Designation: D7542 – 21

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

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

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

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:

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

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:

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

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):

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

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^{-1} (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
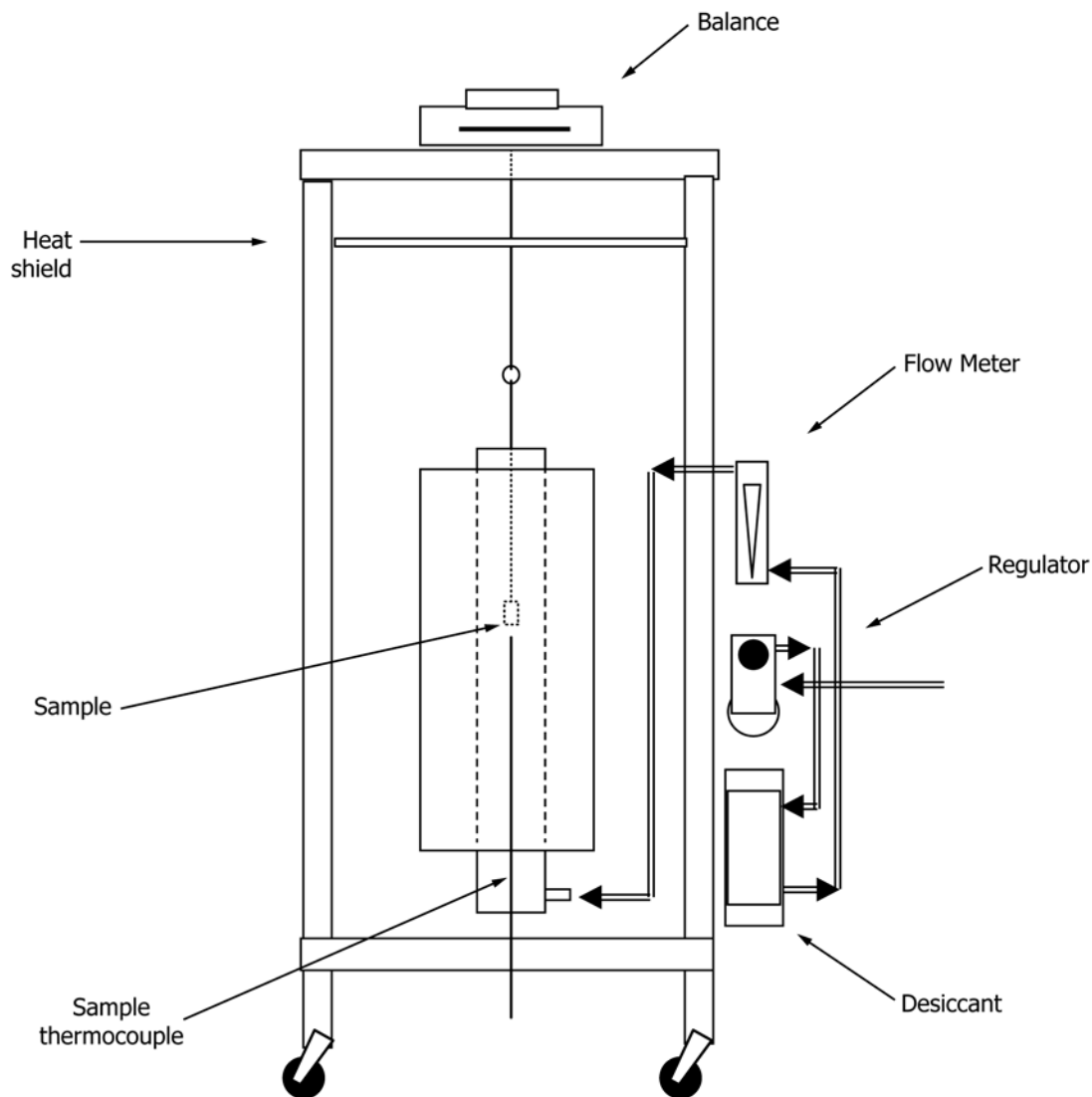
FIG. 1 Oxidation Apparatus

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