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Standard Guide for Impregnation of Graphite with Molten Salt[1]

This standard is issued under the fixed designation D8091; 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 This guide covers procedures for the impregnation of graphite with molten salt under a consistent pressure and temperature. Such procedures are necessary if the user wishes to prepare graphite specimens for testing that represent material that has been exposed to a molten salt environment in a molten salt nuclear reactor. The user will need to ensure that impregnation temperature and pressure conditions reflect those pertaining to the molten salt environment, noting that the properties of the material will change once it becomes irradiated.

NOTE 1—The term impregnation is used throughout this guide as this is the correct term for the described process. Other terms such as infiltration and intrusion may be encountered by the user in other texts and the term intrusion is commonly used to describe penetration of open porosity in graphite in a molten salt reactor environment.

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

1.3 *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.*

1.4 *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:*[2]

B923 Test Method for Metal Powder Skeletal Density by Helium or Nitrogen Pycnometry

C559 Test Method for Bulk Density by Physical Measurements of Manufactured Carbon and Graphite Articles

D7775 Guide for Measurements on Small Graphite Specimens

3. Terminology

3.1 *Definitions:*

3.1.1 *impregnation pressure (P_I), n*—the differential pressure between the cover gas pressure and the pore pressure of the graphite specimen.

3.1.1.1 *Discussion*—If the impregnation starts at a pore pressure of atmospheric pressure, the impregnation pressure is the gauge pressure of the cover gas; if the impregnation starts at a pore pressure of "0" (vacuum), the impregnation pressure is the gauge pressure plus atmospheric pressure. For a pore pressure between 0 and atmospheric pressure, the impregnation pressure is (gauge pressure + atmospheric pressure – pore pressure).

3.1.2 *impregnation temperature (T_I), n*—the system temperature before the graphite specimen has been immersed in the molten salt.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Parameter D_o, n*—a measure of the extent of penetration of the graphite porosity by the molten salt expressed in terms of the open pore volume of the specimen.

3.2.1.1 *Discussion*—If there was no damage to the microstructure of the graphite during impregnation, then parameter D_o based upon open pore volume would be unity at saturation. This parameter is applicable when damage to the graphite microstructure during impregnation is absent or low. Mercury porosimetry studies indicate that the threshold pressure for microstructural damage is 13.8 MPa to 20.0 MPa (2000 psi to 3000 psi).[3,4] This threshold should be used as a guide by users when evaluating D_o. At high impregnation pressures, closed porosity may be broken into by the molten salt and parameter

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[2] 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.

[3] Dickinson, J. M., Shore, J. W., "Observations Concerning the Determination of Porosities in Graphites," *Carbon*, Vol 6, 1968, pp. 937–941.

[4] Baker, D. J., Morris, J. B., "Structural Damage in Graphite Occurring during Pore Size Measurements by High Pressure Mercury," *Carbon*, Vol 9, 1971, pp. 687–690.

*A Summary of Changes section appears at the end of this standard

D_o based upon open pore volume could have values greater than unity. At such pressures, the user may wish to express parameter D in terms of total (open and closed) pore volume, termed D_t. Evaluation of this parameter is provided in 9.2.

4. Summary of Guide

4.1 This guide provides guidance on the impregnation of graphite with molten salt. The guide gives the various factors which need to be considered to perform the impregnation procedure. These include pretreatment of graphite specimens, immersion of graphite in the molten salt, safe handling of the molten salt, and selection and control of the impregnation pressures and temperatures.

5. Significance and Use

5.1 The molten salt reactor is a nuclear reactor which uses graphite as reflector and structural material and fluoride molten salt as coolant. The graphite components will be submerged in the molten salt during the lifetime of the reactor. The porous structure of graphite may lead to molten salt permeation, which can affect the thermal and mechanical properties of graphite. Consequently, it is important to assess the effect of impregnation of molten salt on the properties of the as-manufactured graphite material.

5.2 The purpose of this guide is to report considerations that should be included in the preparation of graphite specimens representative of that after exposure to a molten salt environment. The degree to which the molten salt will infiltrate the graphite will depend upon a number of factors, including the type of graphite and the type and extent of porosity, the properties of the molten salt, the impregnation pressure and temperature, and the duration of the exposure of the graphite to the molten salt.

5.3 The user of this guide will need to select impregnation parameters sufficiently representative of those in a molten salt reactor based on parameters provided by the designer. Alternatively, the user may select a standard set of impregnation conditions to allow comparisons across a range of graphites.

5.4 This guide is not intended to be prescriptive. A typical apparatus and associated procedure are described. Some indication of the sensitivity of the procedure to graphite type and impregnation conditions is given in He, et al.[5]

5.5 There are four major practical issues that must be addressed during the impregnation process:

5.5.1 The density of molten salt is greater than that of graphite. A specially designed tool is required to submerge graphite samples in the molten salt during the impregnation process.

5.5.2 Some molten salts (for example, FLiBe) are poisonous and it is therefore necessary to provide containment by performing procedures within a glove box.

5.5.3 The graphite must be kept away from air to avoid oxidation at high temperature. This can be achieved by performing the impregnation process within a glove box with a controlled atmosphere.

5.5.4 Pressure control of the molten salt can be difficult to achieve. A specially designed autoclave is needed to hold the specimen and molten salt.

5.6 In order to assess the quantity of molten salt in the graphite, parameter D is used as a variable in measuring the mechanical and thermal material properties. Parameter D_o is the ratio of salt volume to open pore volume. Parameter D_t is the ratio of salt volume to total pore volume. The saturated value of D_o can be greater than 1 when the molten salt impregnation takes place at high pressure. It is postulated that the internal microstructure of graphite has been damaged by the high impregnation pressure and some closed pores have been opened. In this case, the parameter D_t is more appropriate to represent the impregnation process.

6. Apparatus

6.1 *Autoclave:*

6.1.1 Since fluoride molten salts are toxic and a small amount of water can significantly affect the wetting behavior of graphite, the conditions for the procedure should be strictly controlled during molten salt impregnation. The schematic diagram of an impregnation setup is shown in Fig. 1.

6.1.2 An autoclave is used as a sealed container and should meet a pressure leakage rate <0.25 %/h at the maximum operation pressure. To avoid corrosion by molten salt, the autoclave should be made of a high temperature and corrosion-resistant alloy.

6.1.3 A graphite crucible is placed inside the autoclave to hold the molten salt. There should be enough clearance between the wall of autoclave and graphite crucible to prevent damage of the graphite crucible due to differences in thermal expansion.

6.1.4 The graphite specimens must be secured in a specimen holder. For example, the specimen holder might comprise two graphite plates with the specimens placed between the plates (see Fig. 2).

NOTE 2—The graphite plates contain holes to allow access by the molten salt to the end-faces of the specimens. The user should ensure that

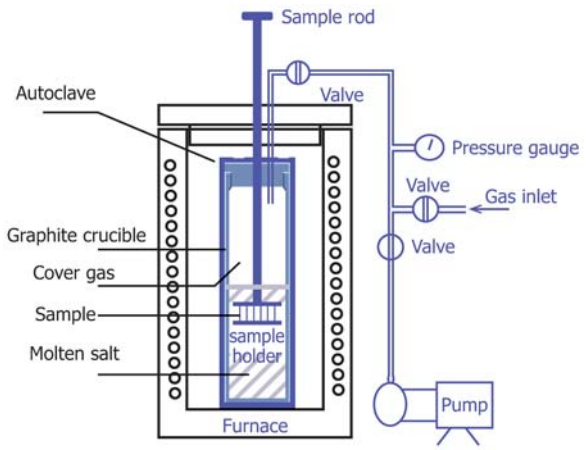

FIG. 1 Schematic Diagram of the Procedural Setup

[5] He, Zhoutong, et al., "Molten FLiNaK Salt Infiltration into Degassed Nuclear Graphite Under Inert Gas Pressure," *Carbon*, Vol 84, 2015, pp. 511–518.

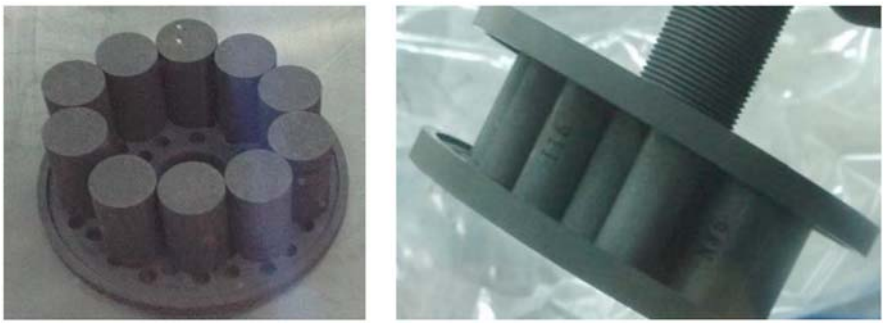

FIG. 2 Sample Holder: Graphite Plates and Sample Rod

the design of these plates does not influence molten salt penetration of the specimens.

NOTE 3—If the user is using this guide to impregnate specimens for comparative purposes, it is recommended that a single specimen volume and geometry should be employed. If different specimen volumes and geometries are necessary to accommodate tests that follow, it is advisable that the user quantifies the extent of impregnation over a bounding range of volumes and geometries to ensure a consistent set of test results.

6.1.5 In this example, the specimen holder is fixed to a sample rod. The specimen rod can move up and down inside the autoclave to ensure that the entire graphite specimen holder is submerged in the molten salt during the procedure.

6.1.6 High purity inert gas (>99.99 %) is pumped into the autoclave and is used to adjust the impregnation pressure of molten salt. A pressure gauge should be installed to measure the gas pressure inside the autoclave.

NOTE 4—The schematic in Fig. 1 shows an arrangement where the void above the molten salt is pressurised with inert gas. The user may wish to perform impregnation on specimens that have been held under vacuum prior to immersion in the molten salt. This might be desirable if the impregnation data need to be aligned with separate pore volume measurements such as mercury porosimetry. In this case, the user would need to configure the impregnation setup accordingly.

6.2 *Electric Furnace*—An electric furnace with temperature control is used to heat the autoclave. The furnace should be able to provide the desired temperature of T_1 °C ± 20 °C.

6.3 *Analytical Balance*—An analytical balance is used to measure the weight of the graphite sample before and after the impregnation procedure. The error of the scale should be less than ±0.1 mg.

6.4 *Glove Box:*

6.4.1 All the testing equipment, including the autoclave, the electric furnace, and the analytical balance should be placed inside a glove box. A hoist system may be installed inside the glove box to aid lifting the autoclave and the graphite crucible.

6.4.2 The water and oxygen contents inside the glove box should be less than 1 ppm to prevent external contamination or oxidation. The glove box is maintained at negative pressure to prevent release of toxic salt vapor/dust from the glove box.

6.4.3 The glove box can be divided into two zones. One zone may be used for temporary storage of graphite specimens and the weighing of graphite specimens; the other contains the furnace and the impregnation equipment.

7. Procedure

7.1 Graphite specimens must be individually marked (for example, surface laser etching) or tracked.

7.2 For regular specimen geometries, the volume V (cm^3) should be evaluated from the dimensions measured in accordance with Test Method C559. For non-regular specimen geometries, the volume must be evaluated by another method such as immersion method (Guide D7775).

7.3 The graphite crucible and graphite specimen must be dried in an oven at a temperature above 110 °C for 2 h to remove any sorbed water.

NOTE 5—The presence of moisture may affect impregnation. To avoid this, the user may wish to first degas the specimen under vacuum. Also, 110 °C is the minimum recommended drying temperature and the user should assess the optimum temperature for this step of the procedure.

7.4 The dry mass of graphite specimen is measured at room temperature by using the analytical balance inside the glovebox and recorded as W_1 (g).

7.5 Calculate graphite bulk density, ρ_{bulk} (g/cm^3), from dry mass and the volume V (cm^3) measured at 7.2 using:

$$\rho_{bulk} = \frac{W_1}{V} \tag{1}$$

7.6 Measure the total displaced skeletal volume of graphite specimen, V_{skel} (cm^3) by using helium (or nitrogen) pycnometry (according to Test Method B923). If using a commercial gas pycnometer, this result will be automatically calculated by the software.

7.7 Calculate graphite skeletal density, ρ_{skel} (g/cm^3), from dry mass and skeletal volume measured at 7.6, according to:

$$\rho_{skel} = \frac{W_1}{V_{skel}} \tag{2}$$

Commercial gas pycnometers would provide this result directly as the average of a series of repeated measurements.

7.8 Calculate open pore volume of the whole specimen, V_o (cm^3), from the bulk density, skeletal density, and dry mass according to:

$$V_o = W_1\left(\frac{1}{\rho_{bulk}} - \frac{1}{\rho_{sket}}\right) \tag{3}$$

7.9 Calculate the total pore volume of the whole specimen, V_t (cm^3), from the bulk density, graphite crystal density (ρ_{cryst} = 2.24 g⁄cm^3), and dry mass, according to:

$$V_t = W_1\left(\frac{1}{\rho_{bulk}} - \frac{1}{\rho_{cryst}}\right) \tag{4}$$

7.10 The autoclave should be preheated at a temperature above 110 °C for at least 2 h.