Application Note

Instrument: ONH836

Oxygen, Nitrogen, and Hydrogen in Refractory Metals

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Summary

Refractory metals are a group of metallic elements known for their exceptionally high melting points, strength, and resistance to wear and corrosion even at extreme temperatures. Examples include Molybdenum, Tantalum, Niobium, Rhenium, and Zirconium with Titanium being the most common.

Refractory metals like Titanium 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. 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.

Method Reference

ASTM E1409: Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique

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.

Note: Please reference the appropriate Safety Data Sheets (SDS) for safe handling of all reference materials and samples.

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, 502-822 Nickel Capsule, and 501-598 Nibble Nickel Flux 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.

Note: Due to limited availability of refractory reference materials, steel reference materials can be used to calibrate.

Method Parameters

General Parameters		
Gas Type	*Helium*	*Argon*
Sample Introduction	Automated Sample Drop	Automated Sample Drop
Analysis Delay	30 s	50 s
Auto Analyze on Mass Entry	No	No
Outgas Before Mass Entry	No	No
Outgas At End Of Analysis	No	No
Wait for User to Load Sample	Yes	Yes
Sample Drop Detection	Disabled	Disabled
Nominal Mass	1.0000 g	1.0000 g
Vacuum On Time	18 s	18 s

Element Parameters		*Helium*			*Argon*	
Parameter	*Oxygen*	*Nitrogen*	*Hydrogen*	*Oxygen*	*Nitrogen*	*Hydrogen*
Integration Delay	5 s	15 s	10 s	3 s	10 s	10 s
Starting Baseline	2 s	2 s	2 s	2 s	2 s	2 s
Use Comparator	No	No	No	No	No	No
Integration Time	30 s	65 s	65 s	45 s	85 s	90 s
Use Endline	Yes	Yes	Yes	Yes	Yes	Yes
Ending Baseline	2 s	2 s	2 s	2 s	2 s	2 s
Range Select	Auto	--	--	Auto	--	--
Range Lower Limit	1950	--	--	1950	--	--
Range Upper Limit	2100	--	--	2100	--	--

Furnace Parameters

Parameter	*Helium*	*Argon*
Furnace Control Mode	Power	Power

Outgas Parameters

Parameter	*Helium*	*Argon*
Cycles	2	2
Power Mode	Constant	Constant
Power	5300* W	4500* W
Time	20 s	20 s
Cool Time	5 s	5 s

Surface Oxide Removal Parameters

Parameter	*Helium*	*Argon*
Remove Surface Oxide	No	No

Analyze Furnace Parameters

Parameter	*Helium*	*Argon*
Step 1 Power Mode	Constant	Constant
Power	4800* W	4100* W

**May vary, depending on line voltage. Level can be adjusted to facilitate recovery and/or reduce crucible burn-through.*

Approximate Cycle Time

Parameter	*Helium*	*Argon*
Time	~4.5 Minutes	~5.0 Minutes

Automation Parameters (if equipped)

Parameter	*Helium and Argon*
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. From the Analysis Screen, use the Login Bar to add three or more blank replicates (minimum of three).
    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. 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. From the Analysis Screen, use the Login Bar to add the desired number of calibration/drift replicates (minimum of three).
    b. Weigh approximately 0.10 to 0.15 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. Perform 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. From the Analysis Screen, use the Login Bar to add the desired number of sample replicates.
    b. Weigh approximately 0.10 to 0.15 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. Perform steps 3d through 3j for each sample to be analyzed.

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. From the Analysis Screen, use the Login Bar to add three or more blank replicates (minimum of three).
    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. 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. From the Analysis Screen, use the Login Bar to add the desired number of calibration/drift replicates (minimum of three).
    b. Weigh approximately 0.10 to 0.15 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. Perform 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. From the Analysis Screen, use the Login Bar to add the desired number of sample replicates.
    b. Weigh approximately 0.10 to 0.15 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. Perform steps 3c through 3j for each sample to be analyzed.

Typical Results - Solid Samples

Data was generated utilizing a linear, force through origin calibration for Oxygen determination using LECO 503-521 (Lot 0805) LCRM Titanium Pin (0.349 % O). A linear, force through origin calibration was utilized for Nitrogen determination using LECO 502-947 (Lot 0740) LCRM Titanium Pin (0.013 % N), and a linear, force through origin calibration was utilized for Hydrogen determination using LECO 503-560 (Lot 0816) LCRM Titanium Pin (141.8 ppm H). The Oxygen calibration was verified using LECO 503-548 (Lot 0796) LCRM Titanium Pin (0.068 % O). The Nitrogen and Hydrogen calibrations were verified using LECO 503-521 (Lot 0805) LCRM Titanium Pin (0.0022 % N, 17 ppm H).

	Helium				*Argon*			
Sample	*Mass (g)*	*O (%)*	*N (%)*	*H (ppm)*	*Mass (g)*	*O (%)*	*N (%)*	*H (ppm)*
Titanium Pin	0.1180	0.109	0.0041	117.8	0.1192	0.101	0.0041	117.2
503-554	0.1180	0.109	0.0034	117.5	0.1182	0.101	0.0052	116.8
Lot 0816	0.1179	0.109	0.0037	118.3	0.1170	0.106	0.0040	119.8
119.5 ± 5.9 ppm H	0.1188	0.109	0.0044	119.0	0.1175	0.100	0.0050	117.2
	0.1175	0.107	0.0042	122.5	0.1182	0.100	0.0048	116.7
	$\bar{x}$ =	***0.109***	***0.0040***	***119.0***	$\bar{x}$ =	***0.102***	***0.0046***	***117.5***
	s =	***<0.001***	***0.0004***	***2.0***	***s =***	***0.002***	***0.0005***	***1.3***
Titanium Pin	0.1184	0.110	0.0041	66.2	0.1185	0.101	0.0046	62.9
503-556	0.1179	0.109	0.0042	67.7	0.1188	0.101	0.0050	62.0
Lot 0816	0.1185	0.110	0.0048	66.3	0.1193	0.102	0.0045	62.2
66.0 ± 5.1 ppm H	0.1190	0.111	0.0044	66.2	0.1185	0.102	0.0042	67.2
	0.1191	0.110	0.0042	65.7	0.1190	0.102	0.0049	71.1
	$\bar{x}$ =	***0.110***	***0.0043***	***66.4***	$\bar{x}$ =	***0.102***	***0.0047***	***65.1***
	s =	***0.001***	***0.0003***	***0.7***	***s =***	***<0.001***	***0.0003***	***4.0***
Titanium Pin	0.1189	0.077	0.0022	32.1	0.1193	0.073	0.0024	30.4
503-558	0.1188	0.074	0.0019	26.2	0.1190	0.071	0.0031	29.6
Lot 0819	0.1200	0.075	0.0025	31.2	0.1177	0.071	0.0026	30.4
0.076 ± 0.006 % O	0.1177	0.074	0.0024	30.5	0.1190	0.072	0.0026	28.3
0.0024 ± 0.0006 % N	0.1187	0.075	0.0024	28.8	0.1197	0.072	0.0021	26.7
28 ± 4 ppm H	$\bar{x}$ =	***0.075***	***0.0023***	***29.7***	$\bar{x}$ =	***0.072***	***0.0026***	***29.1***
	s =	***0.001***	***0.0002***	***2.3***	***s =***	***0.001***	***0.0004***	***1.6***
Titanium Pin	0.1212	0.318	0.0025	19.9	0.1203	0.316	0.0025	24.8
503-569	0.1209	0.316	0.0024	19.9	0.1208	0.316	0.0026	21.9
Lot 0829	0.1205	0.317	0.0027	23.5	0.1213	0.315	0.0033	21.9
0.319 ± 0.005 % O	0.1202	0.316	0.0026	21.5	0.1211	0.317	0.0025	22.5
0.0027 ± 0.0006 % N	0.1204	0.318	0.0022	21.1	0.1204	0.317	0.0029	26.0
21 ± 4 ppm H	$\bar{x}$ =	***0.317***	***0.0025***	***21.2***	$\bar{x}$ =	***0.316***	***0.0028***	***23.4***
	s =	***0.001***	***0.0002***	***1.5***	***s =***	***0.001***	***0.0003***	***1.9***

$\bar{x}$ = sample mean; s = sample standard deviation

Typical Results - Powder/Chip Samples

Data was generated utilizing a linear, force through origin calibration for Oxygen determination using LECO 503-522 (Lot 0804) LCRM Titanium Pin (0.288 % O). A linear, force through origin calibration was utilized for Nitrogen determination using LECO 501-320 (Lot 0598) Titanium Pin (0.035 % N)), and a linear, force through origin calibration was utilized for Hydrogen determination using LECO 502-707-HAZ (Lot 1000) LCRM Titanium Powder (276 ppm H). The Oxygen and Nitrogen calibrations were verified using LECO 503-558 (Lot 0819) LCRM Titanium Pin (0.076 % O, 0.0024 % N). The Hydrogen calibration was verified using LECO 502-947 (Lot 0740) LCRM Titanium Pin (14 ppm H).

	Helium				*Argon*			
Sample	*Mass (g)*	*O (%)*	*N (%)*	*H (ppm)*	*Mass (g)*	*O (%)*	*N (%)*	*H (ppm)*
Tantalum Powder	0.1196	0.149	0.0062	6.5	0.1166	0.139	0.0060	8.3
	0.1185	0.147	0.0062	6.1	0.1160	0.139	0.0057	7.3
	0.1178	0.146	0.0065	6.1	0.1209	0.141	0.0060	7.5
	0.1167	0.147	0.0063	6.7	0.1156	0.141	0.0062	7.1
	0.1162	0.142	0.0062	5.0	0.1193	0.141	0.0060	7.3
	$\bar{x}$ =	***0.146***	***0.0063***	***6.1***	$\bar{x}$ =	***0.140***	***0.0060***	***7.5***
	s =	***0.002***	***0.0002***	***0.7***	***s =***	***0.001***	***0.0002***	***0.4***
Zirconium Chips	0.1187	0.155	0.0050	14.6	0.1174	0.149	0.0053	14.5
	0.1175	0.155	0.0051	12.6	0.1162	0.149	0.0049	14.7
	0.1193	0.154	0.0049	11.8	0.1163	0.149	0.0046	14.6
	0.1160	0.158	0.0053	13.4	0.1188	0.144	0.0044	15.3
	0.1184	0.154	0.0049	12.8	0.1165	0.145	0.0037	16.3
	$\bar{x}$ =	***0.155***	***0.0050***	***13.0***	$\bar{x}$ =	***0.147***	***0.0046***	***15.1***
	s =	***0.002***	***0.0001***	***1.0***	***s =***	***0.003***	***0.0006***	***0.7***

$\bar{x}$ = sample mean; s = sample standard deviation

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