Remnants of soda lime silicate glass cookware failure, from *Consumer Reports* testing.

(Credit:*Consumer Reports*.)

Shattering glass cookware

R.C. Bradt and R.L. Martens

The shattering of glass cookware in household kitchens has been reported in *Consumer Reports* articles,[1,2] television documentaries, complaints to the United States Consumer Products Safety Commission[3] and Internet postings.[4] This article examines the issue from a three fold technical perspective: (i) reviewing the reported scenarios of the incidents, which are suggestive of thermal stress fracture; (ii) comparing the thermal shock resistance of borosilicate glass with soda lime silicate glass; and (iii) examining new and broken glass cookware. Together, these related perspectives suggest the thermal stresses that develop during temperature changes are the primary cause of the explosion-like breakages. The substitution of higher thermal expansion soda lime silicate glass for borosilicate glass in the manufacturing is a contributing factor.

Exploding[†] or shattering glass cookware surfaced as an issue of concern during the past two decades, and reports of problems have been chronicled in several news stories. Collectively, the accumulated complaints suggest that there may be a fracture problem with some glass cookware products. However, none of the coverage has specifically addressed the scientific aspects of the reported failures. This article examines the technical aspects of the sudden, explosion-like failure of glass cookware products.

Background

Corning Inc. pioneered the development and market for glass cookware. The glass cookware products originally manufactured by Corning were made of a low thermal expansion borosilicate glass eventually marketed as Pyrex.[5] (Many glass scientists also associate the name Pyrex with the original borosilicate glass products. Even today, Corning still produces high-quality borosilicate laboratory glassware under the name and trademark of Pyrex.)

The original Pyrex cookware was promoted as "oven to icebox" or "icebox to oven" cookware,[6] presumably because the low coefficient of thermal expansion of the borosilicate glass made it highly resistant to the thermal stresses that develop during these types of temperature changes.

Corning retains the Pyrex registered trademark, but, in 1994, the company began licensing other companies to manufacture products under the Pyrex brand (see "From battery jars to kitchens: A short history of glass cookware," page 35). Today, the Pyrex brand is manufactured for consumer markets in the US, North America, South America and Asia by World Kitchens LLC (Rosemont, Ill.)[7] under a license from Corning. A separate company, Arc International (Arques, France),[8] manufactures and markets Pyrex brand cookware for the European, Middle East and African consumer markets. Independently, the Anchor Hocking Glass Company[9] (Lancaster, Ohio) makes its own line of glass cookware, and has been doing so for many decades under its own brand names.

Compositions of glass cookware

According to the World Kitchens website,[10] Corning changed to a soda lime silicate composition for the glass cookware, and this is the Pyrex tech-

[†]Exploding and shattering have been applied interchangeably in reports describing cookware fractures because of accounts of glass shards being propelled for some distance.[1–4] The term "explosion" as applied here is not the same as the pressure explosion of a carbonated beverage container.

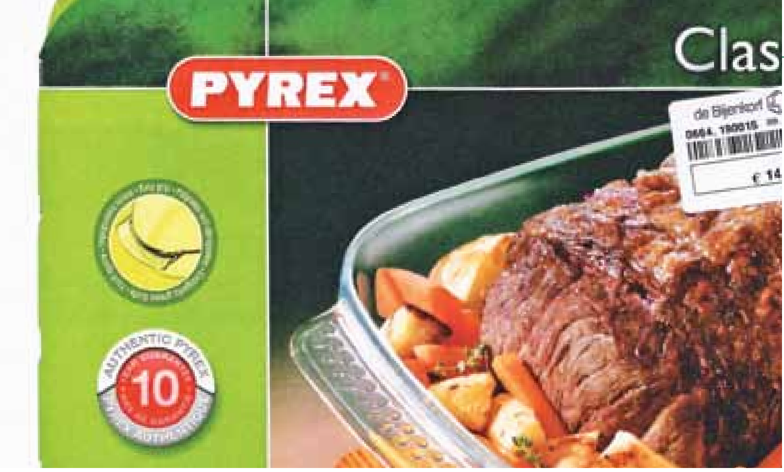


Figure 1. An Arc International label for its Pyrex glass cookware products, from cookware purchased in Europe.

nology that World Kitchens (then Borden) bought from Corning in 1998. World Kitchens acknowledges that the glass cookware it markets under the Pyrex brand name is made from a soda lime silicate glass composition.

On its own, Anchor Hocking developed a "me too" line of cookware that also is based on a soda lime silicate glass.

These soda lime silicate glass cookware products appear to be commercial successes. However, they are not made of a low thermal expansion, thermal stress resistant borosilicate glass as originally developed by Corning.

Arc International produces a line of glass cookware products. These are of a borosilicate glass composition, which it markets with the phrase "Authentic Pyrex" on the label (Figure 1). ††

The three companies that currently manufacture glass cookware—World Kitchens, Anchor Hocking and Arc International—use different silicate glass chemistry formulations. The authors confirmed this by examining the glass chemistry formulations used in the products from each of the three companies using energy dispersive spectroscopy on a FEI Quanta 200 3D scanning electron microscope equipped with an X-ray analyzer Model Apollo XVF from EDAX. The Arc International cookware was determined to be a borosilicate glass with a distinctive, readily identifiable boron peak. It evidently is the original Corning Pyrex composition.[5] The tests confirmed, as expected, that neither the World Kitchens nor the Anchor Hocking products are borosilicate glasses, but are soda lime silicate glasses of slightly different compositions. The chemical spectra clearly show the boron peak in the Arc International glassware, but the World Kitchens and Anchor Hocking glassware are free of boron. They are distinguishable by their calcium and magnesium peaks.

Indications of thermal stress fracture of glass cookware

Before going further, two things should be noted. First, the manufacturers of soda lime silicate glass cookware claim that it has superior mechanical strength and is less likely to fracture on impact, for example by dropping it, a not unreasonable concern in kitchen settings. Second, because of the extensive handling of glass cookware, it is expected that surfaces will become damaged or scratched over time. With these provisos noted, the focus of the authors has been to isolate the effects resulting from thermal stress. What follows below focuses only on the thermal shock properties of the two glass types.

Generally speaking, thermal stress fracture of glass is not an uncommon event. For example, impingement of bright sunlight on a portion of large windows can cause them to crack from the shady cold edge, and cold water splashing on hot glass marine light covers frequently fractures them. Much is known and understood about thermal stresses and thermal shock fracture.[11] The nature of the published reports of the shattering incidents with the soda lime silicate glass cookware suggests a thorough consideration of thermal stresses because the failure incidents are often associated with significant temperature changes.[1–4]

The documented and reported glass cookware incidents[1–4] suggest that the thermal stress resistance of present day soda lime silicate glass cookware is less than that of low-expansion borosilicate glass, such as the original Pyrex. For example, some of the glass cookware items have been reported to fracture immediately on a change in temperature, while other cookware fractures occur during a short time after removing the cookware with its contents from a hot oven. (See *Consumer Reports* example, Figure 2.) Fractures that occur at a time interval after a temperature change, such as after removal of the cookware from a hot oven, are characteristic of thermal stress failures. However, there also are reports of failure while the cookware with its contents is inside the oven. These thermal gradients may have different origins, such as might develop

(Credit: Consumers Union.)

Figure 2. Heat test: Frames from video of tests conducted by *Consumer Reports*[1] shows bakeware made of soda lime silicate glass shattering after being heated in a 450°F degree oven and placed on a wet countertop.

††The authors were not able to find any reports of Arc International Pyrex cookware failing in an explosive manner.

if frozen contents are placed in the cookware before being inserted into a hot oven.

As described in *Introduction to Ceramics*, by Kingery, Bowen and Uhlmann,[12] delayed thermal stress fractures will often occur after temperature changes. This is because the maximum thermal stress is achieved only as a temperature gradient develops after the temperature change. That delay time for thermal stress fracture depends on the heat transfer conditions of the cookware and the heat capacity of the contents within. For example, preparing a roast, a chicken or a ham in a glass cookware dish would each have different heat capacities and present different heat transfer conditions, and the cooking temperatures of their surroundings would be different as well. Therefore, time delay intervals to fracture are expected to vary. The reports that the soda lime silicate glass cookware experiences these delayed shattering fractures suggests that the thermal stresses that develop exceed its strength.

The time dependence of thermal stresses is a function of the heat transfer conditions during the temperature change. These factors determine the magnitude of the temperature gradients and cause the thermal stresses. For example, transferring a hot dish containing a roast directly from the oven to a cold wet stone countertop would be a much more severe thermal shock than putting the same dish on an insulating pad surface.

Because it is impossible to consider all of the possible variations that might occur in household kitchens, a simple, linear elastic approach to a sudden temperature change is applied to estimate and compare the thermal stress resistance of the two glasses.

As noted in Kingery, Bowen and Uhlmann,[12] the simple formula for the fully restrained development of a linear elastic thermal stress, σ_{ts}, from temperature change is

$$\sigma_{ts} = \alpha E \Delta T \quad (1)$$

where α is the coefficient of thermal expansion, E the elastic modulus and ΔT the temperature differential over which the thermal stress or thermal expansion restraint is generated. The ΔT may occur during either heating or cooling. Note that this simple estimate does not include the heat transfer factors, nor time factors, nor does it account for the size and shape of the glass cookware pieces in question. Equation (1) is applicable to an instantaneous, rapid temperature change.

To compare the thermal shock fracture resistance of borosilicate and soda lime silicate glasses, Equation (1) is rearranged to express the ΔT values required to achieve fracture by the thermal stresses generated in the glass cookware during a temperature change. These ΔT values can be compared with typical cooking temperatures and other temperature changes that are regularly encountered in a household kitchen. Equating σ_{ts} to the fracture stress of the glass, σ_f, then rearranging Equation (1) yields

$$\Delta T = \sigma_f / \alpha E \quad (2)$$

where the thermal stress, σ_{ts}, is now σ_f, the failure strength of the glass object.

A typically used benchmark value for glass strength, as noted by Mould[13] and also by Kurkjian[14] is about 5,000 pounds per square inch (about 30 megapascals). The elastic moduli of the two glasses are slightly different, but similar—about 10,200,000 psi (about 68 gigapascals) for soda lime silicate glass and about 9,100,000 psi (about 62 gigapascals) for borosilicate glass.[15] Their coefficients of thermal expansions are very different. The α of borosilicate is about $3 \times 10^{-6}°C^{-1}$. The α of soda lime silicate glass is about $9 \times 10^{-6}°C^{-1}$, about three times greater.[15]

Substituting these values into Equation (2) yields the ΔT values of the rapid temperature change necessary to initiate thermal shock fracture. For borosilicate glass, the calculated temperature difference is about 183°C (about 330°F), but it is only about 55°C (about 99°F) for the soda lime silicate glass. This is a substantial difference.

Carter and Norton,[16] in their text *Ceramic Materials, Science and Engineering*, use a somewhat more complicated

From battery jars to kitchens: A short history of glass cookware

Today, glass cookware is found in virtually every household kitchen, giving the impression that it has been around a very long time. Many older consumers still associate the Pyrex brand with the Corning company, and most consumers are unaware that the manufacturers of Pyrex and the glass formulation have changed over several decades.

Glass cookware is a commercial product of the early 20th Century. Present-day glass cookware appears to have originated from research at what was then known as the Corning Glass Works to improve the thermal shock resistance of battery jars. Corning developed a low-thermal-expansion borosilicate glass that vastly improved the longevity of the battery jar glasses by reducing their thermal shock fracture in service.[6]

It is an interesting scenario how this glass found its way into household kitchens.[6] During the research studies, one of the Corning scientists, Jesse Littleton, took the bottoms of several of Corning's borosilicate glass jars home for his wife to bake her pies. Her successful culinary endeavors led to the development of a line of cookware and laboratory glassware by Corning that became known as Pyrex.

It was initially called "Py-right," with an obvious "pie" to "py" phonetic association. The glass, itself, was originally called Nonex (NON-EXpanding). This glass appears to have evolved into the famous low-expansion Corning 7740 (tradename Pyrex)[5] and other Corning borosilicate glasses.

In 1997, the company sold its consumer products business, including Pyrex-branded consumer products, to Borden Inc. (now KKR Borden), which changed its name to World Kitchens in 2006.

Corning still owns the Pryex trademark, and it still manufactures Pyrex-branded high-quality laboratory borosilicate glassware. However, most glass cookware in the United States is not the same borosilicate composition as the original Corning Pyrex.

form of Equation (1) that includes heat transfer terms. They address many ceramics as well as glasses. Their results will be compared with the calculations of this simple approach. The $\alpha E \Delta T$ term is common to all mathematical models.

Carter and Norton[13] provide an example (which includes heat transfer terms), estimating thermal stress ΔT values for fracture that are about 270°C (about 486°F) for the borosilicate Pyrex and about 80°C (about 144°F) for soda lime silicate glass. Based on these two independent results, it is evident that the temperature differential—the ΔT for fracture initiation by severe thermal stress—is much larger for the borosilicate glass.

A brochure posted on Corning's website[17] presents thermal stress resistance estimates of several glasses of various compositions, including its 7740 borosilicate glass and a soda lime silicate glass (Corning 0080). The reported thermal stress resistance value for the borosilicate glass is 54°C (97°F), whereas that of the soda lime silicate glass is 16°C (29°F)—a factor of about three. Thermal stress resistance is defined for this calculation as "the temperature differential between two surfaces of a tube or constrained place that will cause a tensile stress of 0.7 kg/mm (1000 psi) on the cooler surface."

It is important to note that, according to this brochure, the primary use of 0080 is Petri dishes, not household cookware. Also, it must be noted that soda lime silicate glass compositions vary widely, and values of thermal properties will vary, too. However, these data illustrate the magnitude of the difference in thermal stress resistance that is possible between the two categories of glasses. The superior thermal stress resistance of borosilicate glass for cookware was confirmed in empirical tests performed on glass cookware objects by *Consumer Reports*.[1,2]

It is informative to compare the ΔT values that have been determined to achieve the fracture stress from the three calculations. Table 1 lists those for the soda lime silicate glass and for Pyrex borosilicate. This tabulation shows that in every instance the ΔT for the soda lime silicate glass is much lower than that for the borosilicate. The difference is about a factor of three times for each despite the differences in the calculations. This is because the thermal expansion of the soda lime silicate glass is about three times that of the borosilicate. Clearly, soda lime glass is much more susceptible to thermal shock than the borosilicate glass because of its higher thermal expansion of coefficient.

Table 1 Calculations of thermal differential, ΔT, for soda lime silicate and borosilicate glass.

Source	ΔT Soda lime silicate	ΔT Pyrex borosilicate
This paper	~55°C (99°F)	~183°C (330°F)
Carter and Norton[16]	~80°C (144°F)	~270°C (436°F)
Corning brochure[17]	~16°C (29°F)	~54°C (97°F)

From the perspective of kitchen applications, a good calibration point is that of boiling water, 100°C (212°F) at sea level. None of the calculations suggest the soda lime silicate glass would be likely to survive a rapid exposure to boiling water. Consistent with these calculations, the October 2011 *Consumer Reports* article describes a boiling water incident that led to explosive fracture of a measuring cup and an accompanying injury.[2]

Based on recipes in the famous cookbook, *The Joy of Cooking*, by Rombauer, Becker and Becker,[18] these calculated ΔT values of concern are well within the temperature ranges of kitchen cooking endeavors. For example, their recommended oven temperatures are 350°F for a pork loin or rib eye roast (after 450°F preheat) and 325°F for a turkey (after 450°F preheat). Relative to room temperature, these cooking temperatures could easily exceed the expected ΔT values for the thermal stress fracture of soda lime silicate glass and could cause thermal shock fracture.

The ΔT value alone does not guarantee thermal fracture of glass cookware. However, because of the low ΔT for soda lime silcate glass, one must exercise extreme caution when using cookware made of this glass. Even at modest kitchen temperatures, there is a definite possibility of thermal shock fracture.

Heat strengthening of soda lime silicate glass cookware

In Consumer Product Safety Commission correspondence,[3] CPSC's SaverProducts.gov website[3] and literature relative to shattering glass cookware, manufacturers have responded that during manufacturing they have taken steps to strengthen the soda lime silicate glass cookware by applying a heat strengthening or a thermal tempering process. The manufacturers assert that the process increases the strength of the glass, its impact resistance and its resistance to thermal stress fracture.[19]

This strengthening approach is discussed by Mencik.[20] In a related publication, Gardon[21] extensively reviews the annealing and tempering processes, of which heat strengthening is a variant. In principle, this approach has technical merit, because increasing the glass cookware strength would be expected to increase the ΔT values for thermal shock fracture initiation. (Recall that the glass strength, σ_F, is in the numerator of Equation (2) for ΔT.)

It is possible to detect residual stresses in glass via photoelasticity. Thus, to test this heat-strengthening issue, the authors bought a half dozen new, unused soda lime silicate cookware pieces, which were then examined in the photoelasticity laboratory at the University of Alabama. The authors observed no strong fringe patterns, which would be indicative of residual stresses, in any of the cookware. Although this could be the result of low-stress optic coefficients of the soda lime silicate glasses, it also suggests that the efficacy of heat strengthening that may have been applied to the cookware during manufacturing was minimal and was not sufficient to significantly increase strength or thermal stress resistance of the soda lime silica cookware.

It is well documented that thermally strengthened glasses also have a characteristic cracking pattern when they fracture. Tempered glass breaks into small equiaxed pieces in a fracture process known as dicing. Automobile glass, for example, fractures by dicing into small fragments. McMaster, Shetterly and Bueno[22] depict this form of fragmentation in their review, and creation of these dicing fragments has been analyzed in detail by Warren.[23]

The authors' examination of fracture pieces of several dishes, including some that were intentionally broken by thermal stress and some by impact, revealed no dicing fragmentation. The soda lime silicate cookware consistently fractured into extended glass shards.

The large shards produced by the fracture of the soda lime silicate cookware imply that the thermal or heat strengthening of the soda lime silicate cookware was not substantive. Figure 3 illustrates a reconstructed "Pyrex" bowl that was purchased new and intentionally thermal shocked in a household kitchen. There is no evidence of dicing fracture. The occurrence of long sharp glass shards is also described in numerous reports on the Internet and in the CPSC literature.

Another tool for evaluating whether there is significant heat strengthening of soda lime silicate glass is fractography, which can reveal information about the stress state of a fractured piece. When a glass object with surface compressive stresses fractures, the propagating crack front in the glass proceeds ahead of the crack at the object surface because the near-surface advance is inhibited by the surface compressive stresses.[24]

Indeed, the crack growth pattern on the fracture surface of shards of soda lime silicate glass cookware, as shown in Figure 4, indicates that the soda lime silicate glass has been heat strengthened. Note the Wallner line ripples on the cross section clearly are trailing at the glass surfaces, indicative of surface compressive stresses. (Wallner lines are slight ripples on a fracture surface that are indicative of the direction of crack propagation and the state of stress.)

Thus, although the cookware definitely has been heat strengthened as stated by the manufacturer,[19] it does not appear to be sufficient to increase substantially the thermal stress fracture resistance of the cookware, nor is it sufficient to create a desirable dicing fracture pattern for the glass cookware.

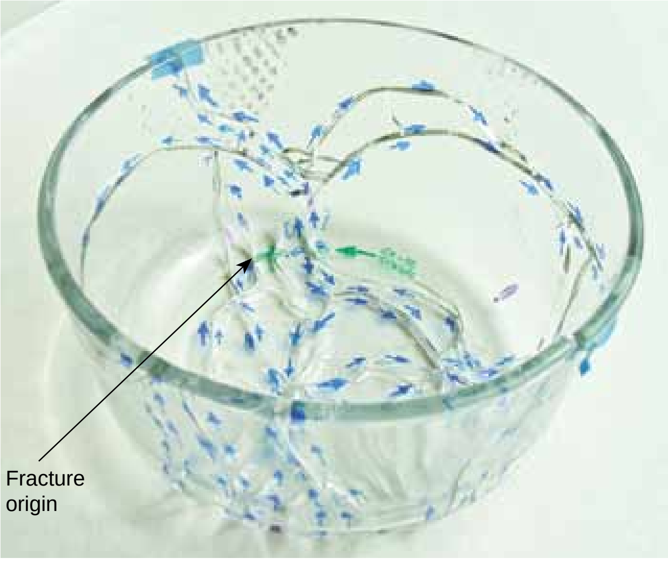
Extensive, in-depth fractography of the fracture surfaces of shards from a large number or series of different reconstructed broken soda lime silicate cookware pieces would make it possible to identify the causes of individual failure events. Such studies, as described by Quinn[25] in *Fractography of Ceramics and Glasses*, are recommended, but are beyond the scope of this article.

Conclusions about shattering glass cookware

The above analyses of shattering soda lime silicate glass cookware indicate that the phenomenological cause of these fractures is thermal stress fracture that develops from temperature changes to which the glass cookware is subjected in the household kitchen. This conclusion is substantiated by three observations: (i) occurrence of the shattering incidents during temperature changes; (ii) the frequent presence of a time delay to fracture initiation after a temperature change; and (iii) calculated temperature differentials, the ΔT values for the initiation of thermal shock fracture during temperature changes of soda lime silicate and borosilicate glasses. In addition, the creation of fracture shards instead of desired dicing of broken pieces of cookware suggests that manufacturers' heat strengthening is insufficient.

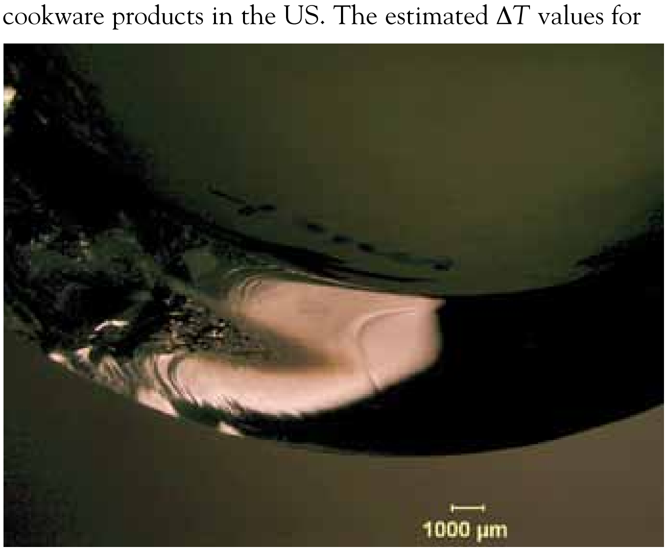
Fracture-initiating temperature differentials can be exceeded during household kitchen cooking. However, not all kitchen procedures create ΔT values that are sufficient to cause thermal stress fracture of the soda lime silicate glass cookware. Time-dependent heat transfer conditions also will affect the magnitude of the thermal stresses that develop.

The original Corning Pyrex borosilicate glass is considerably more resistant to thermal stress fracture than the soda lime silicate glasses that currently are used for most glass cookware products in the US. The estimated ΔT values for



(Credit: G. Quinn.)

Figure 3. A reconstructed soda lime silicate Pyrex bowl fractured by thermal shock. Arrows outline the crack paths.



(Credit: Fractograph supplied by G. Quinn.)

Figure 4. The fracture surface of a soda lime silicate glass cookware bowl (from bowl in Figure 3) as it formed during thermal shock failure. Note the Wallner lines trailing along the surfaces, inside and out, are indicative of heat strengthening of the glass during manufacturing.[22]

thermal stress fracture of that borosilicate glass suggest that normal kitchen cooking temperatures are unlikely to cause thermal stress failures. However, the estimated ΔT values for thermal stress fracture of soda lime silicate glass cookware are well within the range of kitchen temperatures.

Estimates of the ΔT temperature differentials indicate that soda lime silicate glass cookware can be expected to survive moderate temperature changes that are experienced in a household kitchen. However, documented reports of incidents of dramatic shattering failures during what most kitchen cooks would consider normal use suggests that the margin of safety for avoiding thermal stress failures of soda lime silicate cookware is borderline. It does not appear to be adequate for all household cooking. Caution is in order when using soda lime silicate cookware in applications that may involve temperature changes, as print warnings on the product labels indicate.

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A 1936 advertisement for the original Pyrex borosilicate glass cookware.

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