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M. D. Feit , M. J. Matthews, T. F. Soules, J. S. Stolken

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Densification and residual stress induced by CO₂ laser-based mitigation of SiO₂ surfaces[†]

M.D. Feit^{*}, M.J. Matthews, T.F. Soules, J.S. Stolken, R.M. Vignes, S.T. Yang and J.D. Cooke
Lawrence Livermore National Laboratory, 7000 East Avenue, L-491, Livermore, CA 94551

ABSTRACT

Knowing the ultimate surface morphology resulting from CO₂ laser mitigation of induced laser damage is important both for determining adequate treatment protocols, and for preventing deleterious intensification upon subsequent illumination of downstream optics. Physical effects such as evaporation, viscous flow and densification can strongly affect the final morphology of the treated site. Evaporation is a strong function of temperature and will play a leading role in determining pit shapes when the evaporation rate is large, both because of material loss and redeposition. Viscous motion of the hot molten material during heating and cooling can redistribute material due to surface tension gradients (Marangoni effect) and vapor recoil pressure effects. Less well known, perhaps, is that silica can densify as a result of structural relaxation, to a degree depending on the local thermal history. The specific volume shrinkage due to structural relaxation can be mistaken for material loss due to evaporation. Unlike evaporation, however, local density change can be reversed by post annealing. All of these effects must be taken into account to adequately describe the final morphology and optical properties of single and multiple-pass mitigation protocols. We have investigated, experimentally and theoretically, the significance of such densification on residual stress and under what circumstances it can compete with evaporation in determining the ultimate post treatment surface shape. In general, understanding final surface configurations requires taking all these factors including local structural relaxation densification, and therefore the thermal history, into account. We find that surface depressions due to densification can dominate surface morphology in the non-evaporative regime when peak temperatures are below 2100K.

Keywords: fused silica, laser damage mitigation, densification, structural relaxation

1. INTRODUCTION

The potential usefulness of the (10.6 μm) CO₂ laser for mitigation of the growth of already initiated laser damage in silica upon further laser exposure was pointed out by Milam¹ et. al. in 1982. Vigorous investigation² of this approach, however, didn't begin for another 20 years when the need for damage growth mitigation became more evident. Since then LLNL, CEA^{3,4} and other laboratories⁵ have continued to develop laser based mitigation strategies. It is important to control the morphology of the surfaces resulting from such mitigation because mitigated sites modulate the incoming laser beam and can potentially cause deleterious downstream intensification. It has been difficult in the past to predict and control the final surface morphology both because of the complicated physical processes involved and incomplete knowledge of crucial process variables such as surface temperature. In this paper, after a brief listing of involved physical processes, we point out the importance of structural relaxation and the unique properties of fused silica glass in contributing to the volume and morphology (and residual stress) of the mitigated material. Both experimental and theoretical advances have led to a better understanding and control of the processes involved.

Historically, two types of motivation have been behind experimental developments for CO₂ laser mitigation. In the first, the goal is to remove laser damaged material via evaporation. Since this implies high temperatures, short pulse high peak power laser pulses are typically used. In the second type approach, the goal is to heal the damaged material via some combination of material flow and thermal annealing. This implies lower temperatures for longer times so typically involves longer lower peak power pulses. In practice, however, it usually has been difficult to make these clear distinctions because of the unique properties of fused silica. In particular, both the viscosity⁶ and the evaporation⁷ rate of silica vary by many orders of magnitude over the relatively small temperature range of practical interest. With the viscosity dropping and the vaporization rate increasing, so it can be difficult to obtain significant fluid flow without the temperature being high enough for evaporation to set in⁸.

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Along with evaporation/recondensation and material flow, surface morphology can also be affected by gradients in surface tension (Marangoni effect), by laser heating causing surface dehydration⁹ which affects density and viscosity, and by environmental¹⁰ and non-uniform structural changes^{11, 12} due to heating/cooling history (local density and residual stress).

Improvements¹³ in real time measurements of process temperature made it clear vaporization was unimportant in certain processes. It was the realization that volume losses not due to evaporation could affect the resulting mitigated surface morphology (Fig. 1) that indicated the importance of understanding the origin of such effects.

Fig. 1: (a) Apparent “crater” on surface after low temperature mitigation treatment. (b) Disappearance of “crater” after annealing sample in an oven.

We discuss volume loss (densification) effects here. Such densification also results in residual stress. The practical importance of choosing cooling programs to reduce such stresses is described¹⁴ in an accompanying paper in these proceedings.

2. VOLUME CHANGE DUE TO STRUCTURAL RELAXATION

Several causes of densification in fused silica have been noted in the literature ranging from response to large hydrostatic pressure to response to long time high energy fluence low pulse energy ultraviolet laser exposure. We consider here the effect of structural relaxation accompanying rapid cooling from high temperatures. Fused silica is a material, like water, which can become less dense as it solidifies. The phase diagram (Fig. 2) for low OH content type I and II silicas shows^{15, 16} that specific volume first decreases and then increases (material becomes less dense) as the temperature is lowered at some rate. At some point, the structure essentially becomes frozen in. This is characterized by the so-called fictive temperature. If the glass is cooled faster, a structure corresponding to a higher fictive temperature is frozen in at a smaller specific volume (higher density). Thus, the density of the cooled solid material can vary locally depending on the cooling history.

Since we now can accurately monitor both the temperature and fictive temperature distributions, it is possible to estimate the order of magnitude of the structural relaxation volume change by taking into account the local dilatation due to fictive temperature in a procedure analogous to thermoelastic stress theory¹⁷. This involves solving the elastic equilibrium and stress-strain equations (Eq. 1 below) for the local displacements using Youngdahl stress functions¹⁸. When this is done using known physical properties¹⁵ and measured fictive temperatures¹² for the conditions corresponding to Fig. (1), a surface depression of the right order of magnitude is found. This gives confidence that structural relaxation is the mechanism involved and the theoretical description can be included in a more comprehensive theoretical treatment of the mitigation process.

$$\sigma_{rr} = -\frac{E\gamma\Delta T_f}{1-2\nu} + \frac{\nu E(\epsilon_{rr} + \epsilon_{zz} + \epsilon_{\theta\theta})}{(1-2\nu)(\nu+1)} + \frac{\epsilon_{rr}E}{\nu+1}$$

$$\sigma_{\theta\theta} = -\frac{E\gamma\Delta T_f}{1-2\nu} + \frac{\nu E(\epsilon_{rr} + \epsilon_{zz} + \epsilon_{\theta\theta})}{(1-2\nu)(\nu+1)} + \frac{\epsilon_{\theta\theta}E}{\nu+1}$$

$$\sigma_{zz} = -\frac{E\gamma\Delta T_f}{1-2\nu} + \frac{\nu E(\epsilon_{rr} + \epsilon_{zz} + \epsilon_{\theta\theta})}{(1-2\nu)(\nu+1)} + \frac{E\epsilon_{zz}}{\nu+1}$$

$$\frac{\partial\sigma_{rr}}{\partial r} + \frac{\partial\sigma_{rz}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0$$

$$\frac{\partial\sigma_{zz}}{\partial z} + \frac{\sigma_{rz}}{r} = 0$$

Eq.(1): Stress-strain relations (left) and elastic equilibrium conditions (right) in cylindrical coordinates. Here the ϵ 's are components of the strain, σ 's are components of the stress, E is Young's modulus, ν is Poisson's ratio. The quantity ΔT_f is the change in fictive temperature from that at infinity and γ is a measured¹⁶ coefficient that relates fictive temperature to dilation.

Such a comprehensive theoretical numerical description has been assembled including effects of temperature dependent properties such as thermal conductivity, viscoelastic relaxation, surface tension, and structural relaxation. Initial simulations show a complex interaction of the various physical processes. For example, Fig. 3 shows the effect of including or not including structural and viscous relaxation in modeling a low temperature mitigation site. Such simulations are beginning to capture some of the complex observed site morphologies. Fig. 4 shows experimental type III site profiles resulting from identical heating, but different linear ramp down cooling profiles. The more gradual the cooling, the smaller the apparent volume change. Corresponding simulations using type II properties are qualitatively similar (Fig. 4b).

Fig. 2: Specific volume vs. temperature for low OH silicas from Brueckner¹⁵. Higher cooling rates lead to higher fictive temperature and higher ultimate density glass. Higher OH content type III silica has a shallower minimum and dependence of solid thermal expansion rate on fictive temperature.

Fig. 3: Simulated final low temperature type II mitigated silica surface profiles with and without structural relaxation. Inclusion or exclusion of structural relaxation, i.e. densification, changes the qualitative shape of the surface. This effect is most important when evaporation is insignificant, i.e. at low peak temperatures.

The experimental volume losses for high OH content silica shown in Fig. (4a) decrease dramatically as the cooling rate is slowed. This is shown quantitatively in Fig. 5 where volume loss is plotted as a function of the ramp down time. The volume loss is considerably larger for no ramp down, i.e. quenching. Simulations for low OH content silica shown in Fig.(4b) show the same trend.

Fig. 4: (a) Experimental type III site profiles in which laser power is held for 10 sec and then ramped down over 1-100 sec. (b) Simulated type II site comparing effects of 1 sec and 10 sec ramp down in temperature.

Fig. 6 shows experimental and simulated volume losses as a function of achieved surface temperature as the laser power of a 400 μm beam is varied from 1.6 to 2.8 W. The theoretical curves assume activation energies of 4.5 eV for viscosity and 3.6 eV for evaporation. These activation energies were best estimates taken from the literature. The evident change in slope near 2100K indicates a changeover from structural relaxation to evaporation as the dominant mechanism determining volume change.

Fig. 5: Experimentally determined volume loss at surface as a function of cool down ramp time. The volume loss for quenched cooling is much larger.

Fig. 6: Comparison of experimental (points) and theoretical (curves) as a function of surface temperature. Only the incident laser power is varied in the experiment. Theoretical curves were calculated by a coupled thermo-mechanical finite element model including only structural relaxation or evaporative volume losses, respectively. The sudden increase in slope indicates the onset of evaporation.

3. SUMMARY

The surface morphology of CO₂ laser mitigated fused silica sites reflects both the complex physical properties of silica glass and the strong temporal and spatial variations of heating and cooling during processing. While evaporation is the dominant volume loss mechanism at high temperatures, densification due to structural relaxation plays a significant role at lower temperatures and high cooling rates. The relative importance of highly temperature dependent properties such as viscosity (viscous flow), evaporation and densification varies with process variables. Improved experimental diagnostics and measurements along with more comprehensive theoretical models are leading to improved understanding that will aid in designing mitigation protocols that result in desired morphologies.

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