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ABSTRACT
This work reports on a pump–probe laser-based heating and sensing metrology to study the failure mechanisms of materials during extreme heat fluxes localized near surfaces, the localization of which is controlled by the focus of the laser beam and sensed by the reflection of a secondary probe laser. We focus the demonstration of these power density at failure tests on the damage mechanisms of commercially pure titanium metal during and after high heat fluxes induced from the absorbed laser energy. Using this steady-state thermoreflectance pump–probe metrology, a localized region of the material was irradiated at a low modulated frequency, while the average change in the thermoreflectance signal was monitored. We observe surface and cross-sectional oxidation of the titanium, revealing correlations between microstructural evolution events and shifts in thermoreflectance trends as a function of absorbed power density. Furthermore, the damage morphology was shown to be heavily influenced by the size of the heater (dictated by the radius of the pump laser beam), which controlled the relative degree of thermomechanical, melting, and oxidative decohesion failure mechanisms in the samples. The analysis of the temperature distribution coupled with the observed microstructural damage gives rise to a high-throughput experimental technique to induce desired deformation modes through cyclic thermal testing.

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I. INTRODUCTION
The fundamental thermophysical design of next-generation energy storage, power generation, manufacturing, and hypersonic systems relies on the understanding of material responses during high-temperature operation in order to take advantage of the high enthalpies, efficiencies, and energy densities intrinsic to these higher quality heat sources. Resultantly, with these extremely high temperatures come major challenges in understanding the durability and failure thresholds of materials in these extreme environments to ensure operational reliability and efficiency. Typically, structural and/or thermal materials used in extreme environment applications undergo laboratory-based testing under simulated environmental conditions within a controlled setting. However, typical thermal cycling tests involve lengthy experimentation periods—a disadvantage accompanied by high equipment costs and great efforts to maintain the severe test conditions throughout the duration of testing. Additionally, failure analysis following traditional cyclic testing is largely dependent on specimen geometry, among other parameters,
leading to inconsistency in reported material parameters such as yield strength and number of cycles to failure.\textsuperscript{25-26} 

Titanium and Ti alloys are widely used across a broad range of engineering applications due to their desirable material properties such as excellent corrosion resistance, high melting temperature, and a high strength-to-weight ratio.\textsuperscript{11,12} As a refractory metal, Ti readily forms its native passive oxide, which is both highly protective and extremely stable. However, the metal's exceptionally high affinity for oxygen, which imparts its ability to easily form and repair its protective oxide, leaves the metal–oxide system highly susceptible to deleterious oxidation events and altered material properties above intermediate temperatures, which have been well-studied phenomena since the work of Kofstad.\textsuperscript{13-17} Furthermore, the ubiquity of Ti in aerospace, marine, automotive, and microelectronic applications\textsuperscript{11,12,26,27} has facilitated thermal cycling studies in both ambient and elevated temperatures in order to assess thermal fatigue properties and develop lifetime predictions.\textsuperscript{18-21} In this work, we develop a pump–probe laser-based heating and sensing metrology to study the deformation and failure mechanisms of un-alloyed titanium during extreme heat fluxes localized near surfaces. Pump–probe techniques such as time-domain thermoreflectance (TDTR)\textsuperscript{22-24} and steady-state thermoreflectance (SSTR)\textsuperscript{25,26} are commonly used to characterize the thermal properties of a material by monitoring thermoreflectance changes as a function of time or laser power, respectively. However, these pump–probe thermoreflectance methodologies traditionally operate in pump power regimes that induce small perturbations in the sample temperature, avoiding temperature changes that are much greater than a few percent of ambient and thus leading to irreversible material changes.

While laser surface engineering and ablation studies of materials have been performed for several decades,\textsuperscript{27-33} few have exploited the use of high-powered, continuous wave (CW) lasers modulated at low frequencies with locked-in probe lasers as sensors. These testing methods effectively produce the standard 1000-cycle thermal fatigue test in mere minutes. Using this technique, high-throughput capabilities may produce an accelerated assessment of damage and failure thresholds under various conditions. Additionally, with beam spot sizes on the order of micrometers to tens of micrometers and a heat penetration depth on the order of the beam radius,\textsuperscript{26,34} there are very few limitations on material sizes and geometries in order to perform these tests, contrasting with traditional cyclic and thermomechanical testing techniques. This enhanced precision is particularly favorable in the case of testing non-commercial materials with limited availability during early development, such as novel additively manufactured compositions\textsuperscript{35-37} and high-entropy materials,\textsuperscript{38-40} in which destructive testing may be deprioritized due to material availability and fabrication costs in specialized facilities.

Rooted in temperature-dependent changes of the material’s dielectric function, any changes in electronic band structure, microstructure, defect densities, interfaces, phase, chemical composition, etc., can impact the thermoreflectance coefficient. Our metrology described herein relies on the monitoring of the change in thermoreflectance of localized, intensely heated surfaces in order to determine the onset of irreversible reactions and damage in the heated volume of the material. Large pump power densities are purposely used to induce non-perturbative temperature rises, i.e., near surface, on commercially pure (CP) bulk titanium. The material can reach predicted temperature rises several times those of ambient, which facilitate thermomechanical and thermochemical changes. The localization of these induced microstructural changes is controlled by the focus of a CW pump laser beam heat source and a secondary CW probe laser sensor, utilizing similar detection schemes to the recently developed SSTR technique.\textsuperscript{26} The pump beam is modulated at a low frequency allowing the sample surface to either reach the steady state with a time-invariant temperature gradient during beam exposure or otherwise damage during heating. The thermoreflectance change thus provides a means to utilize optical methods to elucidate the laser-induced damage threshold of a material using lock-in detection to track and record the thermoreflectance of the reflected probe laser. This approach has the advantage of achieving ultrahigh heat fluxes typical in extreme environments, such as hypersonic transport and reentry, and sensing energy density changes in material failure without the spatial limitation indicative of traditional emissivity-based pyrometry. The aforementioned practical limitations commonly associated with high-temperature testing are inherently reduced using these methods, which entail extremely high-throughput cyclic testing and thermal damage initiation in frequency-modulated simulated environments comparable to service and operational conditions.

We focus on the demonstration of these “power density at failure” tests on studying the material response and deformation mechanisms of bulk titanium during and after induced high heat fluxes from the absorbed laser energy, again as measured through the thermoreflectance signal of the probe. As will be discussed in more detail in Secs. III and IV, the thermoreflectance profiles suggest that the power density at the onset of damage in titanium correlates to a temperature rise well below the predicted melting temperature of titanium. Thus, our metrology also necessarily includes post-mortem characterization of the thermally cycled sample surfaces, in which the thermomechanical, thermochemical, and thermal fatigue damage features are analyzed to determine the sample-specific catastrophic failure mechanism, or combination thereof. Furthermore, through variation of the heater spot size between power density at failure measurements, we gained the ability to study the role of the geometry of the hot spot relative to the sample surface on thermal failure. In terms of measurable parameters within the scope of this work, this relationship was examined through the effects of heat flux and distribution within the hot spot on the spatially resolved damage morphology.

This paper is organized as follows: in Sec. II, we detail our experimental apparatus and analysis procedure. More specifically, we describe our technique to measure the power density at failure for bulk CP Ti, through \textit{in situ} monitoring of the reflected laser probe response during pump laser heating. Next, the results of the power density at failure measurements and sample characterization images are presented and related to their respective testing conditions, i.e., pump power and spot size. The thermal damage on the Ti samples was evaluated through post-mortem microstructural analysis as described previously. The likely failure mechanisms are discussed in terms of heater size and depth, which in turn relate the heat-transfer mechanisms, oxidation kinetics, and mechanical behavior to the resultant damage morphology. We conclude by proposing a means to predict the power density at failure through analysis of the common trends in signal response and temperature rise across all testing conditions.


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II. METHODS

The experimental setup is centered around a CW solid-state pump laser (Spectra-Physics® Millenia eV™) and a CW diode probe laser (Coherent® OBIS LX™). The output power range of the pump laser is 0.5–15 W at a wavelength of 532 nm, while the output range of the probe laser is 1–100 mW at a wavelength of 785 nm. To produce the modulated heating event on the sample surface while still allowing long enough time during pump exposure for the sample to reach the steady state, the pump beam was modulated using an optical chopper (Thorlabs MC2000B), producing a square wave at a frequency of 100 Hz. The modulation of the pump is kept constant at 100 Hz for all heating events in this study. The incident probe power was maintained below 10 mW, with a radius of approximately 10 μm to ensure negligible heating introduced by the probe beam (<10 K). The pump and probe lasers are overlapped near the sample surface using a longpass dichroic mirror (Thorlabs DMLP550) and were subsequently focused through an objective lens to the sample. The reflected probe beam was back-aligned along its forward path to a photodetector (Thorlabs DET10A), which was connected to the lock-in amplifier (LIA) (Stanford Research Systems SR830) synced to the modulation frequency of the pump and set to a sensitivity of 20 mV/nA. The LIA signal was maximized, optimizing the pump–probe overlap at the targeted region of the sample.

The experimental samples used in this study were 0.25-mm thick CP titanium foils (99.99% Ti) purchased from Sigma Aldrich. The foil surfaces were prepared by mechanical polishing to a mirror surface finish using progressions of abrasive SiC papers and diamond particle slurries, up to grades 1200-grit and 0.3-μm particle size, respectively. The samples were measured within a stainless-steel chamber with an embedded 0.5-in. thick quartz optical transmission window (Thorlabs UDP05). A reduced-oxygen test environment was created by purging the test chamber with ultra-high purity argon gas (Praxair 99.999% Ar) for 10 min prior to experimentation, then maintaining gas flow throughout the duration of testing. The heater size was varied through the use of objective lenses of different magnifications, utilizing the spot-size variability of the pump focused through a 10×, 5×, or 2× objective. The sample sets are referred to as Ti-4, Ti-6, or Ti-18, categorized according to the pump focused through a 10×, 5×, or 2× objective. The sample sets are referred to as Ti-4, Ti-6, or Ti-18, categorized according to the incident pump radius under which the sample was irradiated.

The pump and probe radii at the sample surface were measured using the knife-edge technique.41

Initial experimentation involved varying the pump power density and monitoring the thermoreflectance signal from the reflected probe as a function of the absorbed power density. The signal amplitude measured by the LIA was monitored as the absorbed pump power was increased by 3–10 mW every 30 s stepwise, sweeping through the pump output power range. The calibration procedure is further described in Sec. A of the supplementary material.

We develop the following critical-point analysis of each thermoreflectance profile to identify the power densities at which deviations in signal rise behavior occurred. The power densities at which the first derivative of the signal profile, $\frac{d\Delta R}{dp}$, was undefined or equal to zero, were designated as a critical point, $p_{x,n}$, where $x$ refers to the sample name which in turn refers to the pump radius, and $n$ refers to the position that the critical point occurs in sequence (Fig. 1 and Fig. S2 in the supplementary material). In the lower perturbation regime, the thermoreflectance of metals is well known to vary linearly with temperature.42 However, upon non-perturbative heating leading to large temperature rises, nonlinearities in thermoreflectance can occur.43 Thus, $p_{x,n}$ represents the onset of non-perturbative heating of the metal. Beyond this transition to non-perturbative heating, multiple undefined points were identified in sequence within select regions of continued increased power, such as in the profile around $p_{x,iii}$ shown in Fig. 1, as well as within raw data exhibiting both noise and measurement error. Our previous work identified strong undulations in thermoreflectance signals of thin gold films to be related to gold delamination from the substrate and thus an onset of a failure mechanism.44 We thus posit that this region of large fluctuating changes in our thermoreflectance signal is indicative of early stages of sample damage, and thus further proceduralize our analysis of these data here in terms of a critical-point analysis. To provide a more rigorous definition of the critical points, the signal profiles were further analyzed through the second derivative, $\frac{d^2\Delta R}{dp^2}$. Within each cluster of potential critical points identified through the first derivative, a transition exists in which a positive second derivative transitions to a negative value, which rapidly transitions to a positive value until the next set of potential critical points; i.e., around the discontinuous regions of the function. In other words, the overall positive curvature of the profile briefly transitions to a negative curvature, then
returns to positive at a defined point. This point was designated as the critical point, or critical power density, as the point delineates the proposed threshold power density at which a new morphological process is thought to initiate; this topic is expounded further in the upcoming analysis.

The critical points were subsequently evaluated to identify the power density values near the onset of damage, as evidenced by a decay in signal or through other observed shifts in trend as described above. Measurements were then performed on pristine samples in which the pump was stepped directly to a fluence near the suspected damage threshold and maintained constant for 30 s, allowing the irradiated sample to reach the steady-state temperature rise. After 30 s, the pump beam was fully blocked from the sample, which was then left to cool to ambient temperature within the test chamber before removal.

Post-mortem analyses were conducted using scanning electron microscopy (SEM) in conjunction with focused ion beam (FIB) milling for imaging of the surfaces and cross-sectional damage profiles. Back-scattered and secondary-electron images were collected at an accelerating voltage of 15 kV using a FEI Quanta 650 ESEM and a FEI Helios UC G4 Dual-Beam FIB. Cross sections were obtained using a Ga⁺ source to deposit an ∼1 μm thick protective carbon layer followed by ion milling through the region of damage. Energy-dispersive x-ray spectroscopy (EDS) was used to analyze the elemental composition of the regions of damage.

The average resultant temperature rise, $T$, of the sample during pump heating was approximated from the solution to the radially symmetric heat diffusion equation for a semi-infinite solid,

$$T = \frac{P A}{\pi \kappa r_i^2}, \quad \text{(1)}$$

where $P$ is the incident power, $A$ is the absorbance of the material, $r_i$ is the incident pump radius, and $x$ is the thermal conductivity of the material, which we measure at room temperature using TDTR to be $21 \pm 4 \text{ W m}^{-1} \text{ K}^{-1}$ for Ti in this study, which is consistent with literature values for the thermal conductivity of bulk Ti. Note, for a material that can be considered semi-infinite relative to the heater radius, $\epsilon$ is a constant given by $2 \sqrt{\pi}$. Temperature-dependent thermal conductivity studies of CP Ti in the literature report values between ∼17 and 25 W m$^{-1}$ K$^{-1}$ for measurements within the range of ∼73 and 1327 °C. Because these thermal conductivities vary relatively little within a very large temperature range, and because these values fall within the evaluated uncertainty of the measured Ti foil, the rate of change is thus evaluated using a constant thermal conductivity equal to the value measured at room temperature. The absorbed power, $PA$, is the absorbed fraction of the incident power, which was determined using the measured spectral reflectance of Ti metal determined using the calibration procedure as described in Sec. A of the supplementary material.

The average temperature rise at each power density was estimated using both Eq. (1) and the numerical solution to the heat equation subjected to a radially symmetric surface heating event, which allows us to predict the spatially variation temperature rise within the pump spot during laser heating to steady-state conditions.

### III. RESULTS

#### A. Thermoreflectance measurements

The thermoreflectance signal response, $\Delta R/R_0$, is shown in Fig. 2(a) as a function of pump power. The uncertainty in power density arises from the errors in the measured incident pump radius and fluence step size as well as from the uncertainty in the thermal conductivity of Ti, while the uncertainty in signal magnitude is the standard deviation of the average amplitude measured over five samples. We note that for thermoreflectance data acquired prior to material failure (e.g., prior to critical points in $\Delta R/R_0$), $R_0$ is relatively constant, and the change in signal is associated solely with the modulated response, $\Delta R$.

The power densities corresponding to critical values are designated as $p_{c,n}$, where $x$ is the pump beam radius and $n$ represents each critical-point iteration in sequence ($n = i, ii, iii, iv$), as described previously. These critical power densities are represented within Fig. 2(a) with filled symbols. Four common regimes bound by the critical...
B. Temperature profile

The heat flux through the Ti sample is visualized with temperature profiles (Fig. 3) calculated using the steady-state temperature rise model as described by Braun et al. The distributions demonstrate the temperature rise throughout the substrate at pk,x with respect to the radial position from the pump beam center. The maximum and average temperatures of the heated region at failure are estimated to be \(\sim 0.37T_m\) and \(\sim 0.24T_m\), respectively, again well below the melting temperature of pure Ti metal as observed using the previous method. Further, a larger temperature gradient exists through the penetration depth of the heater in the cross-plane direction than in the in-plane direction near the Ti surface, particularly in the Ti-4 and Ti-6 samples. Therefore, congruent melting of the bulk material in both the in-plane and cross-plane directions was deemed highly unlikely to be the failure mechanism exhibited under irradiation at these power densities.

C. Microstructural damage at the failure threshold

Representative SEM images are shown in Figs. 4(a)–4(c) of Ti surfaces irradiated at the recorded power density correlating to the measured data point immediately preceding pk,x, i.e., the power density correlating to the signal maximum, pk,x. Figures 4(d)–4(f) show the images of Ti surfaces irradiated at this power density at failure. The Ti-18 samples were imaged at 1000×, Ti-6 at 3000×, and Ti-4 at 5000×.

Prior to pk,x, a region of outward growth is observed on each sample surface, with a radius roughly on the order of the focused pump beam; this extrinsic growth is indicative of thermal oxidation of Ti metal. However, while cracking due to outward expansion is present on the Ti-4 and Ti-18 surface damage [Figs. 4(a) and 4(c)], a circular crack creating a recessed ring on the sample surface is observed around the deformation zone of Ti-6 [Fig. 4(b)].

At pk,x, the complete detachment of the damaged surface reveals a circular pit within each surface [Figs. 4(d)–4(f)]. The perimeter of the damage shows material with smoothed edges as well as small spheres surrounding the edges on the planar surface, suggesting partial melting of the material during the heating event. Concentric circles surround the Ti-18 pit and spread outward in a rippled fashion, providing further evidence of resolidified melt. Additionally, the Ti-18 sample shows apparent surface alteration beyond the spot radius on the Ti substrate, including a raised surface beyond the incident beam radius, and surface cracks expanding radially outward through this raised region until reaching the planar metal surface. The cracking observed on the Ti-4 and Ti-18 surfaces contrasted with the buckling within the Ti-6 surface suggests that the stress states within the Ti-6 bulk are opposite to those within the Ti-4 and Ti-18 bulk, leading to distinctly different failure mechanisms.

The cross-sectional SEM images and corresponding EDS maps are shown in Fig. 5. The cross sections reveal hemispherical pits with raised outer edges [Figs. 5(a)–5(c)] and varying levels of oxygen content [Figs. 5(d)–5(f)]. A distinct oxide layer lining the inner contour of the pit is visible within both the Ti-4 and Ti-6 samples [Figs. 5(d) and 5(e)]. Within the Ti-4 surface, a distinct, heavily oxidized layer is observed, with a mean thickness approaching 1 μm—significantly thicker than that of the native oxide thickness of 3–5 nm. However, as pump radius increases, this
oxide-enriched layer lying along the well of the Ti substrate becomes thinner relative to heater size [Figs. 5(b) and 6(c)]. Ti-4 oxide extends over the cracked edges of the pit, forming a continuous layer across the length of the irradiated region. In contrast, Ti-6 oxide is mapped primarily within the pit and on the Ti surface outside of the pit edges, i.e., preferentially located on either side of the cracked surface.

The Ti-18 EDS shows a vastly different composition compared to the former samples, in which the raised material surrounding the pit is composed primarily of Ti metal underneath a surface oxide layer. The material directly beneath the surface is heavily depleted in oxygen to a depth of the heater radius, beyond which another layer of the same thickness is located which has a higher oxygen content. Additionally, within Ti-18, multiple regions of subsurface cracking and voids are observed deep within the substrate [Fig. 5(c)], indicative of the stress states within the bulk which and their possible contribution to the observed failure mechanism.

IV. DISCUSSION

A. Microstructural-driven thermoreflectance response during laser-induced oxidation

The performed techniques utilize the temperature dependence of both the optical properties of the material and its microstructural
evolution, in that the thermoreflectance response of the titanium is related to the structural and chemical changes induced from laser heating. In order to elucidate a correlation between structural processes and the measured optical material properties, the estimated surface temperatures at each critical point are evaluated with consideration of the oxidation behavior observed in high-temperature oxidation studies, as described in the literature. The critical points are further discussed with regard to their potential as markers for shifts in material properties, i.e., as approximate thresholds marking the initiation points of certain structural processes. The thermoreflectance trends are then correlated to those reported in the literature as a function of temperature. As the sequence of critical power densities across all heater sizes were shown to induce a parallel sequence of approximate temperature rises, each critical point and the intermediate power density regimes are discussed in turn.

1. Critical points vs temperature

The trends observed within the initial regime and at power densities close to the failure threshold are corroborated through previous laser-irradiation and ablation studies. The linear rise observed in regime I indicates temperature rises proportionally to the rise in absorbed power, consistent with the proportional trend as predicted through established thermal models. The signal

FIG. 5. Cross-sectional SEM images of the resultant thermomechanical damage on the surface of and within the bulk of irradiated Ti: (a) Ti-4, (b) Ti-6, and (c) Ti-18. EDS mapping shows an oxygen-rich surface (green) indicating a diffusion-limited thermal oxide layer and significantly reduced oxygen content within the bulk Ti (red): (d) Ti-4, (e) Ti-6, and (f) Ti-18.
between the first critical point and mechanical failure. The latter two critical points suggest a relationship between the temperature rise at these power densities and the onset of intrinsic oxidation via oxygen diffusion from the extrinsic oxide through the bulk, which initiates at about 300 °C. At this temperature, some changes in oxide character observed within the literature are partial dissolution of the metastable oxides inducing a stoichiometric evolution into a surface oxide composed primarily of TiO$_{2}$, intrinsic oxidation of oxygen vacancies at the M–O interface, and, in the presence of a formed hydride, eutectoid transformation with the HCP α, BCC β, and δ hydride phases.

Another phenomenon observed in CP Ti at intermediate temperatures is that of creep deformation under stress and temperature. The boundary between the low- and high-temperature creep deformation occurs at 0.3T$_{m}$ (K) for Ti metal, this occurs at an approximate range of 300–318 °C. Classical creep and metallurgy studies of Ti report a regime initiating at approximately 200 °C in which specimens exhibited lower creep rates, dynamic strain aging, and work hardening/annealing recovery up until 315 °C.

The presence of multiple phases may be one contributing factor to melting point depression. Another possible mechanism considers the structure of the stable thermal oxide at 300 °C, TiO$_{2}$, which is a non-stoichiometric, porous oxide with a highly defective rock-salt structure. The diffusion of oxygen from the metastable oxide and across the metal–oxide interface may induce a lower effective melting temperature through the formation of vacancies within the crystalline solid. The thermal conductivity of this thermal oxide has been reported as 1.3 W m$^{-1}$ K$^{-1}$ far below the literature value of 8.5 W m$^{-1}$ K$^{-1}$ for the thermodynamically favored crystalline oxide, TiO$_{2}$, and even much lower than this crystalline oxide with high densities of point and line defects induced from vacancies.

Temperature distribution maps were generated for the two-layer thermal oxide and Ti substrate system as shown in Fig. 6, analogous to those shown in Fig. 3 for the bare Ti metal. The metal–oxide temperature profiles are presented in length scales normalized to the respective pump beam radius of each sample. The calculations of these temperature distribution maps are generated using a numerical heat-transfer model developed specifically for laser thermoreflectance measurements on multi-layer systems. For our temperature distribution maps, we use a two-layer model (thermal oxide/Ti substrate system) that accounts for the full temperature dependence of material properties that occur during laser decay following the power density at failure is also a trend observed in previous works, which have reported rapid decreases in signal intensity as the material undergoes mechanical damage under irradiation at power densities far beyond the damage threshold. Thus, the abrupt increase and linear trend observed in the reflectance curve followed signal decay following the apex within regime IV was considered a resultant of thermomechanical material failure.

The surface temperature at the center of the irradiated region, i.e., the maximum temperature rise as visualized in Fig. 3, is utilized as the approximate temperature rise considered throughout this analysis due to the maximum probe overlap at the incident beam center. The boundary between regimes (I) and (II) is notable in the post-mortem damage analyses, provides evidence of TiO$_{2}$ influence on the thermomechanical material properties beyond the expected changes in thermal properties for the bulk material with increasing temperature. Additionally, the dynamic oxidation processes characteristic of thermal oxide formation would likely have a significant effect on the mechanisms of heat transfer during irradiation, which could in turn influence the subsequent failure mechanism. Thus, the temperature rise profile is modeled as two layers: a 1 μm-thick thermal TiO$_{2}$ layer on a bulk Ti metal substrate, with a thermal boundary conductance between the oxide and metal taken as 200 MW m$^{-2}$ K$^{-1}$.

2. Temperature-dependent properties

As stated previously, the power density at failure approximated through Eq. (1) yields a temperature rise far below the melting temperature of bulk Ti metal, indicating an alternate mechanism of heat transfer enabled through changes in material properties. While the melting temperature of pure Ti metal is relatively high, the effective melting temperature is estimated to be 1455 °C for α-Ti, several hundred degrees Celsius below the melting point of β-Ti. The presence of multiple phases may be one contributing factor to melting point depression. Another possible mechanism considers the structure of the stable thermal oxide at 300 °C, TiO$_{2}$, which is a non-stoichiometric, porous oxide with a highly defective rock-salt structure. The diffusion of oxygen from the metastable oxide and across the metal–oxide interface may induce a lower effective melting temperature through the formation of vacancies within the crystalline solid. The thermal conductivity of this thermal oxide has been reported as 1.3 W m$^{-1}$ K$^{-1}$ far below the literature value of 8.5 W m$^{-1}$ K$^{-1}$ for the thermodynamically favored crystalline oxide, TiO$_{2}$, and even much lower than this crystalline oxide with high densities of point and line defects induced from vacancies.

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heating, such as changes in optical properties/reflectance and the temperature-dependent thermal conductivities of each layer, as well as the independent steady-state material properties of each layer under irradiation at the power density at failure. Additionally, a thermal boundary conductance parameter between the oxide and substrate layers is incorporated into this model, due to the thermal resistance which arises from the thermal growth of a thin oxide upon a crystalline substrate.27

While the reflectance trends upward with temperature for pure Ti metal,28 the temperature rise is affected by increased scattering due to increased surface roughness during heating,29 resulting in decreased reflectivity, as well as through the high absorbance of the incident pump laser by the oxide, afforded by the strain-induced narrowed bandgap of Ti oxides at optical wavelengths.11,60,61 A temperature profile is produced in which the heat flux is heavily localized to the oxide layer and the metal–oxide interface, achieving temperatures much higher than the melting point of the oxide.

B. Damage mechanisms

Although the estimated temperature rises at each sequence of critical points are roughly equivalent across all measured samples, the distinctive damage morphologies suggest a pump-size dependence on the failure mechanism. The effect of oxide–substrate interfacial area is well-studied across numerous high-temperature oxidation studies and is found to be influential on thermally induced phase changes, lattice defects, and thermomechanical residual stresses.62–66 Similarly, the relationship between heater size and its impact on thermal transport mechanisms are discussed herein within the context of area-dependent microstructural evolution.

As demonstrated in Figs. 3 and 6, the three-dimensional temperature distribution conferred through steady-state pump heating gives rise to spatially dependent microstructural processes, in which flux-gradients arise as a function of the temperature and position.25 Such processes include incongruent oxide formation and dissolution and thermally assisted ion migration through the oxide, interface, and substrate.67–69 The effects of these gradients are pronounced under small spot sizes, as the narrow temperature distribution and high penetration depth produce a highly concentrated region of rapid deformation through the bulk, ultimately leading to fracture and localized melt. Under a much larger incident area, these structural and compositional effects are mitigated, potentially giving rise to unique damage characteristics contingent on size.

An observable effect of the heat distribution dependence on thermomechanical deformation is visible through the melt patterns within the post-mortem Ti, which increases in volume with increasing heater radius, as shown previously [Figs. 4(d)–4(f)]. While the deformation zones of the Ti-4 and Ti-6 samples are confined laterally and depth-wise to their approximate heater size, the deformed region within the Ti-18 sample extends far beyond the incident radius, suggesting enhanced thermal propagation and thus higher thermal conductivity compared to the former samples. A potential cause for this variance could be attributed to the low concentration and/or relatively uniform distribution of thermally induced defects in the Ti-18 sample, which is afforded through its relatively large irradiated area; this is speculated due to the dominant effect of microstructural defects on fatigue.21 Therefore, studies on the effects of defect concentration on thermal transport in TiO2 have shown a decrease in thermal conductivity due to increased phonon scattering with the introduction of vacancies, increased non-stoichiometry, gradual evolution to p-type semiconductor character, and introduction of shear planes seen at high temperatures and low partial pressures of oxygen.11,66 While the thermal oxidation of Ti metal is temperature-dependent, the resultant oxide is heavily influenced by the material structure due to its effect on the concentration of ions and vacancies at the metal–oxide interface, e.g., the stress-dependent non-equilibrium vacancy concentration, as stated above. In other words, our results suggest that Ti-18 has a larger thermal conductivity at elevated temperatures than assumed for our thermal model calculations; this increase may be attributed to differences in defect/oxide composition relative to its Ti-4 and Ti-6 counterparts. The cross-sectional images and accompanying EDS maps [Figs. 4(a)–4(f)] provide insight into the in-plane and cross-plane mechanisms of heat transfer across the metal–oxide interface, which are discussed below through analysis of interfacial residual stresses.

The curvature of the metal–oxide interface is speculated to play a significant role in the mechanisms of heat transfer and subsequently distinct post-mortem morphologies of each sample. The curvature is observed to be inversely proportional to the heater size, indicating a lower magnitude of mismatch strain across the interface within the Ti-18 sample.72 Additionally, this curvature imparts a non-uniform stress distribution within the heated regions of the bulk,66 greatly influencing the morphology through stress-driven microstructural evolution.66,73 This is consistent with the results of the Ti-4 and Ti-6 samples, wherein the curvature is considerably more pronounced due to the smaller heater radius and the mechanical deformation at the metal–oxide interface and the sample surface is apparent. The low curvature of the Ti-18 sample provides a means to relieve oxidative stresses through propagation of the strain deep within the bulk, as shown in Fig. 5(c), in which a large crack parallel to the plane of the sample surface is shown at the bottom of the cross section. The stress is effectively localized within the lattice and alleviates the lateral growth strain at the metal–oxide interface and the thermal stresses that arise through the coefficient of thermal expansion (CTE) mismatch at the metal–oxide interface.73 While the size of the irradiated Ti-18 necessitates a considerable number of misfit defects to compensate for the high mismatch strain, the large interfacial area also allows the defect density to remain low enough to avoid introducing new stress states (i.e., tension within the oxide), effectively decreasing the stress concentration gradient between the competing surface oxide expansion and substrate thermal expansion to avoid separation between the layers at the interface.62 The observed continuity of the oxide layer along the Ti-18 surface profile [Fig. 4(f)] further suggests a low defect density within the oxide, with a degree of lattice coherence at the metal–oxide interface sufficient to overcome the shear strains imposed through oxidation. Within the Ti-18 cross section [Figs. 4(c) and 4(f)], the raised, formerly molten material is comprised of both Ti metal and Ti oxide, providing evidence of continuous heat flow across the metal–oxide interface and propagation through the substrate, ultimately inducing melt.

In contrast, the resolidified material on the Ti-4 and Ti-6 surfaces is composed predominantly of oxide [Figs. 5(d) and 5(e)], which separates entirely from the metal substrate, as a means to resolve the
internal stress states developed during heating. Additionally, no appreciable diffusion of oxygen atoms is observed below the metal–oxide interface; this contrast with Ti-18 provides further evidence of dissimilar interfacial thermal transport mechanisms between samples leading to unique failure mechanisms which are likely dependent on the beam size. The small heater imparts a high heater depth to surface area ratio, amplifying the effects of thermal stresses on the lattice induced through rapid oxidation, thermal expansion, and defect formation. The unique failure mechanisms induced through variance in heater size provide an opportunity to explore the properties of novel materials through a comprehensive failure analysis study. As heat-transfer methods and measured optical properties are specific to each given material, each signal profile will thus provide insight into its unique properties. An example of one such property which differs from the material used in this study is the change in reflectance with temperature at a particular wavelength; the decrease in thermoreflectance with temperature exhibited for Ta metal compared to the inverse trend in Ti metal produces a wildly different measurement profile, as will be expounded upon in future work.

V. SUMMARY: DETERMINING NON-MELTING-BASED FAILURE

The above observations give rise to a tunable method to predict the approximate temperature rise at the onset of a change in one or more material properties and thus determine if the material is damaging due to pure diffusive thermal transport considerations and temperature rises or if this material failure is due to other thermomechanical or thermochemical mechanisms. Through measurements of the rise in signal intensity, this high-throughput tool is developed in which optical properties, microstructural changes, and mechanical behavior under thermal cycling can be broadly surveyed for temperature rises and power densities of interest and subsequently refined for further examination within a vastly reduced timeframe compared to traditional cyclic load testing.

The implications for the use of this method in high-temperature and refractory material studies are numerous. Due to the inaccessibility of most field testing as well as limited availability of novel, newly synthesized materials, this method provides a means to observe properties of said materials through in situ testing; of these properties, the oxidation behavior of these materials is of particular interest, as is a means to engineer material surfaces through localized selective laser melting. Using a volume of material on the order of micrometers and a known heater radius, a rearrangement of Eq. (1) may be used to yield the absorbed power density as a function of surface temperature in the following form:

\[ \frac{PA}{\lambda T} = \kappa c, \]

where \( T \) is the temperature corresponding to the onset of a particular microstructural event as determined through the reflectance measurement and \( c \) is a constant equivalent to the constant \( 2\sqrt{2} \) for a material that can be considered semi-infinite relative to the heater radius. It is useful to linearize Eq. (3) to produce a simplified form,

\[ \frac{PA}{\lambda T} = \kappa c, \]

in which the variable of interest may be analyzed as a function of known experimental and material parameters, as demonstrated through the linearization of the critical power densities shown in Fig. 2(b). Looking forward, it is useful to note that the absorbed power is directly related to the temperature and spot size of the source through the material’s thermal conductivity (i.e., \( PA=\lambda T_0/c \)), offering a potential method similar to STRT for thermal conductivity measurements.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional information on calibration procedures.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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