Application Note

Instrument: ONH836

EMPOWERING RESULTS

Oxygen, Nitrogen, and Hydrogen in Refractory Metals

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Summary

Titanium is a metal that can be combined with elements such as aluminum, vanadium, molybdenum, and tin to produce high-strength, low-density, and corrosion-resistant alloys. Titanium alloys are used by the military, medical devices, sporting goods, and aerospace industries because of these properties, and due to the strict demands of these industries, effort needs to be taken to assure that the material meets the highest of quality standards.

Oxygen and nitrogen are alloying elements in titanium, and are also classified as alpha stabilizing elements as they promote alpha phase alloys. Interstitial oxygen and nitrogen levels can be used to regulate the tensile strength of the material, but due to its high solubility can cause unwanted surface embrittlement. This phenomenon can be leveraged, however, under controlled processing to create surface films that increase surface hardness and wear properties.

One of the most critical chemical specifications of titanium 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.

The LECO ONH836 is a simultaneous oxygen, nitrogen, and hydrogen determinator that utilizes an electrode furnace, inert carrier gas, and both infrared and thermal conductivity detection to meet the analytical needs of the refractory metal industry.

This application note was written specifically for use with the LECO ONH836 series determinator.

Sample Preparation

Sampling and sample preparation of refractory metals such as titanium and zirconium is somewhat different from that of steel. Unlike steel samples, hydrogen is not as mobile in this group of materials; therefore, storage in liquid nitrogen or dry ice is not required. However, it is important to keep the sample cool when cutting or sectioning. Sample preparation for oxygen and nitrogen determination has been different from that of hydrogen determination. Typically, titanium and zirconium samples are chemically etched to remove surface contamination when oxygen and nitrogen are determined. However, etching can introduce hydrogen into the sample. ASTM method E 1409 "Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique", as updated in 1996, permits either etching or abrading (filing) of the test specimen. ASTM E 1447 "Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method" permits surface preparation by abrading (if necessary to remove contamination). Differences in sample preparation present somewhat of a dilemma regarding simultaneous determination of O, N, and H in titanium. However, abrading samples with a file to remove surface contamination will yield accurate O, N, and H results. The ONH836 utilizes a high-power electrode furnace to quickly and efficiently release the target gases from within the sample, which allows for a very rapid simultaneous determination of oxygen, nitrogen, and hydrogen.

Accessories

782-720 Graphite Crucibles

782-721 Lower Electrode Tip for 782-720 crucibles without automation

618-376 Lower Electrode Tip for 782-720 crucibles with automation

502-344 Nickel Baskets

501-598 Nibble Nickel Flux

501-073 Graphite Powder

502-822 Nickel Capsule (for chip and powder materials)

Note: LECO 502-344 Nickel Baskets and 502-822 Nickel Capsule are prepared using a proprietary procedure to ensure low and precise O, N, and H content. They can be used directly from the bottle without additional cleaning. To avoid contamination, handle with clean forceps only. The 618-376 Lower Electrode Tip is only required if the instrument is equipped with automation.

Reference Materials

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

*Method Parameters***

General Parameters

Sample Introduction	Automated Sample Drop
Analysis Delay	30 s
Auto Analyze on Mass Entry	No
Outgas Before Mass Entry	No
Wait for User to Load Sample	Yes
Vacuum On Time	18 s

Element Parameters	*Oxygen*	*Nitrogen*	*Hydrogen*
Integration Delay	5 s	15 s	10 s
Starting Baseline	2 s	2 s	2 s
Use Comparator	No	No	No
Integration Time	30 s	65 s	65 s
Use Endline	Yes	Yes	Yes
Ending Baseline	2 s	2 s	2 s
Range Select	Auto	—	—
Range Lower Limit	800	—	—
Range Upper Limit	950	—	—

Furnace Parameters

Furnace Control Mode	Furnace Power

Outgas Furnace Settings

Cycles	2
Power Mode	Constant
Power	5500* W
Time	20 s
Cool Time	5 s

Surface Oxide Removal

Remove Surface Oxide	No

Analyze Furnace Settings

Step 1 Power Mode	Constant
Power	4800* W

Approximate Cycle Time 3.5 Minutes

**May vary, depending on line voltage. Level can be adjusted to facilitate recovery and/or reduce crucible burn-through.*
***The method parameters listed in the table above are optimized for the use of helium as a carrier gas. The use of argon as a carrier gas will require lengthened integration times, as well as reduced outgas and analysis power levels. Please contact the LECO Technical Services Laboratory for additional details.*

Automation Parameters (if equipped)

General Parameters

Auto Cleaner State	Enabled
Auto Cleaner Mode	During Analysis
Clean Time	8 s

Procedure - Solid Samples

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
    a. Login a minimum of 3 Blank replicates.
    b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open. Place a 502-344 Nickel Basket into the loading head.

    Note: samples using automation should be placed in the appropriate autoloader position before starting the analysis sequence. Once the sequence has started, the automatic analysis will start and end automatically.

    c. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
    d. Clean the upper and lower electrode manually, or, if applicable, remove the crucible and press the analyze button to clean with the automatic cleaner.
    e. Add approximately 0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
    f. Firmly place the crucible on the lower electrode tip or appropriate autoloader position.
    g. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
    h. Repeat 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. Login a minimum of 3 Standard replicates.
    b. Weigh approximately 0.10 to 0.14 grams of a calibration/drift standard, enter the mass and standard identification into appropriate replicate fields.

    Note: LECO Reference Materials do not require preparation. See preparation statement on the reference material certificate.

    c. Place the calibration/drift standard in a 502-344 Nickel Basket, and if applicable, place the sample into the appropriate autoloader position.
    d. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.

    Note: samples using automation should be placed in the appropriate autoloader position before starting the analysis sequence. Once the sequence has started, the automatic analysis will start and end automatically.

    e. Place the nickel basket containing the calibration/drift standard into the open port at the top of the loading head.
    f. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
    g. Clean the upper and lower electrode manually, or, if applicable, remove the crucible and press the analyze button to clean with the automatic cleaner.
    h. Add approximately 0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
    i. Firmly place the crucible on the lower electrode tip or appropriate autoloader position.
    j. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
    k. Repeat steps 3b through 3j a minimum of three times for each calibration/drift standard used.
    l. Calibrate/drift following the procedure outlined in the operator's instruction manual.
4. Analyze samples.
    a. Login Sample with the appropriate number of replicates.
    b. Weigh approximately 0.10 to 0.14 g of appropriately prepared sample, enter mass and sample identification into appropriate replicate fields.
    c. Place the weighed sample into a 502-344 Nickel Basket.
    d. Repeat steps 3d through 3j for sample analysis.

Typical Results - Solid Samples

Sample	Mass (g)	O%	N%	H ppm
LECO	0.12	0.1917	0.0358	20.0
501-996		0.1926	0.0364	19.2
0.193% O		0.1938	0.0370	21.9
0.036% N		0.1943	0.0367	20.9
20.5 ppm H		0.1916	0.0354	18.6
		0.1933	0.0359	19.3
		0.1942	0.0361	22.4
		0.1932	0.0360	21.3
		0.1944	0.0354	21.9
		0.1910	0.0353	19.6
	X =	***0.1930***	***0.0360***	***20.5***
	s =	***0.0012***	***0.0006***	***1.3***
LECO	0.1	0.1701	0.0087	26.6
501-664		0.1702	0.0091	27.7
0.169% O		0.1710	0.0088	26.2
0.009% N		0.1706	0.0081	26.4
		0.1703	0.0088	24.7
		0.1733	0.0090	26.4
		0.1700	0.0089	25.7
		0.1696	0.0090	27.6
		0.1688	0.0087	26.3
		0.1694	0.0090	26.1
	X =	***0.1703***	***0.0088***	***26.4***
	s =	***0.0012***	***0.0003***	***0.8***
LECO	0.1	0.1346	0.0039	10.3
502-047		0.1383	0.0041	11.9
0.137% O		0.1362	0.0039	10.2
		0.1380	0.0041	12.4
		0.1383	0.0039	12.5
		0.1346	0.0039	11.0
		0.1347	0.0037	10.5
		0.1356	0.0042	9.3
		0.1360	0.0043	10.9
		0.1352	0.0038	10.1
	X =	***0.1361***	***0.0040***	***10.9***
	s =	***0.0015***	***0.0002***	***1.0***
LECO	0.1	0.0501	0.0027	18.9
501-653		0.0523	0.0030	22.4
0.053% O		0.0495	0.0022	19.9
0.003% N		0.0507	0.0029	22.2
		0.0534	0.0027	19.3
		0.0509	0.0031	27.9
		0.0505	0.0028	24.5
		0.0501	0.0026	19.4
		0.0497	0.0025	25.8
		0.0514	0.0025	26.8
	X =	***0.0509***	***0.0027***	***22.7***
	s =	***0.0012***	***0.0003***	***3.4***

Procedure – Powder/Chip Samples

Note: Oxygen and Nitrogen determination in chip and powder samples is typically performed using 502-822 Nickel Capsules. To optimize recovery, it is recommended to add ~0.4 g of 501-598 Nibbled Nickel Flux to the nickel capsules, prior to analysis.

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
   a. Login a minimum of three Blank reps.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open. Insert a 502-822 Nickel Capsule containing ~0.4 g of 501-598 Nibbled Nickel Flux (leave capsule open) into the open port at top of the loading head.

   Note: samples using automation should be placed in the appropriate autoloader position before starting the analysis sequence. Once the sequence has started, the automatic analysis will start and end automatically.

   c. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
   d. Clean the upper and lower electrode either manually or remove the crucible and press the analyze button to clean with an automatic cleaner if applicable.
   e. Add approximately 0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
   f. Firmly place the crucible on the lower electrode tip or appropriate autoloader position.
   g. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat 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. Login a minimum of three Standard reps.
   b. Weigh approximately 0.10 to 0.12 grams of a calibration/drift standard into a 502-822 Nickel Capsule; enter the mass and standard identification into appropriate rep fields. If applicable, place the nickel capsule in the appropriate autoloader position.

   Note: LECO Reference Materials do not require preparation. See preparation statement on the reference material certificate. Solid Standards may be used to calibrate when chip or powder standards are not available.

   c. Add ~0.4 g of 501-598 Nibbled Nickel Flux to the nickel capsule, covering the calibration/drift standard (leave capsule open).
   d. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.

e. Place the Nickel Capsule containing the sample into the open port at the top of the loading head.
f. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
g. Clean the upper and lower electrode either manually or remove the crucible and press the analyze button to clean with an automatic cleaner if applicable.
h. Add approximately 0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
i. Firmly place the crucible on the lower electrode tip or appropriate autoloader position.
j. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
k. Repeat steps 3b through 3j a minimum of three times for each calibration/drift standard used.
l. Calibrate/drift following the procedure outlined in the operator's instruction manual.

4. Analyze Samples.
   a. Login Sample with the appropriate number of reps.
   b. Weigh approximately 0.10 to 0.12 grams of appropriately prepared sample into a 502-822 Nickel Capsule, enter mass and sample identification into appropriate rep fields. If applicable, place the nickel capsule in the appropriate autoloader position.
   c. Repeat steps 3c through 3j for sample analysis.

Typical Results - Powder/Chip Samples

Sample	*Mass (g)*	*O%*	*N%*	*H ppm*
CRM	0.1048	0.116	0.0147	45.0
NBS 173	0.1070	0.111	0.0147	39.8
Ti Alloy	0.1105	0.120	0.0155	39.7
Chips	0.1002	0.120	0.0156	39.6
	0.1060	0.119	0.0144	41.1
	X=	***0.117***	***0.0150***	***41.0***
	s=	***0.004***	***0.0005***	***2.3***
CRM	0.1072	0.0741	0.0067	53.4
NBS 176	0.1096	0.0763	0.0068	57.1
Ti Alloy	0.1028	0.0781	0.0067	54.0
Chips	0.1086	0.0771	0.0068	57.8
	0.1076	0.0750	0.0062	52.7
	X=	***0.0761***	***0.0067***	***55.0***
	s=	***0.0016***	***0.0002***	***2.3***
Tantalum	0.1137	0.102	0.0027	112.0
Powder	0.1106	0.106	0.0029	111.1
	0.1179	0.099	0.0029	110.9
	0.1070	0.105	0.0029	111.9
	0.1101	0.100	0.0029	111.5
	X=	***0.103***	***0.0028***	***111.5***
	s=	***0.003***	***0.0001***	***0.5***
CRM	0.1089	0.165	0.0102	30.2
NBS 174	0.1060	0.159	0.0096	28.9
Ti Alloy	0.1029	0.161	0.0100	30.4
Chips	0.1055	0.161	0.0095	28.8
	0.1073	0.168	0.0095	31.0
	X=	***0.163***	***0.0098***	***29.9***
	s=	***0.004***	***0.0003***	***1.0***
CRM	0.1148	0.155	0.0036	12.2
NIST 360b	0.1117	0.150	0.0038	10.4
Zirconium Alloy	0.1029	0.153	0.0036	11.9
Chips	0.1095	0.155	0.0040	14.9
0.0045% N	0.1045	0.147	0.0037	12.8
	X=	***0.152***	***0.0038***	***12.4***
	s=	***0.003***	***0.0002***	***1.6***

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