Paul A. Temple was born in East Chain, MN, on January 21, 1940. He received the B.A. degree in mathematics from Mankato State University, Mankato, MN, and the M.S. and Ph.D. degrees in physics from Iowa State University, Ames, and Kansas State University, Manhattan, respectively.

He was a member of the faculty of the Physics Department of Northwest Missouri State University, Maryville, from 1965 until 1976. In 1974 he received a National Research Council

Post-Doctoral Fellowship for research on the electronic properties of metal surfaces, within the Research Department of the Naval Weapons Center, China Lake, CA, where he has been a permanent Staff Member since 1976. He is a Member of the Advanced Optical Technology Branch, with major interests in the characterization of low absorption optical materials and in the investigation of laser damage mechanisms in dielectrics and metals.

M. J. Soileau, photograph and biography not available at the time of publication.

Effect of Surface Preparation Methods on Laser-Induced Pitting of Copper Mirrors at the 10.6 μm Wavelength

STEVEN C. SEITEL, JAMES O. PORTEUS, DONALD L. DECKER, WILLIAM N. FAITH,
AND DARRELL J. GRANDJEAN

Abstract—Ten precision Cu laser mirrors prepared by eight different methods were evaluated at 10.6 μm for resistance to spatially selective laser-induced damage (pitting). Surfaces essentially free of pitting and with melt thresholds close to that of intrinsic Cu were produced by electron-beam melting bulk Cu, followed by diamond turning; by diamond turning with a 20° negative top rake angle; by chemical vapor deposition of pure Cu on a diamond-turned Cu substrate; and by polishing bulk Cu on a hard lap with high pressure. The electron-beam melted surface was the most damage resistant, but residual stresses left by the melting process degraded the optical surface figure. A special cleaning method was developed to remove optically absorbing contaminants trapped by surface defects.

I. INTRODUCTION

Spatially selective laser-induced damage is the premature failure at isolated "weak points" of a figured optical surface. It may occur at fluences much lower than necessary to damage the surrounding surface. In Cu laser mirrors evaluated at infrared wavelengths [1], [2], the usual manifestation is one or more small surface pits, occurring away from the point of maximum fluence. In this paper, the terms "selective damage" and "pitting" are interchangeable. Pitting is believed due to randomly distributed surface defects [2]. Some are easily recognized as scratches or depressions, and some are too

small or too subtle to be identified with a Nomarski phase contrast microscope.

In small-spot laser damage studies of Cu mirrors reported from this laboratory [1]–[8], it was possible to extract damage thresholds which were characteristic of a defect-free surface. Selective failures did not occur often enough to alter appreciably these "uniform" values provided that the irradiated spot size was small compared to the average separation of defects. The distinction between selective and uniform damage is lost when spot size approaches defect separation (typically 1 mm). In large-spot applications, defect-related selective damage very well may be the factor which limits mirror performance. The problem is not confined to Cu mirrors. Similar effects have been observed in dielectric mirrors prepared on metallic substrates [9] and in antireflection-coated LiNbO₃ Q-switches [10], [11].

Attempts to minimize pitting in Cu mirrors by methods which reduce defect count or size have been reported. Vapor deposition of Cu on SiC substrates produced a surface remarkably free of pitting, but the uniform melt threshold was lowered by the relatively low thermal conductivity of the substrate [5]. Visibly perfect surfaces were prepared by diamond machining high-density forged Cu [2]. However, these surfaces pitted frequently, suggesting that forging reduces defect size but increases concentration.

This paper reports laser damage measurements made on Cu mirrors prepared by a number of different methods in a fur-

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The authors are with the Naval Weapons Center, China Lake, CA 93555.

ther attempt to reduce pitting. Uniform damage thresholds for surface melting, slip, and light emission were measured to establish basic mirror performance. Susceptibility to pitting was then determined by exposing many sites at low fluence. Finally, a special cleaning procedure was tested for efficacy in reducing selective damage.

II. EXPERIMENTAL

Testing was performed in the Laser Damage Facility at the Naval Weapons Center (NWC). A detailed description of the experimental arrangement for this study is given by Porteus *et al.* in a companion paper in this issue [4]. Briefly, the sample to be tested was placed in an evacuable chamber, and laser radiation was focused on the surface with a lens. The target surface was observed before, during, and after irradiation by means of a 20 power microscope.

The 10.6 μm radiation source was a single-mode, single-frequency CO_2 laser obtained by hybridizing a Lumonics pulsed TEA laser with a low-pressure continuous wave discharge section in the same optical cavity [12]. A single transverse mode was selected with an aperture. The frequency spread of the Doppler-broadened gain profile in the low-pressure section was smaller than the separation of adjacent longitudinal cavity modes. Thus, when operated above the lasing threshold, the low-pressure section provided a well-defined, single-mode "start" flux to the pulsed TEA section.

The output pulse was approximately 2 μs in duration, as shown in Fig. 1. The gain-switched spike characteristic of conventional pulsed TEA lasers has been suppressed almost completely, and there is no evidence of longitudinal mode beating. The spatial distribution of radiation at the target surface was very nearly Gaussian, as shown in Fig. 2. The spot diameter, measured at the $1/e^2$ intensity points, was 238 μm .

Sample preparation methods are identified by type in Table I. At least one sample of each type was prepared in this laboratory or elsewhere.¹ Substrates were bulk Cu and Mo, and in one case, Mo, to which a thin sheet of Cu had been brazed. Surface processing methods included some that had shown promise in earlier measurements [5], [13] such as chemical vapor deposition (type 6) and sputter deposition with dispersion hardening (type 7). The vapor-deposited Cu was applied on a 2 μm thick layer to a diamond-machined Cu substrate, with no additional finishing. The dispersion-hardened Cu was sputtered onto a polished Mo substrate and subsequently polished. Sample types 4 and 8 were prepared by melting the surface with a scanning electron beam and finishing by diamond machining. It was difficult to produce an acceptable optical finish on these samples, since the substrate surface had been distorted as much as 0.25 mm by

Fig. 1. Temporal shape of the CO_2 hybrid laser pulse. The first peak is the vestige of a gain-switched spike. Full width at half peak intensity is 2 μs .

Fig. 2. Pinhole scan across the CO_2 hybrid laser pulse in the target plane. The error bars represent one standard deviation in the average of five consecutive pulses at each position. The solid line represents the least squares best fit Gaussian.

the melting process. Two unconventional "hard"-finishing methods were included in the study. In both of these, the surface was deliberately cold-worked, either by high-pressure polishing of bulk Cu on a hard lap (type 2), or by diamond turning bulk Cu with a 20° negative top rake angle (type 3). Cold working has been shown to increase resistance to laser-induced surface slip, and the resulting distorted surface layer may also "heal" small defects in the starting material [2]. The Cu sample prepared by conventional polishing (type 1) provides a reference to the earlier work [2].

Duplicates of types 2 and 6 were used as controls in testing a special cleaning procedure designed to remove contaminants trapped by surface pits. Special cleaning consisted of a series of ultrasonic rinses in acetone which was then removed by blowing with clean, dry nitrogen. Just before testing, the samples were wet with clean acetone and dried by drawing a lens tissue in one direction over the surface. The risk of scratching or abrasion is significant, and special cleaning was applied only to those samples finished at NWC or where more than one

¹Sample type 1 was provided by Design Optics, Sunnyvale, CA; type 2, by AVCO-Everett Research Laboratories, Inc., Everett, MA; type 3, by NWC, China Lake, CA; and type 5, by Battelle Memorial Institute Pacific Northwest Laboratories, Richland, WA. Types 4 and 8 were prepared by United Technologies Research Center, East Hartford, CT, and diamond machined at NWC. Type 6 was prepared at NWC and overcoated by the Westinghouse Research and Development Center, Pittsburgh, PA. Type 7 was prepared by Battelle and diamond turned at NWC.

TABLE I
SAMPLE PREPARATION

Sample type	Substrate		Surface	
	Material	Fabrication	Process	Finish
1	Bulk Cu	Machined	{	Conventional polish
2				"Hard" polish
3				"Hard" diamond turning
4			Electron beam	Conventional diamond turning
5				Conventional diamond turning
6	Bulk Mo	Conventional diamond turning	Chemical vapor deposit	None
7		Polished	Dispersion-hardened sputter deposit	Conventional polish
8		Brazed sheet Cu	Electron beam	Conventional diamond turning

sample of a given type was available for testing. Samples not specially cleaned were blown off with nitrogen just before testing.

Uniform damage thresholds for light emission, surface slip, and surface melting were determined for each sample to establish basic mirror performance. Complete details of the procedure are presented in the companion paper [4]. Briefly, approximately 50 sites on the surface were exposed, each to a single pulse. The laser energy was varied from well below to well above the damage point, and threshold values were extracted from the data by maximum likelihood analysis [7].

Selective damage then was studied by exposing up to 300 sites on a 0.5 mm square grid at constant low energy. Fewer shots were required to evaluate those samples that damaged readily. Laser fluence was 225 ± 25 J/cm² for all samples, about half the melt threshold for intrinsic Cu in this case [4]. Since selective damage seldom occurred exactly on-axis, the actual fluence was less. The surface was viewed through the 20 power microscope during each exposure, and notation was made of visible surface changes, light emission, and whether or not an existing defect was involved. For example, a typical observation might be that a flash was observed at an existing off-axis pit and that the appearance of the pit was altered. Sites which damaged then were examined with a Nomarski phase contrast microscope to characterize the associated defects.

III. RESULTS

Basic mirror performance is summarized in Table II. A sample is identified by preparation type and by whether it was specially cleaned. Samples are ranked in decreasing order by melt threshold. The first five samples have melt thresholds greater than 400 J/cm². For comparison, the calculated threshold for intrinsic Cu is 415 J/cm² [4]. The brazed Cu on Mo sample, 8-A, damaged much more readily than the rest. This sample had a bluish color over much of its surface and, apparently, was degraded by the diffusion of brazing alloy to the surface during initial preparation. The high tabulated melt threshold for the conventionally polished sample 1-A is misleading, as explained below.

Table III contains the results of the selective damage tests. Samples are ranked according to the damage frequency, given

TABLE II
UNIFORM DAMAGE THRESHOLDS

Sample ^a	Threshold (J/cm ²)		
	Slip	Melt	Flash
4-A	259±15	442±16	472±13
3-A	196±5	439±17	484±11
5	175±11	426±24	464±23
2-A	200±21	424±12	486±13
6-A	297±9	411±8	419±5
2	118±17	397±10	473±54
1-A	111±12	394±29	159±18
7	231±13	367±3	455±16
6	206±11	355±35	457±11
8-A	57±5	173±22	207±29

^aA-Suffix indicates specially cleaned sample.

in the second column. This figure of merit was obtained by calculating the percentage of exposed sites with a permanent, highly localized, laser-induced change in appearance. Sites which only flashed were not included. The remaining columns are the raw data, tabulated by total number of sites exposed, by failure mode, and by whether failure occurred at an existing defect which was visible through the 20 power microscope.

The electron-beam melted sample 4-A pitted least and also had the highest melt threshold (cf. Table II), but was difficult to finish, as discussed previously. All three top-ranked samples were diamond turned to an optical finish at NWC at some point in their preparation [14]. It is important to note that the performance of a diamond-machined surface depends strongly upon turning technique and instrument accuracy, as well as upon the starting material, and, consequently, similar substrates machined in other laboratories may behave differently.

As shown at the bottom of the table, samples 8-A and 1-A pitted frequently. When these were examined with the Nomarski microscope, most of the "pitting" proved to be uniform surface failure by melting and massive surface slippage. This was to be expected for 8-A, since its uniform damage

TABLE III
SELECTIVE DAMAGE FREQUENCY^a

Sample ^b	Dmg. ^c freq. (%)	No. shots	No defect ^d			Defect ^d		
			Change	Flash	Both	Change	Flash	Both
4-A	1.0	295	1	3	2	0	3	0
3-A	1.4	295	3	2	0	1	1	0
6-A	1.9	267	0	0	2	0	1	3
2-A	2.4	294	3	0	0	4	9	0
7	4.8	294	8	10	1	4	2	1
6	9.1	298	10	1	14	2	9	1
2	9.9	132	4	7	5	4	9	0
5	13.9	287	29	16	6	3	9	2
1-A	67.6 ^e	37	0	7	25	0	2	0
8-A	77.0 ^e	113	37	1	50	0	0	0

^aTest was conducted at 225±25 J/cm².^bA-Suffix indicates specially cleaned sample.^cPercentage of sites with permanent surface change.^dVisible under 20X magnification.^eUniform damage.

thresholds were well below 225 J/cm². The discolored portions of the surface damaged far more often than the remainder. Uniform damage is also to be expected for the conventionally polished sample 1-A, but the reasoning is more complicated. The key observation here is that, for this sample only, the flash threshold is *less* than the tabulated melt threshold. Light emission corresponds to the formation of a highly absorbing surface plasma, which expands rapidly, exceeding the spot size in less than 100 ns [15]. Much of the laser pulse is intercepted by the plasma and coupled into the target over an enlarged area so that the peak fluence is reduced. For this reason, the significance of the tabulated melt threshold is questionable and should not be used to rank this particular sample.

A strong correlation between pitting and surface defects is not apparent in the raw data in Table III. Defects associated with selective damage are often too small to be observed at 20 power magnification. As an example, the left-hand micrograph in Fig. 3 shows a damage site on the top-ranked sample 4-A. In the upper left-hand corner, there is a scratch which may have been introduced during special cleaning. This scratch was not visible with the 20 power microscope, yet pits and flashes along it account for all the permanent changes and most of the flashes observed on this sample.

The right-hand side of Fig. 3 shows visible defects where flashes were observed on the vapor-deposited sample 6-A. These appear as small light spots on and just below the visible grain boundary. These defects do not necessarily originate in the deposited layer, which is only 2 μm thick. The thermal diffusion depth for Cu under the present conditions is about 19 μm so that substrate defects may contribute to selective damage.

Fig. 4 shows selective damage on the hard-finished samples.

Fig. 3. Nomarski micrographs of selective damage sites on the electron-melted bulk Cu sample 4-A (left) and on the chemical vapor-deposited Cu sample 6-A (right). Damage is described in the text.

On the diamond-turned sample 3-A, shown on the left, the damage is a ring of pits. These appear to be associated with dimple-like depressions, visible with the Nomarski microscope, which occurred outside the damaged area. These depressions may have acted as traps for contaminants or may have produced increased absorption as a result of their geometry. The right-hand side of Fig. 4 shows a large visible defect where a flash was observed on the hard-polished sample 2-A. The nature of the defect is not clear in this case.

There is evidence that special cleaning reduces the frequency of selective damage. Sample pairs 2, 2-A and 6, 6-A provide

Fig. 4. Nomarski micrographs of selective damage sites on the "hard" diamond-turned bulk Cu sample 3-A (left) and on the "hard"-polished bulk Cu sample 2-A (right). Damage is described in the text.

comparisons of nominally identical surfaces, with one surface from each pair being specially cleaned. In both cases, the cleaned sample damaged much less frequently. Also, the top four samples from Table II were specially cleaned, while the next four were not. The two lowest ranked samples were specially cleaned but failed uniformly, as described above. The fact that special cleaning reduces pitting suggests that failure often is due to contaminants trapped during mirror fabrication by surface voids or other defects, rather than to geometrical optical concentration by the defects themselves.

IV. CONCLUSIONS

Copper mirrors prepared by different methods were evaluated at $10.6\ \mu\text{m}$ for resistance to laser-induced selective damage and to determine the uniform damage thresholds. Since only one or, at most, two samples of each type were available for damage testing, the results presented here must be interpreted with caution. The data are not sufficient to say that one particular processing method tested is to be preferred above all others for producing defect-damage-resistant mirrors. Indeed, the optical quality of a surface is strongly dependent upon the skill of the preparer, the details of the finishing process, and the starting materials. Nominally identical samples prepared in different laboratories might rank differently. The significance of the results reported here is that essentially defect-free surfaces have been prepared by several new methods which offer the promise of improved copper mirror performance.

Electron-beam surface melting, followed by diamond machining and special cleaning, produced a surface free of pitting, except along a single scratch which may have been introduced during cleaning. This sample also had the highest melt threshold measured, being very close to the computed value for intrinsic Cu. It was difficult to produce a good optical surface on this sample because of substrate surface deformation.

Surfaces with good selective damage resistance and high melt thresholds also were produced by vapor deposition of

Cu on a diamond-machined bulk Cu substrate and by diamond turning bulk Cu with a 20° negative top rake angle. High-pressure polishing of Cu on a hard lap also produced a damage-resistant surface.

Special cleaning to remove optically absorbing contaminants trapped by surface defects improved selective damage resistance. Special cleaning may scratch the surface. Scratches, depressions, and other surface blemishes often obviously are associated with pitting; however, damage sometimes occurs at visibly perfect locations. Further studies using electron and surface analytical microscopy, together with small-spot selective damage testing, are required to identify the more subtle surface anomalies contributing to selective damage.

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Steven C. Seitel was born in Burbank, CA, on February 27, 1944. He received the Ph.D. degree in physics from Montana State University, Bozeman, in 1972.

He studied photodissociation of atmospheric molecules as a Post-Doctoral Research Associate at the Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder. Since 1974 he has been with the Naval Weapons Center, China Lake, CA. Presently he is a member of the Quantum Surface Dynamics Branch,

and his interests include laser component development, optical materials improvement, and nonlinear optical processes.

James O. Porteus was born in Wilmington, DE, on October 25, 1929. He received the B.S. degree from the University of Delaware, Newark, in 1951 and the Ph.D. degree from Cornell University, Ithaca, NY, in 1958, both in physics.

He joined the Naval Weapons Center, China Lake, CA, in 1959, where he became involved in surface physics research with emphasis on inelastic low-energy electron diffraction. In 1967 he became Head of the Quantum Surface

Dynamics Branch. Currently, he supervises and is actively engaged in research on the interaction of laser radiation with solid surfaces.

Dr. Porteus is a member of the American Physical Society, the American Vacuum Society, and Sigma Xi.

Donald L. Decker was born in Pomona, CA, on August 30, 1939. He received the B.S. degree in physics and mathematics in 1961, the M.S. degree in physical optics and solid-state physics, and the Ph.D. degree in experimental physics in 1968, all from the University of California, Riverside.

In 1968 he received a National Research Council Post-Doctoral Fellowship for work on the optical properties of the alkali metals, within the Research Department of the Naval Weapons Center, China Lake, CA. Since 1971 he has been a Permanent Staff Member. He is currently Head of the Advanced Optical Technology Branch, where his major research interest is in the fabrication and characterization of low optical absorption and low scatter optical components primarily for laser applications.

William N. Faith was born in Los Angeles, CA, on June 16, 1935. He received the A.A. degree in industrial arts from Ventura College, Ventura, CA, in 1955.

Since 1965 he has been with the Quantum Surface Dynamics Branch at the Naval Weapons Center, China Lake, CA. He is a specialist in ultrahigh vacuum technology and surface analysis and is currently engaged in laser damage studies.

Darrell J. Grandjean was born in Los Angeles, CA, on July 28, 1944. He received the A.S. degree in machine tool/metal working in 1974 from Cerro Coso Community College, Ridgecrest, CA.

He has been a Journeyman Craftsman in the machine tool and welding trades. He joined the Naval Weapons Center, China Lake, CA, in 1974, at which time his primary duties included design, fabrication, and testing of precision prototype hardware. Presently, he is a member of the Advanced Optical Technology Branch, where he is engaged in surface physics research with emphasis on single-point diamond machining, including the design of optical components, hardware, and fixturing associated with the submicro-inch toleranced diamond-machining field.