Designation: C1720 – 21

Standard Test Methods for Determining Liquidus Temperature of Waste Glasses and Simulated Waste Glasses[1]

This standard is issued under the fixed designation C1720; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover procedures for determining the liquidus temperature (T_L) of nuclear waste, mixed nuclear waste, simulated nuclear waste, or hazardous waste glass in the temperature range from 600 °C to 1600 °C. This test method differs from Practice C829 in that it employs additional methods to determine T_L. T_L is useful in waste glass plant operation, glass formulation, and melter design to determine the minimum temperature that must be maintained in a waste glass melt to make sure that crystallization does not occur or is below a particular constraint, for example, 1 volume % crystallinity or $T_{1\%}$. As of now, many institutions studying waste and simulated waste vitrification are not in agreement regarding this constraint (**1**).[2]

1.2 Three methods are included, differing in (*1*) the type of equipment available to the analyst (that is, type of furnace and characterization equipment), (*2*) the quantity of glass available to the analyst, (*3*) the precision and accuracy desired for the measurement, and (*4*) candidate glass properties. The glass properties, for example, glass volatility and estimated T_L, will dictate the required method for making the most precise measurement. The three different approaches to measuring T_L described here include the following: Gradient Temperature Furnace Method (*GT*), Uniform Temperature Furnace Method (*UT*), and Crystal Fraction Extrapolation Method (*CF*). This procedure is intended to provide specific work processes, but may be supplemented by test instructions as deemed appropriate by the project manager or principle investigator. The methods defined here are not applicable to glasses that form multiple immiscible liquid phases. Immiscibility may be detected in the initial examination of glass during sample preparation (see 9.3). However, immiscibility may not become apparent until after testing is underway.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C162 Terminology of Glass and Glass Products

C829 Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method

C859 Terminology Relating to Nuclear Materials

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E2282 Guide for Defining the Test Result of a Test Method

2.2 *NIST Standards:*[4]

SRM-773 National Institute for Standards and Technology (NIST) Liquidus Temperature Standard

SRM-674b NIST X-Ray Powder Diffraction Intensity Set for Quantitative Analysis by X-Ray Diffraction (XRD)

SRM-1416 Aluminosilicate Glass for Liquidus Temperature

SRM-1976a NIST Instrument Response Standard for X-Ray Powder Diffraction

SRM-1976c Instrument Response Standard for X-Ray Powder Diffraction

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[1] These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.13 on Spent Fuel and High Level Waste.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.

2.3 *Other Standard:*[5]

ISO/IEC 17025:2017 American National Standards Institute/National Conference of Standards Laboratories (ANSI/NCSL) General Requirements for the Competence of Testing and Calibration Laboratories

3. Terminology

3.1 For terms not defined herein, refer to Terminology C859 and C162.

3.2 *Definitions:*

3.2.1 *air quenching*—to pour or place a molten glass specimen on a surface, for example, a steel plate, and cool it to the solid state.

3.2.2 *anneal*—to prevent or remove processing stresses in glass by controlled cooling from a suitable temperature, for example, the glass transition temperature (T_g) (modified from Terminology C162).

3.2.3 *annealing*—a controlled cooling process for glass designed to reduce thermal residual stress to an acceptable level and, in some cases, modify structure (modified from Terminology C162).

3.2.4 *cleaning glass*—glass or flux used to remove high viscosity glass, melt insolubles, or other contamination from platinum-ware.

3.2.5 *crystallize*—to form and/or grow crystals from a glass melt during heat-treatment or cooling.

3.2.6 *crystallization*—the progression in which crystals are first nucleated and then grown within a host medium.

3.2.6.1 *Discussion*—Generally, the host may be a gas, liquid, or another crystalline form. However, in this context, it is assumed that the medium is a glass melt.

3.2.7 *crystallization front*—the boundary between the crystalline and crystal-free regions in a test specimen that was subjected to a temperature gradient heat-treatment.

3.2.8 *furnace profiling*—the process of determining the actual temperature inside of a furnace at a given location; this involves different steps for different types of furnaces.

3.2.9 *glass*—an inorganic product of fusion that has cooled to a rigid condition without crystallizing (see Terminology C162); a noncrystalline solid or an amorphous solid (**2**).

3.2.10 *glass sample*—the material to be heat-treated or tested by other means.

3.2.11 *glass specimen*—the material resulting from a specific heat treatment.

3.2.12 *glass transition temperature* (T_g)—on heating, the temperature at which a glass transforms from a solid to a liquid material, characterized by the onset of a rapid change in several properties, such as thermal expansivity.

3.2.13 *gradient furnace*—a furnace in which a known temperature gradient is maintained between the two ends.

3.2.14 *inhomogeneous glass*—a glass that is not a single amorphous phase; a glass that is either phase separated into multiple amorphous phases or is crystallized.

3.2.15 *liquidus temperature* (T_L)—the maximum temperature at which thermodynamic equilibrium exists between the molten glass and its primary crystalline phase.

3.2.15.1 *Discussion*—T_L is the maximum temperature at which a glass melt crystallizes.

3.2.16 *melt insoluble*—a crystalline, amorphous, or mixed phase material that is not appreciably soluble in molten glass, for example, noble metals, noble metal oxides.

3.2.17 *mixed waste*—waste containing both radioactive and hazardous components regulated by the Atomic Energy Act (AEA) (**3**) and the Resource Conservation and Recovery Act (RCRA) (**4**), respectively.

3.2.17.1 *Discussion*—The term "radioactive component" refers to the actual radionuclides dispersed or suspended in the waste substance (**5**).

3.2.18 *mold*—a pattern, hollow form, or matrix for giving a certain shape or form to something in a plastic or molten state. **Webster's Dictionary**[6]

3.2.19 *nuclear waste glass*—a glass composed of glass-forming additives and radioactive waste.

3.2.20 *observation*—the process of obtaining information regarding the presence or absence of an attribute of a test specimen or of making a reading on a characteristic or dimension of a test specimen (see Terminology E2282).

3.2.21 *preferred orientation*—when there is a stronger tendency for the crystallites in a powder or a texture to be oriented more one way, or one set of ways, than all others.

3.2.21.1 *Discussion*—This is typically due to the crystal structure. **IUCr**[7]

3.2.22 *primary phase*—the crystalline phase at equilibrium with a glass melt at its liquidus temperature.

3.2.23 *radioactive*—of or exhibiting radioactivity; a material giving or capable of giving off radiant energy in the form of particles or rays. **American Heritage**[8] **Webster's**[6]

3.2.23.1 *Discussion*—Example of particles or rays formed by the disintegration of atomic nuclei are α, β, and γ; said of certain elements, such as radium, thorium, and uranium and their products.

3.2.24 *Round-Robin*—an interlaboratory and intralaboratory testing process to develop the precision and bias of a procedure.

3.2.25 *section*—a part separated or removed by cutting; a slice, for example, representative thin section of the glass specimen. **Webster's**[6]

3.2.26 *simulated nuclear waste glass*—a glass composed of glass forming additives with simulants of, or actual chemical species, or both, in radioactive wastes or in mixed nuclear wastes, or both.

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[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[6] Merriam-webster.com.

[7] IUCr Online Dictionary of Crystallography, 2011.

[8] American Heritage Dictionary, 1973.

3.2.27 *surface tension*—a property, due to molecular forces, by which the surface film of all liquids tends to bring the contained volume into a form having the least possible area.

3.2.28 *test determination*—the value of a characteristic or dimension of a single test specimen derived from one or more observed values (see Terminology E2282).

3.2.29 *test method*—a definitive procedure that produces a test result (see Terminology E2282).

3.2.30 *test observation*—see *observation*.

3.2.31 *uniform temperature furnace*—a furnace in which the temperature is invariant over some defined volume and within some defined variance.

3.2.32 *vitrification*—the process of fusing waste with glass making chemicals at elevated temperatures to form a waste glass (see Terminology C162).

3.2.33 *volatility*—the act of one or more constituents of a solid or liquid mixture to pass into the vapor state.

3.2.34 *waste glass*[6]—a glass developed or used for immobilizing radioactive, mixed, or hazardous wastes.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *ASTM Type I water*—purified water with a maximum total matter content including soluble silica of 0.1 g/m^3, a maximum electrical conductivity of 0.056 μΩ^{-1}/cm at 25 °C, and a minimum electrical resistivity of 18 MΩ × cm at 25 °C.

3.3.2 *set of samples*—samples tested simultaneously in the same oven.

3.3.3 *standard*—to have the quality of a model, gauge, pattern, or type. **Webster's**[6]

3.3.4 *standardize*—to make, cause, adjust, or adapt to fit a standard (**5**); to cause to conform to a given standard, for example, to make standard or uniform. **Webster's**[6]

3.4 *Abbreviations:*

3.4.1 *AEA*—Atomic Energy Act

3.4.2 *ANSI*—American National Standards Institute

3.4.3 *ASTM*—American Society for Testing and Materials

3.4.4 *CF*—crystal extrapolation method

3.4.5 C_F—crystal fraction in a sample or specimen

3.4.6 *EDS*—energy dispersive spectrometry

3.4.7 η—viscosity

3.4.8 *FWHM*—full width of a peak at half maximum

3.4.9 *GF*—gradient temperature furnace

3.4.10 *GT*—gradient temperature furnace method

3.4.11 *HF*—hydrofluoric acid

3.4.12 *HLW*—high-level waste

3.4.13 *ID*—identification

3.4.14 *MSE*—mean squared error

3.4.15 *NBS*—National Bureau of Standards

3.4.16 *NCSL*—National Conference of Standards Laboratories

3.4.17 *NIST*—National Institute for Standards and Technology (formerly NBS)

3.4.18 *OM*—optical microscope or optical microscopy

3.4.19 *PDF*—powder diffraction file

3.4.20 *RCRA*—Resource Conservation and Recovery Act

3.4.21 *RIR*—relative intensity ratio

3.4.22 *RLM*—reflected light microscopy

3.4.23 *SD*—standard deviation

3.4.24 *SEM*—scanning electron microscope or scanning electron microscopy

3.4.25 *SRM*—Standard Reference Material

3.4.26 *SSE*—sum of squared errors

3.4.27 $T_{1\%}$—temperature where glass contains 1 volume % of a crystalline phase

3.4.28 T_a—primary UT measurement above T_L

3.4.29 T_c—primary UT measurement below T_L

3.4.30 T_g—glass transition temperature

3.4.31 T_L—liquidus temperature

3.4.32 *TLM*—transmitted light microscopy

3.4.33 T_M—melting temperature for glass preparations

3.4.34 *UF*—uniform temperature furnace

3.4.35 *UT*—uniform temperature furnace method

3.4.36 *WC*—tungsten carbide

3.4.37 *XRD*—X-ray diffraction

4. Summary of Test Method

4.1 These test methods describe methods for determining the T_L of waste or simulated waste glasses. Fig. 1 illustrates an example T_L for a simple two-component liquid on an arbitrary binary phase diagram.

4.1.1 *Gradient Temperature Furnace Method (GT)*—This method is similar to Practice C829, "Standard Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method," although it has been modified to meet the specific needs of waste and simulated waste glass measurements. The most pronounced differences between this method and the Practice C829 "boat method" are the sample preparation and examination procedures.

4.1.1.1 Samples are loaded into a boat, for example, platinum alloy (Fig. 2) with a tight-fitting lid, and exposed to a linear temperature gradient in a gradient furnace (Fig. 3) for a fixed period of time. The temperature, as a function of distance, *d*, along the sample, is determined by the location within the gradient furnace, and the T_L is then related to the location of the crystallization front in the heat-treated specimen (Fig. 4).

4.1.1.2 Following the heat-treatment, the specimen should be annealed at, or near, the glass transition temperature, T_g, of the glass (this should be previously measured or estimated) to reduce specimen cracking during cutting and polishing.

4.1.1.3 The specimen should then be scored or marked to signify the locations on the specimen located at different depths into the gradient furnace, that is, locations heat-treated at specific temperatures.

4.1.1.4 If the specimen is optically transparent, it can be observed with transmitted light microscopy (TLM) or reflected light microscopy (RLM) to look for bulk or surface

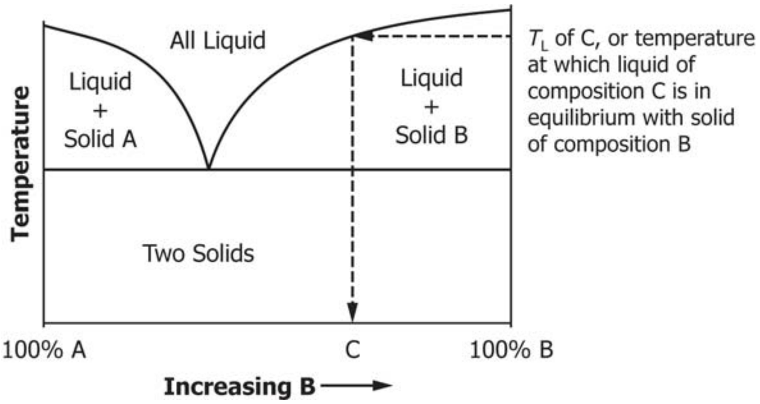


FIG. 1 Binary Phase Diagram of Components A and B with T_L of Composition C Highlighted

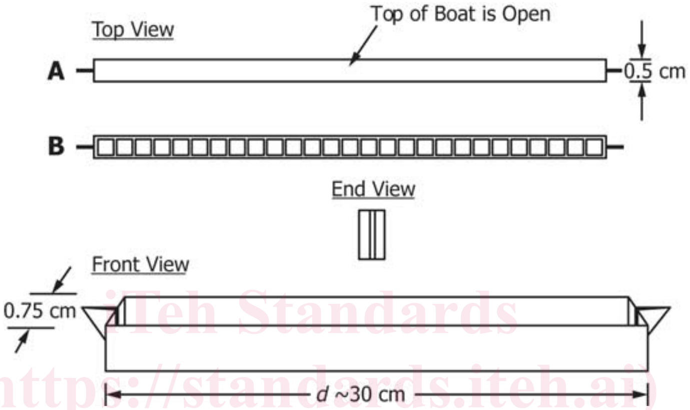


FIG. 2 GF Boat Diagram: (*A*) Single Chamber Crucible Design (*B*) Single Chamber Design Loaded with a Set of Samples (that is, Smaller Crucibles)

FIG. 3 Photograph of Typical Gradient Temperature Furnace

crystallization, respectively. If the specimen is not optically transparent or is barely optically transparent (for example, in glasses with high quantities of Fe_2O_3), a cut or fractured section of the glass can be polished very thin (that is, a thin section can be made) to allow for observation. Another option for surface observations is scanning electron microscopy (SEM). This method provides a quick measurement of T_L in the absence of convective flow of glass in the gradiant furnace, which distorts the location of the crystallization front (that is, the crystallization front is likely not constant at a given temperature (see Fig. 4)).

4.1.1.5 The temperature gradient and increased volatility at higher temperatures cause gradients in surface tension, which in turn cause convective flow. This method is ideal for glasses with a T_L less than roughly 1000 °C or glasses with a low volatility near the T_L. If the temperature range spanned by the crystallization front is too high for the desired tolerance, *UT* or *CF* should be used for a more precise T_L measurement. *GT* is

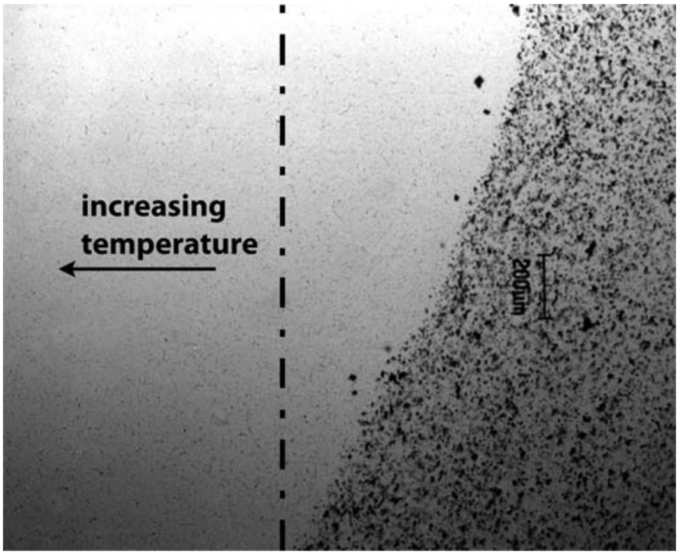


FIG. 4 OM Micrograph of the Crystallization Front in a GT Specimen

not easily used to measure the T_L on radioactive glasses because of the size of the gradient furnace and the complicated sample analysis required. This method is not recommended for glasses with a T_L in a temperature range of very low glass viscosity (that is, $\eta < 50$ Pa·s).

4.1.2 *Uniform Temperature Furnace Method (UT)*—This method is similar to the methods used in phase diagram determination and can be used for making more precise measurements than those determined with *GT*.

4.1.2.1 In this method, a glass sample is loaded into a crucible (for example, platinum alloy, see Fig. 5) with a tight-fitting lid and subjected to temperatures for a fixed period of time (for example, 24 h ± 2 h). Following heat-treatment, the specimen can be observed by optical microscopy (OM) for the appearance or absence of crystalline or other undissolved materials with methods similar to those previously described (4.1.1). Crystalline material present in the meniscus (that is, in the upper corners of the heat-treated specimen) can be an artifact of this process and should be reported separately. The locations of the crystals within the heat-treated specimen need to be reported (that is, the melt-crucible interface, meniscus, melt-air interface, or the bulk) on the *liquidus temperature data sheet* (see Appendix X1). The crystal locations used to define T_L should be clearly documented when reporting T_L. Typically, crystals in any location except for the meniscus (where composition can be affected by volatility) are used. In some circumstances, surface crystallization can be excluded from T_L determination.

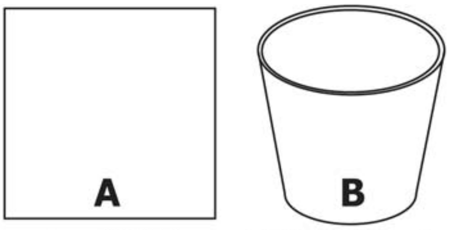
4.1.2.2 The T_L is then given by the temperature range between the highest temperature at which a specimen contains crystals (T_c) and the lowest temperature without crystals in the specimen (T_a); the T_L is then typically defined as the average of T_a and T_c.

4.1.2.3 This method is more time consuming as it requires more heat-treatments than *GT*, although it minimizes the effects of volatility and eliminates the convection-driven uncertainty in crystallization front measurements. This method is used for high precision measurements (on the order of ±5 °C), is more easily applied to radioactive glasses, and can be used to measure T_L values as high as 1600 °C with typical high-temperature furnaces (for example, furnaces with $MoSi_2$ heating elements), and even higher with specialized equipment and high-temperature crucibles. This method may be used for glasses with a high volatility near T_L under certain circumstances.

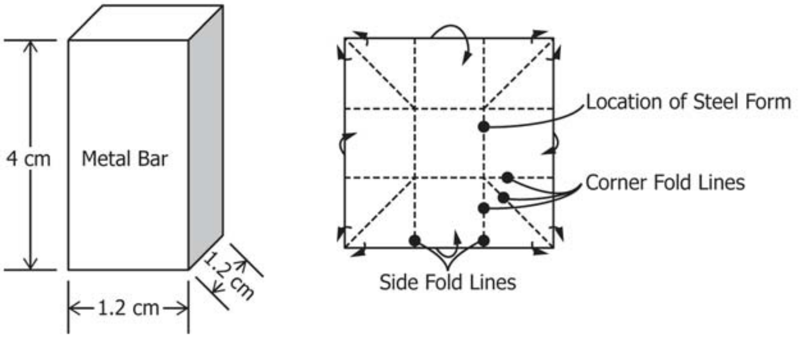
4.1.3 *Crystal Fraction Extrapolation Method (CF)*—This method is an alternate method that uses a UT specimen to measure the crystal fraction, C_F (in mass % or volume %), of a crystalline phase or phases in a sample heat-treated at multiple temperatures, $T << T_L$. The C_F at each temperature is measured with XRD, RLM, TLM, SEM, or combinations thereof, by mass and/or volume %, and then T_L is achieved by extrapolating C_F as a function of temperature to zero crystals. This method is more suited for glasses with a higher volatility near the T_L than the previous methods. When multiple crystalline phases are present, XRD is an effective method for quantifying C_F as a function of temperature and is very effective at determining the T_L of each phase independently; this would be more difficult by *GT* and *UT*. *CF* yields the additional benefit of equilibrium crystal fractions as a function of temperature, which can sometimes tend to be non-linear at $C_F > 5$ mass % to 10 mass % crystallinity for most crystalline phases. Different techniques for *CF* are described below.

4.1.3.1 *Volume Fraction of Crystal(s) in the Specimen* (12.4.2)—With TLM, RLM, or SEM as well as image analysis software, it is possible to measure the area fraction of crystals in an image or micrograph of the specimen. The area fraction is then equivalent to the volume fraction if the image is representative of the bulk of the specimen, and the effective depth of the image is insignificant. If this process is done at different temperatures, the T_L can be extrapolated as a function of temperature.

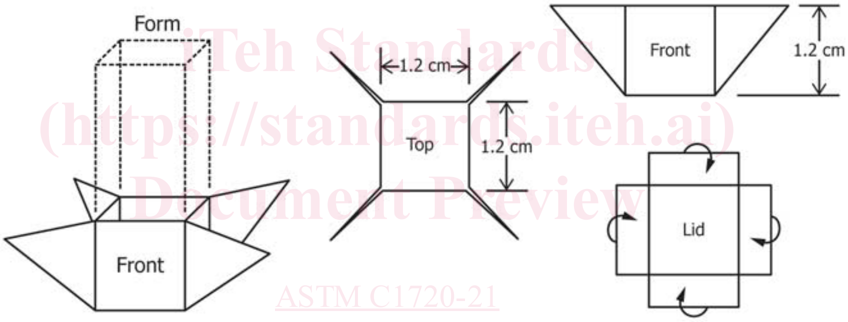
NOTE 1—The mass fraction of crystals in the specimen can be estimated if the densities of the glass and the crystal(s) are known.



(1) 3.6- × 3.6-cm square piece of foil (A) or conical thimble (B) made of inert material, for example, platinum alloy



(2) For the cubic crucible, take foil in (1) and draw an "×" pattern from corner to corner (excluding the center square) to help locate the form used and where to fold the corners.



(3) Fold the corners along the diagonal lines. Then fold the sides up next to the form.

FIG. 5 *UT* and *CF* Crucible Schematic

4.1.3.2 *Number Fraction of Crystal(s) in the Specimen* (12.4.3)—In the same fashion as described in 4.1.3.1, count the number of crystals in an image or micrograph of the specimen at different temperatures. If this process is done at different temperatures, the T_L can be extrapolated as a function of temperature.

4.1.3.3 *Mass Fraction of Crystal(s) in the Specimen by Adding a Known Crystalline Phase* (12.4.4)—Adding a known mass fraction of a known, standard crystalline material (for example, NIST SRM-674b) allows the standardization of the XRD pattern. The standards and the unknown specimen should be run independently before mixing to verify that there is not overlap between the peaks of the standard and the peaks in the unknown specimen because this will make quantification difficult and less accurate. The standardized pattern can then be used to generate quantitative (if the crystal structure has been refined) or semi-quantitative (if the crystal structure has not been refined) C_F analysis with Rietveld **(6-8)** refinement software or the relative intensity ratio (RIR) method (12.4.5).

4.1.3.4 *Mass Fraction of Crystal(s) in the Specimen by Comparing it to the Calibration Curve* (12.4.5)—In this method, samples with known concentrations of the crystalline phases being analyzed are prepared and tested using XRD. The peak area's (full width at half maximum or FWHM, total crystal peak area, or highest peak area) and known crystal fractions are used to generate a calibration curve. The peak area of the unknown specimen is then used in the calibration equation to determine a quantitative (if interpolated) or semi-quantitative (if extrapolated) crystal fraction.

4.1.3.5 *Volume Fraction of Crystal(s) in the Specimen With C_F Data From XRD Analysis*—Commonly, melter constraints are in terms of a volume % of crystallinity, for example, $T_{1\%}$. Once C_F data are obtained in mass % by XRD, the remaining mass of glass, m_g, is calculated as a difference given by

$$m_g = m_t - \sum_{i=1}^{N} m_{c,i} \qquad (1)$$

where:

m_t = the total mass (that is, the value is normalized to one and thus component values are mass fractions), and
$m_{c,i}$ = the mass fraction of the *i*-th crystalline phase observed and quantified by XRD.

By converting the mass fractions of the *i*-th component additives, m_i, into mole fractions, M_i, the density of glass, ρ_g, can be computed with the following expression:

$$\rho_g = \frac{\sum_{i=1}^{N} M_i m_{m,i}}{\sum_{i=1}^{N} M_i V_{M,i}} \tag{2}$$

where:

$m_{m,i}$ = the molecular mass of the *i*-th oxide, and
$V_{M,i}$ = the molar volume of the *i*-th component additive explained elsewhere (**9**).

The total volume of each heat treatment, V_{HT}, is calculated with

$$V_{HT} = \frac{m_g}{\rho_g} + \frac{\sum_{i=1}^{N} m_{c,i}}{\rho_{c,i}} \tag{3}$$

where:

$\rho_{c,i}$ = the density of the *i*-th crystalline component.

The volume % of the *i*-th crystalline component, $V_{c,i}$, in the heat-treated specimen is denoted by

$$V_{c,i} = 100 \times \frac{m_{c,i}}{(\rho_{c,i} \times V_{HT})} \tag{4}$$

The values of $V_{c,i}$ can then be plotted as a function of temperature and a linear correlation fit to the data with

$$V_{c,i} = m \times T + b \tag{5}$$

where:

$T_{1\%}$ = $(V_{c,i} - b)/m$ when $V_{c,i} = 1$ ($T_{1\%}$)

5. Significance and Use

5.1 This procedure can be used for (but is not limited to) the following applications:

(1) support glass formulation development to make sure that processing criteria are met,

(2) support production (for example, processing or troubleshooting), and

(3) support model validation.

6. Apparatus

6.1 *Equipment for GT:*

6.1.1 Resistance-heated tubular gradient furnace capable of achieving temperatures of 550 °C to 1150 °C with gradients in the range of roughly 1 °C/mm (Fig. 3). For glasses with an estimated T_L > 1150 °C, furnaces with elements capable of high temperatures need be used, for example, $MoSi_2$.

6.1.2 Calibrated thermocouple and temperature readout device appropriate for the estimated temperature range that will be used for testing. Type K thermocouples can be used within 95 °C to 1260 °C, Type R thermocouples can be used within 870 °C to 1450 °C, and Type S thermocouples can be used within 980 °C to 1450 °C without special calibrations or qualifications.

6.1.3 Resistance furnace and controller used for annealing (capable of maintaining constant temperatures between 400 °C and ~900 °C) with a temperature accuracy of 10 °C.

6.1.4 Specimen boat made of material inert to the sample (for example, platinum alloy) with approximate dimensions of 0.5 cm × 1 cm × 10 cm to 30 cm (width × height × length), respectively; an example specimen boat is shown in Fig. 2. If the test glass viscosity is below 5 Pa·s at the measurement temperature, it is recommended that a round-based crucible be used. A separate option with Method A is to fill the long boat with several small individual boats with individual lids (Fig. 2-B).

6.1.5 Diamond cutoff saw.

6.1.6 Variable speed polisher.

6.1.7 Silicone rubber mold for mounting of GT glass specimen in epoxy.

6.1.8 OM for TLM and/or RLM.

6.1.9 SEM/EDS.

6.1.10 XRD.

6.2 *Equipment Needed for UT:*

6.2.1 Resistance furnace capable of maintaining constant temperatures T ~550 °C to 1600 °C (that is, $MoSi_2$ heating elements) or furnace capable of $T \leq 1200$ °C for glasses with $T_L \leq 1150$ °C.

6.2.2 Calibrated thermocouple and temperature readout device appropriate for the estimated temperature range that will be used for testing (6.1.2).

6.2.3 Specimen boat (or crucible) and tight fitting lid made of material compatible with the sample (for example, platinum alloy) with suggested dimensions of 1.2 cm × 1.2 cm × 1.2 cm (width × height × length, respectively) (Fig. 5-1A). Another option is a round-bottom, thimble-shaped crucible (Fig. 5-1B).

6.2.4 Diamond cutoff saw.

6.2.5 Variable speed polisher.

6.2.6 OM for TLM and/or RLM.

6.2.7 SEM/EDS.

6.2.8 XRD.

6.3 *Equipment Needed for CF:*

6.3.1 This includes the same equipment as described previously in 6.2 because a UT specimen is required for the measurement technique, although additional materials are also required.

6.3.2 Image analysis software for measuring the C_F present in a micrograph collected with OM, SEM, etc.

6.3.3 Crystal structure/unit cell refinement software for quantifying crystal fractions by spiking in a known mass% of a known crystalline material.

6.3.4 Known crystalline material (for example, SRM-674b) that does not overlap with crystalline peaks in unknown specimen.

7. Reagents and Materials

7.1 Reagents and materials used in conjunction with the various methods outlined in this procedure.

7.1.1 *Reagents:*

7.1.1.1 ASTM Type 1 water.

7.1.1.2 Cleaning solvents, for example, ethanol, isopropanol, acetone.

7.1.1.3 Abrasive media for polishing (such as SiC or diamond).

7.1.1.4 Glass microscope slides.

7.1.1.5 Glass cover slides.

7.1.1.6 Meltable adhesive (such as wax).

7.1.1.7 Solvent-soluble adhesives (such as methyl methacrylate-based adhesives).

7.1.1.8 Non-temperature sensitive adhesives (such as cyanoacrylate or other epoxy).

7.1.2 *Materials:*

7.1.2.1 Furnace appropriate to method being used, for example, GF, UF (required heating elements dependent on temperature needs).

7.1.2.2 Material for making crucibles or boats, for example, sheets of platinum alloy or pre-formed crucible(s).

7.1.3 *Calibrated Thermocouples*—Type K thermocouples can be used within 95 °C to 1260 °C, Type R thermocouples can be used within 870 °C to 1450 °C, and Type S thermocouples can be used within 980 °C to 1450 °C without special calibrations or qualifications.

7.1.3.1 Standard reference material for calibrating furnace, for example, SRM-773 or SRM-1416.

7.1.3.2 OM or SEM for making visual observations of heat-treated specimens.

7.1.3.3 XRD for making C_F measurements.

7.1.3.4 XRD standard reference material for peak location and C_F calibration (for example, SRM-1976a or 1976c).

8. Hazards

8.1 The hazards associated with this procedure should be evaluated by each institution before conducting work.

8.2 The primary hazards encountered when following this procedure are sharp objects (for example, metal foil for crucibles, glass shards, and saws), high-temperature surfaces (for example, furnace surfaces, heat-treated specimens fresh out of a furnace, tongs used to remove specimens from a furnace), electrical hazards (for example, exposed heating elements such as $MoSi_2$), and radiation hazards (for example, if working with radioactive glasses). When handling a glass specimen, protective gloves should be worn to prevent injury. The furnaces used for heat-treatment of the glass samples outlined in this procedure are at temperatures of 600 °C to 1600 °C; thus, temperature-resistant or insulated gloves should be worn when putting samples into the furnace or when removing specimens from the furnace. Electrically insulating gloves could also be used in conjunction with (that is, underneath) the leather gloves to electrically isolate the user's hands from potential contact of the tongs or tweezers with exposed electrical elements when removing heat-treated specimens. It is pertinent that the operator of the XRD is cautious of the hazards associated with the technique and is trained to the institution's safety procedures for operating the equipment.

9. Sampling, Test Specimens, and Test Units

9.1 Specific test instructions will contain all or part of the following information: preferred T_L measurement method, tolerance goals, estimated T_g (needed for the gradient temperature furnace method only), an estimated T_L or temperature range (based on model predictions), heat treatment time, and data recording requirements.

9.2 *GF Preparation:*

9.2.1 A gradient furnace is constructed of two or more independent heating zones, and thus the gradient can be adjusted as needed to obtain a low-pitched ($\Delta T/\Delta d$ is low, where T is temperature and d is distance from a reference point inside the furnace) or sharp gradient ($\Delta T/\Delta d$ is high), a parameter that should be optimized within the gradient furnace accordingly depending upon the expected crystallization rate of the sample ($\Delta C_F/\Delta T$). If $\Delta C_F/\Delta T$ is low (for example, ≤ 1 mass % ΔC_F increase over ≥ 100 °C is considered low), the gradient can be low-pitched, and in cases where $\Delta C_F/\Delta T$ is high (for example, ≥ 1 mass % ΔC_F increase over ≤ 10 °C is considered extremely high), the gradient can be high-pitched.

9.3 *Sample Preparation for GF, UT and CF:*

9.3.1 Glass samples for T_L analysis are typically melted, ground to a powder and mixed, remelted, and then quenched on a steel plate. Once quenched, analyze the glass sample with OM, SEM, and/or XRD to make sure that the sample is free of crystalline and/or immiscible phases. Melt insolubles (for example, noble metal oxides) are acceptable, but should be reported. If the sample is crystal free and homogeneous, then follow 9.3.2 – 9.3.4. However, if the glass is crystallized or otherwise inhomogeneous, then skip to step 9.3.5.

9.3.2 According to Practice C829, the particle sizes recommended for T_L determination of the SRM-773 or SRM-1416 glass with *GF* Method (boat method) is < 0.85 mm (–20 mesh) and with *UT* Method (perforated plate) is between 1.70 mm and 2.36 mm (+12/-8 mesh). However, in practice, glass particles that are too small (that is, ≤ 0.100 mm) when heat-treated can introduce a significant degree of bubbles into the melt, especially in moderate and high viscosity glasses ($\eta > 10$ Pa·s), which can dramatically affect heat transfer as well as visibility through a heat-treated glass specimen. Also, it is difficult to clean glass particles that are too small (that is, ≤ 0.100 mm). Glass particles that are too large (that is, > 4 mm) will not fit in the previously described crucibles. Thus, the recommended particle size for these measurements is between 0.422 mm and 4 mm or (+40/-5 mesh); thus the glass should be sieved and this size retained. These sizes are used because sizes << 0.422 mm will promote crystal nucleation and growth during heat treatments, and sizes >> 4.0 mm pose a issues when attempting to load glass into the crucible because the packing density is reduced significantly. Carefully crush the glass, being cautious not to introduce contamination (that is, no direct contact with steel). Use a mill or mortar and pestle composed of material harder than the glass (for example, SiC, WC, or equivalent) to crush the sample to the desired size.

9.3.3 Wash the sample by ultrasonic cleaning for 2 min in a clean glass beaker or equivalent container by submerging glass particles in ASTM Type 1 water, which fills the container above the glass by an equivalent volume. Decant the water and repeat the ultrasonic cleaning twice more (2 min each cleaning) with fresh ASTM Type 1 water. Ultrasonically clean the sample a fourth time for 2 min with ethanol. Decant the ethanol and dry the sample at ≥ 90 °C for ≥ 1 h in an open beaker in an oven designed for drying combustibles. The washing steps can be performed using alternative, non-polar solvents (for example, pentane, hexane) if a reaction with water or between the cleaning solvent and the glass is suspected.

9.3.4 Transfer the cleaned and dried glass sample into a clean, marked container or bag while being careful not to contaminate the glass with dust, dirt, oils, or salts or cross-contaminate the sample with other samples. Seal the container or bag and store in a clean, dry environment until ready for testing.

9.3.5 Glasses that are crystallized, inhomogeneous, or phase separated should be prepared by grinding the entire batch to a very fine powder. The grinding and mixing will best homogenize the sample. It is essential to reduce the effects of sample inhomogeneity when making T_L measurements.

10. Preparation of Apparatus

10.1 *Furnace Setup*—The furnace should be capable of sustaining temperatures that will be used for heat treatments with ≥ 50 °C between the furnace's maximum operating temperature and the heat-treatment temperature. The furnace should have a calibrated temperature monitoring capability. The furnace should have an over-temperature control to prevent damage to the furnace by potential heating past the maximum safe operating temperature of the furnace. See 6.1 and 6.2 for further information.

10.2 *Specimen Preparation for Analysis*—See 12.2.4 for instructions on preparing specimens for *GT* , 12.3.2 for instructions on preparing specimens for *UT*, and the 12.4 subsections for instructions on preparing specimens for the different *CF* methods.

10.3 *Analysis Equipment:*

10.3.1 *OM*—OM can be used to observe heat-treated specimens in TLM and/or RLM mode (depending on specimen optical transparency and morphology). For image analysis with *CF*, the microscope should be equipped with a micrograph acquisition system such as a digital camera.

10.3.2 *SEM*—Specimen preparation for general SEM observations typically requires that the specimen be coated with an electrically-conductive coating (for example, C, Au, Pd) unless the SEM can analyze low-conductivity specimens. For high-resolution SEM micrograph acquisition, specimens can either be polished (best if done to optical quality) to expose the features of interest on a surface of the specimen, or they can remain unpolished.

10.3.3 *XRD*—Typical specimen preparation for XRD involves grinding a heat-treated specimen to a powder. To verify peak locations, the powdered specimen should be doped with an approved XRD standard, for example SRM-1976a or SRM-674b.

11. Calibration and Standardization

11.1 *Calibration*—The test equipment, including thermocouples and thermocouple readouts, must be calibrated, at least annually, in accordance with a consensus standard, for example, ANSI/NCSL 17025:2017.

11.1.1 Furnaces must be profiled for temperature at least once every six months and checked for accuracy at least once every six months during active projects. Profiling of the gradient furnace shall be performed according to Practice C829 (see 11.1.1.1).

11.1.1.1 The gradient furnace can be profiled by inserting a calibrated thermocouple into the furnace, while empty, and measuring the equilibrium temperature at different distances, *d*, from a location (typically, a stopper inserted at the back end). Use the gradient furnace temperature profile to determine the length of the specimen boat and the position where the boat is placed in the gradient furnace. If the gradient is non-linear, the different heating zones can be adjusted accordingly until the desired gradient and gradient shape are achieved. The temperature gradient in the GF should be close to linear (±1 °C over the temperature range of interest) with a gradient of no more than 1.2 °C/mm. Then, the gradient furnace should be operated with standard reference materials for temperature calibration, for example, SRM-773 or SRM-1416.

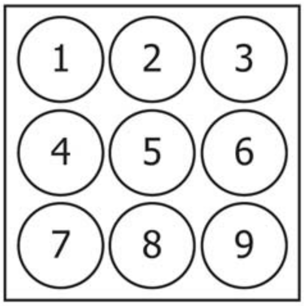
11.1.1.2 To profile a uniform temperature furnace, temperature uniformity among the locations where the sample crucible shall be located inside the furnace must be verified. If a temperature value at a specific location on the sample stage at a given temperature is ±2 °C different from the average temperature over the other profiling locations, then data collected at that location and temperature should not be used for the T_c/T_a values used to determine T_L.

An example of uniform temperature furnace profiling is given by using a calibrated thermocouple. The first profiling step is to create a sample stage inside of the furnace in the middle of the hot zone of the furnace. Then, make sure that there are an adequate number of holes through the top of the furnace that are large enough to fit the width of a thermocouple (~0.6 cm) directly above the positions labeled on the sample stage. Holes not in use should be plugged to prevent heat loss that could potentially lead to undesirable temperature gradients. If using the example in Table 1, then nine holes must be made in the top of the furnace directly above the locations being profiled.

11.1.1.3 The furnace is to be profiled through a temperature range of a given test. For instance, if the furnace is going to be used to test samples in the range of 810 °C to 1290 °C, then the furnace should be profiled at 800 °C, 1300 °C, and a regular temperature increment in between (for example, every 100 °C from 800 °C to 1300 °C). Note that not all types of thermocouple can be calibrated through this entire range, so make sure that a calibration curve is used for each type of thermocouple to extrapolate the actual temperature value from the voltage reading on the thermocouple readout if a specific type of thermocouple is being used outside of the recommended temperature validity range (for example, Type R/S at $T \geq$ 1450 °C).

11.1.1.4 At each temperature, place the calibrated thermocouple through the hole in the top of the furnace and rest the end of the thermocouple at the location where the sample crucible shall be located on the sample stage. Note that electrical safety procedures must be followed when working near electrical hazards. Let the temperature come to thermal equilibrium (for example, 5 min to 20 min) at each location and record the reading from the thermocouple in the profiling table

TABLE 1 Furnace Profiling Diagram



Reported Temperature	Position								
	1	2	3	4	5	6	7	8	9
800	801	800	802	798	799	801	802	799	798
900	901	902	902	898	899	900	899	902	901
1000	1001	1002	1001	999	998	999	1000	1001	1001
1100	1098	1100	1100	1101	1102	1099	1100	1098	1099
1200	1201	1202	1202	1200	1201	1199	1198	1199	1200
1300	1304	1302	1302	1301	**1305**	1301	1300	1299	1298
1400	1401	1400	1401	1402	**1405**	1400	1401	1402	1398

NOTE 1—This is shown as an example for a square sample stage. The tabulated data to the right of the diagrams shows how the thermocouple readouts are entered at each reported temperature for each position on the sample stage. Locations at temperatures that are more than ±2 °C from the average temperatures collected at a specific temperature are to be omitted from use for T_a or T_c values—these values are to be labeled as red, bold, or underlined, or combinations thereof.

(see example in Table 1). If a temperature value at a given specific location on the sample stage at a given temperature is ±2 °C different from the average temperature collected at a specific temperature over all the profiling locations, then data collected at that location and temperature should not be used for the T_c/T_a values used to determine T_L. When measuring T_c and T_a values used to determine T_L, it is ideal to run these heat-treatments at locations on the stage that are within the required tolerance.

11.1.2 The XRD should be calibrated every six months or at the completion of any maintenance. To do this, perform an XRD scan on a 2θ calibration standard (for example, SRM-1976a or SRM-1976c) and verify that the diffraction peak locations (that is, degrees, 2θ) and intensities match those of the standard. If peaks are not in the correct locations, then the instrument must be realigned.

11.2 *Accuracy Check*—At least one standard glass with T_L traceable to a round robin study or NIST standard (such as SRM-773 or SRM-1416) shall be tested with each new batch of T_L measurements or on a regular frequency to determine the accuracy of each furnace over time. The minimum frequency shall be once annually or with each change of furnace profile or gradient, whichever comes first. The measured value must be within the tolerance expected for the standard glass, or the furnace must be re-configured and the standard re-measured. The data from these tests should be maintained, plotted, and analyzed to check for trends, biases, or increases in variation as part of a defined measurement control program. This can provide continuous validation of the test method and basis for bias adjustments.

12. Procedure

12.1 Liquidus temperature measurements of a glass specimen shall be determined by one of three methods: *Gradient Temperature Furnace Method (GT)*, *Uniform Temperature Furnace Method (UT)*, or *Crystal Fraction Extrapolation Method (CF)*. The appropriate method for the samples to be tested shall be specified in the applicable test instructions. For *GT* specimens, proceed to 12.2; for *UT* specimens, proceed to 12.3; for *CF* specimens, proceed to 12.4.

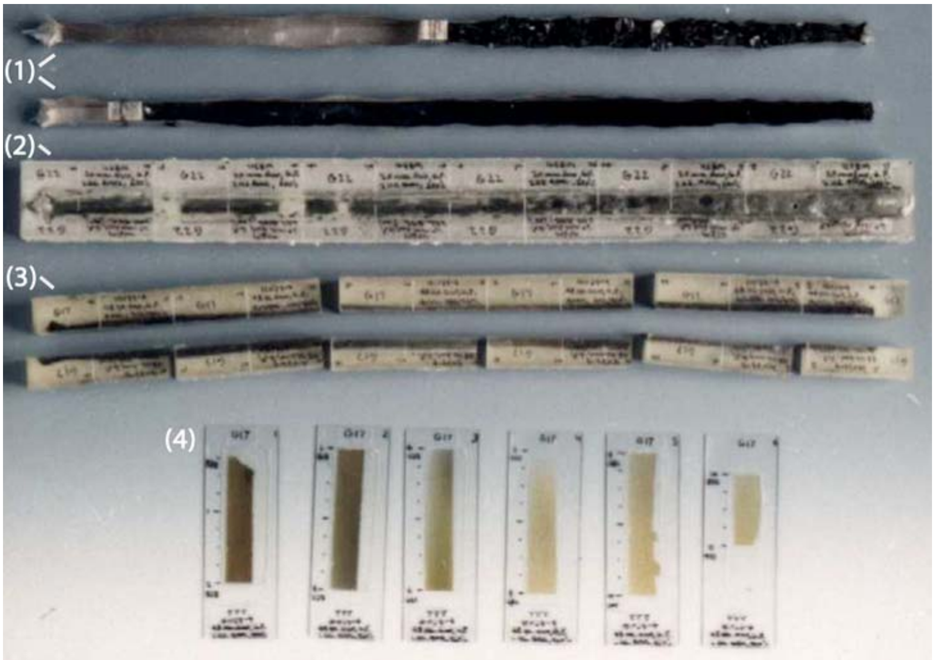
12.2 *Gradient Temperature Furnace Method (GT):*

12.2.1 Place test glass sample in a boat (6.1) and slide into a preheated and profiled gradient furnace (11.1.1.1) through the cooler end of the furnace. Position the boat in the furnace at the desired test temperature range. Let the glass sample soak for the time specified in the test instruction. The typical heat treatment time is 24 h ± 2 h, although this is dictated by the time required to reach thermodynamic equilibrium.

12.2.2 At the completion of the heat treatment, remove the boat with the specimen from the gradient furnace and place into a preheated annealing furnace with the temperature near the measured or estimated T_g for ≥ 2 h and then slowly cool the furnace to room temperature.

12.2.3 Remove the boat from the annealing furnace and mark the specimen in a way to correlate locations on the specimen with *d* and *T* values (4.1.1). Remove the test specimen from the boat, attempting to keep the specimen intact. Depending on the crystallization rate of the glass tested, the low-temperature end of the heat-treated specimen might appear to be a heavily crystallized glass ceramic. Place the specimen in a mold, for example, silicone rubber, large enough to fit the entire specimen or, at the very least, the region of intended interest (estimated T_L ± 5 cm). Cover the specimen entirely with a single batch of epoxy. Allow the epoxy to cure and harden. Remove the specimen from the mold. The process of mounting the specimen in resin will improve the ability to keep the specimen intact during cutting and polishing.

12.2.4 Use a saw equipped with a diamond cut-off blade to cut the specimen in half longitudinally, along the temperature gradient, and polish the cut side of one of the halves. Adhere the polished side to a single or to multiple glass microscope slides (for example, with cyanoacrylate or CrystalBond); it is typically easier to polish multiple small sections (≤ 5 cm, each) versus one large section. Cut the remainder of the specimen parallel to the slide, leaving ~2 mm thick of specimen adhered to the slide, and polish a thin section of the specimen with a variable speed polisher. Make sure to permanently mark the identification of the specimen, the gradient profile, and the profile measurement increments on the glass slide. Fig. 6 shows examples of GF specimens at different stages of the process.



NOTE 1—In sequence from the top are (*1*) partially-filled platinum boats containing (top) as-prepared glass chunks and (bottom) a heat-treated specimen, (*2*) an entire heat-treated GF specimen mounted in epoxy and labeled accordingly, (*3*) epoxy-mounted GF specimens cut longitudinally into smaller sections, and (*4*) thin sections of GF specimens.

FIG. 6 Different Stages of Preparation for GT Specimens

12.2.5 After the specimen thin-section has been prepared, analyze the specimen with OM and/or SEM to determine the location of the crystallization front (Fig. 4). In the absence of convection, the T_L of a glass is equal to or higher than the temperature of the crystallization front. The crystallization front may span a range of several degrees as shown in Fig. 7. In this case, record the range of temperatures in which the crystallization front occurs. If the temperature range of the crystallization front falls outside the tolerance goals, the sample must be retested with a smaller gradient or with Methods *UT* or *CF*.

12.2.6 The T_L should be taken as the temperature in the center of the crystallization front temperature range (see Fig. 4) unless other evidence suggests that a different temperature within the range should be selected.

12.2.7 Determine the crystalline phase with OM and/or SEM. Additional analysis can be done to provide more definitive information such as EDS and/or XRD if requested by the test originator.

12.2.8 Record date, sample name, gradient profile, primary phase, analysis technique, crystallization front temperature range, and liquidus temperature measurement for each glass in a Laboratory Record Book or data sheet.

12.3 *Uniform Temperature Furnace Method (UT):*

12.3.1 Place the test glass specimen in a box or conical crucible (6.2) and place it into a preheated and profiled uniform temperature furnace. Position the crucible in the furnace at the proper location as per the furnace profiling from 11.1.1.2. Let the glass sample soak for the specified time. It is recommended that tests be run ≥ 24 h for $T \geq 900$ °C, ≥ 48 h for T ~800 °C, ≥ 72 h for T ~700 °C, ≥ 84 h for T ~650 °C, and ≥ 96 h for T < 650 °C to reach equilibrium, although these times are sample dependent and subject to change on a per-glass basis.

12.3.1.1 The equilibrium can be determined for a given sample at a specific temperature by running several identical samples in parallel and removing them from the furnace at different time points to monitor the C_F as a function of time. The time at which C_F plateaus is considered equilibrium. If the samples are held at too high of a temperature (sample dependent), certain components in the specimen could volatilize off and change the composition of the melt, thus artificially changing the properties and altering the measurement of true thermodynamic equilibrium.

12.3.2 At the completion of the heat treatment, air-quench the specimen and remove the test glass specimen from the crucible. Water quenching can be used for samples that are

FIG. 7 Crystallization Front in GT Specimen with Convective Flow Patterns