ASTM INTERNATIONAL

Designation: D7542 – 21

Standard Test Method for
Air Oxidation of Carbon and Graphite in the Kinetic Regime[1]

This standard is issued under the fixed designation D7542; 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 test method recommends a standard procedure for measuring oxidation rates in air of various grades of nuclear graphite and/or manufactured carbon. Following the standard procedure recommended here, one can obtain kinetic parameters that characterize the oxidation resistance in standard conditions of tested materials and that can be used to for materials selection and qualification, and for quality control purposes in the fabrication process.

1.2 This test method covers the rate of oxidative weight loss per exposed nominal geometric surface area, or per initial weight of machined test specimens of standard size and shape, or both. The test is valid in the temperature range where the rate of air oxidation of graphite and manufactured carbon is limited by reaction kinetics.

1.3 This test method also provides a standard oxidation temperature (as defined in 3.1.7), and the kinetic parameters of the oxidation reaction, namely the apparent activation energy and the logarithm of pre-exponential factor in Arrhenius equation. The kinetic parameters of Arrhenius equation are calculated from the temperature dependence of oxidation rates measured over the temperature range where Arrhenius plots (as defined in 3.1.8) are linear, which is defined as the "kinetic" or "chemical control" oxidation regime. For typical nuclear grade graphite materials it was found that the practical range of testing temperatures is from about 500 °C to 550 °C up to about 700 °C to 750 °C.

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

1.5 *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.*

1.6 *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]

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

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

E898 Practice for Calibration of Non-Automatic Weighing Instruments

E1582 Test Method for Temperature Calibration of Thermogravimetric Analyzers

E1970 Practice for Statistical Treatment of Thermoanalytical Data

3. Terminology

3.1 *Definitions:*

3.1.1 Definitions are ordered by oxidation rates first, followed by activation energy as calculated from oxidation rates.

3.1.2 *area-normalized oxidation rate* (OR_a), *n*—rate of weight loss due to oxidation of a machined test specimen at a given temperature, divided by the nominal geometric surface area of the specimen.

3.1.2.1 *Discussion*—The rate of weight loss is determined by a linear fit of the weight loss plotted against time in the range from 5 % to 10 % loss of original specimen weight. The units of area-normalized oxidation rate, OR_a, are g h^{-1} m^{-2}.

3.1.3 *weight-normalized oxidation rate* (OR_w), *n*—rate of weight loss due to oxidation of a machined specimen at a given temperature, divided by the initial weight of the specimen.

3.1.3.1 *Discussion*—The rate of weight loss is determined by a linear fit of the weight loss plotted against time in the range from 5 % to 10 % loss of original specimen weight. The units of weight-normalized oxidation rate, OR_w are:

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

$$[g_{(oxidized)}][g_{(specimen)}]^{-1} h^{-1} \text{ (or, equivalent, } h^{-1}) \qquad (1)$$

3.1.4 *nominal geometric surface area, n*—exposed area (A) of the test specimen determined by measuring its diameter (D) and height (H) before testing and using the formula:

$$A = 2\pi D^2/4 + \pi DH \qquad (2)$$

The units of nominal geometric surface area are m^2.

3.1.5 *weight-normalized standard oxidation rate (SOR$_w$), n*—value of weight-normalized oxidation rate corresponding to 1 % weight loss in 24 h (equivalent to $SOR_w = 4.17 \times 10^{-4}$ g g^{-1} h^{-1}).

3.1.6 *area-normalized standard oxidation rate (SOR$_a$), n*—value of area normalized oxidation rate corresponding to 1 % weight loss in 24 h. Area-normalized standard oxidation rate, SOR_a, depends on the initial specimen density. For carbon and graphite samples (density 1.2 to 2.2 g cm^{-3}) SOR_a varies between 2 and 4 g h^{-1} m^{-2}.

3.1.7 *standard oxidation temperature (SOT), n*—temperature in degrees Celsius at which a sample would reach the standard oxidation rate, that is, it would lose by oxidation 1 % of its initial weight in 24 h.

3.1.7.1 *Discussion*—In this procedure, SOT is estimated by plotting the decimal logarithm of oxidation rate data determined at several temperatures against the reciprocal of the absolute temperature (in Kelvin) of the measurement. The plot should yield a straight line. The temperature at which the line predicts a rate corresponding to 1 % weight loss in 24 h (equivalent to $SOR_w = 4.17 \times 10^{-4}$ g g^{-1} h^{-1}) is the standard oxidation temperature (*SOT*).

3.1.8 *activation energy (E$_a$), n*—measure of temperature effects on the rate of oxidation in the kinetic, or chemical control, regime. Activation energy is calculated from the Arrhenius equation:

$$OR = Z\exp(-E_a/RT) \qquad (3)$$

where:

OR = oxidation rate,
R = 8.314 J mole^{-1} K^{-1} is the universal gas constant,
T = absolute temperature (in Kelvin), and
Z = pre-exponential factor.

The activation energy and pre-exponential factor are calculated from linearized form of Arrhenius equation, that is, from the slope and intercept of the linear plot of the logarithm of oxidation rate versus the inverse of absolute temperature (1/T):

$$\log_{10}(OR) = \log_{10} Z - E_a/(2.303\,RT) \qquad (4)$$

Activation energy is expressed in units of kJ/mol. Pre-exponential factor is expressed in the same units as the oxidation rates, namely g h^{-1} m^{-2} (for Z_a calculated from area-normalized oxidation rates, OR_a) or g g^{-1} h^{-1} (for Z_w calculated from weight-normalized oxidation rates, OR_w).

4. Summary of Test Method

4.1 This test method provides the rate of oxidation in air of cylindrical test specimens with standard size, machined of carbon and graphite. During tests, the specimens hang freely from a continuously recording balance in a stream of dry air preheated at a preselected test temperature. The nominal geometrical surface area of the specimen is determined before testing. The linear rate of weight loss between 5 % and 10 % of the specimen's initial weight is determined during exposure. Experience has shown that this is the most linear part of the curve because weight loss below 5 % of the specimen starting weight includes an induction period where reactive surface is created. For weight losses above 10 % of the specimen starting weight, the sample dimensions may become significantly distorted. The area-normalized oxidation rate (OR_a) is calculated by dividing the rate of weight loss by the original nominal geometric surface area of the specimen. The result is reported in g h^{-1} m^{-2}. The weight-normalized oxidation rate (OR_w) is calculated by dividing the rate of weight loss by the original weight of the specimen. The result is reported in g g^{-1} h^{-1}. The results can be used to compare the oxidation resistance of different graphite materials and to estimate their service life at equivalent oxidation conditions.

4.2 In order to calculate the kinetic parameters of the oxidation reaction and the standard oxidation temperature, the procedure is repeated with fresh specimens for a total of four temperatures. An Arrhenius plot is obtained as explained in 3.1.8. Only those data points in the linear range of the Arrhenius plot should be used for calculation of slope and intercept. If deviation from linearity of Arrhenius plots is observed at high temperatures for certain materials, the data outside the linear segment should not be used, and more oxidation rate measurements should be performed at lower temperatures. For typical nuclear graphite materials it was found that the practical range of testing temperatures is from about 500 °C to 550 °C up to about 700 °C to 750 °C.

5. Significance and Use

5.1 This test method can be used to measure the rate of oxidation for various grades of manufactured carbon and graphite in standard conditions, and can be used for quality control purposes.

5.2 The following conditions are standardized in this test method: size and shape of the graphite specimens; their placement in the vertical furnace with upwards air flow; the method for continuous weight variation measurement using an analytical scale with under-the-scale port; the air flow rate, which must be high enough to ensure that oxidation is not oxygen-starved at the highest temperature used; the initial and final points on the weight loss curve used for calculation of oxidation rate.

5.3 This test method also provides kinetic parameters (apparent activation energy and logarithm of pre-exponential factor) for the oxidation reaction, and a standard oxidation temperature. The results characterize the effect of temperature on oxidation rates in air, and the oxidation resistance of machined carbon or graphite specimens with standard size and shape, in the kinetic, or chemically controlled, oxidation regime. This information is useful for discrimination between material grades with different impurity levels, grain size, pore structure, degree of graphitization, or antioxidation treatments, or a combination thereof.

5.4 Accurately determined kinetic parameters, like activation energy and logarithm of pre-exponential factor, can be
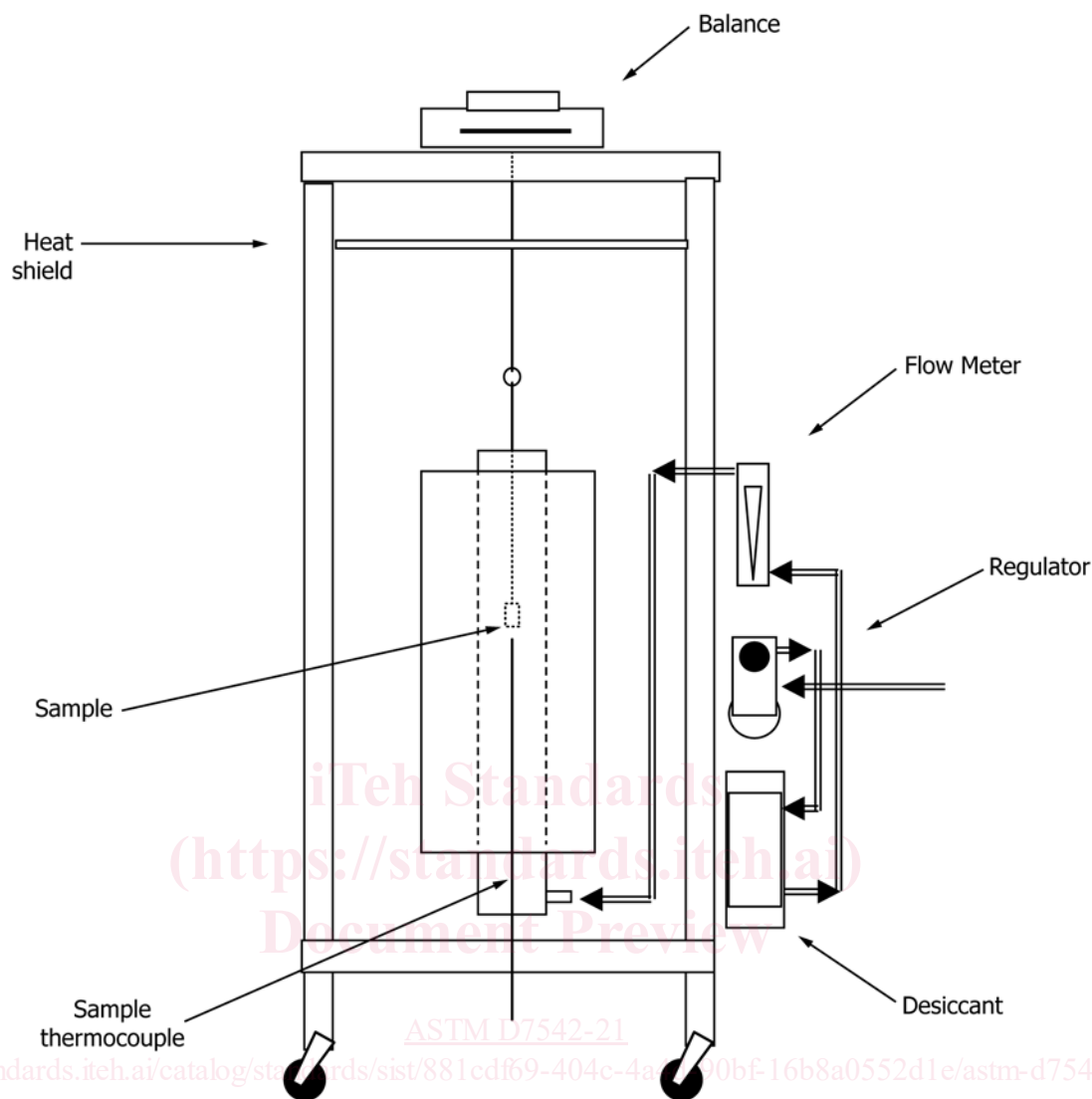
FIG. 1 Oxidation Apparatus

used for prediction of oxidation rates in air as a function of temperature in conditions similar to those of this test method. However, extrapolation of such predictions outside the temperature range where Arrhenius plots are linear (outside the kinetic or chemically controlled regime of oxidation) should be made with extreme caution. In conditions where (*1*) oxidation rates become controlled by a mechanism other than chemical reactions (such as in-pore diffusion or boundary transport of the oxidant gas), or (*2*) the oxidant supply rate is not large enough to prevent oxidant starving conditions at high temperature, prediction of oxidation rates using kinetic parameters determined with this test method will produce overestimated results.

6. Interferences

6.1 Specimens shall not be contaminated during handling. They should be machined without oil, using diamond or carbide tools, and handled with cotton gloves.

6.2 The specimen and the air supply to the furnace shall be free of moisture. A desiccant column shall be used on the air supply line.

7. Apparatus

7.1 *Oxidation Apparatus,* Shown schematically in Fig. 1 and consisting of the following:

7.1.1 *Vertical Tube Furnace*—Capable of obtaining 900 °C. A three-zone furnace with proportional–integral–derivative (PID) controllers is recommended. Temperature control accuracy should be ±2 °C. The temperature of each zone should be independently controlled by its thermocouple. A separate sample temperature thermocouple should also be used; it is recommended that the sample temperature thermocouple is located in the gas stream below the sample within maximum 5 mm of it. It should indicate the temperature of the gas stream just before the sample (sample temperature). Safety interlocks
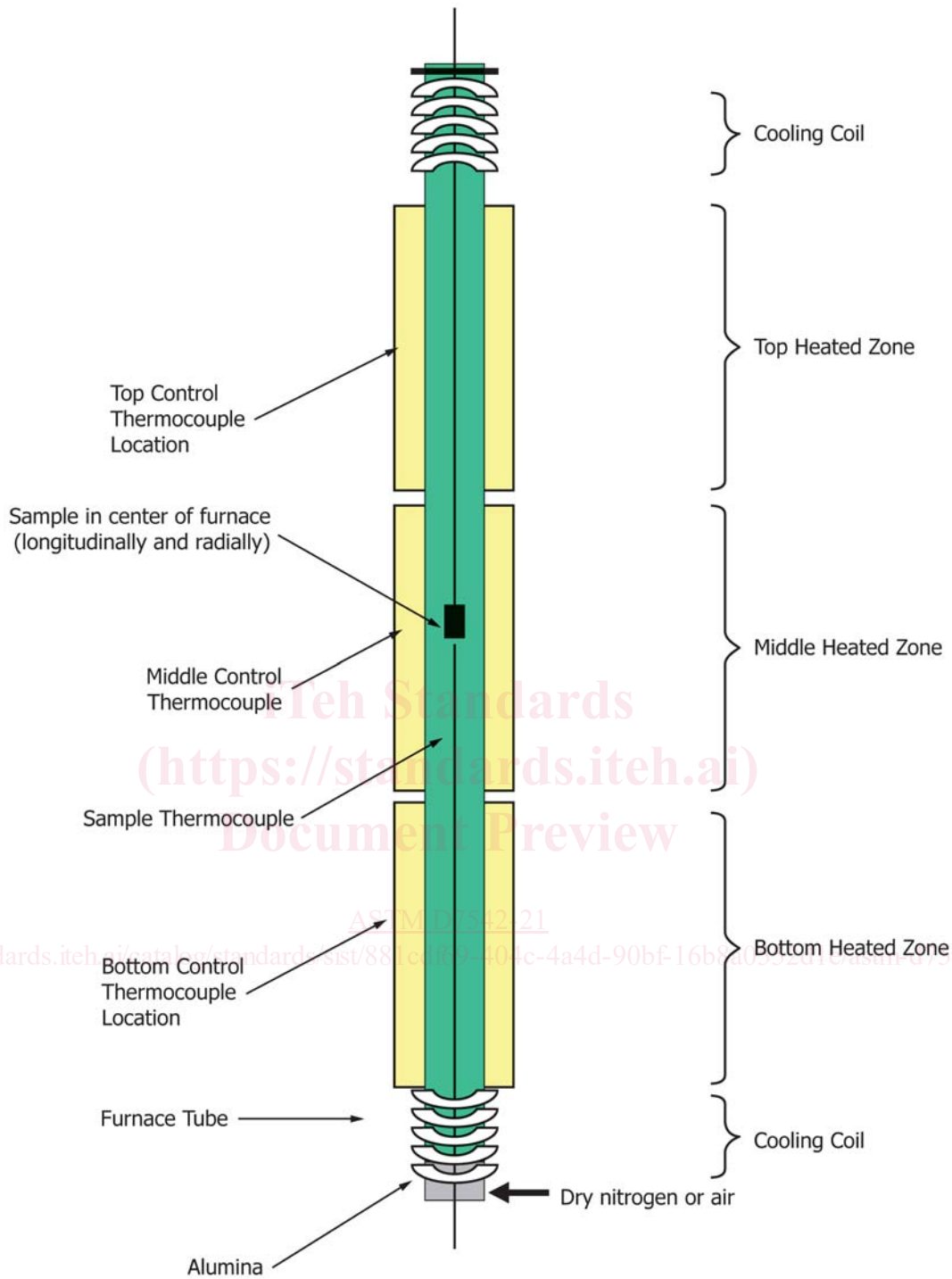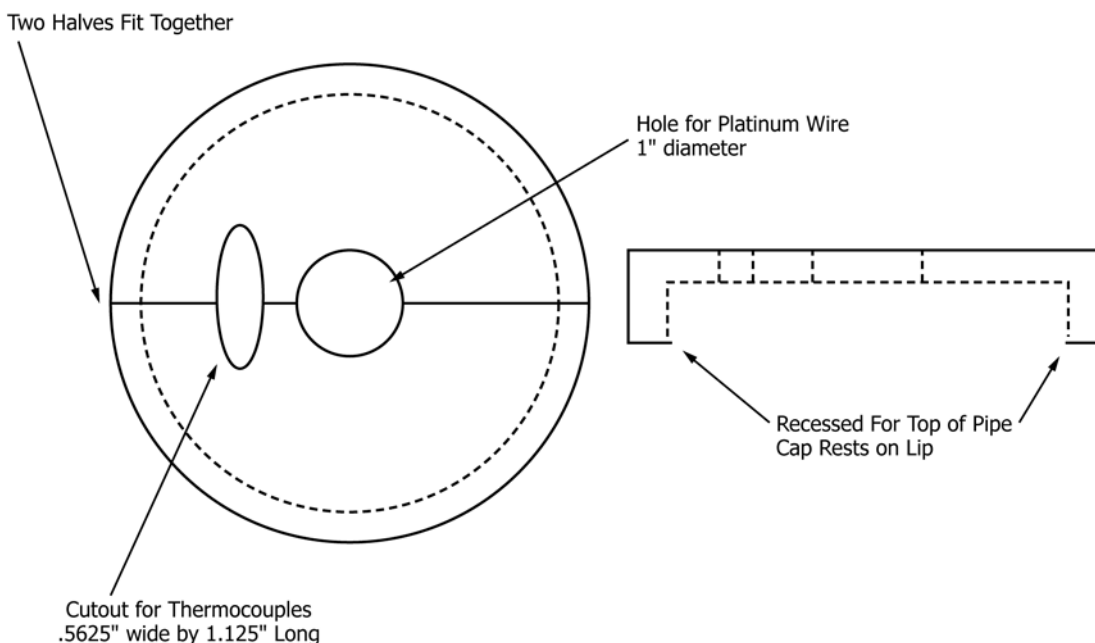
FIG. 2 Tube Furnace

Two Halves Fit Together

Hole for Platinum Wire 1" diameter

Recessed For Top of Pipe Cap Rests on Lip

Cutout for Thermocouples .5625" wide by 1.125" Long

FIG. 3 Top Cover

with thermocouples placed on the outside of the pipe are recommended for each zone.

7.1.2 *Oxidation Resistant Furnace Tube*—Such as Inconel[3] 2½ in. schedule 40 pipe (7.30 cm outer diameter; 6.27 cm inner diameter) should be used. Tubes of alumina or quartz with equivalent inner diameter may also be used. It is recommended that the ends extending from the furnace, especially the top end of the tube, are cooled by water circulating through copper tubing wrapped around the furnace tube (see Fig. 2).

7.1.3 *Top Cover Block*—Manufactured from a refractory material, such as boron nitride, and should be used as thermal shield protection for the analytical balance (Fig. 3). Alternately, a grooved copper plate can be used, having a copper tube threaded through the grooves for water circulation. The role of thermal shield is to ensure that the analytical balance placed on top of the vertical furnace is maintained as constant temperature, as close as possible to room temperature, as required for proper operation. The same effect can be obtained by allowing sufficient air gap between the top end of the furnace tube and the analytical scale, and by removing the hot gases coming from the furnace tube through a snorkel connected to the local ventilation system.

7.1.4 *Platinum Wire and Platinum Basket*—For holding suspended specimen (Fig. 4).

7.2 *Analytical Balance*—With weigh-below port feature, at least 200 g capacity, ±0.001 g resolution.

7.3 *Air Flow Meter*—0 L/min to 10 L/min, ±5 % full-scale accuracy.

FIG. 4 Platinum Wire Basket

7.4 *Nitrogen Flow Meter*—0 L/min to 10 L/min, ±5 % full-scale accuracy.

7.5 *Desiccator*—Charged with indicating desiccant for storage of conditioned specimens before use.

7.6 *Cotton Gloves*—For handling specimens.

8. Reagents and Materials

8.1 *Alumina or Silica Beads or Spheres,* −12 / +32 mesh.

8.2 *Air Supply,* desiccated.

8.3 *Nitrogen Supply (99.99 %),* desiccated.

8.4 *Desiccant Column.*

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[3] Inconel is a trademark of Special Metals Corporation. The sole source of supply of the apparatus known to the committee at this time is Special Metals Corporation, 4317 Middle Settlement Rd., New Hartford, NY 13413-5392. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

9. Hazards

9.1 *Burns*—The test involves high temperatures. Appropriate steps should be taken to avoid contact with hot surfaces. Guarding is recommended.

9.2 *Fire*—Hot surfaces could be a source of ignition.

10. Sampling and Test Specimens

10.1 At least four test specimens with standard size and shape are required. It is recommended to prepare a total of 8 or 10 specimens for duplicate measurements at a minimum of four temperatures.

10.2 The standard size of test specimens for the oxidation test is a cylinder with a 25.4 mm diameter and 25.4 mm length. Machining should be done with carbide or diamond tools. The machining tolerances should be ±0.15 mm. Surface finish is not critical.

10.3 Wipe the specimens with lint-free paper to remove dust from machining.

10.4 Condition the specimens at 110 °C to 150 °C for a minimum of 3 h. Remove and cool in a desiccator for a minimum of 30 min. Keep specimens in desiccator until ready to perform test.

11. Calibration and Standardization

11.1 The recommended practice for calibration of temperature scale for thermogravimmetry is Practice E1582.

11.2 The recommended test method for testing top-loading, direct-reading laboratory scales and balances is Test Method E898.

12. Procedure

12.1 Measure the diameter (*D*) and height (*H*) of the specimen to the nearest ±0.03 mm.

12.2 Assemble the furnace as shown in Fig. 1. Charge the bottom of the furnace with about 5 cm layer of alumina or silica beads to act as a gas distributor.

12.3 Hang the wire basket on the weigh-below hook of the analytical balance. Ensure that the wire is in the middle of the furnace chamber and does not touch the walls of the furnace tube. Tare the balance. Remove the wire basket and insert the specimen. Re-hang the basket and specimen in the furnace. Weigh the specimen to the nearest ±0.01 g and record weight as *W*.

12.4 Start flowing dry nitrogen through the tube at a flow rate of 10 L/min. Allow the furnace to stabilize at the test temperature for 60 min. After 60 min, verify that the weight of the specimen is stable to the nearest ±0.01 g and record weight as W_o. This is the initial weight of the dry specimen before oxidation.

12.5 Switch the gas flow from dry nitrogen to dry air with an air flow of 10 L/min. It is recommended to verify in preliminary tests that the rate of oxidation does not vary by more than 5 % with the rate of air flow at the highest test

temperature used. If variations larger than 5 % are found, the test temperature is too high and a lower test temperature should be used.

12.6 Record the weight, sample temperature, and elapsed time often enough so that changes between readings are always less than 0.1 % of the initial weight, W_o. An automated data collection system is recommended. The frequency of data collection should be adjusted depending on the anticipated duration of test.

12.7 Continue the test until the specimen has lost about 15 % of its initial weight, that is, its weight becomes 0.85 W_o. Stop the automated data collection program (if it is being used) and save the data.

12.8 After cooling, remove the specimen by disconnecting the wire at the balance.

12.9 Using fresh specimens each time, repeat steps 12.1 – 12.8 above at least at three different test temperatures. A minimum of four different test temperatures should be used, typically between 500 °C and 750 °C, spaced at 50 °C to 100 °C one from another. Selection of test temperatures should be based on the oxidation resistance of the particular graphite or carbon sample. The oxidation rates increase rapidly with the increase in temperature, and the time needed to complete the test will vary strongly. At low temperatures the time required to complete the test may be 24 h or longer, but at high temperatures the test may terminate in 1 h or 2 h. The test temperatures should be selected such that the Arrhenius plots (exemplified in Fig. A2.1) yield a straight line. All high temperature data deviating from the straight line should not be used for the analysis. Experience has shown that a reasonable temperature range for high density graphite (1.75 g.cm⁻³ to 1.85 g.cm⁻³) is between 600 °C and 750 °C. For low density materials (1.2 g.cm⁻³ to 1.5 g.cm⁻³) the temperature range is between 500 °C and 650 °C.

12.10 It is recommended to perform at least two replicate measurements at each of the four temperatures selected. Using duplicate measurements allows for statistical treatment of data, and determination of precision of test results calculated from the slope and intercept of Arrhenius plot, as outlined by Practice E1970.

13. Calculation or Interpretation of Results

13.1 Calculate the nominal geometric surface area of each specimen (*A*, in m²) before testing.

$$A = 10^{-6} (2\pi D^2/4 + \pi DH) \qquad (5)$$

D = specimen diameter in mm, and
H = specimen height in mm.

13.2 Calculate the sample weight values corresponding to 5 % and 10 % weight loss from the initial weight of the specimen, W_o.

$$\text{weight value for } 5\% \text{ weight loss} = 0.95\,W_o \qquad (6)$$

$$\text{weight value for } 10\% \text{ weight loss} = 0.90\,W_o \qquad (7)$$

13.3 Calculate the slope of the weight loss versus time (*S*, in g/h) from the linear regression fit of the weight versus time data from between 5 % and 10 % weight loss. Because data is

recorded at least every tenth of a percent of weight loss, there are always at least 100 points used in the slope calculation.

13.4 At each temperature, calculate the area-normalized oxidation rate (OR_a, in g h^{-1} m^{-2}) by using the following equation:

$$OR_a = -S/A \qquad (8)$$

S = slope of weight loss in g h^{-1}, and
A = area of specimen in m^2.

13.5 At each temperature, calculate weight-normalized oxidation rate (OR_w, in g g^{-1} h^{-1}) by using the following equation:

$$OR_w = -(S/W_o) \qquad (9)$$

S = slope of weight loss in g h^{-1}, and
W_o = initial weight of specimen in g.

13.6 Evaluate area-normalized Standard Oxidation Rate (SOR_a) in g h^{-1} m^{-2} for the series of uniform graphite grade specimens to be tested, based on the average sample weight $\bar{W}$ (in grams) and area $\bar{A}$ (in m^2) of specimens, measured before testing:

$$SOR_a = (0.01 \times \bar{W}/24)/\bar{A} \qquad (10)$$

The weight-normalized Standard Oxidation Rate is $SOR_w =$ 4.17 × 10^{-4} g g^{-1} h^{-1} and is independent of the graphite grade used.

13.7 To obtain the Standard Oxidation Temperature (SOT), the oxidation rate shall be measured at a minimum of four different temperatures in the range where the Arrhenius plot (introduced in 3.1.8 and described in 13.9) is linear.

13.8 Calculate absolute test temperatures (in Kelvin) using $T = t + 273$, where t is the test temperature in degrees Celsius.

13.9 Using either one of area-normalized oxidation rate (OR_a) or weight-normalized oxidation rate (OR_w), plot the logarithm of the oxidation rates, $\log_{10}(OR)$, against the reciprocal of the absolute test temperatures, $1/T$. The resulting Arrhenius plot should be a straight line with a negative slope (see Fig. A2.2). Determine the intercept and the slope of the plot as $Intercept$ and $Slope$. A linear regression fit of the data can be used in place of a graphical solution. The correlation coefficient (R^2) shall be at least 0.985. The $Slope$ is expressed in Kelvin (K). The $Intercept$ may be reported (optionally) as the logarithm of pre-exponential factor in Arrhenius equation, and has no units associated with it.

13.10 Calculate the Standard Oxidation Temperature (SOT) in degrees Celsius for the series of samples using:

$$SOT = Slope/[log(SOR) - Intercept] - 273 \qquad (11)$$

NOTE 1—The factor for conversion of natural to decimal logarithms was reduced during algebraic transformations of Arrhenius equation and it is absent from Eq 11.

NOTE 2—Although the $Intercept$ and the SOR in the above formula have different values when using area-normalized oxidation rates (OR_a) or weight-normalized oxidation rates (OR_w), the calculated result for Standard Oxidation Temperature (SOT) is independent of the method used for normalization of oxidation rates.

13.11 Calculate the Activation Energy in kJ/mole using the formula:

$$E_a = -0.019138 \times Slope \qquad (12)$$

where the numerical factor 0.019138 = 2.303 × 8.314 × 0.001 includes the gas constant and the conversion factor of natural to decimal logarithms. The result is not dependent on the method used for normalization of oxidation rates.

13.12 If replicate measurements were made at each test temperature (recommended), follow Practice E1970 for statistical treatment of data, and determine the precision of results calculated from slope and intercept of Arrhenius plots. This practice describes the mathematical process of calculating the mean value and standard deviation of test results for activation energy and logarithm of pre-exponential factor.

14. Report

14.1 For the Oxidation Rate at a preselected temperature report either one of weight-normalized or area-normalized oxidation rates (the former is preferred). Also report specimen dimensions and specimen weight before oxidation, apparent density of the specimen before oxidation (according to Test Method C559), weight loss interval (in percentage of initial weight) used for determination of oxidation rate, the average test temperature over that weight loss interval, the air flow rate, and the calculated oxidation rate. A plot of the weight loss data showing the trend line and correlation coefficient (R^2) in the linear segment is preferred, as shown in Fig. A1.2.

14.2 For the Standard Oxidation Temperature and Activation Energy, report the average test temperatures where oxidation rates were measured, and the SOT and E_a values calculated as explained at 13.10 and 13.11. An Arrhenius plot of the decimal logarithm of oxidation rates versus reciprocal of the absolute test temperatures, showing the trend line and the correlation coefficient (R^2) is preferred. Examples or Arrhenius plots derived from area-normalized and weight-normalized oxidation rates are shown in Fig. A2.1 and Fig. A2.2.

14.3 Optionally, for the logarithm of pre-exponential factor of Arrhenius equation, report $\log_{10} Z = Intercept$, where $Intercept$ is calculated from the best linear fit of Arrhenius plot, as explained at 13.9. Specify the method used for normalization of oxidation rates. Weight-based normalization is preferred.

14.4 If replicate oxidation rate measurements were made at each test temperature, follow Practice E1970 and report mean value and standard deviation for activation energy and logarithm of pre-exponential factor in Arrhenius equation.

15. Precision and Bias[4]

15.1 The precision of this test method was determined in an interlaboratory study (ILS) conducted in 2006–2008 on two nuclear-grade and one specialty-grade graphite materials. The materials were designated, respectively, as Samples A, Samples B, and Samples C.

15.2 Five organizations participated in the ILS, including commercial graphite manufacturers and research laboratories. They used either existing equipment, already in use for quality

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