LAB REPORT CS/ONH 28

G8 GALILEO

Determination of Hydrogen in Aluminum and Aluminum-alloys

Introduction

In aluminum processing, hydrogen has a strong influence on the quality and properties of the finished product. The high solubility of hydrogen gas in molten aluminum decreases up to two orders of magnitude during solidification of the melt. This can result in the accumulation of hydrogen in voids or along grain boundaries, but it can also lead to pore-formation, cracking or blistering and thus material failure.

Especially during further processing of high purity aluminum, i.e., rolling into thin sheets or foils, these hydrogen-filled pores inside the material can lead to degradation, resulting in uselessness of the finished product.

The obvious solution for this problem is to keep the level of hydrogen, and thus the number of pores, as low as possible. To ensure a low porosity and produce high quality material, the maximum amount of hydrogen in high purity aluminum is limited to around 0.2 to 0.3 ppm.

Aluminum alloys, such as those used for production of casting components, are even more sensitive to hydrogen. Typical alloying elements like i.e., silicon and copper, reduce the hydrogen solubility in molten and solid aluminum. To avoid hydrogen-related pores, 0.06 to 0.1 ppm of hydrogen are commonly set as upper limit in Al-Si cast alloys.

The G8 GALILEO ONH is a high-end analyzer designed for the rapid determination of oxygen, nitrogen, and hydrogen in solid materials. This analyzer is based on the inert gas fusion (IGF) principle, which involves fusion of the sample material in a graphite crucible at high temperatures. The special “H in Al” mode with automatic melting point detection via the built-in pyrometer enables the accurate and precise measurement of hydrogen traces in pure aluminum as well as aluminum alloys.

Measuring Principle

The working principle of the G8 GALILEO H analyzer for the determination of hydrogen in aluminum is the so-called carrier gas method with melt extraction and thermal conductivity detection.

The aluminum sample is heated until its melting point in a graphite crucible under a flowing inert gas stream. The freely programmable temperature of the electrode furnace is monitored and controlled by a contact free optical sensor. A special temperature/time program makes sure that evaporation of the low melting material is significantly reduced to minimize contamination of the furnace area and potential memory effects.

After outgassing of the crucible, the sample is automatically dropped into the pre-heated graphite crucible. The evolved measuring gas H_2 is swept by the carrier gas N_2 to the highly stable and sensitive thermal conductivity cell (TCD) with two measuring ranges. Removal of interfering gases, like CO, is performed by oxidizing CO to CO_2 with Schütze reagent and subsequent adsorption of CO_2 on a molecular sieve.

The shielded, open design rotating sample port of the G8 GALILEO can transfer even large samples into the crucible without jamming or usage of additional capsules and allows observation of the melting process during the analysis.

Sample Preparation

The required sample dimension for the analysis with automatic melting point detection is 16 x 9.5 mm. It is highly important to ensure that these dimensions are met.

Sample pieces from ingots and wrought products are sectioned using a water-cooled cut-off saw. Final preparation of the resulting square bars or sample rods, i.e., taken from the melt with a mold, is performed with a lathe. Lathe chuck and tool must be clean and free of lubricants or, when a micro-spray coolant system is used, the lubricant must be removed by thoroughly washing the sample with isopropanol. The sample piece is machined to a diameter of 9.5 mm. Nominal lathe speed is 1500 to 3000 rpm, advance at 0.03 to 0.04 mm/revolution. It is important that the entire surface layer is removed and that the surface is free of pores and as plane as possible.

From the prepared rods, sample pieces with a length of 16 mm are produced - preferably furnished with a bevel at one end to allow better sliding into the graphite crucible. The resulting sample weight is around 3 g.

The surface of the samples must be clean and free of grease. Thus, prepared samples can be stored in isopropanol but should be analyzed as soon as possible. Prior to the analysis the sample is washed in acetone and dried with a cold blow dryer.

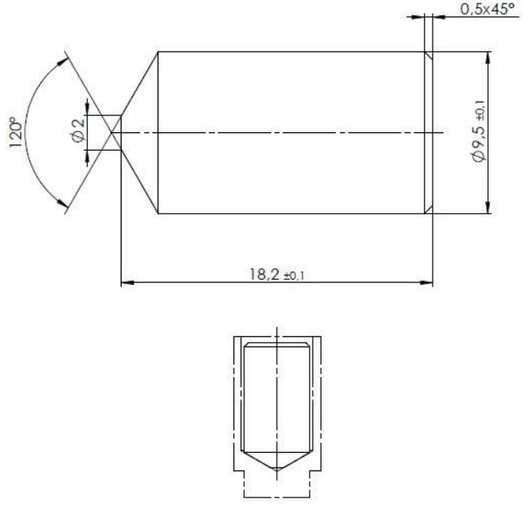

Figure 1
Dimensions and cross-section of the suggested sample size for the determination of hydrogen in high purity aluminum and Al-Si-alloys.

Consumables and Accessories

- Graphite crucible Al
- Crucible carrier Al
- Sample port Al
- Sample funnel Al
- Schütze reagent
- Molecular sieve
- Carrier gas: Nitrogen, 99.996%
- Calibration gas: Helium 99.999% or Hydrogen (preferably 5 % H_2 in Nitrogen)

Method Parameters

The general settings for Al analysis should be programmed via **Sample (Power control)**.

Analysis:

▪ Startdelay	15 s	0%
▪ Max. of startcomp.	20 s	
▪ Analysis time	35 s	29%*
▪ Endcompensation	90 s	0%
▪ Max. of endcomp.	15 s	
▪ Crucible cooling:	10 s	

Outgas:

▪ Purge before outgas	5 s	
▪ Outgas	80 s	45%
▪ Purge after outgas	20 s	

*The appropriate power level of each instrument may vary between 25-35% depending on the power supply and configuration.

In addition to the general analysis settings, the aluminum mode must be selected under Extras. The parameters for the Aluminum mode should be programmed as followed:

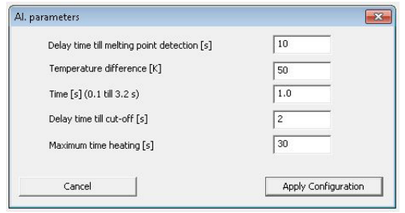

Figure 2
Aluminum mode parameters for high purity aluminum

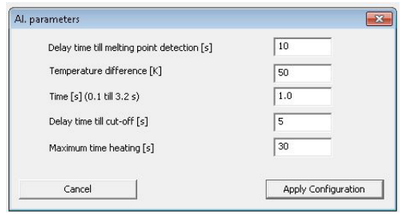

Figure 3
Aluminum mode parameters for Al-Si-alloys

Figure 4
Left: pure aluminum sample after analysis, right: Al-Si-alloy after analysis.

Principle of the Automatic Melting Point Detection

The G8 GALILEO is equipped with a contact-free optical measurement of the real crucible temperature. After degassing of the crucible and automatic drop of the sample into the pre-heated crucible, the pyrometer enables the detection of the point of fusion of the aluminum sample. The necessary melting energy is obtained from the hot graphite crucible. Thus, the temperature of the crucible decreases by some hundred degrees during melting of the aluminum sample.

As soon as this decrease is detected by the pyrometer, the power of the furnace is switched off and the sample continues melting smoothly without evaporation of the material. The analysis is continued without heating to allow continuous degassing of hydrogen from the sample.

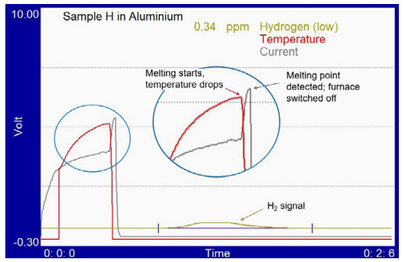

Figure 5
Aluminum mode parameters for high purity aluminum

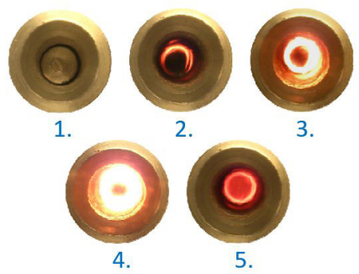

Figure 6

1. Loaded Al sample on the closed sample port. After degassing and cooling of the crucible the sample automatically drops into the crucible. The sample port remains open.
2. Heating starts
3. The crucible turns red hot and heats the Al sample by radiation
4. Sample starts melting. The fusion enthalpy leads to cooling of the crucible; the temperature decay is detected by the optical pyrometer
5. The furnace, and thus heating, is switched off, the analysis continues until all hydrogen is released.

Figure 7
The sample can be easily removed from the reusable crucible

Calibration

The system can be calibrated using either the optional built-in gas dosing unit with ten different volumes, or by using certified reference materials.

Due to the low concentrations of hydrogen in aluminum, it is recommended to use a mixture of 5% H_2 in pure nitrogen gas for calibration.

Example of a gas calibration signal

- 5 % H_2 in N_2
- Vol. 4 of the gas dosing unit = 0.2616 ml

⇒ 1.17 µg Hydrogen absolute

Alternatively, He can be used as calibration gas.

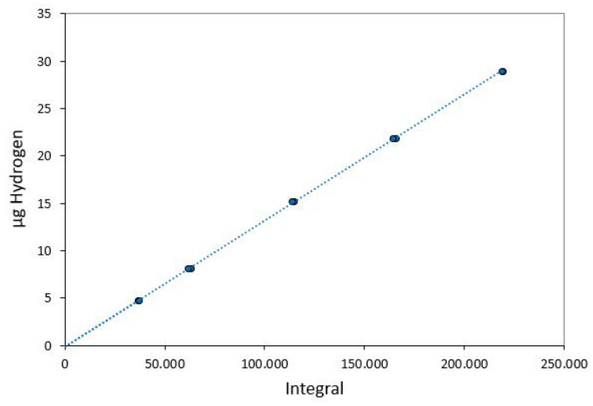

Figure 8
Plot of two cycles of five calibration volumes with He calibration gas measured with the gas calibration unit of the G8 GALILEO.

Procedure

I. Determination of the blank value

Before measuring the first sample, carry out 5-10 blank measurements using the same graphite crucible that you are planning to use for sample analyses. Place the graphite crucible onto the lower electrode, select 1 g as sample weight and "Blank" as sample code and analyze.

II. Sample measurement

1. Place the graphite crucible used for the blank measurements onto the lower electrode

2. Weigh the prepared sample, transfer the mass to the software and apply

3. Place the sample into the sample port and start the analysis

4. After the analysis has finished, remove the sample from the crucible and re-use the crucible to continue with further samples. Clean upper and lower electrode and replace the glass wool in the dust trap at regular intervals.

Typical Results

The following repetitive measurements of production samples demonstrate the reproducibility of the G8 GALILEO and the method outlined:

Sample 1	
Mass / g	Hydrogen / ppm
3.1484	0.3085
3.1483	0.3252
3.1497	0.3147
3.1473	0.3148
3.1478	0.3144
Mean1)	**0.3155**
STD1)	**0.0060**

1) Mean = arithmetic average; STD = absolute standard deviation (1σ)

Sample 2	
Mass / g	Hydrogen / ppm
3.1493	0.0572
3.1556	0.0538
3.1533	0.0621
3.1532	0.0547
3.1619	0.0563
Mean1)	**0.0568**
STD1)	**0.0032**

1) Mean = arithmetic average; STD = absolute standard deviation (1σ)

Sample 3	
Mass / g	Hydrogen / ppm
3.1556	0.1628
3.1511	0.1646
3.1526	0.1585
3.1503	0.1648
3.1532	0.1650
Mean1)	**0.1632**
STD1)	**0.0027**

1) Mean = arithmetic average; STD = absolute standard deviation (1σ)

Sample 4	
Mass / g	Hydrogen / ppm
3.1538	0.2627
3.1506	0.2724
3.1487	0.2524
3.1504	0.2619
3.1499	0.2714
Mean1)	**0.2642**
STD1)	**0.0082**

1) Mean = arithmetic average; STD = absolute standard deviation (1σ)

Summary

The additional aluminum package, ease of use, fast and easy maintenance as well as the high precision make the G8 GALILEO the ideal instrument for quality and process control in the aluminum industry.

The G8 GALILEO further provides the possibility to measure oxygen, nitrogen and hydrogen by inert gas fusion and allows a variety of modular system modifications, also making automation, diffusible hydrogen, and argon analysis possible. For further information, please refer to our brochure or contact us directly.

Acknolwedgements

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