Application Note

Instrument: H836EN

Determination of Hydrogen in Reactive and Refractory Metals

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Introduction

Refractory metals such as titanium and zirconium can be combined with elements such as aluminum, vanadium, molybdenum and tin to produce high-strength, low-density, and corrosion-resistant alloys. These alloys are used by military, medical, sporting, and aerospace industries because of these properties. Due to the strict demands of these industries, effort needs to be taken to assure that the material meets the highest quality standards. One of the more critical chemical specifications of these alloys is the Hydrogen content. Too high of a Hydrogen content can cause hydrides to precipitate, which can lead to embrittlement and subsequent cracking when the alloy is stressed. Hydrogen pickup typically occurs during downstream processing steps such as heat treating, pickling, and cleaning. As a result, monitoring the Hydrogen content throughout these processing steps is a critical quality control procedure.

Instrument Model and Configuration

The H836EN instrument is designed for wide-range measurement of Hydrogen content of steel, iron, refractory metals, and other inorganic materials. A pre-weighed sample is placed in a graphite crucible, which is heated in an impulse furnace to release analyte gases into a flowing stream of Argon carrier gas. Evolved Oxygen reacts with the graphite crucible to form CO and CO_2. Separate reagents remove moisture from the analyte gases present as H_2O and convert CO to CO_2 which is then scrubbed from the analyte gases by an additional reagent. A molecular sieve column is used to separate the analyte gases, H_2 and N_2. Then a thermal conductivity (TC) cell is used for the detection of Hydrogen (H_2).

Sample Preparation

A clean representative sample is required for proper Hydrogen determination. Solid samples should be sectioned in such a manner as to avoid overheating, preferably by shearing. If necessary, abrade sample surfaces with a clean file, rinse in acetone, and air dry to remove surface contamination. Cleaned samples must be handled with tweezers or forceps to prevent contamination. Chip and powder samples should be a uniform mesh size. ASTM E1447, "Standard Test Method for Determination of Hydrogen in Reactive Metals and Reactive Metal Alloys by Inert Gas Fusion with Detection by Thermal Conductivity or Infrared Spectrometry," outlines proper sample preparation procedures for reactive and refractory metals and their alloys and is an excellent source of information.

Note: LECO Reference Materials typically do not require preparation prior to analysis. Refer to preparation statement on the reference material certificate.

Method Reference

ASTM E1447 - Standard Test Method for Determination of Hydrogen in Reactive Metals and Reactive Metal Alloys by Inert Gas Fusion with Detection by Thermal Conductivity or Infrared Spectrometry.

Accessories

619-895 High Temperature Graphite Crucibles, 761-739 Tin Flux Pellets, 502-040-100 Tin Capsules, 619-896 Lower Electrode Tip, 766-053 Crucible Tweezers, 760-138 Sample Tweezers.

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials.

*Method Parameters***

General Parameters	
Sample Introduction	Automated Sample Drop
Analysis Delay	70 s
Wait for User to Load Sample	Yes
Vacuum On Time	20 s
Element Parameters	
Integration Delay	30 s
Starting Baseline	2 s
Use Comparator	Yes
Comparator Level	0.10 %
Minimum Integration Time	90 s
Maximum Integration Time	110 s
Furnace Parameters	
Furnace Control Mode	Current
Outgas Parameters	
Cycles	3
Current Mode	Constant
Current	900 A†
Time	30 s
Cool Time	5 s

Analyze Furnace Settings

Step 1

Current Mode	Constant
Current	850 A[†]
Time	60 s

Step 2

Current Mode	Constant
Current	0 A
Time	30 s

***Refer to 836 Series Operator's Instruction Manual for parameter definitions.*

[†]May vary based on the line voltage. Adjust to improve recovery or to reduce crucible burn-through.

Procedure - Solid Samples

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
   a. Log in a minimum of three Blank replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Press the Analyze button on the instrument screen again, and the loading head slide-block will close, and the lower electrode will open.
   d. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   e. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.
   f. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.
   g. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis sequence will start and end automatically.
   h. Perform steps 2b through 2g a minimum of three times.
   i. Set the blank following the procedure outlined in the operator's instruction manual.
3. Instrument calibration/drift correction.
   a. Log in a minimum of three Standard replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Weigh ~0.15 g to 0.3 g of a suitable calibration/drift sample and enter the mass and sample identification into the appropriate replicate fields.
   c. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   d. Place the calibration/drift sample into the open port at the top of the loading head.
   e. Press the Analyze button on the instrument screen again and the loading head slide-block will close, and the lower electrode will open.
   f. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   g. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.

   Note: The flux to sample mass ratio must be greater than 3.3 as per ASTM D1447.

   h. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.
   i. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis equence will start and end automatically.
   j. Perform steps 3b through 3i a minimum of three times for each calibration/drift sample utilized.
   k. Calibrate/drift following the procedure outlined in the operator's instruction manual.
4. Analyze Samples.
   a. Log in a Sample with the appropriate number of replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Weigh ~0.15 g to 0.3 g of a prepared sample and enter the mass and sample identification into the appropriate replicate fields.
   c. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   d. Place the sample into the open port at the top of the loading head.
   e. Press the Analyze button on the instrument screen again, and the loading head slide-block will close, and the lower electrode will open.
   f. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   g. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.
   h. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.
   i. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis sequence will start and end automatically.
   j. Perform steps 4b through 4i for each sample being analyzed.

Procedure – Chip/Powder Samples

Note: Chip and powder samples should be a uniform mesh size. Chip samples with particle sizes of +40 mesh (420 microns) may be analyzed following the procedure outlined for analysis of solid samples. Chip samples with particles sizes of -40 mesh must be analyzed following the procedure outlined below.

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
   a. Log in a minimum of three Blank replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Place a 502-040-100 Tin Capsule (leave capsule open) into the open port at the top of the loading head.
   d. Press the Analyze button on the instrument screen again, and the loading head slide-block will close, and the lower electrode will open.
   e. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   f. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.
   g. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.

h. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis sequence will start and end automatically.
i. Perform steps 2b through 2h a minimum of three times.
j. Set the blank following the procedure outlined in the operator's instruction manual.

3. Instrument calibration/drift correction.
   a. Log in a minimum of three Standard replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Weigh ~0.15 g to 0.3 g of a suitable calibration/drift sample into a 502-040-100 Tin Capsule and enter the mass and sample identification into the appropriate replicate fields.

   Note: Solid reference materials may be utilized to calibrate when chip or powder reference materials are not available.

   c. Press the Analyze button on the instrument screen. After a short delay the loading head slide-block will open.
   d. Place the tin capsule containing the calibration/drift sample into the open port at the top of the loading head.
   e. Press the Analyze button on the instrument screen again, and the loading head slide-block will close, and the lower electrode will open.
   f. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   g. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.
   h. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.
   i. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis sequence will start and end automatically.
   j. Perform steps 3b through 3i a minimum of three times for each calibration/drift sample utilized.
   k. Calibrate/drift following the procedure outlined in the operator's instruction manual.

4. Analyze Samples.
   a. Log in a Sample with the appropriate number of replicates and select the appropriate Method. Then select the appropriate Furnace Method.
   b. Weigh ~0.15 g to 0.3 g of a sample into a 502-040-100 Tin Capsule and enter the mass and sample identification into the appropriate replicate fields.
   c. Press the Analyze button on the instrument screen. After a short delay the loading head slide-block will open.
   d. Place the tin capsule containing the sample into the open port at the top of the loading head.
   e. Press the Analyze button on the instrument screen again, and the loading head slide-block will close, and the lower electrode will open.
   f. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   g. Add two pellets of 761-739 Tin Flux to a 619-895 Graphite Crucible.
   h. Firmly place the graphite crucible containing the tin flux on the lower electrode tip.
   i. Press the Analyze button on the instrument screen and the lower electrode will close. The analysis sequence will start and end automatically.
   j. Perform steps 4b through 4i for each sample being analyzed.

Typical Results

Results for solid samples are based on a linear, forced through origin calibration utilizing 503-518 (Lot: 0802) LCRM Titanium Pins (176 ppm Hydrogen). Results for powder/chip samples are based on a linear, forced through origin calibration utilizing 502-706 (Lot: 1000) LCRM Titanium Powder (279 ppm Hydrogen).

Solid Samples

Sample	*Mass (g)*	*Hydrogen (ppm)*
LECO 502-891	0.2449	103
Lot: 0749	0.2401	115
Titanium Pin	0.2282	109
103 ppm ±7 ppm H	0.2416	114
	0.2531	108
	Avg =	***108***
	s =	***5***
LECO 503-507	0.2452	83
Lot: 0797	0.2442	84
Titanium Pin	0.2438	85
79 ppm ±5 ppm H	0.2447	82
	0.2451	80
	Avg =	***83***
	s =	***2***
LECO 503-519	0.2452	18
Lot: 0803	0.2435	20
Titanium Pin	0.2441	19
20 ppm ±3 ppm H	0.2443	18
	0.2433	18
	Avg =	***19***
	s =	***1***
LECO 502-890	0.2399	8.5
Lot: 0747	0.2423	8.0
Zirconium Pin	0.2377	8.0
9.1 ppm ±2.4 ppm H	0.2366	7.1
	0.2421	8.4
	Avg =	***8.0***
	s =	***0.5***

Powder/Chip Samples

Sample	*Mass (g)*	*Hydrogen (ppm)*
Reagent Grade	0.2522	7.3
Tantalum	0.2501	7.8
	0.2512	7.7
	0.2502	7.3
	0.2507	7.7
	Avg =	***7.6***
	s =	***0.3***
LECO 502-708-HAZ	0.2503	259
Lot: 1000	0.2521	260
Titanium Powder	0.2522	261
259 ppm ±10 ppm H	0.2509	261
	0.2525	260
	Avg =	***260***
	s =	***1***
NBS 176	0.2502	54
Titanium Chips	0.2497	54
	0.2508	53
	0.2493	53
	0.2503	54
	Avg =	***54***
	s =	***1***
NIST 360b	0.2512	16
Zirconium Alloy Chips	0.2512	14
16.01 ppm	0.2501	15
(Informational value only)	0.2502	15
	0.2512	14
	Avg =	***15***
	s =	***1***

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