



Annealing of Fused Quartz

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Abstract

Fused quartz like other vitreous (glassy) materials may have stress after thermal treatment. To avoid this stress, the glass must be cooled properly. The principles of annealing are:

- 1) *elevate the temperature of the glass to point where the stress is relieved*
- 2) *hold at this temperature until the entire body of the glass reaches temperature equilibrium.*
- 3) *cool the glass slowly to a temperature where the glass is rigid.*

The purpose of this paper is to explain these principles in detail.

Key Words: anneal, stress, anneal point, strain point, thermal treatment

Introduction

Fused quartz is widely used for applications where high temperature and high purity are required. Quartz is an attractive material because 1) it is high purity, 99.995% SiO₂ 2) can be used at temperatures as high as 1250°C 3) it offers a great deal of forming

flexibility. Quartz can be machined with diamond tools and flame work the form complex shapes. In the semiconductor industry quartz is used widely to form the process chamber for processing silicon wafers.

When quartz is flame worked, the glass worker may induce thermal stress in the piece. As in metals and other vitreous (glassy) materials, this thermal stress is relieved by annealing. Different terms are used to describe the degree of anneal. Optical Anneal (the highest degree of anneal) refers to an anneal schedule that eliminates all stress that may impact the transmittance of light waves. Commercial Anneal implies a degree of anneal that is practical for commercial applications. Mechanical Anneal is a degree of anneal commonly used for quartz ware used in the semiconductor industry. This degree of anneal satisfies the need for fabricated parts to be dimensionally stable and free of breakage due to thermal stress. The principles of annealing is simple, but can easily be misunderstood resulting in possible breakage of parts during use. Before you can understand the principles of annealing, you need to understand some common terms used to describe the thermal properties of glass.

Thermal Properties

Thermal properties that relate to the annealing process are 1) thermal coefficient of expansion, 2) strain point and 3) anneal point.

Thermal Coefficient of Expansion - is commonly referred to as the "expansion" of the glass. To state it simply, most materials expand when heated and contract (shrink) when cooled. This property is important because not all materials have the same thermal expansion. Figure 1 is a comparison of the thermal expansion of various types of glass. Thermal expansion expresses as $\Delta L/L/^\circ C$. In other words, the change in length per each degree of temperature change. Typical units would be in/in/ $^\circ C$ or cm/cm/ $^\circ C$. Note that fused quartz has an extremely low coefficient of expansion: 0.55×10^{-6} cm/cm/ $^\circ C$ (20-300 $^\circ C$).

Although we express the property as expansion, it is contraction of the quartz upon cooling that we must control in an annealing process.

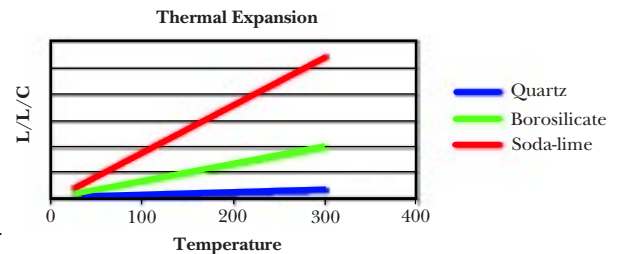


Fig. 1



Viscosity - is a measure of resistance to flow of a material when exposed to a shear stress. Since the range of "flowability" is extremely wide, the viscosity scale is generally expressed logarithmically.

Common terms forexpressing glass viscosity include: strain point, annealing point, and softening point.

Strain Point - the temperature at which the internal stress is substantially relieved in four hours. This point has been defined as a viscosity of $10^{14.5}$ poise, where poise = dyne/cm² sec. At this viscosity the glass is substantially rigid. Strain point for GE 214 / 124 is 1120°C.

Anneal Point - the temperature at which the internal stress is substantially relieved in 15 minutes, a viscosity of $10^{13.2}$ poise. Anneal Point for GE214 /124 is 1215°C. The anneal point should not be confused with the temperature required for annealing (annealing temperature). For most commercial glasses the temperature for annealing is 35-40°C above the strain point. For GE electrically fused quartz the annealing temperature is commonly used as 1150°C.

Softening Point - the temperature at which glass will deform under its own weight, a viscosity of approximately $10^{7.6}$ poise. The softening point of fused quartz has been variously reported from 1500°C to

1680°C. This range results from variation in hydroxyl content (OH)⁻ and minor variations in other trace impurities. Softening Point for GE 214 /124 is 1683°C.

Why Does the Quartz Have Stress

Annealing is performed to remove the stress in the glass. To understand how annealing works, we should understand why the glass has stress. The reason for stress has to do with the thermal expansion discussed above. Let's consider a simple example of a "thick plate of glass.

Temporary stresses due to heating and cooling - When a glass worker heats the plate it will expand or grow due to the thermal expansion property. As you can guess, the surface for the glass heats up first. This means that the surface of the glass will grow first. This sets up a stress in the glass between the interior of the glass and the expanding surface. As the surface grows it

becomes compressed. Figure 1 shows the surface in compression and the interior in tension. If the glass worker heats the glass too fast, the stress between the surface and the interior can exceed the breaking stress of the glass. However, the stress due to heating are only temporary. As both the surface and the interior reach the same temperature, equilibrium is reached and no stress is present.

When the plate is cooled the condition become reversed. Cooling causes the plate to shrink. As the surfaces are cooled they shrink first, putting the interior of the plate in compression. This puts the surface of the glass in tension. Since glass is relatively weak in tension, this cooling time where the glass surface is in tension, is the critical time during thermal treatment. If cooling happens too rapidly, tension on the surface along with an imperfection on the surface can cause the glass to fail. Here again, these stresses due to cooling are temporary stress. However, if the principles of annealing are not applied permanent stress can result from cooling.

Permanent stress (Cooling through the transition range) - During cooling where the glass becomes rigid, permanent stress can be produced. This occurs in the temperature range between the anneal point and the strain point. Since the surfaces cools first, it becomes rigid first. The interior of the plate is still hot

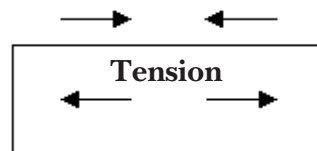


Fig. 1

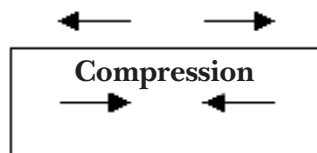


Fig. 2



and continues to shrink until it becomes rigid. As it shrinks it is putting the surfaces in compression. Since the surface is in compression, the inside of the glass is in tension. Thus, there is permanent stress in the glass; compression on the surface and tension on the inside as in Figure 3.

This plate example is very simple. In practice, the articles heated and cooled are much more complex.

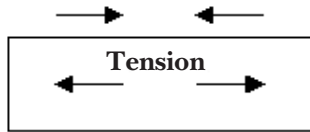


Fig. 3

In the real world, the cooling that causes permanent stress may vary from place to place on the part. For example, cooling may be different from inside a tube to outside. Thin sections will cool faster than a thick section. However, permanent stress can be controlled and minimized by following a proper cooling cycle or annealing cycle.

Annealing Cycle

From the discussion above you saw that cooling can cause permanent stress. A proper annealing cycle will minimize or prevent these permanent stress from developing. The concept is to cool the glass slow enough to prevent these stresses from developing. This slow cool

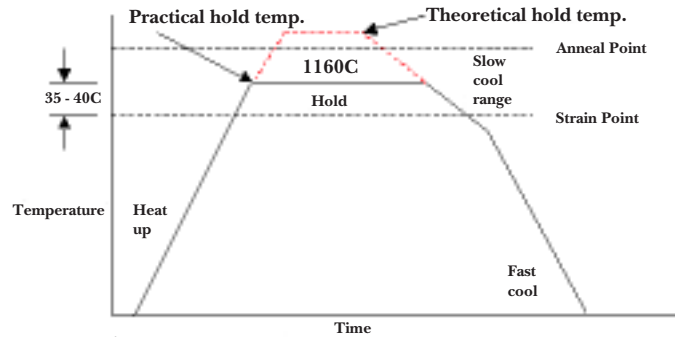


Fig 4

ing allows the surfaces of the glass to cool at the same rate as the interior. If the interior and the surfaces cool at the same rate they will also shrink at the same rate. Therefore, there will be no stress setup within the glass due to the difference in the shrinkage (contraction) of the glass.

An Anneal cycle consists of heat up rate, hold temperature /time and cool down rate. See figure 4.

Heat Up Rate

Heat up is the gradual increase in temperature until you reach the hold temperature. The rate of heating is not the most critical part of the annealing cycle. The rate depends on the type of glass. The main issue is the avoid the rapid heat up that will cause excessive temporary stress discussed earlier. All glasses can withstand some temporary stress during heat up. Because heat up produces compression on the surfaces, breakage due to temporary stress of heat up is less likely than on cool down. In particular, quartz with its low rate of thermal expansion can withstand

very rapid heat up. Different glasses may require different rates of heating. The difference between glasses is directly related to the rate of the thermal expansion. Glass

with high thermal expansion, must be heated more slowly. While quartz, a very low expansion glass, can be heated more rapidly.

Hold Temperature

The hold temperature is also very much dependent on the type of glass. The objective is bring the entire glass body to temperature equilibrium at the annealing temperature. The desired temperature is a temperature where the glass relaxes without deforming. Most literature describes the theoretical annealing temperature as a temperature approximately 10°C above the annealing point. However, for GE electrically fused quartz the practical annealing temperate is approximately 1160°C (approximately 40°C above the strain point) This temperature below the annealing point is commonly used to prevent deformation of delicate parts. This annealing temperature will vary dependent on the viscosity characteristics of the quartz. Electrically fused quartz (GE214) has a higher use temperature than flamed fused quartz. Thus electrically fused



quartz also has an annealing temperature higher than flame fused quartz. This difference is approximately 50°C.

The time required at the hold temperature will depend on the size of the load in the annealing furnace and the type of product. For instance, a thin walled tube will require very little hold time in the furnaces. The heat process and the fact that the tube is heated in side and out in an annealing furnace assures that the entire body of the quartz reached the hold temperature quickly. On the other hand, a fabricated parts with a thick flanges will require a longer time. This additional time is require for the entire body (surfaces and interior) to reach the hold temperature. In practice 30 minutes at the hold temperature is adequate for most parts.

Practical annealing temperature -

In practice fabricators of quartz components for the semiconductor industry use different annealing cycles that have proved to be a practical combination of time and temperature that to satisfy the characteristics of the components made and the annealing furnaces. For example, various companies incicate use of the following hold times and temperatures:

- 1160°C for 60 to 120 minutes depending on parts thickness
- 1185°C for 20 minutes
- 1155°C for 30 minutes

These cycle are aimed at achieving a mechanical anneal of approximately 200 psi. measured photo-elastically.

Slow Cool Down (the critical time for permanent stress)

The cool down portion of the annealing cycle is the most critical part of the annealing cycle. During cooling permanent stresses will develop if the cooling is not controlled properly. In particular, the early part of the cooling cycle is most critical. This is where the quartz becomes rigid. In the range from the hold temperature to 10°C below the strain point the glass is becoming rigid. If cooling is too fast in this range, stress will develop. The rate of cooling in this range depends on the effectiveness of the cooling. For instance, if the cooling is from one side only, then the cooling must go slower than if the cooling takes place form both surfaces; two side cooling.

This slow cooling will enable all points within the quartz to cool at the same rate.

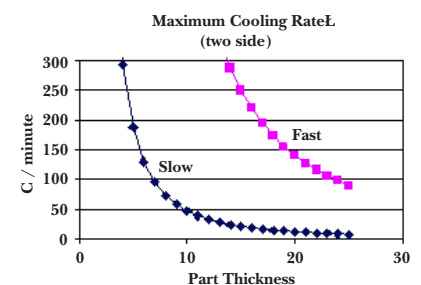
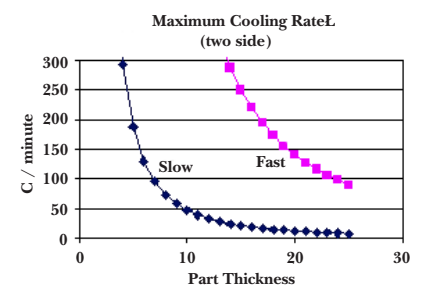
Using the information in the Handbook of Glass Engineering by E.B. Shand, the following formula was developed for quartz to estimate the cooling rate for critical slowing cooling range. This cooling rate is based on thefollowing values:

Young's modulus (E) = 10.5x10⁶ psi

Thermal diffusivity (K) = .0014 in²/sec
 Poisson's ratio (ν) = .17
 Thermal expansion (α) = .55X10⁻⁶/in/in/°C
 Thickness (t) = in
 σ_i = acceptable stress at the mid-plane. This residual stress or design stress, depending on the application, may be in the range of 1.7x10⁵ to 20.4x10⁵ Pa (25 to 300psi). As a general rule, it is possible to cool up to 100°C/hour for sections less than 1" thick

$$R_{C/sec} = \frac{24 K \sigma_i (1-\nu)}{E \alpha t^2}$$

The following graphs show the range of cooling rates for various thicknesses of parts. The slow cooling is derived from a desire to keep the maximum tension to 25 psi. the fast cooling curve allows for a maximum stress of 3000 psi.





The first graph showing cooling from two side while the second graph shows cooling from one side only. In practice, residual stress after annealing or design stress, depending on the application, may be in the range of 25 to 300 psi

Fast Cool Down (only temporary stress)

When the quartz reaches a temperature 10°C below the strain point the cooling can be accelerated down to room temperature. Thermal stress which result from this rapid cooling from below the strain point to room temperature will be temporary stress; not present when the quartz reaches room temperature.

Stress Measurement

Stresses from differential cooling that locked in at room temperature can be detected with a polariscope. A polariscope is a device that provides a source of polarized light for examination of the quartz glass. When the quartz glass contains stress, the polarized light is retarded relative to the unstressed glass. The retardation of this light appears as different colors in the polariscope.

The details of stress measurement can be quite complicated and are beyond the scope of this paper.

Summary

Because of the low thermal expansion (CTE) characteristics of fused quartz, items made with fused quartz can withstand rapid changes in temperature (thermal shock). Correspondingly, the low CTE makes quartz items less likely to have thermal stress due to improper cooling. However, to insure that items made from quartz have stress within acceptable limits, it is necessary to anneal parts that have been flame worked. The principles of annealing can be achieve is different ways. Fabricators of fused quartz components have developed specific annealing schedules that best suite the size and shape of the components made; the characteristic of their anneal equipment; and the degree of anneal desired.

A practice schedule for quartz items made with GE fused quartz includes a peak hold temperature of 1160°C with a 30 minute hold and slow cooling to 1050°C.

References

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