INTERNATIONAL

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Standard Test Method for Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique[1]

This standard is issued under the fixed designation E 1409; 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 covers the determination of oxygen in titanium and titanium alloys in concentrations from 0.01 % to 0.33%0.5 % and the determination of nitrogen in titanium and titanium alloys in concentrations from 0.003 % to 0.11%.. 0.11 %.

1.2 The values stated in both inch-pound and SI units are to be regarded separately as the standard. The values given in parentheses are for information only.

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionarywarning statements are given in 8.8.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E 1019Test Method for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E 1914 Practice for Use of Terms Relating to the Development and Evaluation of Methods for Chemical Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this method, refer to Terminology E 135 and E1914and Practice E 1914.

4. Summary of Test Method

4.1 This test method is intended for use with automated, commercially available, inert gas fusion analyzers. These analyzers typically measure both oxygen and nitrogen simultaneously or sequentially utilizing parallel measurement systems.

4.2 The test sample, plus flux, is fused in a graphite crucible under a flowing inert gas stream (Ar, He)(argon, helium) at a temperature sufficient to release oxygen and nitrogen. Oxygen combines with carbon to form carbon monoxide (CO) and nitrogen is released as N_2. Depending on instrument design, the CO is oxidized to carbon dioxide (CO_2) or left as CO and swept by the inert gas stream into either an infrared or thermal conductivity detector. The detector output is compared to that of reference materials and the result is displayed as percent oxygen. The nitrogen is swept by the inert gas stream (helium gas) into a thermal conductivity detector. The detector response is compared to that of reference materials and the result is displayed as percent nitrogen.

4.3 In a typical instrument for the determination of nitrogen, the sample gases are swept with inert gas through heated rare earth/copper oxide that converts CO to CO_2 and H and hydrogen (H_2 to H) to water (H_2O. The CO O). The CO_2 is absorbed on sodium hydroxide impregnated on clay, and the H_2O is removed with magnesium perchlorate. The nitrogen, as N_2, enters the measuring

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf.

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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] Withdrawn.

cell and the thermistor bridge output is integrated and processed to display percent oxygen.

5. Significance and Use

5.1 This test method is primarily intended as a test for compliance with compositional specifications. It is assumed that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

6. Interferences

6.1 The elements usually present in titanium and its alloys do not interfere but there is some evidence to suggest that low purity flux can cause some adsorption of the released oxygen.

7. Apparatus

7.1 *Instrument*—Fusion and measurement apparatus, automatic oxygen and nitrogen determinator consisting of an electrode furnace, provision for scrubbing impurities from analytical gas stream; infrared or thermal conductivity measurement system(s), or both, and auxiliary gas purification ~~systems.~~systems (Note 1).

NOTE 1—The apparatus and analysis systems have been previously described in Test Method E 1019. Several models of commercial oxygen and nitrogen determinators are available and presently in use by industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instruction manual for operational details.

7.2 *Graphite Crucibles*—The crucibles must be made of high-purity graphite and be of the dimensions recommended by the instrument manufacturer.

7.3 *Flux*—Wire baskets must be made of high-purity nickel and the dimensions must meet the requirements of the automatic sample drop, if present, on the instrument. (See Note 2.)

NOTE 2—In some instruments, nitrogen and oxygen are run sequentially and platinum is the required flux for nitrogen. High-purity platinum can be substituted for nickel in the same ratio of flux to sample.

7.4 *Tweezers*—Six-inch tweezers made of solvent and acid-resistant plastic.

8. Reagents

8.1 *Acetone*—Residue after evaporation must be ~~< 0.0005%.~~ <0.0005 %.

8.2 *Graphite Powder*—High-purity as specified by the instrument manufacturer.

8.3 *Inert Gas*—Use the purity and type specified by the instrument manufacturer.

8.4 *Magnesium Perchlorate, Anhydrous*[4]—Used in the instrument to absorb water. Use the purity specified by the instrument manufacturer.

8.5 *Nickel Flux Cleaning Solution*— Prepare a fresh solution by combining 75 mL of acetic acid, 25 mL of nitric acid (HNO_3~~and 2 mL of HCl.~~), and 2 mL of hydrochloric acid (HCl).

8.6 *Rare Earth/Copper Oxide*—Reagent used in some instruments to oxidize CO to CO_2 for thermal conductivity detection. Use the purity specified by the instrument manufacturer.

8.7 *Sodium Hydroxide on Clay*[5]—Reagent used in some instruments to absorb CO_2. Use a purity specified by the instrument manufacturer.

8.8 *Titanium Sample Pickle Solution*— Prepare a fresh solution of 3 parts 30 % hydrogen peroxide (H_2O_2~~and 1 part 48% HF. HNO~~) and 1 part 48 % hydrofluoric acid (HF). HNO_3 may be substituted for 30 % H_2O_2 (see Note 3). (**Warning**—HF causes serious burns that may not be immediately painful; refer to the paragraph about HF in the Safety Precautions Section of Practices E 50.)

NOTE 3—In 2004, alternative sample preparation procedures (Section 12) were tested by seven laboratories. Three laboratories processed the sample materials by picking their samples in HF-H_2O_2 (8.8). Two laboratories utilized the HF-HNO_3 alternative pickle solution (8.8). Two laboratories utilized abrasion (in this case diamond saw and shear) in accordance with 12.4. The prepared samples were distributed among the laboratories for analysis. Six laboratories analyzed these samples in random order under a single operator, single-day, single calibration sample run. The results of this testing are given in Tables X1.1 and X2.1 for oxygen and nitrogen, respectively. In both cases, the analysis of the ANOVA indicates that there is no significant difference at the 95 % level of confidence for either oxygen or nitrogen due to the preparation technique.

9. Hazards

9.1 Use care when handling hot crucibles and operating furnaces to avoid personal injury by either burn or electrical shock.

9.2 For precautions to be observed in the use of HF and other reagents in this test method, refer to Practices E 50.

10. Preparation of Apparatus

10.1 Assemble the apparatus as recommended by the manufacturer. Make the required power, gas, and water connections. Turn on the instrument and allow sufficient time to stabilize the equipment.

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[4] Known commercially as Anhydrone.

[5] Known commercially as Ascarite II.

10.2 Change the chemical traps and filters as required. Test the furnace and analyzer to ensure the absence of leaks. Make a minimum of two test runs using a sample as directed in 14.3 and 14.4 to condition the newly changed filters before attempting to calibrate the system or to determine the value of the blank.

11. Nickel Flux Preparation

11.1 Nickel is necessary to flux the titanium fusion reaction but contamination can be present on the surface of the nickel ~~were~~wire baskets that must be removed before use.

11.2 Immerse the flux in nickel flux cleaning solution for 50 s to 60 s, then rinse in running water for 2 min to 3 min. Pour flux onto paper towels to remove excess water. Place flux in sealable glass container, rinse with acetone and decant. Replace with fresh acetone and store flux under acetone until used. (See Notes 4 and 5.)

NOTE 4—Nickel is necessary to flux the titanium fusion reaction but significant oxidation can be present on the surface of nickel wire baskets that can cause interference with the analysis. Ultra high-purity nickel baskets are commercially available that do not require the nickel cleaning procedure above. Their sufficiency must be verified by satisfactory blank determinations.

NOTE 5—The fluxing agent must be of proper size to be introduced through the sample drop mechanism and into the graphite crucible.

12. Sample Preparation

12.1 The optimum test sample is a pin approximately ⅛ in. (5 mm) in diameter and nominally weighing 0.12 g to 0.15 g. Cut the sample to this approximate weight range.

12.2 Leach the test sample in the titanium sample pickle solution ~~(see 8.8,~~ (**Warning**~~in~~ —See 8.8~~, and~~.) (see Note 4) until the surface is clean. This will normally require approximately 5 s from the time of the initial vigorous reaction between the sample and the solution.

12.3 Immediately remove the reacting test sample with tweezers and rinse it twice with water and once with acetone and allow to air dry. This test sample should now weigh between 0.100 g and 0.140 g.

12.4 Alternatively, clean surfaces may be prepared on the test sample by filing or cutting off all outside edges, retaining only fresh surfaces, and finishing by rinsing with acetone and air drying. The test sample should now weigh between 0.100 g and 0.140 g.

12.5 All subsequent operations on the test sample and flux must be done without introducing contamination to either. Use only clean tweezers and never let the test sample or flux contact the analyst's skin. In the event this does happen, rinse the sample plus nickel basket with acetone and air dry before analysis.

13. Standardization

13.1 *Standardants*—Select only titanium or titanium alloy reference materials. Select one containing approximately 0.2 % oxygen and approximately 0.02 % nitrogen. The accuracy of the test method is dependent upon the accuracy of the methods used to certify the oxygen and nitrogen concentrations of the reference materials, as well as upon their homogeneity. Thus, wherever possible, reference materials used to confirm instrument standardization should be National Institute of Standards and Technology (NIST) Standard Reference Materials or other certified reference materials.

13.2 *Gas Dosing*—Automatic and manual gas dosing, recommended by some manufacturers, can be used to set up the instrument, but instrument response must be verified by standardization with titanium reference materials because of the fusion characteristics of the furnace/sample combination.

13.3 *Initial Adjustment of Measurement System (that is, "warm-up")*—Weigh a titanium material (not necessarily a titanium reference material) to the nearest milligram, place it in a nickel basket and transfer it to an outgassed graphite crucible containing graphite powder (Note 6). Proceed as directed in 14.3 and 14.4. Repeat in triplicate. (Outgassing is accomplished automatically either as part of the continuous analysis cycle used with the automatic sample drop, or as the first step in a two-stage cycle associated with the manual addition of the sample to the crucible.)

NOTE 6—In some instruments the addition of graphite powder (0.1 g to 1.0 g depending on crucible size and style) is designed to optimize furnace performance and facilitate the release of nitrogen from the test sample. Refer to the instrument manufacturer's instructions for recommended graphite powder additions (Note 2).

13.4 *Determination of Blank*—Proceed as directed in 14.3 and 14.4 with a graphite crucible containing graphite powder (Note 2 and Note 6) and analyze the nickel basket but without a sample. Determine the average blank of three to five individual runs (maximum allowable blank average: 0.0005 % oxygen; 0.00007 % nitrogen) and enter this value into the appropriate mechanism of the analyzer. Problems with inconsistent or high blank values must be corrected before the analysis can be continued. If the unit does not have provision for automatic blank compensation, then the blank value must be manually subtracted from the total result prior to any other calculation. Refer to the manufacturer's instructions for proper blanking procedures (Note 7).

NOTE 7—Typical leak checks should be 0.0 mm Hg to 0.5 mm Hg. The maximum allowable leak check is 0.7 mm Hg.

13.5 *Standardization*—Follow the standardization procedure recommended by the manufacturer using titanium reference materials.

13.5.1 Weigh a titanium reference material to the nearest milligram, place it in a nickel basket and transfer it to an outgassed graphite crucible containing graphite powder if appropriate (Note 6).