Oxygen and Nitrogen Determination in Refractory Metals and Their Alloys

LECO Corporation; Saint Joseph, Michigan USA

Instrument: ON736

Introduction

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 device, 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 their high solubility, they 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.

The LECO ON736 is a simultaneous oxygen and nitrogen 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 ON736 series determinator.

Sample Preparation

A clean and representative sample is required in order to obtain optimum results. Solid samples should be removed of surface contamination prior to analysis. Typically, titanium samples are chemically etched to remove surface contamination when oxygen and nitrogen are determined. ASTM Method E1409 "Determination of Oxygen and Nitrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Technique", permits either chemical etching or abrading (filing) of the test specimen. Other refractory metals, such as zirconium, molybdenum, tantalum, niobium, rhenium, and hafnium are typically abraded, rinsed with a solvent such as acetone, and dried with warm air. Care must be taken to remove all traces of the solvent prior to analysis. For porous materials, such as tungsten, it is advisable to avoid the use of solvents as it can be difficult to remove all traces of the solvent by drying. Chip samples are typically rinsed with a solvent such as acetone, provided the material is not porous. Powder samples are typically analyzed without additional preparation. Refer to the ASTM methods below for additional details.

Method

ASTM E1409, ASTM E1569

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, 502-822 Nickel Capsules,
501-073 Graphite Powder, 501-598 Nibbled Nickel Flux

Reference Materials

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

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 three Blank replicates
   b. Press the Analyze icon on the instrument screen. After a short delay, the slide-block will open.

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

   c. Place a 502-344 Nickel Basket into the loading head or into the appropriate autoloader position.
   d. Press the Analyze icon on the instrument screen again, the 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 ~0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
   g. Firmly place the crucible on the lower electrode tip or the appropriate autoloader position.
   h. Press the Analyze icon on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
   i. Repeat 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. Login a minimum of three Standard replicates.
   b. Weigh 0.10-0.15 g of a reference material, enter the mass and sample identification into the appropriate replicate fields.

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

Inorganic Application Note

c. Place the reference material into a 502-344 Nickel Basket.
d. Press the Analyze icon on the instrument screen. After a short delay, the slide-block will open.

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

e. Place the nickel basket containing the reference material into the open port at the top of the loading head.
f. Press the Analyze icon on the instrument screen again, the slide-block will close and the lower electrode will open.
g. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
h. Add ~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 the appropriate autoloader position.
j. Press the Analyze icon 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 reference material utilized.
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 0.10-0.15 g of a prepared sample, enter mass and identification into the appropriate replicate fields.
   c. Place the weighed sample into a 502-344 Nickel Basket.
   d. Repeat steps 3d through 3j for sample analysis.

*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*
Integration Delay	0 s	10 s
Starting Baseline	2 s	2 s
Use Comparator	No	No
Integration Time	35 s	65 s
Use Endline	Yes	Yes
Ending Baseline	2 s	2 s
Furnace Parameters		
Furnace Control Mode	Power	
Outgas Furnace Settings		
Cycles	2	
Power Mode	Constant	
Power	5500* W	
Time	20 s	
Cool Time	5 s	
Surface Oxide removal		
Remove Surface Oxides	No	
Analyze Furnace Settings		
Step 1 Power Mode	Constant	
Power	4750* 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.*

Typical Results—Solid Samples*

Name	Mass (g)	Oxygen %	Nitrogen %
502-880	0.1114	0.108	0.0023
Titanium Pin	0.1160	0.111	0.0024
O: 0.110 ± 0.004 %	0.1178	0.110	0.0025
N: 0.002 ± 0.001 %	0.1177	0.109	0.0024
	0.1140	0.109	0.0024
	Avg =	***0.109***	***0.0024***
	s =	***0.001***	***0.0001***

Name	Mass (g)	Oxygen %	Nitrogen %
Molybdenum Rod	0.1038	0.0113	<0.0005
	0.1038	0.0121	<0.0005
	0.1068	0.0121	<0.0005
	0.1050	0.0115	<0.0005
	0.1128	0.0118	<0.0005
	Avg =	***0.0117***	***<0.0005***
	s =	***0.0003***	**-**

502-890	0.1019	0.140	0.0020
Zirconium Pin	0.1194	0.139	0.0019
O: 0.141 ± 0.005 %	0.1220	0.140	0.0022
N: 0.0020 ± 0.0003 %	0.1167	0.140	0.0021
	0.1209	0.140	0.0021
	Avg =	***0.140***	***0.0021***
	s =	***0.0004***	***0.0001***

Tantalum Sheet	0.1236	0.0024	<0.0005
	0.1031	0.0028	<0.0005
	0.1071	0.0021	<0.0005
	0.1140	0.0026	<0.0005
	0.1076	0.0030	<0.0005
	Avg =	***0.0026***	***<0.0005***
	s =	***0.0004***	**-**

**Note: Results based on a linear force through origin calibration utilizing LECO 502-888 (Lot #0746-37) Titanium LRM @ 0.354 ± 0.008 % Oxygen and 502-879 (Lot #0572) Titanium LRM @ 0.014 ± 0.002 % Nitrogen.*

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 replicates.
   b. Press the Analyze icon on the instrument screen. After a short delay, the slide-block will open.

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

   c. Place a 502-822 Nickel Capsule (leave capsule open) into the loading head.
   d. Press the Analyze icon on the instrument screen again, the 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 ~0.05 g of 501-073 Graphite Powder to a 782-720 Graphite Crucible.
   g. Firmly place the crucible on the lower electrode tip or the appropriate autoloader position.
   h. Press the Analyze icon on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
   i. Repeat 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. Login a minimum of three Standard replicates.
   b. Weigh 0.10-0.12 g of a reference material, enter the mass and sample identification into the appropriate replicate fields.

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

   c. Place the reference material into a 502-822 Nickel Capsule.
   d. Press the Analyze icon on the instrument screen. After a short delay, the slide-block will open.

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

   e. Place the nickel capsule containing the reference material into the open port at the top of the slide-block.
   f. Press the Analyze icon on the instrument screen again, the slide-block will close and the lower electrode will open.
   g. Clean the upper and lower electrode either manually or with an equipped automatic cleaner.
   h. Add ~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 the appropriate autoloader position.
   j. Press the Analyze icon 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 reference material utilized.
   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 0.10-0.12 g of a prepared sample, enter mass and identification into the appropriate replicate fields.
   c. Place the weighed sample into a 502-822 Nickel Capsule.
   d. Repeat steps 3d through 3j for sample analysis.

*Typical Results—Powder/Chip Samples**

Name	*Mass (g)*	*Oxygen %*	*Nitrogen %*
NIST 360b	0.1168	0.151	0.0046
Zirconium Alloy Chips	0.1177	0.150	0.0038
	0.1177	0.150	0.0036
	0.1154	0.149	0.0045
	0.1140	0.145	0.0048
	Avg =	***0.149***	***0.0043***
	s =	***0.002***	***0.0005***
Titanium Alloy Powder	0.1047	0.163	0.0286
	0.1131	0.163	0.0286
	0.1193	0.164	0.0288
	0.1173	0.162	0.0304
	0.1124	0.161	0.0297
	Avg =	***0.163***	***0.0292***
	s =	***0.001***	***0.0008***

Name	*Mass (g)*	*Oxygen %*	*Nitrogen %*
Tungsten Chips	0.1145	0.0326	<0.0005
	0.1158	0.0316	<0.0005
	0.1157	0.0352	<0.0005
	0.1137	0.0332	<0.0005
	0.1081	0.0359	<0.0005
	Avg =	***0.0337***	***<0.0005***
	s =	***0.0018***	***-***
Tantalum Powder	0.1146	0.172	0.0252
	0.1168	0.175	0.0246
	0.1191	0.176	0.0249
	0.1112	0.175	0.0251
	0.1140	0.173	0.0257
	Avg =	***0.174***	***0.0251***
	s =	***0.001***	***0.0004***

**Note: Results based on a linear force through origin calibration utilizing LECO 502-888 (Lot #0746-37) Titanium LRM @ 0.354 ± 0.008 % Oxygen and 502-879 (Lot #0572) Titanium LRM @ 0.014 ± 0.002 % Nitrogen.*

LECO Corporation | 3000 Lakeview Avenue | St. Joseph, MI 49085 | Phone: 800-292-6141 | 269-985-5496
info@leco.com • www.leco.com | ISO-9001:2015 Q-994 | *LECO is a registered trademark of LECO Corporation.*
LCRM = LECO Certified Reference Material, LRM = LECO Reference Material and are registered trademarks of LECO Corporation.

Form No. 203-821-550 8/20—REV2