Original Paper

Effects of melting conditions on platinum-inclusion content in phosphate laser glasses

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Results from small-scale glass melting experiments aimed at reducing the density of platinum particles in phosphate laser glasses are discussed. The platinum particles originate from the crucibles used to melt the laser glass and can cause optical damage in glasses used in high-peak-power lasers. The melting experiments examine the effects of a) temperature and temperature gradients; b) processing time; and c) O_2 atmosphere on the formation and dissolution of platinum inclusions in LG-750 phosphate laser glass. Results show that most platinum inclusions originate early in the melt cycle, with thermal gradients within the melter being one of the major causes. By using oxidizing conditions (O_2), the platinum inclusions can be dissolved into the glass during the course of the melt cycle. Results from the laboratory-scale melting experiments have been incorporated into a proprietary laser-glass melting process. The laser glass prepared under these conditions has an average of less than 0.1 platinum inclusions/l, which represents a 1000-fold reduction over the previously available phosphate laser glasses.

Einfluß der Schmelzbedingungen auf den Gehalt an Platineinschlüssen in Phosphatlasergläsern

Es werden die Ergebnisse von Glasschmelzversuchen im Labormaßstab diskutiert, deren Ziel es war, den Anteil von Platineinschlüssen in Phosphatlasergläsern zu reduzieren. Die Platinteilchen stammen von den zur Laserglasschmelze verwendeten Tiegeln und können in optischen Gläsern, wie sie in Hochleistungslasern eingesetzt werden, zu Fehlern führen. Durch die Schmelzversuche wurde der Einfluß von a) Temperatur und Temperaturgradienten, b) Behandlungsdauer und c) Sauerstoffatmosphäre auf die Entstehung und Auflösung von Platineinschlüssen in LG-750-Phosphatlaserglas untersucht. Die Ergebnisse zeigen, daß sich die meisten Platineinschlüsse recht früh während des Schmelzvorganges bilden, wobei Temperaturunterschiede im Schmelzaggregat eine der Hauptursachen sind. Unter oxidierenden Bedingungen (O_2) können die Platineinschlüsse während des Schmelzablaufs im Glas gelöst werden. Die aus den Schmelzversuchen gewonnenen Erkenntnisse wurden in einem patentrechtlich geschützten Laserglasschmelzverfahren angewendet. Ein unter diesen Bedingungen hergestelltes Laserglas weist im Durchschnitt weniger als 0,1 Platineinschlüsse/l auf, was eine 1000fache Reduzierung gegenüber herkömmlichen Phosphatlasergläsern bedeutet.

1. Introduction

Platinum and platinum alloys have been successfully used as container materials in the glass melting industry since the 1940s. In contrast to most ceramic refractories, platinum is largely chemically inert to a wide range of glass compositions; consequently, very high-quality, homogeneous optical glasses can be produced in platinum melters [1].

Although relatively inert, platinum still produces some level of contamination in the glasses. This contamination is in the form of either microscopic platinum particles (inclusions) and/or low levels (ppb to ppm) of dissolved platinum. In most applications, the level of contamination is sufficiently small not to affect the optical performance of the glass. However, with the advent of high-peak-power lasers in the 1960s, it was discovered that platinum inclusions produced fracture sites when irradiated above a certain fluence threshold [2 to 4]. Since

that time, considerable effort has gone into trying to reduce or eliminate platinum inclusions in both laser glasses and other laser optical components (e.g., lenses).

In 1985, when the LLNL (Lawrence Livermore National Laboratory) 120 kJ Nova laser (used for Inertial Fusion Research) was first operated, the large (7 l) phosphate glass laser disks experienced isolated, bulk damage due to platinum inclusions [5 to 7]. Most of the damage sites are distinguished by a series of radial fractures that form a circular pattern perpendicular to the beam direction. This damage morphology is shown in the schematic drawing and photographs given in figures 1a, b and 2a, b, respectively. The damage occurred at fluences above about 2.5 J/cm^2 (at normal incidence) at a pulse length of 1 ns. Further details of the mechanism of laser damage due to platinum inclusions are discussed elsewhere [4, 5, and 8 to 18].

To verify that the damaging inclusions were indeed platinum, glass samples were core-drilled from several damage sites in the laser disks. The cores were then

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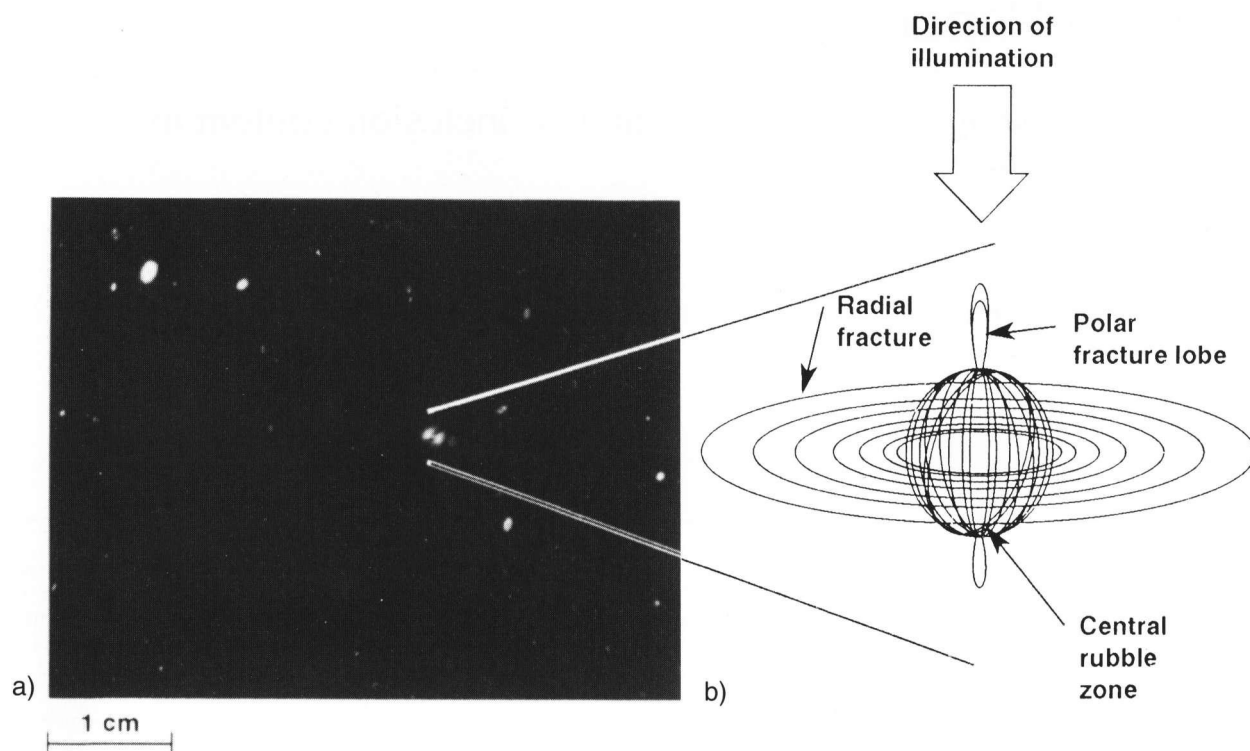
Figures 1a and b. Schematic representation of the typical morphology of laser-induced damage in laser glasses caused by a platinum inclusion. Generally, there is a major radial fracture normal to the direction of beam propagation, with two minor lobes extending above and below the radial fracture plane; a) photograph of damage sites in laser glass, b) typical geometry of many fracture sites.

cleaved at the plane of the damage fracture and submitted for Scanning Electron Microscopy (SEM) analysis. Figures 3a and b show a typical Back-Scattered Electron (BSE) image of one such sample at two different levels of magnification, with the typical conchoidal fracture pattern of the laser damage site. At the center of the photograph is a high-atomic-number particle that can be clearly seen by the white image it produces in the high-magnification BSE photograph. Energy dispersive x-ray analysis of several such particles verified that they were platinum.

It was anticipated that use of a phosphate laser glass in the design of high-peak-power lasers would reduce the risk of platinum-inclusion damage because of the greater solubility of platinum in phosphate than in silicate or fluorophosphate laser glasses. Platinum present in the dissolved (ionic) state represents no damage threat. Unfortunately, even though the phosphate glass was far superior to both silicate and fluorophosphate alternatives, it still contained platinum inclusions in concentrations of about 10 to 1000/l and in size from less than about 5 (visual detection limit) to approximately 100 μm [6 and 7].

The occurrence of platinum in glass has been the subject of study for many years and has recently been reviewed [5]. In prior work related specifically to laser glasses, two general approaches were used to try to reduce or eliminate the source of platinum inclusions. The first was to develop glasses and melting conditions tha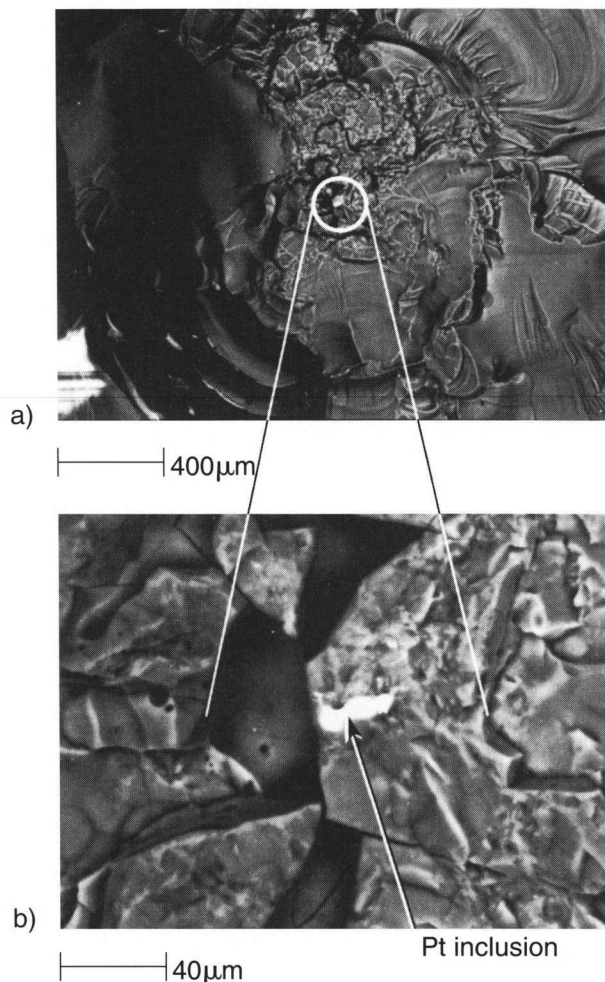t minimize platinum levels, and the second was to melt in a platinum-free environment. Following the first approach, Ginther [19] attempted to develop a silicate glass of a composition that would be resistant to platinum contamination. His approach was to eliminate volatile alkali and alkaline earth oxides from the glass formulation. Experiments by Ginther showed that oxygen, produced by the dissociation of these components under reducing conditions, contributed to vapor-phase transport of platinum to the glass melt. Thus, he reasoned that by eliminating these components the platinum content in the glass could be significantly reduced. His experiments indeed showed reduction in platinum although no large-scale melting experiments were conducted nor was the glass ever laser damage tested. Ginther prepared his samples by induction heating and noted that induction heating will produce greater levels of platinum contamination than does resistance heating, simply because induction heating heats the platinum surface to a higher temperature than the rest of the melt. Ginther suggests that the lower thermal gradients produced by resistance heating should lead to lower platinum contamination.

One of the most significant studies of platinum inclusions in silicate glasses was reported by Hornyak and Abendroth [20] who worked primarily with the ED-2 silicate laser glass formulation. ED-2 is a proprietary silicate glass composition that is essentially a lithium disilicate also containing CaO, Al_2O_3, and CeO_2. In their study, Hornyak and Abendroth investigated the effects
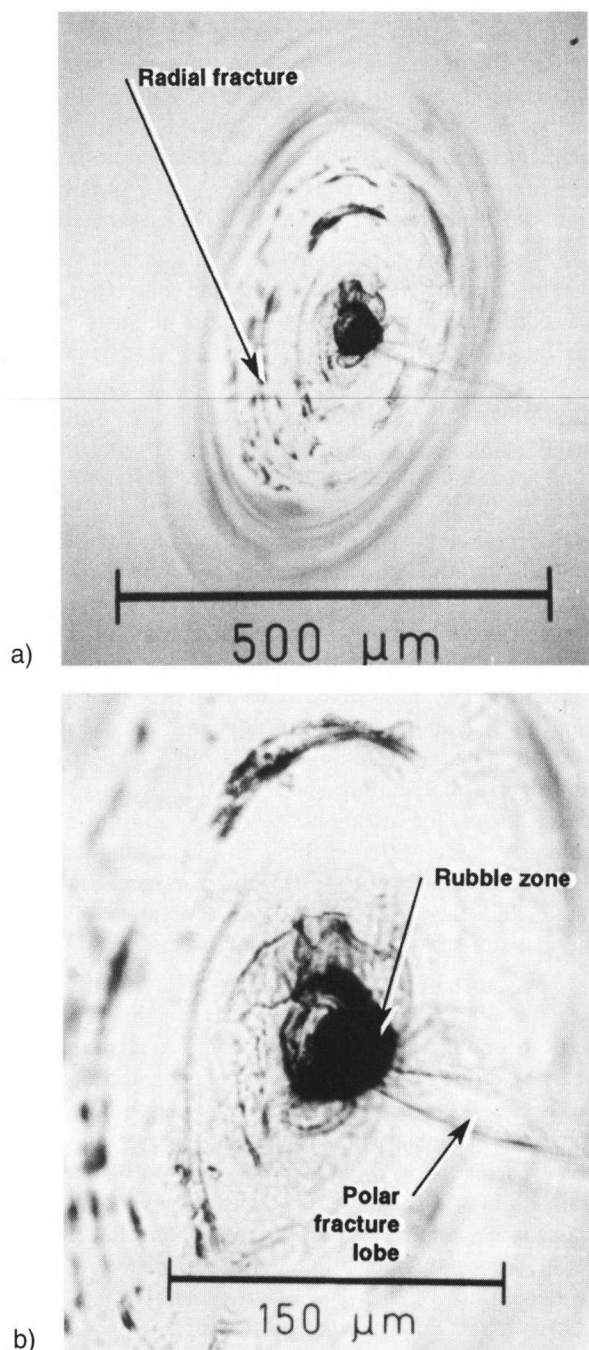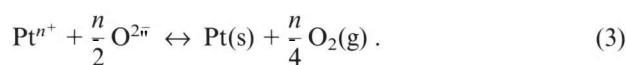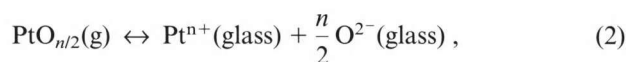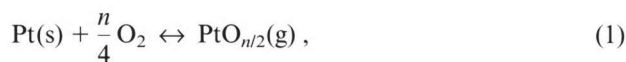
Figures 2a and b. Optical photographs of damage sites (figure a taken at low magnification, figure b taken at higher magnification) showing the characteristic radial fracture and lobes as discussed in figures 1a and b. The highly fractured spherical region surrounds the location of the original inclusion.

Figures 3a and b. SEM back-scattered electron images of a cleaved damage site (figure a taken at low magnification, figure b taken at higher magnification). The remaining kernel from the original platinum inclusion is the small white particle that can be seen near the center of figure b.

of O_2 partial pressure on platinum solubility in ED-2. They reported that platinum particles were not observed in ED-2 glass melted in air or O_2 but that use of a neutral atmosphere produced massive numbers of metallic inclusions. Hence, their work indicated that the melt redox conditions control the solubility of platinum in the silicate glass melts.

Hornyak and Abendroth proposed the following reaction mechanism to account for the effects of O_2 partial pressure on the incorporation of platinum in the glass:

$$Pt(s) + \frac{n}{4} O_2 \leftrightarrow PtO_{n/2}(g) , \qquad (1)$$

$$PtO_{n/2}(g) \leftrightarrow Pt^{n+}(glass) + \frac{n}{2} O^{2-}(glass) , \qquad (2)$$

$$Pt^{n+} + \frac{n}{2} O^{2\bar{n}} \leftrightarrow Pt(s) + \frac{n}{4} O_2(g) . \qquad (3)$$

They measured the solubility of platinum in ED-2 glass at 1450 °C as a function of oxygen partial pressure and correlated the solubility with the oxidation state in the melt by simultaneously measuring the Ce^{3+}/Ce^{4+} ratio in the glass. Assuming a constant $O^{2\bar{n}}$ activity in the melt, the equilibrium constant for equation (3) is simply:

$$K_{eq} = \frac{k(P_{O_2})^{n/4}}{[Pt^{n^+}]} .\tag{4}$$

Thus, the slope of the platinum solubility data can be related to the valence state of platinum by

$$\lg [Pt^{n^+}] \equiv \frac{n}{4} \lg [P_{O_2}] - \lg k' ,\tag{5}$$

where n = valence state of the dissolved platinum, P_{O_2} = oxygen partial pressure (in bar), k' = a constant.

From their data, Hornyak and Abendroth [20] determined a value of n of approximately 1.6 to 1.9 which, they suggest, indicates an oxidation state of 2. Hornyak and Abendroth then applied their observations to ED-2 glass production. By using the Ce^{3+}/Ce^{4+} couple as an indicator of platinum solubility, they measured the rate of platinum incorporation in the glass during the melting, refining, and homogenization cycles. Their results showed that most (70%) of the platinum entered the glass during the charging cycle, and only a small increase in platinum was observed during refining and homogenization. However, they also found that, if the cycle time of the process was increased, the platinum might exceed the solubility limit and be precipitated.

As mentioned, the second approach to eliminate platinum inclusions from laser glass was to perform the melt in non-platinum systems. For example, workers at Sovirel in France [3], used ceramic melters to prepare platinum inclusion-free glass. Dielectric inclusions from the ceramic still produced laser damage although at a somewhat higher threshold (about 22 J/cm² at 30 ns); the damage density was greater than 300/l.

Perhaps the most recent report of a platinum-free glass is that by Wilson [21] of BK-7 silicate glass being melted in ceramic melters. The authors procured a large blank of this glass and subjected it to laser damage testing at approximately 8 J/cm² at 8 ns (1.05 μm). The density of damage sites was greater than 100/l and, in one instant, resulted in a massive 3-cm-diameter fracture region that propagated through the entire glass thickness. The source of the damage is apparently dielectric inclusions originating from the ceramic melter.

Although ceramic pot melters in principle eliminate the problem of platinum inclusions, ceramic melters commonly adversely affect several other factors such as ceramic inclusions, optical homogeneity, absorption loss, and cost.

2. Preparation of phosphate laser glass and sources of platinum inclusions

The original phosphate laser glass used in the Nova laser was prepared in a two-step batch melting process. Although the details of the process are proprietary, the following description highlights the key steps of the process. In the first step, a cullet glass is made by melting the raw starting materials. The cullet glass is usually melted in a relatively inert ceramic refractory crucible, and a bubbling gas is often added to remove unwanted volatile products, particularly water. The product of this melt step is poured onto a cold surface, where it fractures into smaller pieces as a result of thermal stresses. The cullet is generally full of bubbles, striae, and possibly some small particles of undissolved starting material.

The glass produced from the cullet melt is used in the final melting step which (for the original Nova glass) was conducted in a nominal 40-l platinum crucible. During this second melt step, the glass is homogenized to provide the striae-free, high optical quality glass necessary for laser applications. This homogenizing process involves two stages [22]. The first is a refining process conducted at high temperatures where the viscosity of the glass is low, allowing bubbles to rise to the surface. The second stage is a homogenization process which is generally conducted at temperatures lower than either the melting or refining stages. During homogenization the melt is continuously stirred. The continuous mixing provides a thorough distribution of all components within the glass melt, which is necessary for the elimination of striae and assurance of uniformity of the refractive index over the entire casting. Finally, the melt is cooled to a temperature such that the viscosity of the glass is proper for casting into a mold of the appropriate size and shape. After casting, the glass undergoes a coarse annealing step, is inspected for inclusions and striae, and then is fine-annealed to remove residual thermal stresses due to the forming process.

The source of platinum inclusions in laser glasses has been the subject of many studies and is generally agreed to be from one or more of the following: a) abrasion and wear; b) attack on the platinum crucible by reduced species in the glass (e.g., silicon); c) direct dissolution of the crucible in the melt, with subsequent precipitation of the dissolved platinum; d) selective dissolution of platinum grain boundaries, with the subsequent release of platinum grains into the melt; and/or e) vapor-phase transport as $(PtO_{2(g)})$ and a re-deposition as metallic platinum either on the surface of the glass or at a location within the melter where it may drop back into the glass.

In principle, abrasion and wear can be eliminated as a source by care in processing. Also, in the case of phosphate glasses, the oxygen fugacity in the melt is sufficiently high that reduced species are not formed that can attack the crucible. Therefore, precipitation, selective dissolution of grain boundaries, and vapor-phase transport are the three most likely sources of platinum inclusions in phosphate laser glasses. Consequently, the primary focus of this study is to differentiate between these three mechanisms and to understand the processing conditions that affect either inclusion formation or solubility in the melt.

Platinum inclusions formed by vapor-phase transport stem from the peculiar properties of platinum metal. Platinum is an unusual metal in that it forms a volatile oxide $(PtO_{2(g)})$ when heated above approximately 700°C

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in an oxygen-containing atmosphere [23 and 24]. Above this temperature, platinum oxide exists only as a gas; upon contact with a solid or liquid surface, it deposits platinum metal. The vapor pressure of platinum oxide in equilibrium with platinum (at 1 bar O_2) is much greater than that of the pure platinum metal at typical glass melting temperatures.

Alcock and Hooper [24] and Schäfer and Tebben [25] have studied the thermodynamics of PtO_2 formation over a temperature range from 1000 to 1600 °C and from 1000 to 1200 °C, respectively. Alcock and Hooper showed that, for O_2 pressures at or below atmospheric, the oxide formed is PtO_2 (versus e.g., PtO or Pt_3O_4); thus, at equilibrium the amount formed is directly proportional to the oxygen partial pressure:

$$Pt^0 + O_2 \leftrightarrow PtO_2 . \tag{6}$$

The equilibrium constant for this reaction is simply

$$K_{eq} = \frac{P_{PtO_2}}{(a_{Pt})(P_{O_2})} \tag{7}$$

where P_{PtO_2} = PtO_2 partial pressure, P_{O_2} = oxygen partial pressure, and a_{Pt} = platinum activity (which for the pure metal is unity).

The equilibrium constant is related to the Gibbs free energy (ΔG^0) of the reaction via the classic thermodynamic expression:

$$\Delta G^0 = -RT \ln K_{eq} \tag{8}$$

which, upon substitution of equation (7) for K_{eq}, gives

$$\Delta G^0 = -RT \ln \frac{P_{PtO_2}}{(P_{O_2})} \tag{9}$$

where R = the molar Boltzmann constant (= 8.315 J/(mol · K)) and T = temperature in K.

Alcock and Hooper [24] measured the PtO_2 vapor pressure in 1-bar O_2 between 1100 and 1500 °C and found the data could be accurately represented by

$$\lg(P_{PtO_2}) = -\left(\frac{8585 - 0.204\, T}{T} \right) \tag{10}$$

giving a Gibbs free energy (in J/mol) of

$$\Delta G^0 = 164\,400 - 3.91\, T . \tag{11}$$

Thus, from equation (9), the equilibrium PtO_2 pressure at other oxygen partial pressures and temperatures can be easily calculated:

$$P_{PtO_2} \equiv P_{O_2} \cdot \exp\left[\frac{-164\,400 + 3.91\, T}{RT} \right] . \tag{12}$$

For comparison, the corresponding vapor pressure (in bar) of the pure platinum metal can be calculated using the following expression from Hampson and Walker [26]:

$$P_{Pt} = 1.333 \cdot 10^{-3} \cdot \exp\left[\frac{-63\,494 + 22.20\, T}{T} \right] . \tag{13}$$

Note that over the temperature range of interest (1000 to 1200 °C) and at 1 bar O_2, the vapor pressure of PtO_2 is more than about 10^6 greater than that of platinum. Therefore, in the presence of an oxygen-containing atmosphere, the rate of platinum transport (as PtO_2) is greatly accelerated. Since the oxide vapor pressure depends linearly on the O_2 pressure (equation (13)) then P_{O_2} would have to be 10^{-6} bar to have the PtO_2 vapor pressure equivalent to that of the metal. Thus, in oxidizing systems, platinum can be transported to the molten glass as PtO_2 and then redeposited on the glass as pure platinum metal.

The notion that PtO_2 transport can lead to Pt^0 inclusion formation in optical glasses was clearly illustrated by Ginther [19]. He conducted a series of experiments in which a silicate glass was melted in a ceramic crucible that was in close proximity but physically separated from platinum metal. When the melt was carried out in O_2, platinum inclusions were found in the glass; when an inert gas (N_2) was used, no platinum particles were observed.

Based on these experiments, it would appear that preparing glass in an inert gas environment would eliminate platinum-inclusion formation. Unfortunately, this is not the case. The oxygen partial pressure produced by decomposition of oxide-glass components is often sufficient to produce platinum transport and inclusion formation. This, of course, was the basis for the work by Ginther [19] on low oxygen pressure glasses that was discussed in section 1.

3. Experimental procedures

All experiments were conducted using small-scale melts of LG-750 laser glass in either 0.5 or 2 l platinum pots. LG-750 is a commercial metaphosphate laser glass manufactured by Schott Glass Technologies, Inc., Duryea, PA (USA). Although the composition of LG-750 is proprietary to Schott, the essential ingredients are phosphorous, aluminum, barium, potassium and neodymium with some additional minor additives. The starting material (i.e., cullet glass) for most of these experiments was prepared in one large melt to ensure uniformity among the experiments. For convenience, most of the melts were heated inductively. However, to test the suggestion by Ginther [19], that induction heating leads to greater temperature gradients and hence
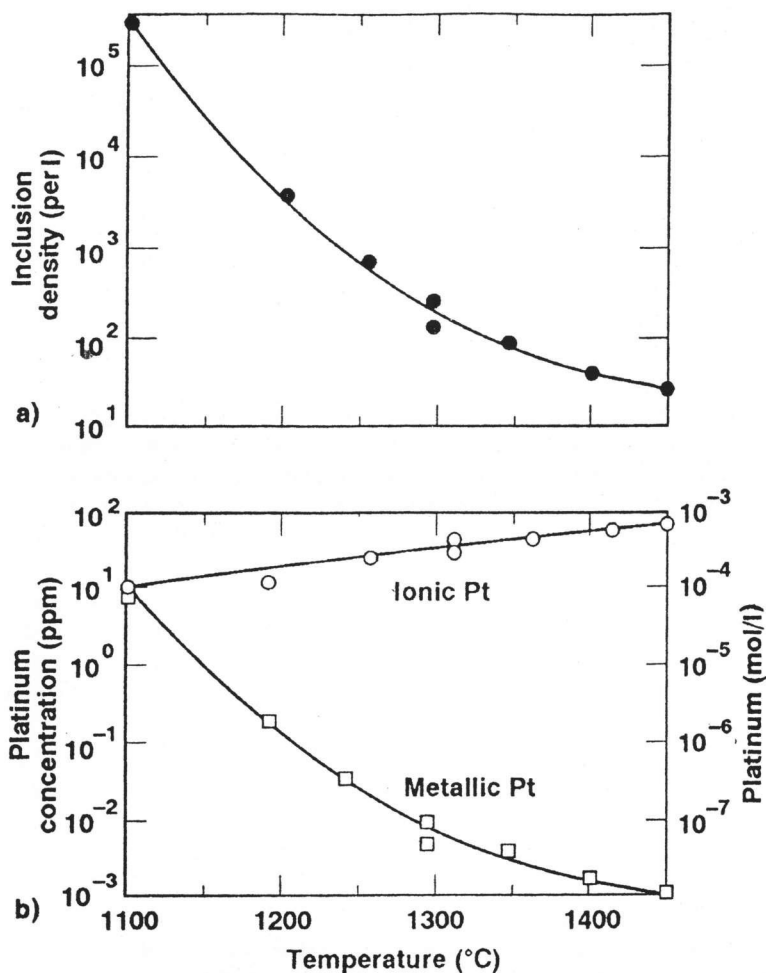
Figures 4a and b. Platinum-inclusion density (figure a) and metallic (□) and ionic (○) platinum concentration (figure b) versus refining temperature for a series of 0.5-l melts of LG-750 phosphate laser glass. The metallic platinum concentration was calculated from the inclusion density shown in figure a and assuming an inclusion radius of 10 μm.

higher platinum-inclusion density, several melts were also prepared by resistance heating.

The increase in platinum transport caused by temperature gradients also implies that the method of cullet addition to the platinum pot would affect the melt experiments. Consequently, in nearly all experiments a standard technique was used to add cullet to the melt.

First, the cullet was placed in the platinum melting crucible at room temperature. Second, the crucible was then heated to the desired experimental temperature, and finally additional room-temperature cullet was added until the proper glass level was reached.

In later experiments, the method of cullet addition (for a given melting condition) was varied to determine whether the method of addition had an effect on the platinum-inclusion density.

Each melt was cast into a steel mold and annealed to produce a glass slab for analysis of platinum content. From this casting, two transmission samples were prepared for monitoring the ionic platinum content. The concentration of ionic platinum was related to absorption in the 400-nm region, using the correlation developed by Campbell et al. [5].

The bulk of the casting was used to produce an inspection block through which a 3.5-mm diameter,

50-mW HeNe laser beam was systematically scanned. Every inclusion observed was marked and then inspected under suitable illumination and magnification to independently verify the identity of the site. Inspection blocks that contained large numbers of particles were analyzed by counting the total number of sites found in a specific volume element. The concentration of metallic platinum resulting from each melt was then estimated by assuming a uniform size distribution for 10-μm-radius spherical particles. This estimate probably represents an upper bound for the actual metallic content. Most inclusions were in the 5 to 10 μm size range, although the observed size distribution was quite large.

4. Results and discussion from phosphate laser glass melting experiments

4.1. Influence of refining temperature on platinum-inclusion density

The melts used to investigate the impact of refining temperature on platinum content of phosphate glass all employed an identical refining procedure, which consisted of a 2 h treatment under a nitrogen cover gas followed by 2 h under oxygen. The refining temperature was varied from 1100 to 1450 °C.
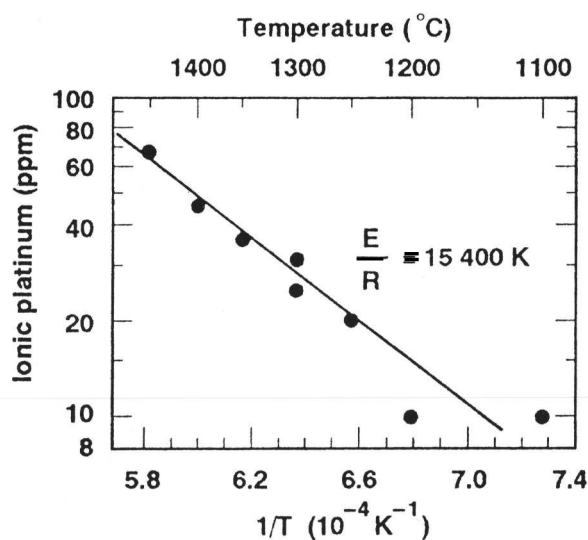
Figure 5. Ionic platinum concentration versus $1/T$ for LG-750 phosphate laser glass; data from figures 4a and b. The activation energy. E, can be determined from the slope of the curve, E/R, where R is the gas constant.

Figures 4a and b display the metallic and ionic platinum contents resulting from these melts. Immediately obvious from these data is the large disparity between the ionic and metallic platinum concentrations except with the melt at 1100 °C. Three conclusions can be drawn from these experiments:
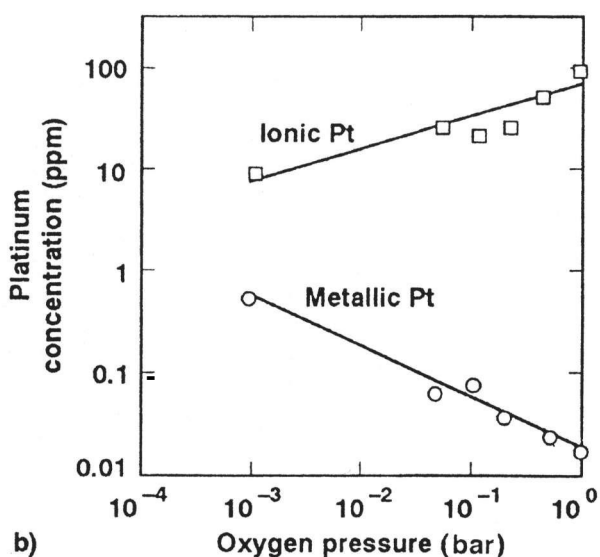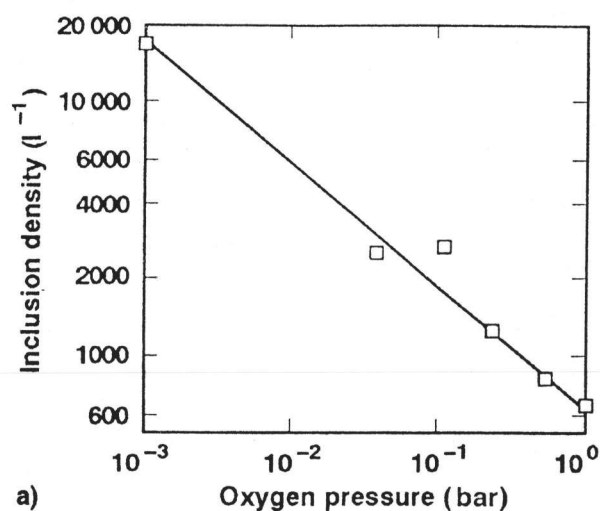
a) The metallic platinum concentration decreases dramatically with increases in refining temperature.

b) The ionic platinum concentration increases with temperature.

c) In general, if ionic platinum producing even a modest 400-nm absorption were converted into metallic platinum, a typical melt refined at 1300 °C would have more than 10^6 inclusions/l.

The observed increase in ionic platinum has been shown to come mainly from direct dissolution of the crucible walls [5]. Consequently, the increased dissolution of platinum inclusions with higher refining temperatures is expected to have only a minor effect on the ionic platinum content of the melt.

Figure 5 is an Arrhenius-type plot of the logarithm of ionic (dissolved) platinum content versus T^{-1}. The data at higher temperatures show a linear relationship characterized by an activation energy, E, of about 126 kJ/mol.

4.2. Influence of oxygen content in the melt atmosphere

A series of 0.5-l pot melts were prepared in which the oxygen content of the gas flowing over the melt was varied from approximately 10^{-3} to 1.0 bar. The inclusion densities were determined by the microscopic examination techniques mentioned in section 3. Figures 6a

Figures 6a and b. Platinum-inclusion density (figure a) and metallic ($\bigcirc$) and ionic ($\square$) platinum concentrations in LG-750 phosphate laser glass (figure b) as a function of oxygen partial pressure used during the melt refining step. The metallic platinum concentration was calculated from the inclusion density given in figure a and assuming an inclusion radius of 10 μm.

and b summarize the data graphically and clearly show the dramatic improvement that strongly oxidizing conditions have on reducing the number of platinum inclusions. The disadvantage in using highly oxidizing conditions is the increase in absorption, particularly below 400 nm, due to optical absorption by ionic platinum. For high platinum-ion concentrations, the corresponding 400-nm absorption could affect the efficiency of neodymium pumping by xenon flashlamps. The effect of ionic platinum on the transmission is clearly shown in the spectra in figure 7 of a sample of LG-750 glass melted under oxidizing conditions. The transmission was measured for three sample thicknesses. Note the main Pt^{n+} absorption is in the 400 to 450 nm region, in agreement with that reported by earlier researchers [27 to 32].
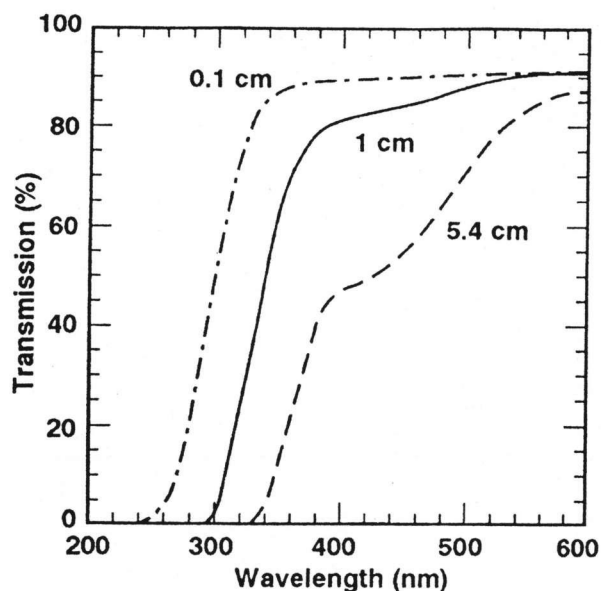
Figure 7. Effect of ionic platinum on the transmission spectra for three different thicknesses of LG-750 phosphate laser glass melted under oxidizing conditions (O_2 gas environment).

The relatively large background concentration of inclusions observed even under the most highly oxidizing conditions is probably an artifact of the procedure used to charge the crucible at the beginning of the experiment. In these small-scale experiments, it is difficult to control all the melt variables during the melt cycle, which can lead to higher than normal background levels of inclusions.

4.3. Effect of refining time under oxygen

A series of 2-l melts was completed to investigate the affect of refining time under 100 % oxygen on the result-ant platinum-inclusion density (table 1). The standard

conditions for this series of melts used two sequential refining periods. The first period was conducted under 100 % N_2 ($P_{O_2} \approx 10^{-3}$ bar) for about 2 h. This was fol-lowed by a second period under 100 % O_2 and of vari-able duration. The exceptions to this pattern are melt 40.2, which had only one 2-h refining period under 100 % O_2, and melt 83.2, which had a single 2-h refining time under 100 % N_2. All melts were refined at 1300 °C.

For these melts, the platinum crucible had a total surface area of approximately 1145 cm², of which 920 cm² was submerged below the melt and 225 cm² was exposed to the atmosphere above the melt. The ionic platinum was calculated from the 400-nm absorption, using a correlation developed previously [5]:

$$[Pt^{n+}] = 637 \cdot \alpha_{400\,nm} \tag{14}$$

where $[Pt^{n+}]$ is the ionic platinum content in ppm and $\alpha_{400\,nm}$ is the absorption coefficient at 400 nm in cm^{-1}. Note that the ionic platinum concentration increases nearly linearly with time at a rate of approximately $2.8 \cdot 10^{-4}$ mole platinum per liter per hour or, when expressed in terms of the platinum area exposed to the melt, $6.1 \cdot 10^{-7}$ mole Pt/(cm² · h) (figure 8).

The metallic (platinum inclusion) concentration showed considerable variability in this series of melts. As mentioned before, this is believed to be a consequence of the procedure used to charge the crucible. Neverthe-less, the highest inclusion density was observed for the melt prepared under 100 % N_2 (no O_2 refining); this melt also had the lowest dissolved (ionic) platinum content. Thus, refining under N_2 favors platinum-inclusion for-mation.

These results also suggest that a substantial number of platinum inclusions enter the melt during the fill pro-cedure (approximately 5000/l for these particular melts). Exposure to oxygen appears to result in the dissolution

Table 1. Effect of variable refining time at 1300 °C and an oxygen pressure of 1 bar on platinum content in 2-l melts of LG-750 phosphate glass

melt number	time in h at 1 bar O_2	metallic platinum			ionic platinum		
		particles in l^{-1}	concentration[1]		absorption coefficient (in cm^{-1}) at 400 nm	concentration	
			in ppb	in mol/l		in mol/l	in ppm
83.2	0	4900	157	$2.3 \cdot 10^{-6}$	0.016	$1.5 \cdot 10^{-4}$	10
39.2	1	725	23	$3.3 \cdot 10^{-7}$	0.055	$5.1 \cdot 10^{-4}$	35
65.2	1.5	78	2.5	$3.6 \cdot 10^{-8}$	0.061	$5.7 \cdot 10^{-4}$	39
37.2/2	2	950	30	$4.4 \cdot 10^{-7}$	0.071	$6.6 \cdot 10^{-4}$	45
37.2/3	2	410	13	$1.9 \cdot 10^{-7}$	0.093	$8.6 \cdot 10^{-4}$	59
37.2/4	2	56	1.7	$2.6 \cdot 10^{-8}$	0.078	$7.3 \cdot 10^{-4}$	50
37.2/5	2	12	0.4	$5.5 \cdot 10^{-9}$	0.086	$8.0 \cdot 10^{-4}$	55
37.2/6	2	38	1.2	$1.8 \cdot 10^{-8}$	0.093	$8.6 \cdot 10^{-4}$	59
40.2	2	96	3.0	$4.4 \cdot 10^{-8}$	0.081	$7.5 \cdot 10^{-4}$	52
66.2/1	3	185	5.8	$8.5 \cdot 10^{-8}$	0.128	$12 \cdot 10^{-4}$	82
66.2/3	3	205	6.5	$9.5 \cdot 10^{-8}$	0.119	$11 \cdot 10^{-4}$	76
38.2/1	4	810	25	$3.7 \cdot 10^{-7}$	0.108	$10 \cdot 10^{-4}$	69
38.2/2	4	37	1.2	$1.7 \cdot 10^{-8}$	0.140	$13 \cdot 10^{-4}$	89

[1]) Calculated from the platinum-inclusion density assuming a particle radius of 10 µm.
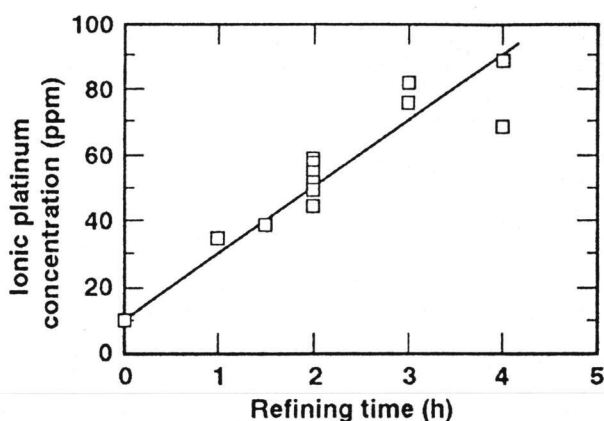
18

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Figure 8. Ionic platinum concentration versus refining time at 1300 °C and 1-bar O_2 pressure for LG-750 phosphate laser glass.

Figure 9. Schematic diagram of a cold cullet particle dropping into a heated platinum crucible (temperature $\approx$ 1100 to 1200 °C) containing an equilibrium PtO_2 pressure of $\approx 10^{-6}$ bar.

of platinum inclusions as well as continued introduction of ionic platinum into the melt due to dissolution of the crucible walls. The increased ionic platinum is primarily from dissolution of the crucible walls, with only a very small contribution from the dissolution of inclusions [5].

4.4. Effect of temperature gradients on platinum-inclusion formation

Temperature gradients can lead to transport of platinum (as PtO_2), with the subsequent formation of inclusions. In typical melting experiments, thermal gradients often exist, first, during the start of melting when cold cullet is being added to the melt and, second, between different hot and cold regions of the melter. As a consequence, platinum inclusions can form directly on the glass, when cold cullet is added to a melter, or indirectly, when platinum condenses in some cooler region and then falls or refluxes back into the crucible.

In these particular experiments, there are two main sources of thermal gradients that could lead to platinum-inclusion formation:

a) induction heating,
b) addition of cold cullet to a hot platinum crucible.

As pointed out by Ginther [19], induction heating can lead to sizable temperature gradients between the heated (receptor) platinum crucible and the glass melt. Resistance heating, on the other hand, produces smaller gradients and should produce less PtO_2 transport and hence fewer inclusions.

Similarly, addition of cold cullet to a hot platinum crucible can, in principle, cause solid platinum to condense on the relatively cool surface of the cullet. This is illustrated schematically in figure 9. Here, a cold piece of cullet added to a hot platinum crucible "sweeps" through a volume (V_s) of gas within the crucible. Assuming all the PtO_2 within that volume precipitates as
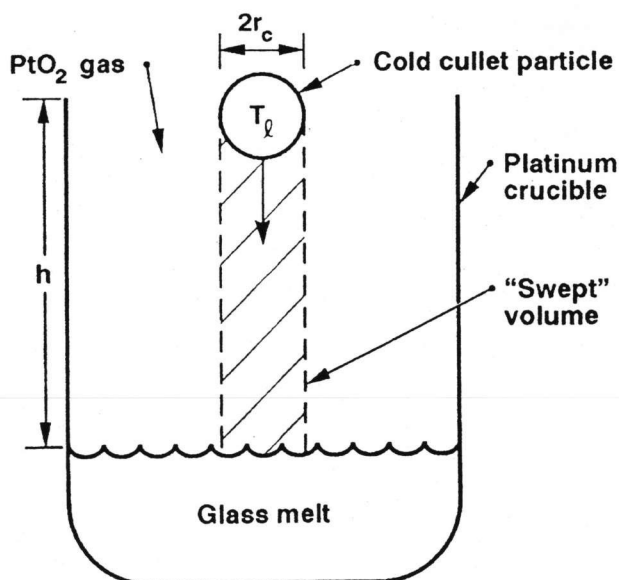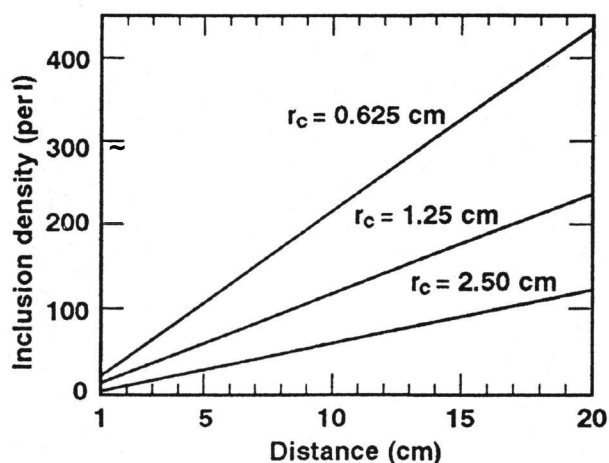

Figure 10. Calculated density of inclusions, 10 μm in radius, resulting from metallic platinum accumulation on a cold cullet particle of radius r_c 0.625, 1.25, and 2.50 cm as the particle falls a given distance through a heated platinum crucible.

Pt^0 on the cullet, then it is possible to calculate an inclusion density in the glass. The volume of gas "swept" V_s (in cm³) is simply

$$V_s = \pi r_c^2 h \qquad (15)$$

where r_c = radius of the cullet (in cm), h = height (in cm) of the free fall.

Assuming the platinum oxide behaves as an ideal gas, then the number of moles (N_{Pt}) of platinum in the swept volume is

Table 2. Effect of thermal gradients on platinum-inclusion density in small-scale experimental melts of LG-750 phosphate glass

melt number	heating method	cullet temperature	relative thermal gradient	platinum inclusions/l
34.5	induction	cold	greatest	1700
35.5	resistive	cold	–	38
81.5	resistive	hot (1050 °C)	smallest	6

$$\frac{P_{PtO_2} V_s}{R T_H} = \frac{P_{PtO_2} \pi r_c^2 h}{R T_H} \qquad (16)$$

where P_{PtO_2} = equilibrium partial pressure (in bar) of PtO_2 at temperature T_H (in K), and R = gas constant (83 cm^3 · bar/(K · mol)).

Assuming an average inclusion radius of r_i (in cm), then the inclusion density (ϱ_i, (in l^{-1})) in the cullet glass is

$$\varrho_i = \frac{N_{Pt}}{V_c} \left(\frac{M_w}{V_{Pt} \varrho_{Pt}} \right), \qquad (17)$$

where M_w = molecular weight (in g/mol) of platinum, ϱ_{Pt} = density (in g/cm^3) of platinum, V_c = volume (in cm^3) of the glass cullet particle, and V_{Pt} = volume (in cm^3) of the platinum inclusion.

Combining equations (16 and 17) gives the desired result:

$$\varrho_i = \left(\frac{9}{16 \pi} \right) \left(\frac{P_{PtO_2} h M_w}{R T_H r_c r_i^3 \varrho_{Pt}} \right). \qquad (18)$$

This function (equation (18)) is plotted in figure 10 versus free-fall distance for three different cullet sizes. An inclusion radius of 10 μm and a crucible temperature of 1100 °C containing 1 bar O_2 was assumed. This model, of course, is greatly simplified. Nevertheless, it illustrates the potential impact of cold cullet additions on the initial platinum-inclusion concentration in the melt. Thus, the thermal gradients due to cullet addition and induction heating used in these experiments can lead to a sizable background of platinum inclusions.

To quantify the impact of thermal gradients on platinum-inclusion density, several 0.5-l melts were prepared with the aim of reducing the thermal gradients to a minimum. This was done by using resistance heating, by preheating the cullet, or both. The results (table 2) show that minimizing the thermal gradients reduces the platinum-inclusion density.

4.5 Results from production melts of platinum-free laser glass

Results of the research reported here and a companion article [33] have been incorporated into large-scale melting processes that have lead to essentially platinum inclusion-free phosphate laser glass. Although the specific processing details and melter designs are proprietary, the underlying basis for platinum removal is largely: eliminate the source of platinum inclusions as best as possible (i.e., erosion, wear, temperature gradients, etc.); and use oxidizing conditions to dissolve any remaining inclusions in the glass.

Production-scale melting of replacement glass for the Nova laser took place over approximately 18 months. The total production run involved about 350 large laser disks, each having a finished volume of about 7 l.

During production, each laser glass casting was subjected to 100 % quality assurance (QA) testing for the presence of platinum inclusions. This was accomplished by scanning the entire glass casting with a small-diameter laser beam whose output fluence (in J/cm^2) exceeded that of the Nova laser. The QA system used a commercial, Q-switched, YAG laser and movable x-y stage to automatically scan the entire glass volume. The system is fully automated and operates unattended; further details of the system design and operation are given by Weinzapfel et al. [34]. Each glass vendor was supplied with a complete damage-test system that was fully integrated into the production schedule.

The manufacturing goal was to have no more than an average of two inclusions per disk; each disk contains about 7 l of glass, so this translates to an inclusion density of less than 0.3/l. In actual operation, a density of approximately 0.1 inclusion/l (i.e., less than 1 platinum inclusion per disk) was achieved. For comparison, the original Nova laser glass contained, on the average, about 100 inclusions/l. Thus, the replacement glass represents almost a 1000-fold reduction in platinum-particle density. More specifically, 62 % of all the 7-l laser glass disks had zero platinum inclusions and no disks had more than 8.

5. Summary and conclusions

There are two important conclusions from melting experiments designed to examine the affect of various process parameters on the formation and dissolution of platinum inclusions in phosphate laser glasses. First, most platinum inclusions originate early in the melt cycle. This suggests that the major source of platinum inclusions is not the erosion or wear of the platinum crucible but the condensation of PtO_2 vapor as Pt^0 particles due to thermal gradients or other non-equilibrium conditions. Second, platinum inclusions can be dissolved into the phosphate glass during the course of the melt

cycle by using oxidizing conditions (e.g., 100% O_2). These results have been incorporated into production melting processes to produce laser glass containing approximately 0.1 platinum inclusion/l.

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