experiment D-296-6, when the sample of the alloy was heated in nitrogen at 172 W for 21 s, there was complete melting and reaction. The sample recovered from the second experiment was bell-shaped, as if much melt had run from a small volcano and froze. (This latter sample emitted an unexpected burst of brilliant white radiation.) The specimens recovered from both experiments with the alloy heated in nitrogen are shown at the right of Figure 14.

From the photographs in Figures 14 and 15, it seems that titanium is most reactive in nitrogen at the lowest laser powers, with the alloy, Zr_3Al, next, and the zirconium the least reactive. As in oxygen, each metal reacts more extensively at higher laser powers. Titanium and zirconium both seem less reactive in nitrogen (Figures 14 and 15) than in oxygen (Figures 11 and 12): on the other hand, the alloy seems more reactive in nitrogen than in oxygen (compare Figures 13, 14 and 15).

The comments in the previous paragraphs probably should be regarded as tentative at present, however, because the number of experiments performed with the metals heated in nitrogen is limited.

Above: 71.5 W for 22 s. D-298-2
Below: 63.8 W for 18 s. D-298-1

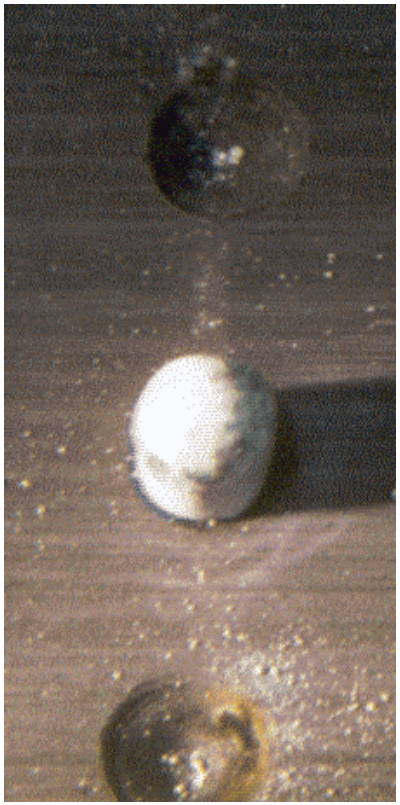
102 W for 26 s. D-273-2.



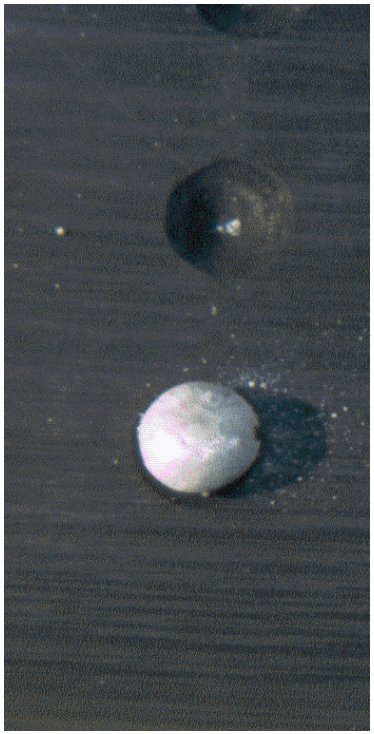
176 W for ~18 s. D-265-2.

Figure 11. Specimens recovered after titanium samples were heated in oxygen with a CO_2 laser.

Above: 71,6 W for 20 s. D-298-4.
Below: 66.3 W for 27 s. D-298-3.



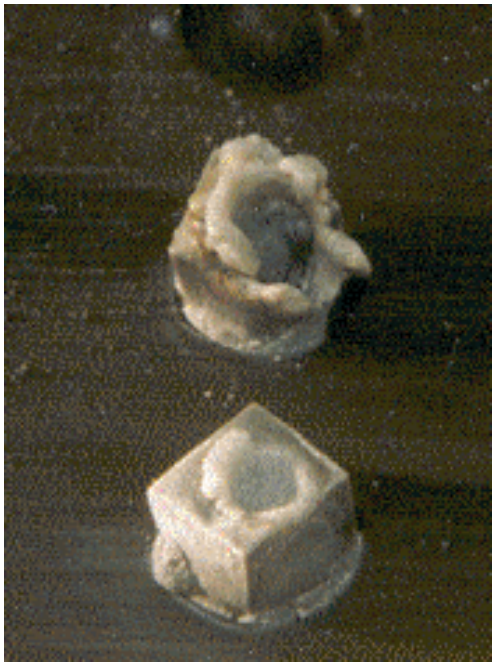
184 W for ~28 s. D-257-2.



182 W for ~98 s. D-257-1.

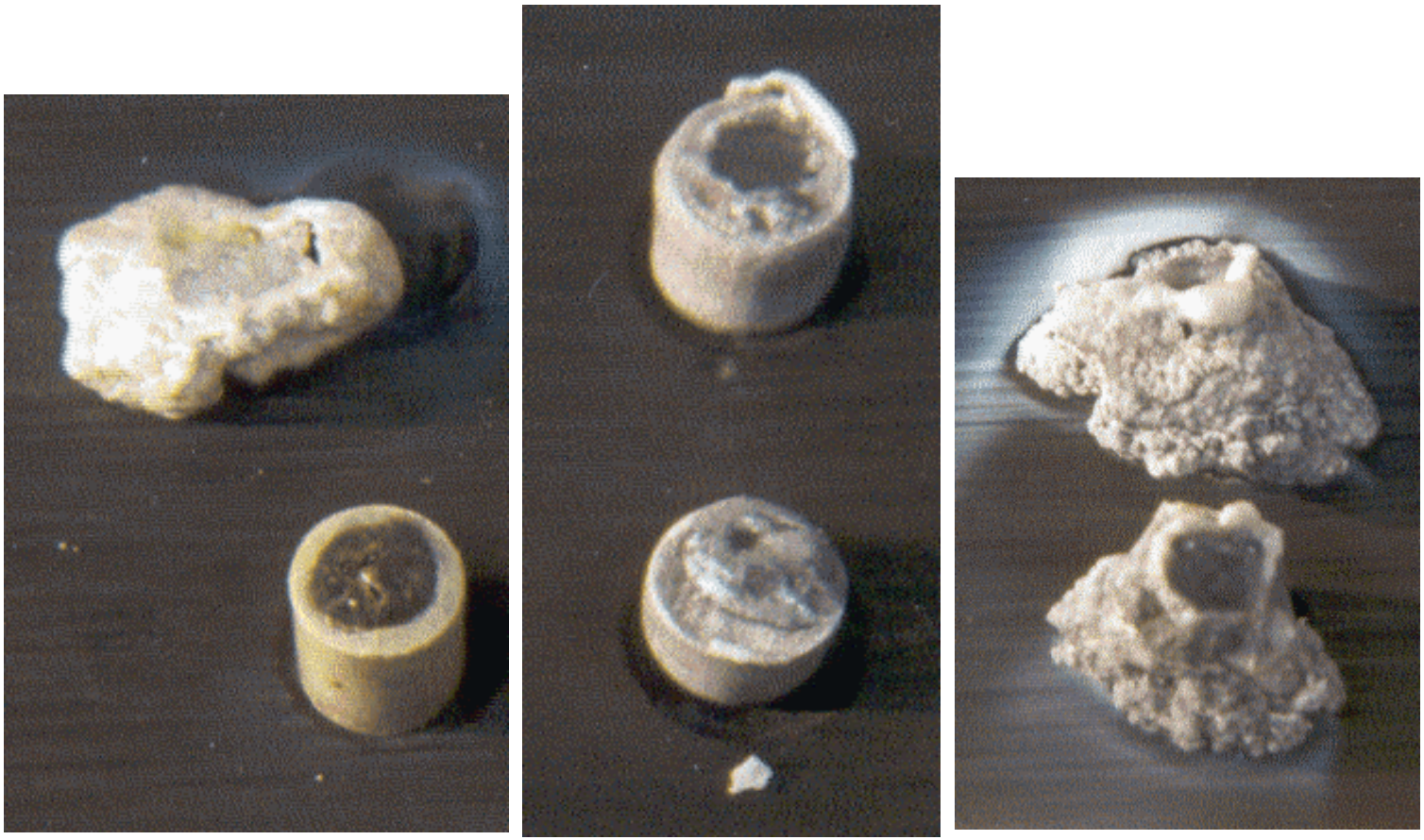
Figure 12. Specimens recovered after zirconium samples were heated in oxygen with a CO_2 laser.

63.8 W for 27 s. D-288-4



Above: 136 W for 18 s. D-293-2.
Below: 80.5 W for 16 s. D-293-1.

Figure 13. Specimens recovered after samples of the alloy, Zr_3Al, were heated in oxygen with a CO_2 laser.



Ti

Above: 104.9 W for 20 s. D-296-2.
Below: 69.4 W for 16 s. D-296-1.

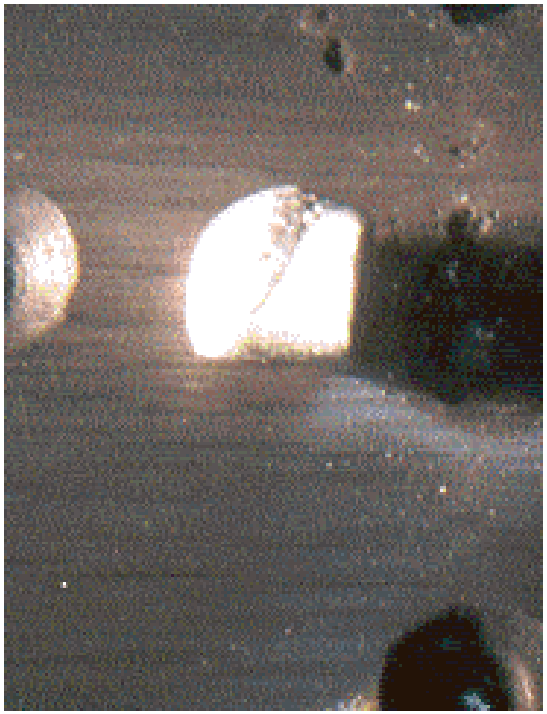
Zr

Above: 146 W for 23 s. D-296-4.
Below: 106.2 W for 22 s. D-296-3.

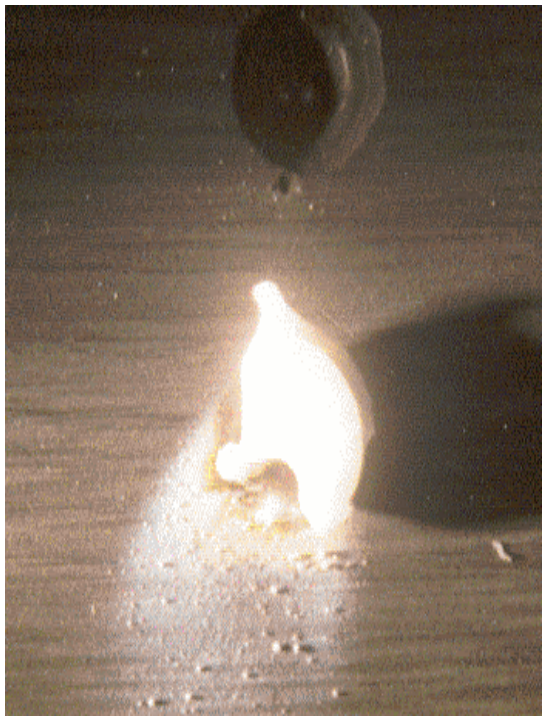
Zr_3Al

Above: 171 W for 21 s. D-296-6.
Below: 143 W for 26 s. D-296-5.

Figure 14. Specimens recovered after samples of titanium, zirconium and the alloy, Zr_3Al, were heated in nitrogen with a CO_2 laser. Distance between tips of the arrowheads is 5 mm.



169 W for ~39 s. D-272-3



175 W for ~160 s. D-272-1

170 W for ~166 s. D-272-2

Figure 15. Specimens recovered after samples of zirconium were heated in nitrogen with a CO_2 laser. Distance between tips of the arrowheads is 5 mm.

Aluminum Oxide Heated in Oxygen

When this work started, we assumed it possible to identify certain temperatures during the heating and ignition of a metal by comparing the luminosity of the specimen with halts that occur when the metal or its oxidation products melt or solidify. We also assumed it possible to use halts produced by the melting or solidification of other materials with known melting temperatures heated with the CO_2 laser in side experiments.

To test this assumption, we turned to aluminum oxide, which (a) is known to melt readily in the laser beam (Nelson et al., 1973), (b) has been recommended as a melting point standard for high temperatures (melting temperature = 2054 ^{o}C) (Schneider, 1970) and (c) has an emittance of essentially 1 in the molten state (Weber et al., 1995).

We obtained alumina ceramic spheres (99.5% Al_2O_3) of two diameters: 3.11 mm and 4.76 mm. Although they contain small impurities, these spheres have brilliant white glossy exteriors. Spheres of slightly impure ceramic were used instead of the 100% Al_2O_3 (single crystal sapphire) because they could be obtained quickly at low cost.

The melting was performed as follows: A sphere was placed in one of the shallow holes in the graphite block and moved into the laser focus. It was necessary to move the ceramic spheres into the focus somewhat more slowly than the metal samples in the ignition experiments because heating too rapidly caused the ceramic to fragment. Once in the focus, the spheres were heated with laser beam powers between 110 W and 177 W for 10 or 15 seconds. The spheres were heated in flowing oxygen to duplicate conditions in similar experiments by Nelson et al. (1973).

Each sphere became brightly luminous during the heating, but extinguished quickly when the laser was turned off. During this rapid cooling, the luminosity decreased initially, then paused briefly before extinguishing altogether. Sometimes, the luminosity dipped slightly and then rose again before the pause. We identify the pause at constant luminosity as the halt that accompanies the solidification of the melt at a temperature of 2054 ^{o}C. We attribute the slight dip before the halt to subcooling of the melt prior to the onset of solidification.

We recorded luminosity-time traces during the heating and cooling of both the smaller and larger alumina spheres: six experiments with 3.11 mm-diameter spheres and two with 4.76 mm-diameter spheres. The experimental conditions are summarized in Table 8. The luminosity-time traces for the smaller spheres are shown in Figures 16 and 17, and for the larger spheres in Figure 18.

In Figures 16 through 18, we have reduced the maximum vertical scale value of each plot to 2 volts compared to the maximum of 3 volts used in Figures 4 through 9. This was done because the luminosities emitted near the melting temperature of aluminum oxide, 2054 ^{o}C, were much lower than those emitted by the burning metals that may reach temperatures in excess of 3000 ^{o}C.

After solidifying, each sphere showed a roughly hemispherical golden-colored zone, presumably where heating and melting had occurred, while the rest of the sphere remained the original brilliant white. There was little apparent change in sphericity caused by the heating, however, although careful measurements were not made.

Table 8. Heating Aluminum Oxide Spheres in Oxygen with a Carbon Dioxide Laser

Expt. No.	Sphere Dia. (in.)	Sphere Dia. (mm)	Laser Power(W)	Heating Time (s)	Halt Level (V)	Remarks
D--294-1	0.125	3.11	110	10	0.31	Manual triggering. Short halt during solidification, not
SOC						during melting.
D-294-2	0.125	3.11	154	11	0.37	Manual triggering. Subcooling and longer halt at higher
SOC						luminosity during solidification.
D-294-3	0.125	3.11	143	13	0.37	Manual triggering. Subcooling and longer halt at higher
SOC						luminosity during solidification.
D-295-1	0.125	3.11	113	10	0.48	Normal triggering. No subcooling, very short halt during
SOC						solidification.
D-295-2	0.125	3.11	180	12	0.55	Normal triggering. Subcooling and longer halt at higher
SOC						luminosity during solidification.
D-295-3	0.125	3.11	180	17	0.56	Normal triggering. Subcooling and longer halt at higher
SOC						luminosity during solidification.
D-295-4	0.188	4.76	177	18	0.81	Normal triggering. No subcooling, very short halt during
SOC						solidification.
D-295-5	0.188	4.76	176	13	0.71	Normal triggering. No subcooling, very short halt during
SOC						solidification.

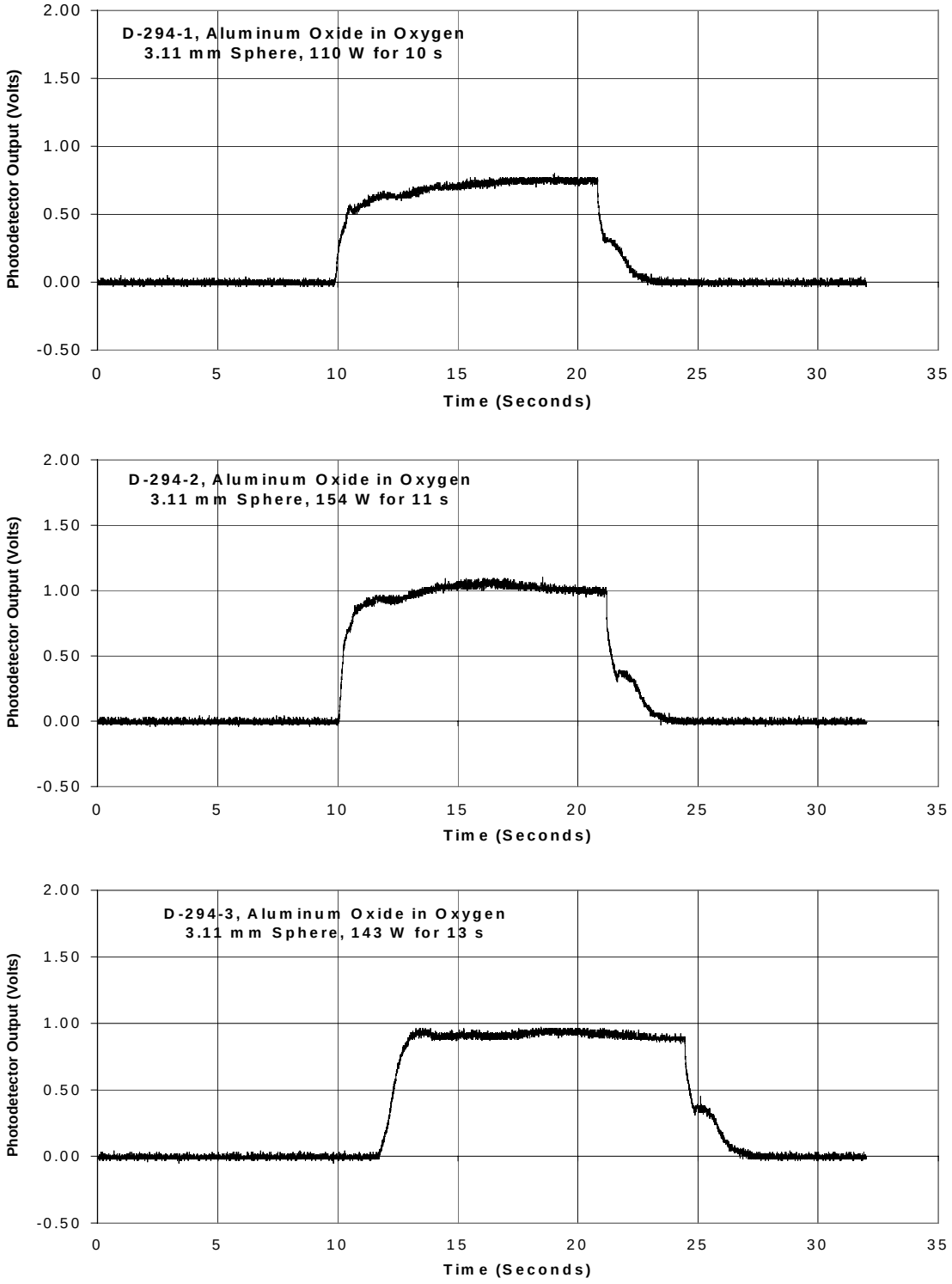


Figure 16. Luminosity-time traces recorded during the CO_2 laser heating and cooling of three 3.11 mm-diameter aluminum oxide spheres. Each experiment was performed in flowing oxygen with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 2 volts.

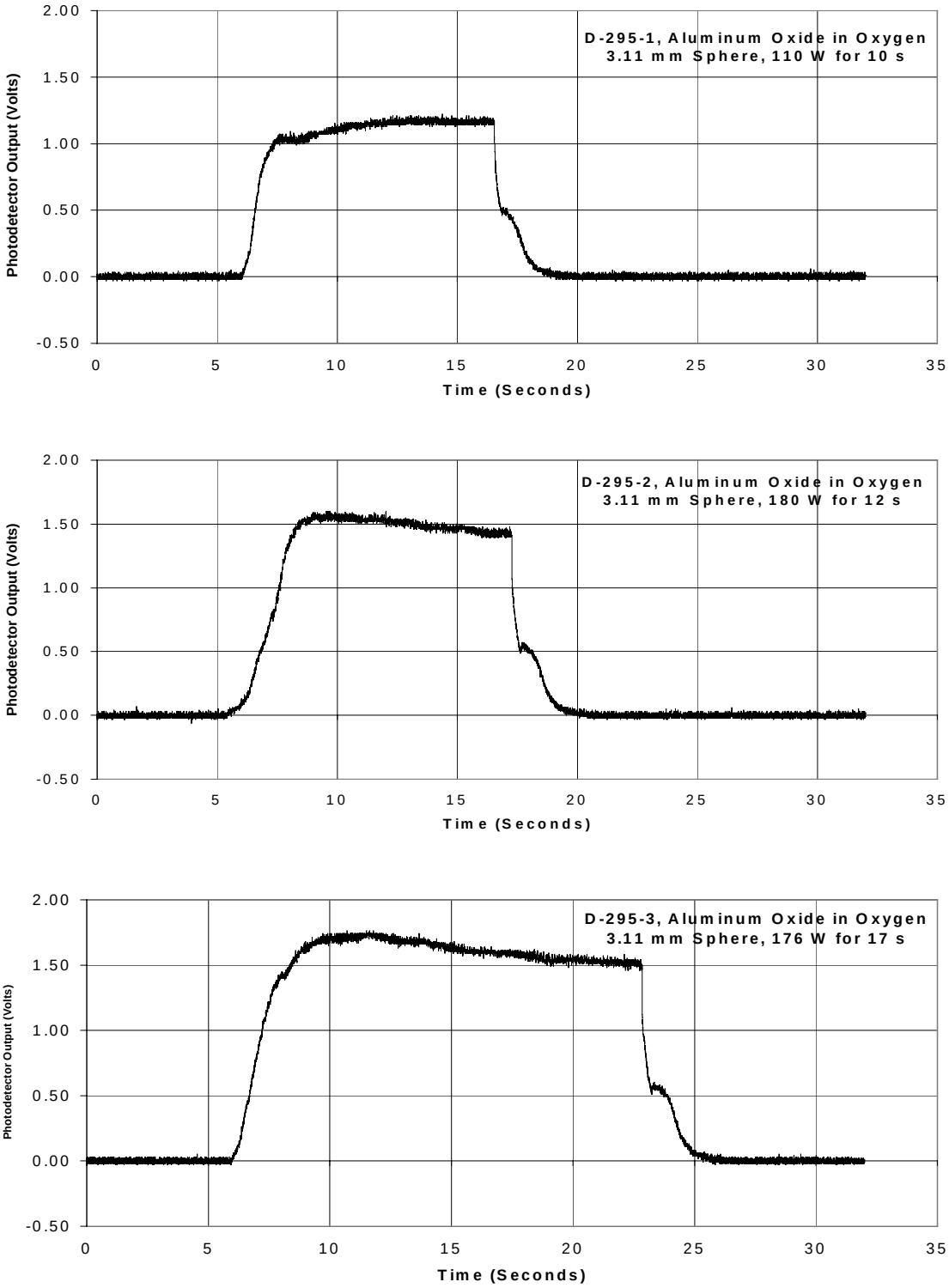


Figure 17. Luminosity-time traces recorded during the CO_2 laser heating and cooling of three 3.11 mm-diameter aluminum oxide spheres. Each experiment was performed in flowing oxygen with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 2 volts.

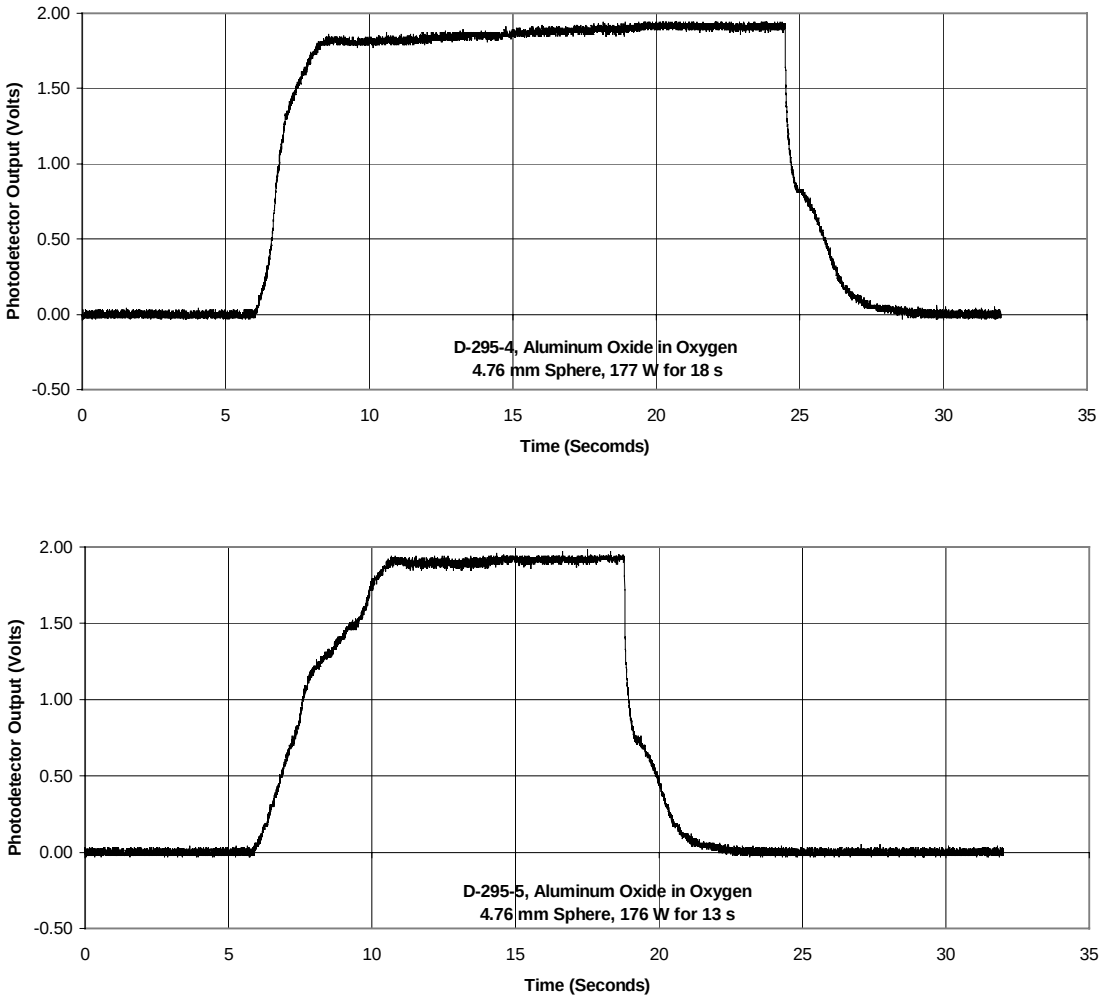


Figure 18. Luminosity-time traces recorded during the CO_2 laser heating and cooling of two 4.76 mm-diameter aluminum oxide spheres. Each experiment was performed in flowing oxygen with standard optical conditions (SOC). The maximum ordinate of each plot has been adjusted to 2 volts.

DISCUSSION

Reproducing the Earlier Studies: Titanium in Oxygen

Our initial efforts were directed toward duplicating the earlier studies of metal combustion at the National Bureau of Standards, Boulder, CO, by Runyan et al. (1974). This involved first reproducing the experimental arrangement—the downward-directed, focused laser beam for heating the metal sample on the graphite block with a gaseous oxidizer flowing across its surface.

Our experimental setup operated essentially as described by these authors. Their suggested use of a graphite block to support the samples during laser heating was especially valuable. We never observed reaction during heating between the graphite and any of the three metals in oxygen or nitrogen or the aluminum oxide in oxygen, even for the highest laser powers and the longest heating times.

After testing our setup, we concentrated mostly on reproducing the luminosity emitted by the metal specimens during hating. In particular, we tried to understand their luminosity-time plot, reproduced in Figure 19, that was produced by heating a sample of titanium (weight ~0.130 g) in flowing oxygen with 100 W of CO_2 laser radiation.

Initially, we started with our maximum beam powers of ~175 W, but realized they were far too large because they seemed to overdrive the luminous emission by specimens of both titanium (weight ~0.111 g) and zirconium (weight = ~0.160 g) heated in both oxygen and nitrogen.

Next, we lowered the beam power to 100 W to replicate those used by Runyan et al. This power also seemed to overdrive the luminosity. But by further reducing the beam power to about 66 W, were able to generate fairly reproducible luminosity-time traces of the sort shown in Figure 4 when titanium specimens were heated in flowing oxygen.

At present, we cannot explain the differences between the traces in Figures 4 and 19. We note that the laser power of 100 W reported by Runyan et al. is higher than the powers of about 66 W we found to be desirable, and also that the time scales in the two figures are not of the same order. It seems likely that they may have made errors in (a) timing and (b) laser power measurements; both may be due to measuring uncertainties in the apparatus of the 1970's.

Heating Metals in Oxygen with the CO_2 Laser

In this section, we shall primarily discuss the experiments performed under standard optical conditions (SOC).

The luminosity-time traces produced in the nine experiments performed under SOC with the samples of the three metals heated in flowing oxygen (see Table 1) are shown in Figures 4, 5 and 6. The samples of both titanium and zirconium were heated with laser beam powers between 66 W and 72 W, while the three samples of the Zr_3Al alloy were heated with progressively increased powers of 66 W, 80 W and 136 W.

When Figures 4, 5 and 6 are compared, it is seen that the most intense luminosities were emitted by the zirconium samples, saturating the photodetector in two of the three experiments. The peak luminosities of the titanium samples were considerably lower, while the peak luminosities of the Zr_3Al alloy samples seemed to remain roughly the same as those of the titanium samples in spite of the increasing laser powers.

Also, the emission times were short for the Zr_3Al alloy samples, somewhat longer for the zirconium samples while those for the titanium samples were by far the longest.

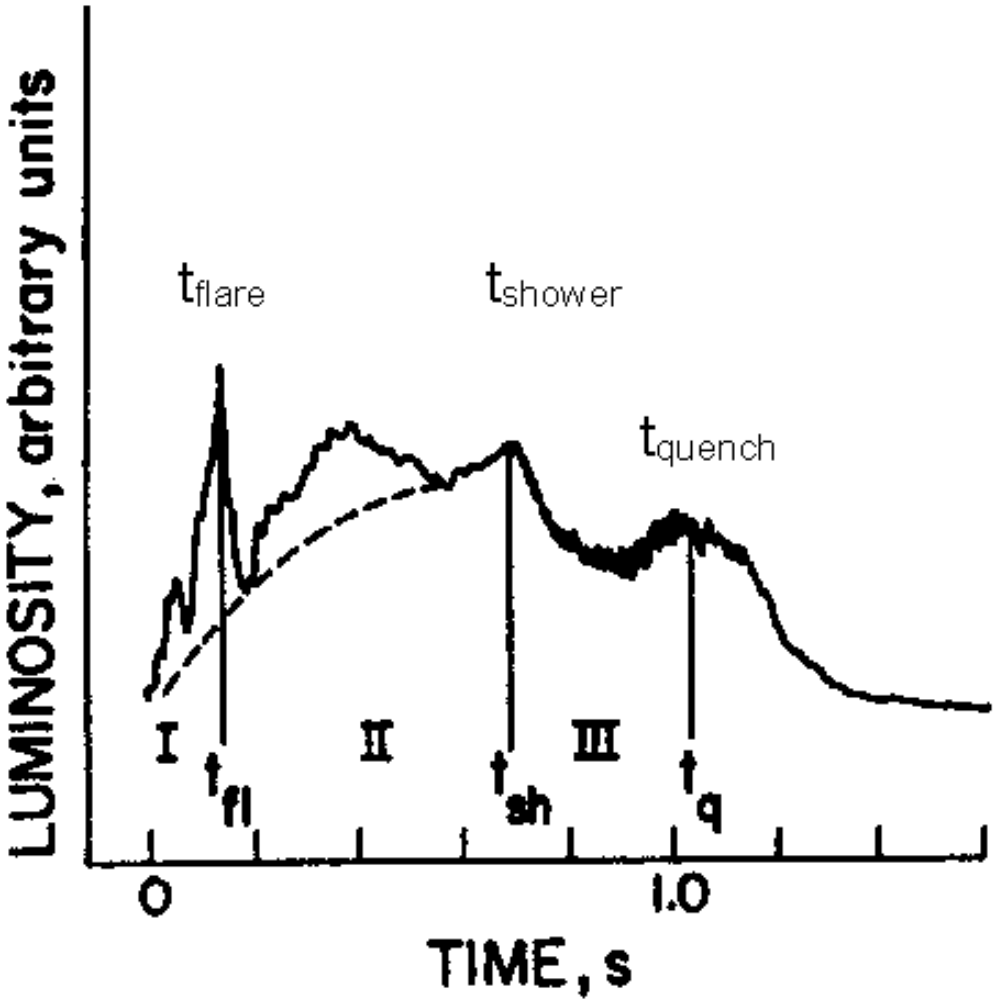


Figure 19. Time resolved brightness curve for bulk titanium (~130 mg) combustion. Reproduced from Runyan, Moulder and Clark (1974).

The emission times seem related to the amount of melting that occurred during the experiments. When the three metals were heated with laser beam powers between 66 W and 72 W, there was very little melting of the Zr_3Al alloy samples, partial melting of the zirconium samples, and complete melting of the titanium samples (see Figures 11, 12 and 13).

The luminosity-time traces were very smooth for the Zr_3Al alloy samples, somewhat more jagged for the zirconium samples while those for the titanium samples were by far the most jagged. The jagged portions of the traces seem to accompany the ejection of sparks by the burning metal sample (see Figure 10). We have observed that the sparks were ejected most copiously from titanium samples heated in oxygen when the traces were the most jagged. The zirconium samples heated in oxygen showed only a brief ejection of sparks, but then only in the jagged portions of the traces. And finally, no sparks were ejected from the Zr_3Al alloy samples during the normal heating with beam powers between 66 W and 72 W; correspondingly, the traces were smooth, as shown in Figure 6. (In experiment D-293-2, when the Zr_3Al alloy sample was heated at 136 W, about twice the laser power used for heating the zirconium and titanium samples, a small ejection of smoke was observed between 6 s and 7 s, corresponding to a small, slightly jagged increase in luminosity.)

Heating Metals in Nitrogen with the CO_2 Laser

In this section, as in the previous section, we shall primarily discuss the experiments performed under standard optical conditions (SOC).

The luminosity-time traces produced in the five experiments performed under SOC with the samples of metal heated in flowing nitrogen (see Table 1) are shown in Figures 7, 8 and 9. These experiments, as well as those performed earlier in the program, indicated that when both zirconium and titanium were heated at laser powers of 65 W to 72 W moderate or good ignitions and reactions were produced in flowing oxygen but there was little or no reaction when the oxidizing gas was flowing nitrogen. Also, heating the Zr_3Al alloy at these powers in flowing oxygen produced essentially no reaction. Therefore, after performing two unsuccessful experiments with titanium heated with 68 W to 69 W in flowing nitrogen (one before SOC were achieved, D-285-1, and the other under SOC, D-296-1), we used higher laser powers for the remainder of the experiments in this gas.

When we increased the laser power from 69.4 W to 104.9 W for experiment D-296-2, the sample of titanium heated in nitrogen produced an excellent ignition, complete melting and the strong luminosity shown in Figure 7. Also, the sample of metal changed from its original cylindrical shape to a frozen globule of billowy, yellowish material, presumably titanium nitride (see Figure 14).

When we heated samples of zirconium in nitrogen with intermediate laser powers of 102.6 W and then 146 W for experiments D-296-3 and D-296-4, there was very little reaction in either experiment–only small dabs of frozen melt were produced on top of cylinders of unmelted metal (see Figure 14). Moreover, the luminosities shown in Figure 8 were considerably lower than the luminosity produced by titanium heated in nitrogen under similar conditions (experiment D-296-2) and shown in Figure 7.

Even when the laser power was increased to the maximum and the heating time increased significantly in experiment D-272-3 (169 W for ~39 s) the sample recovered was still an unmelted cylinder of metal with a bead of frozen material on top, as shown at the left of Figure 15. Only when we heated the zirconium in nitrogen at our maximum powers (170 W to 175 W) for the longest heating times (160 s to 166 s) in experiments D-272-1 and D-272-2 was the melting and reaction complete, as shown at the center and right of Figure 15.

Unfortunately, we cannot compare the luminosity-time measurements for the earlier experiments with zirconium in nitrogen that produced the samples shown Figure 15 (D-272-1, D-272-2 and D-272-3) with those for the later experiments that produced the samples shown Figure 14 (D-296-3 and D-296-4) because they were not recorded in the earlier experiments (see Table 6).

Because (a) the reactivity of the alloy, Zr_3Al, seemed lower than zirconium in oxygen, and (b) zirconium seemed to require more laser power to ignite in nitrogen than in oxygen, we began to heat the alloy in nitrogen with intermediate to high laser powers. In the first experiment, D-296-5, performed with 144 W for 26 s, to our surprise, there was reasonably good ignition, some melting and strong luminosity. But when we increased the laser power to 172 W for 21 s in experiment D-296-6, there was excellent ignition, complete melting and luminosity that started out very strong for about 8 seconds, followed by a burst of extreme luminosity (the brightest of all experiments performed during this program) that lasted another 7 seconds until the laser was turned off (see Figure 9). The solids recovered after both the experiments resembled miniature solidified volcanoes (see Figure 14).

From these experiments, we conclude that in flowing nitrogen, little reaction occurs when titanium and zirconium are heated at the lower laser powers (66 W to 72 W) that easily ignited them in flowing oxygen. But when the laser powers were increased 2- or 3-fold for the heating in nitrogen, good ignition, substantial melting and strong luminous emission can occur with both titanium and zirconium. The alloy, Zr_3Al, was heated only at higher laser powers, so we are unable to compare its behavior with titanium and zirconium heated at the lower powers.

Properties that Govern Ignition

A primary objective of this work is to investigate the combustion chemistry and material physical behavior that govern the ignition of DU in gases typical of a fire environment. In our earlier letter reports (Nelson et al., 2001a, b), we suggested that the melting temperature might strongly influence the ignition and combustion of a metal. If this hypothesis is valid, the higher the melting temperature of the metal, the more difficult it should be to ignite. Therefore, we have studied three metals–zirconium, with a melting point of 1852 ^{o}C, titanium, with a melting point of 1660 ^{o}C, and the alloy, Zr_3Al, with the eutectic temperature of 1350 ^{o}C–for comparison with DU that melts at 1132 ^{o}C. Thus, if the hypothesis is correct, zirconium should be the most difficult to ignite and the Zr_3Al alloy should be the easiest of the three metals studied to date.

But this was not the order observed in flowing oxygen. Instead, we found that the Zr_3Al alloy was the most difficult to ignite, titanium was the easiest and zirconium was in between. In flowing nitrogen, again titanium seemed to be the easiest to ignite, but the comparison between zirconium and the alloy was not as clear. The alloy seemed to be somewhat easier to ignite in nitrogen than the metallic zirconium, but there is uncertainty because the number of experiments performed with the alloy in nitrogen was small.

These results seem to indicate tentatively that the ease of ignition is not as simply related to the melting temperature of the metal as originally hypothesized. Of course, this statement is still premature, based on a limited number of experiments with only three materials, two of which are pure metals and the third a binary alloy.

Proxy Metal

Another objective of this work is to identify an environmentally acceptable metal that can substitute for DU in outdoor fire tests. We hypothesized, again on the basis that melting temperature was a controlling factor in ignition, that the Zr_3Al alloy might be a good candidate for the proxy metal, better than the higher melting zirconium, which also has been proposed as a candidate.

Although our experiments are very limited, they suggest that because the Zr_3Al alloy seems more difficult to ignite in oxygen, it offers little or no advantage over zirconium as a possible proxy. In nitrogen, the comparison between the two metals is less clear because of the small number of experiments. Actually, we are currently leaning toward titanium as the proxy because of its relative ease of ignition in both oxygen and nitrogen. Any decision, of course, must await comparisons with ignition experiments with DU.

Generation of Sparks

Although the sparks shown in Figure 10 seem very interesting, they are usually generated quite late during the heating, ignition and combustion of the specimens, as indicated in Tables 1, 2, 3, 5 and 6. We do not believe, therefore, that they are important to the primary objective of this work—understanding the ignition of the metals.

If sparks form during the combustion of DU in a fire situation, however, they may provide an important mechanism for its dispersal in the environment as aerosol and/or particulate that falls to the ground. Also, sparking could also affect the environment by providing a way for spreading fire throughout a site.

It is intriguing to speculate about the origin and nature of the sparks generated when titanium and zirconium are heated in either oxygen or nitrogen. There is also the question of why the sparks fragment and explode early in their generation (for an example, see the upper photograph in Figure 10) but not later (Runyan et al., 1974). We suggest a simplistic preliminary hypothesis: that the material is boiling as it oxidizes.

While 35 mm color film provides the highest quality images of the sparks (for example, the upper image in Figure 10), only a few photographs can be taken during an experiment. On the other hand, the continuous video record provides hundreds of single-frame images at 30 f/s during an entire experiment (for example, the lower image in Figure 10). Although the video images have lower quality, they often provide the best way to examine the generation of sparks, particularly when the sparks are not ejected too vigorously, for example, late in the heating of zirconium in oxygen, or when the spark emission extends over a long time, for example, when zirconium is heated in nitrogen.

Calibration of Luminosities

An important assumption in this work has been that the "halts" or pauses in the luminosity-time records produced during the melting and solidification of identifiable substances could be used to calibrate the high temperatures produced during the laser heating and subsequent ignition and combustion of a metal. Although halts have been observed in several of our metal combustion experiments (see, for example, Figures 4 and 5), we have not as yet been able to identify either the temperatures or the compositions of the materials at the times of these halts.

To produce halts in a refractory material with a known composition, we have used aluminum oxide, which has been studied carefully in both the liquid and solid states near its melting temperature of 2054 ^{o}C (see Nelson et al., 1973; Schneider, 1970; Weber et al., 1995). Because this oxide has only the single, fixed stoichiometry, Al_2O_3, and is stable in air and inert atmospheres at this temperature (Nelson et al., 1973), it melts and freezes in a straightforward and simple fashion, much like a pure metal. Moreover, it is readily melted with CO_2 laser radiation (Nelson et al., 1973).

The desired halts were observed when we melted 3.11 mm- and 4.76 mm-diameter 99.5% aluminum oxide ceramic spheres. Thus, in Figures 16, 17 and 18, each trace shows a distinct deflection about 0.5 s after the laser is turned off. As mentioned above, we attribute these deflections to the release of heat of crystallization that causes the luminosity to remain essentially constant for a short time before the sample cools to ambient temperature. Another factor associated with the halts may be the change in emittance as aluminum oxide freezes (Nelson et al., 1973; Weber et al., 1995).

We were surprised not to observe halts when the aluminum oxide melted. Note that no deflections could be detected during the laser heating in any trace shown in Figures 16, 17 and 18; the halts occurred only during cooling.

Reproducibility of the Halt Levels

In Table 8, we have presented photodetector output voltages at the halt levels for the eight experiments performed under SOC with laser-heated aluminum oxide spheres. Although they were easily identified in each trace shown in Figures 16, 17 and 18, the halt levels seemed to vary somewhat with laser power, sphere diameter and from day to day. These variations in voltage, of course, cast doubt on the use of halt levels determined with a photodetector as a quantitative way to calibrate temperatures during the ignition of metals.

At present, we cannot account for these variations, because all eight experiments were performed with identical optical conditions (SOC)—the same filters and the same photodetector aimed at the laser focus point in the same way. (The setup for standard optical conditions (SOC) remained unchanged during the last three weeks of experiments in which both aluminum oxide and the three metals were heated with the laser.)

Some possible explanations for the variations:

- It may be that slight horizontal or vertical variations of the position of a heated specimen on the graphite block might change the effective diameter of the emission source seen by the

photodetector. This could change the apparent levels of the halts between experiments even though the solidifying material always was at the same temperature. This also might explain the stronger emission for larger spheres shown in Table 8.

- From the appearance of the both the golden and white zones of the solidified spheres after the experiments, it seems likely that the aluminum oxide spheres did not melt completely in the laser beam. More or less melting also could change the effective diameter of the molten oxide and thus the size of the emission source. This could cause more intense emissions (higher halt levels) for both higher laser powers and larger spheres as shown in Table 8.

- The formation of the golden coloration where the otherwise bright white ceramic spheres were heated is consistent with the presence of impurities. It is possible that variations in the amounts of impurities from sphere to sphere might affect their melting and freezing temperatures and thus cause the luminosities emitted at the halts to vary. Also, it is possible that impurities might segregate differently when larger or smaller amounts of melt are produced, changing the solidification temperatures as the melt compositions vary. If these experiments are continued, spheres of 100% Al_2O_3 (single crystal sapphire) should be used instead of the 99.5% aluminum oxide ceramic used here.

- It is possible that the positioning of the photodetector and filters could change slightly between experiments, perhaps due to vibration or thermal expansion and contraction of the supports. This might account especially for the variations encountered between the first three experiments D-294-1, D-294-2 and D-294-3 and the second group of three, D-295-1, D-295-2 and D-295-3, performed three days later under seemingly identical conditions.

Subcooling

In order to examine the halts more carefully, we have expanded the scales of Figures 16, 17 and 18—that is, decreased the horizontal width of each plot from 35 seconds to 4 seconds—in new plots presented in Figures 20, 21 and 22; the halts are approximately centered in the expanded plots.

In several of these expanded plots (D-294-2, D-294-3, D-295-1, D-295-2 and D-295-3), we observe dips in the luminosity just before the halts. We attribute these dips to subcooling of the molten aluminum oxide before solidification begins and releases heat of crystallization that tends to raise the temperature back to the halt level.

In the experiments performed with the 3.11 mm-diameter spheres (Figures 20 and 21), the subcoolings were observed only with the highest laser powers (143 W to 180 W, D-294-2, D-294-3, D-295-2 and D-295-3), but not with the lower laser powers (110 W and 113 W, D-294-1 and D-295-1). Also, in Figure 22, when the 4.76 mm-diameter spheres were heated at the highest laser powers (176 W and 177 W, D-295-4 and D-295-5), there was essentially no subcooling.

To explain this behavior, we suggest that the ability for the partially melted spheres to exhibit subcooling depends on the volume of melt present when cooling begins; that is, when the laser is turned off. Thus for the smaller spheres, a greater volume of melt would be produced with the higher laser powers. For the larger spheres, even at the highest laser powers, the volume of melt is probably smaller, and the deflection as solidification begins is small, with little tendency to exhibit subcooling.

Another possible explanation might be that the segregation of impurities in the partially molten aluminum oxide sphere might affect the nucleation of the melt during cooling, and thus affect the depths of subcooling.

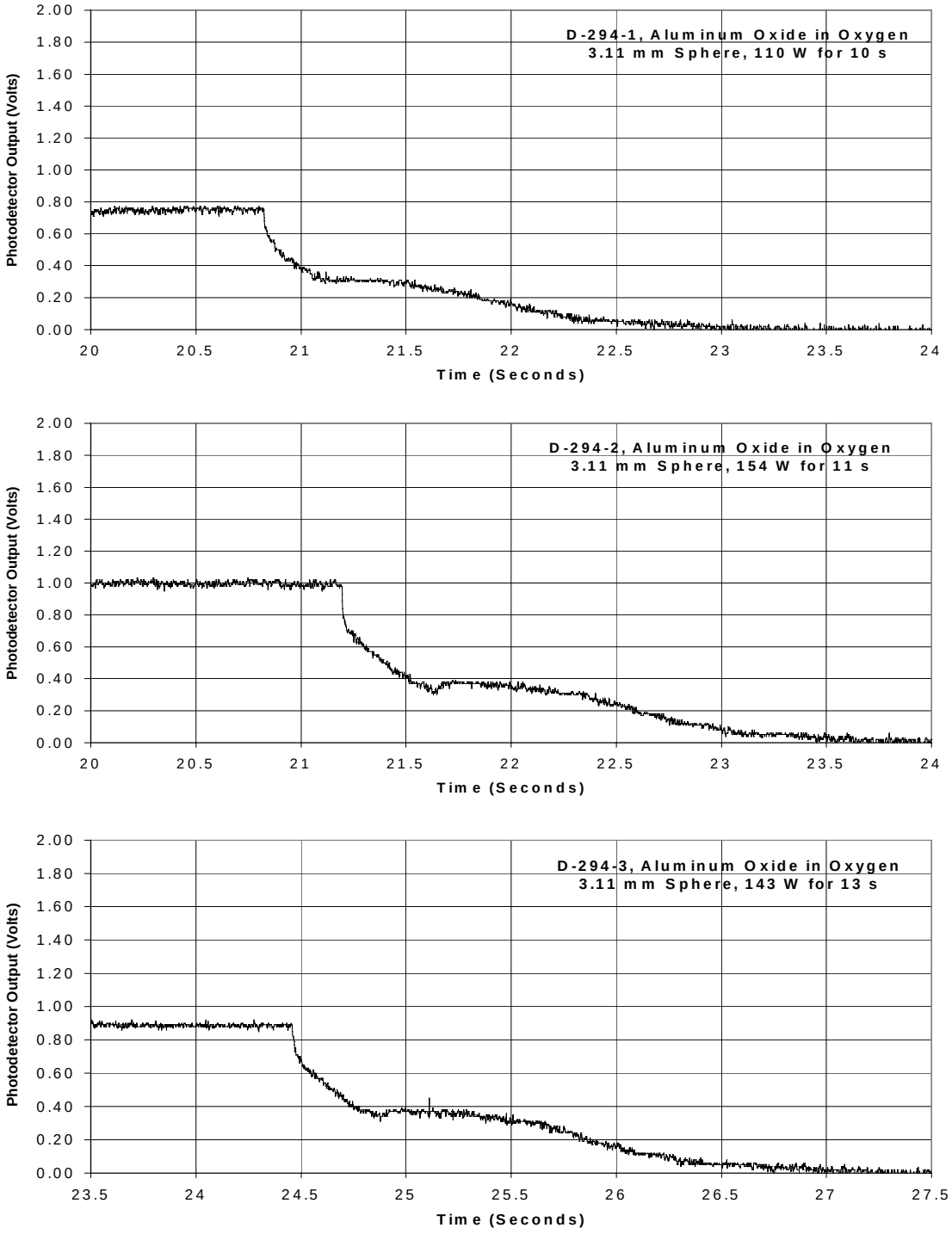


Figure 20. The luminosity-time traces in Figure 16 replotted with expanded horizontal scales to show the solidification halts more clearly.

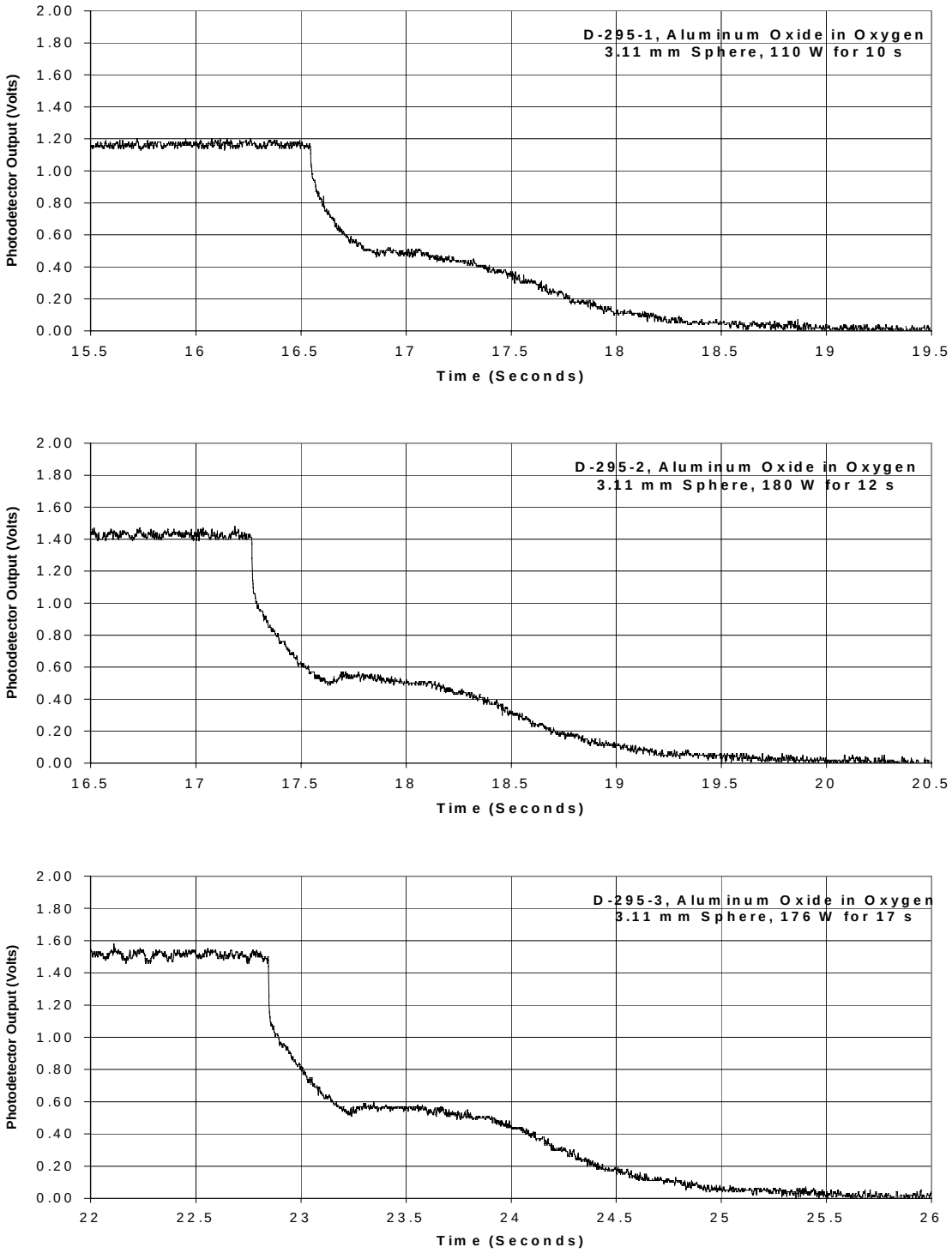


Figure 21. The luminosity-time traces in Figure 17 replotted with expanded horizontal scales to show the solidification halts more clearly.

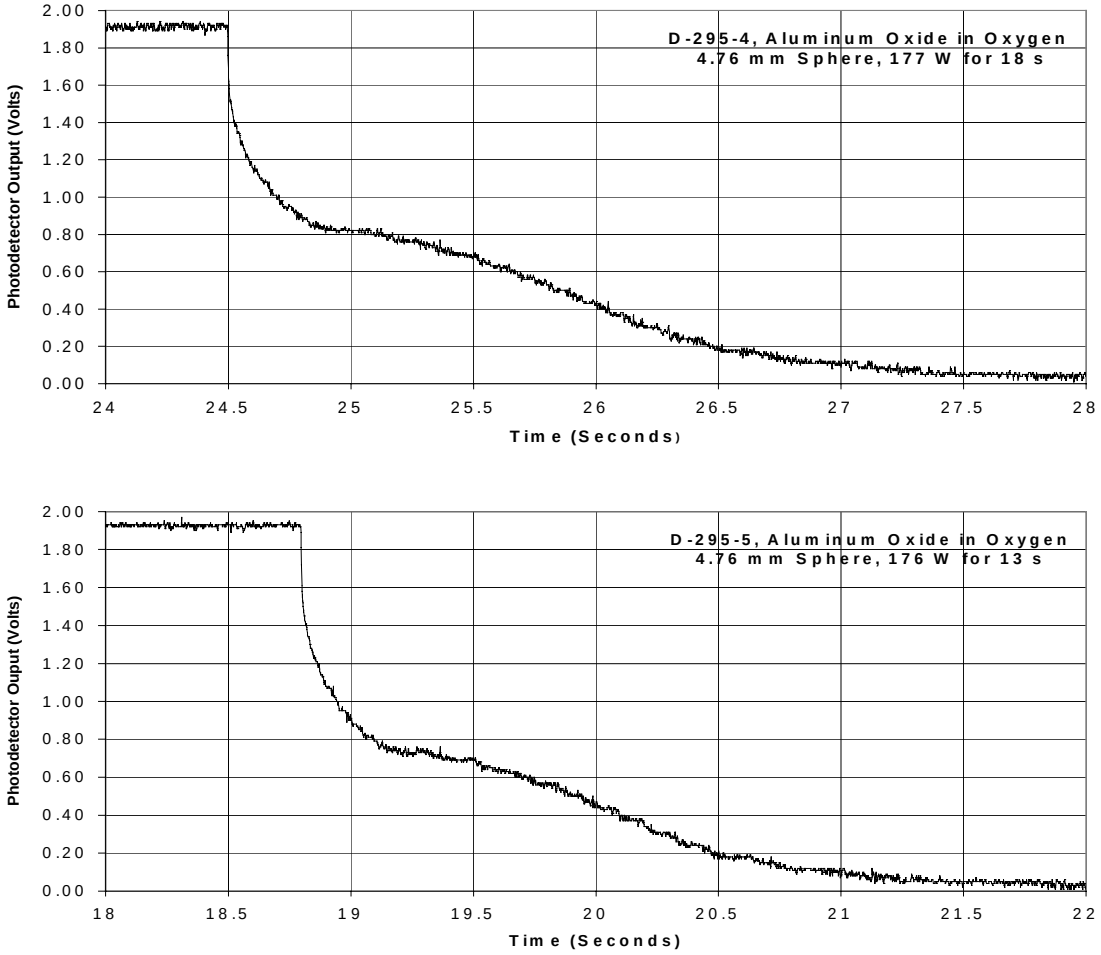


Figure 22. The luminosity-time traces in Figure 18 replotted with expanded horizontal scales to show the solidification halts more clearly.

Luminosity and Temperatures

In this section, we attempt to use the luminosities of solidifying aluminum oxide spheres to define a temperature on our luminosity-time traces. Figure 23 is a composite plot showing luminosity-time traces generated when samples of titanium (experiment D-292-3; see Figure 4), zirconium (experiment D-290-2; see Figure 5) and the alloy Zr_3Al (experiment D-290-3; see Figure 6) were heated in flowing oxygen with CO_2 laser powers between 65 W and 68 W for between 24 s and 29 s. Superimposed on this plot are two horizontal dashed lines that indicate the spread between maximum and minimum halt levels when 3.11 mm-diameter aluminum oxide spheres solidify at 2054 ^{o}C; these values are 0.56 V and 0.31 V, respectively, taken from Table 8. The luminosities of each of the four materials were recorded with standard optical conditions (SOC).

Note that the luminosity of the solidifying aluminum oxide was much lower than the maximum luminosities generated during the combustion of the metals. It is likely that the combustion temperatures of the metals are closer to 3000 ^{o}C and thus emit much more strongly than the solidifying aluminum oxide.

(Note the brief halt during the ignition of the titanium sample in experiment D-292-3; see Figures 4 and 23. It is possible that this corresponds to the melting temperature of titanium, 1660 ^{o}C.)

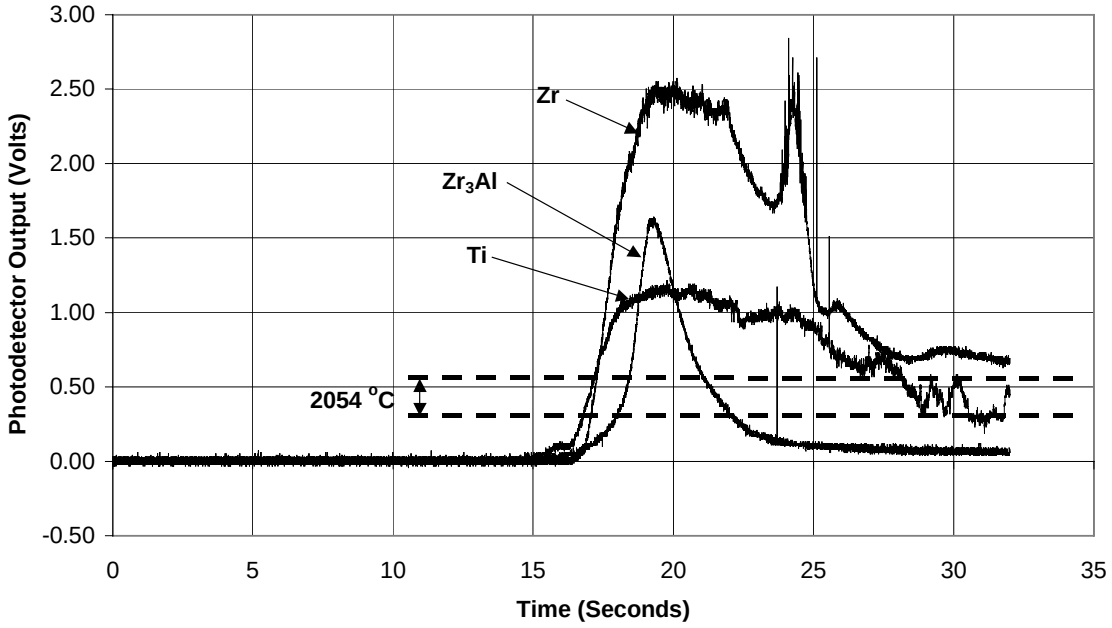


Figure 23. Composite plot showing luminosity-time traces generated when samples of titanium (experiment D-292-3; see Figure 4), zirconium (experiment D-290-2; see Figure 5), and the alloy Zr_3Al (experiment D-290-3; see Figure 6) were heated in flowing oxygen with the CO_2 laser operating between 65 W and 68 W. Dashed lines indicate the maximum and minimum halt levels when 3.11 mm-diameter aluminum oxide spheres solidify at 2054 ^{O}C. All luminosities were recorded with standard optical conditions (SOC).

Suggested Future Activities

We propose these next steps as outlined in our previous letter reports (Nelson et al., 2001a, b):

1. Put the experimental program for DU on hold until a quantitative temperature calibration of the luminosity-time traces can be achieved.

2. Prepare a report of the results obtained during the program for 2001/2002.

3. Request additional funding of about $18K to purchase the Pyro fiber optic automatic emissivity-correcting IR thermometer. If this instrument performs according to the manufacturer's descriptions, it should provide the quantitative information required to complete the program.

4. Continue the program during 2002/2003 based on consultations with the sponsor.

We have developed and tested a technique that provides unique but only semi-quantitative information about the ignition and combustion of metals. Our prediction that "halts" produced by the melting and solidification of the metals, their oxidation products and standard materials could be used to convert luminosities into temperatures did not materialize as quantitatively as hoped. It seems unwise, therefore, to start experiments with DU without being able to provide accurate temperature-time information.

Fiber Optic Pyrometer

We believe that the fiber optic automatic emissivity-correcting infrared thermometer marketed by the Pyrometer Instrument Company, Northvale, NJ, would provide excellent temperature-time measurements during the ignition and combustion of metal samples. The manufacturer claims the following for this instrument:

- Several temperature ranges are available, one of which is 900 ^{o}C to 3000 ^{o}C.
- The instrument uses fiber optics to measure temperatures of targets as small as 1 mm.
- The instrument generates temperature measurements at a rate of 37 per second (27 ms per data point).
- The fiber optics system uses pulsed laser emission to automatically correct each temperature measurement for the instantaneous emissivity of the sample.
- The fiber optics system provides accurate aiming via a light beam projected in reverse through the fiber optics.
- The accuracy of the temperature measurements after the emissivity corrections is ± 3 ^{o}C.

If the purchase of the pyrometer is possible, adequate time should be allowed for ordering and delivery in order to continue the experiments in the spring of 2002.

Calibration of Luminosities with Solidification of Other Materials

In Figure 23, the luminosity produced when molten aluminum oxide solidifies at 2054 ^{o}C is considerably lower than the maximum luminosities emitted when titanium, zirconium and the alloy, Zr_3Al, are heated in oxygen. It would be desirable to add other halt levels produced during the solidification of other materials with melting temperatures higher than aluminum oxide. We suggest that the solidification of other molten oxides, for example,

- Yttrium oxide, Y_2O_3, with a solidification temperature of 2439 ^{o}C (Foex, 1977)
- Calcium oxide, CaO, with a solidification temperature of 2580 ^{o}C (Yamada et al., 1986),
- Zirconium oxide, ZrO_2 with a solidification temperature of 2715 ^{o}C or Y_2O_3-stabilized ZrO_2 (Akapov et al., 2001)
- Magnesium oxide, MgO, with a solidification temperature of 2957 ^{o}C (Valyano et al., 1992)

might provide useful halts that would span the luminosity range indicated in Figure 23. Because radiant heating has been used to study the melting-solidification transitions of these oxides (Y_2O_3 was melted with a solar furnace (Foex, 1977), CaO with a xenon lamp imaging furnace (Yamada et al., 1986) and ZrO_2, Y_2O_3–stabilized ZrO_2 and MgO with a CO_2 laser (Akapov et al., 2001, Valyano et al., 1992)), it is possible that our laser heating techniques also could be used to melt these oxides.

There are also metals that melt/solidify in the same range of temperatures as those achieved when titanium, zirconium and the Zr_3Al alloy are heated in oxygen and nitrogen. Examples are:

- Tungsten, with a solidification temperature of 3410 ^{o}C, and

- Tantalum with a solidification temperature of 2996 ^{o}C.

Our laser heating techniques might not succeed as well with the metals because heating must be done in an inert atmosphere, such as argon, the metals may reflect the radiation from the CO_2 laser and at these very high temperatures there might be reaction between the metal and the graphite support.

If we succeed in obtaining the fiber optic pyrometer, we envision using the solidification of several of these refractory materials to check its operation and calibration. Of particular importance will be the solidification of molten aluminum oxide at 2054 ^{o}C and yttrium oxide at 2439 ^{o}C, because both oxides are regarded as standard materials (Schneider, 1970; Foex, 1977).

Direct Video Imaging of the Samples

During this program, the video camera primarily provided overall imaging of the experimental area. The videorecords allowed us to determine times for various events, for example, the beginning and end of laser heating, the onset and duration of sparking or unusual luminosities. There is little information about the behavior of the heated samples themselves, however.

We suggest that when the experiments are restarted, a second video camera be added to provide direct high magnification imaging of the samples during heating, ignition and combustion. Perhaps the imaging can be done with fiber optics to obtain close-in viewing, especially with the DU experiments which must be performed in an enclosure. If the 3 mm-diameter sample fills a large portion of the video image, it should be possible to observe melting and solidification during ignition and combustion, ejection of smoke and sparks, movements of the samples during heating, and to determine the amounts of molten phase present during melting of standard substances such as aluminum oxide. Because of the intense luminosities at these temperatures, it would be necessary for this camera to view the samples through one or more heavy optical filters. Since both cameras will provide imaging at rates of 30 frames per second, they should nicely complement the proposed fiber optic pyrometer that makes 37 temperature measurements per second. It is likely that the three devices can be synchronized with one or more photoflash discharges.

A second and very important advantage of viewing with the second camera is one of safety for the operators. Thus a highly magnified image can be viewed on one or more video monitors without the eye hazards involved with direct viewing of the intensely emitting specimen.

Experiments at Lower Laser Powers

In the experiments performed during this program, we heated the samples of metal with laser powers between ~65 W and ~180 W. In retrospect, we feel that even the lowest powers may have been too high to correctly subject the samples to temperature conditions representative of a fire environment. Although we cannot tell for sure, we believe the initial temperatures of the metals may have been far above those produced in a fire environment, which are about 1000 ^{o}C.

The fiber optic pyrometer should be able to determine initial temperatures typical of fire environments, because the range of the instrument we are considering is 900 ^{o}C to 3000 ^{o}C. If, as we suspect, the output power of the CO_2 laser is too high, we may be able to reduce it somewhat by lowering the discharge current, although at ~65 W we seem to be approaching the lower limit for stable operation of the discharge through the lasering gas mixture. It may be necessary to operate the laser at a higher power where the discharge is stable and then use a beam splitter to discard a predetermined fraction of the beam into an absorbing cavity in a water-cooled block and use the remainder for heating the samples. Our beam calorimeter (see Figure 2) can measure powers as low as 10 W.

Experiments in Other Oxidizing Atmospheres

Up to this point, we have heated metals in only two gaseous atmospheres—flowing oxygen and flowing nitrogen, both at a local atmospheric pressure of ~0.1 MPa. We have not studied other atmospheres that might be present in typical fire atmospheres, for example, carbon monoxide, carbon dioxide and water vapor. Moreover, we have not attempted gaseous mixtures, the most significant of which would be air. Also, we have not considered the important reduction of the local atmospheric pressures of the oxidizing gases at higher altitude test sites (for example, ~0.085 MP in New Mexico) compared to those closer to sea level (for example, ~0.1 MPa in Madison).

When the experiments are resumed, it would seem wise to perform experiments in one or more of these other oxidizing atmospheres. Perhaps experiments in oxygen and nitrogen and other oxidizing gases and mixtures at reduced pressures would also be valuable.

Experiments with DU

We have made significant preparations for experiments with DU. Some of the accomplishments are:

- We have established working relations with the radiation safety and health physics department at the University of Wisconsin-Madison.

- Fifty 0.5 g samples of metallic DU have been received from Los Alamos National Laboratory and are being stored by the University of Wisconsin's Radiation Safety Officer.

- The protocol for performing the proposed experiments with DU in our laboratory at the University of Wisconsin-Madison has been prepared with guidance from radiation safety and health physics personnel. This protocol has been submitted to and subsequently approved by the Nuclear Regulatory Commission, Washington, DC.

- We have designed, constructed and are testing a prototype combustion chamber for CO_2 laser heating of DU in a flowing gas that will retain all combustion products: solids, aerosols, splatter and sparks. A photograph of this prototype chamber is shown in Figure 24. This chamber consists of: (a) a transparent cylinder with (b) a bottom cover plate on which a graphite block rests, and (c) an upper cover plate with a gas inlet and outlet and a centered KCl window to admit the focused CO_2 laser beam. The sample of DU would be positioned at the focus of the laser in a depression in the graphite block.

  In its final version, the cover plate would be fitted with two additional optical windows, one for viewing the heated sample with the high-magnification video camera, and the other for viewing it with the fiber optic pyrometer. The gas outlet would lead to appropriate HEPA filters for total retention of any particulate matter, spatter or aerosolized material. Also, the chamber could be operated at a lowered internal gas pressure to duplicate the local atmospheric pressures of higher altitude test sites.

  It will be important to check the operation of the chamber with a non-toxic, non-radioactive metal, probably titanium, before proceeding with the DU.

Figure 24. Prototype combustion chamber for CO_2 laser-heating of DU in a flowing gas. It consists of: (a) a transparent cylinder with (b) a bottom cover plate on which a graphite block rests, and (c) an upper cover plate with gas inlet and outlet and a centered KCl window to admit the laser beam. The cover plate also would be fitted with two other windows for viewing the heated sample with a close-up video camera and with a fiber optic pyrometer. The gas outlet would lead to appropriate filters for retention of sparks, spatter and aerosolized material.

CONCLUSIONS

The CO_2 laser heating technique developed at the University of Wisconsin-Madison during 2001 provides excellent capabilities for studying the ignition and combustion of metals. The principal output generated by the technique, luminosity-time traces, at present offers valuable semi-quantitative information about these high temperature processes. The technique has a serious shortcoming, however--that these records cannot be converted reliably to temperature-time traces, the desired end product of the studies. Although we hoped to make these conversions on the basis of luminosities emitted during the melting and solidification of

(a) the metals and their oxidation products, and

(b) standard substances such as aluminum oxide (solidifies at 2054 ^{o}C),

we have concluded that a high-speed pyrometer is needed before studies of DU can continue.

From the luminosity-time traces recorded during the CO_2 laser heating of titanium, zirconium and the alloy Zr_3Al in both oxygen and nitrogen and from examination of the reaction products recovered after solidification, we conclude tentatively that:

- The melting temperature of a metal may not necessarily play a governing role in its ignition.
- Neither zirconium nor the alloy Zr_3Al will provide a good substitute for DU in a fire environment.
- At present, titanium seems the best candidate for the proxy metal.

DU experiments are ready to start but must remain on hold until accurate temperature calibrations of the ignition and combustion of the metals can be achieved.

REFERENCES

Akopov, F. A., Val'ano. G. E., Vorob'v, A. Y., Mineev, V. N., Petrov, V. A, Chernyshov, A. P., and Chernyshov, G. P., 2001, "Rapid Solidification Of ZrO_2-8 Mol% Y_2O_3 Melt," High Temperature (Engl. Trans.) 39 (6): 846-855 Nov.-Dec.

Causey, A. R., et al., 1977, "Irradiation Response of the Ordered Phase Zr_3Al", STP 633-ASTM, 437-454.

Foex, M., 1977, "Research on the Melting Point of Yttrium Oxide," High Temp. High Pressures 9 (3) 269-282.

Nelson, L. S., 1965, "Nature of the Spearpoints Observed During the Combustion of Zirconium Droplets," Nature 207, 741.

Nelson, L. S., Richardson, N. L., Skaggs, S. R., and Keil, K., 1973, "Effects of Oxygen and Argon Atmospheres on Pendant Drops of Aluminum Oxide Melted with Carbon Dioxide Laser Radiation," High Temp. Sci., 5, 138-154.

Nelson, L. S., Brooks, P.W., Bonazza, R., and Corradini, M. L., 2001a, Studies of Metal Combustion, Draft Letter Report submitted to Sandia National Laboratories, Albuquerque, NM, October 1, 2001.

Nelson, L. S., Brooks, P.W., Bonazza, R., and Corradini, M. L., 2001b, Studies of Metal Combustion, Draft Letter Report submitted to Sandia National Laboratories, Albuquerque, NM, December 31, 2001.

Runyan, C. C., Moulder J. C., and Clark, A. F., 1974, "Time-Resolved Spectra of Bulk Titanium Combustion," Combustion and Flame 23, 129-133; see also Moulder J. C., and Clark, A. F., 1977, "Time-Resolved Spectroscopy of Laser-Initiated Metal Combustion," Optical Engineering 16, 393-398.

Schneider, S. J., 1970, "Cooperative Determination of the Melting Point of Alumina," Pure Appl. Chem. 21, 117-122.

Valyano, G. E., Vorobev, A. Y., Petrov, V. A., Titov, V. E., and Chernyshev, A. P., 1992, "Investigation of the Melting and Solidification Temperatures of Magnesia During Radiant Heating with a CO_2 Laser," High Temperature (Engl. Trans.) 30 (5): 761-765, Sep.-Oct.

Weber, J. K. R, Nordine, P. C, and Krishnan, S., 1995, "Effects of Melt Chemistry on the Spectral Absorption-Coefficient of Molten Aluminum-Oxide," Journal of the American Ceramic Society, 78, (11), 3067-3071, Nov.

Yamada, T., Yoshimura, M., and Somiya, S., 1986, "Reinvestigation of the Solidification Point Of CaO by Digital Pyrometry," Journal of the American Ceramic Society 69 (10), C243-C245, Oct.