EURO PM2019 CONGRESS & EXHIBITION

# Relevance of Oxygen and Hydrogen Determination in Additive Manufacturing and Powder Recycling

Session 46, Powders for AM-Recycling

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# Bruker Solutions for AM/PM Elemental and Structural Analysis

**X-Ray Fluorescence (WD-XRF)**
Elemental composition & mapping

**S8 TIGER**

**Inert Gas Fusion – Mass Spectrometry (IGF-MS)**
O, N, H & Ar detection

**G6 LEONARDO**
**G8 GALILEO**

**Combustion Analysis**
C and S analysis in solids

**G4 ICARUS**

**Electron Microscope Analyzers**
Highest resolution Imaging
Topographical & material analysis

**EM ANALYZERS**

**Micro Computed Tomography**
Metrology
Non-destructive inspection
CAD comparison

**SKYSCAN 1272**

**X-Ray Diffraction (XRD)**
Phase composition
Texture
Residual stress

**D8 DISCOVER**

**Mechanical/Tribology Test**
Wear rates & resistance
Friction
Load
Hardness

**UMT TRIBOLAB**

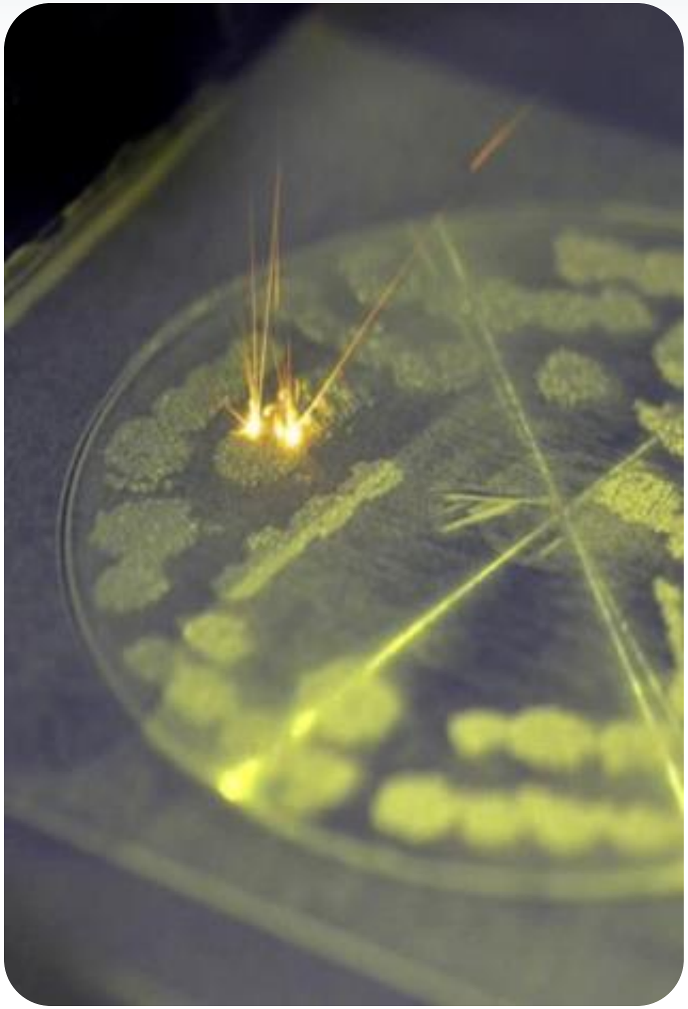
**Nano Indentation (NI)**
Mechanical homogeneity
Fracture
Surface energy
Agglomeration

**TI 980 TRIBOINDENTER**

**3D Optical Microscopy**
Roughness
Metrology
Surface geometry & shape

**NPFLEX**

# Relevance of Oxygen & Hydrogen Introduction



- Chemical reactions on the metal particle surface play an important role during:
  - Powder Production
  - Storage
  - Conditioning for AM
  - Handling in the machine
  - Post Processing / Heat Treatment
  - Powder Recycling

⇒ **Powder Aging** (degradation, oxidation, uptake, corrosion, …)

# Relevance of Oxygen & Hydrogen Effects of “gases in metals”

Laser Beam Melting is related to welding – layer by layer - and shares the same challenges

**Oxygen**

- unwanted, parasite element
- steel: causing ageing brittleness
- Titanium: degrades mech. properties (e.g. ductility)
- bulk (inclusions) vs. surface (oxidation)
- reactive metals like Ti, Mg, Al have high oxygen affinity

**Hydrogen**

- highly unwanted element
- causes harmful, complex embrittlement damages
- can be supplied during: welding, etching, annealing, corrosion for moisture

# Relevance of Oxygen & Hydrogen Factors for Degradation

- Powder degradation will be faster:
  - the smaller the particles are (high specific surface)
  - the higher moisture / oxygen levels are
  - the higher the temperature is
  - the longer the exposition time is

Correlation between particle size and O, H content on AlSi10Mg:

| Particle Size / µm | Oxygen / ppm | Hydrogen / ppm |
|---|---|---|
| 10 - 53 ↓ | 1640 ↑ | 68.2 ↑ |
| 20 - 63 | 998 | 53.7 |
| 40 - 100 | 772 | 38.1 |

# Relevance of Oxygen & Hydrogen
# Surface reaction with moisture

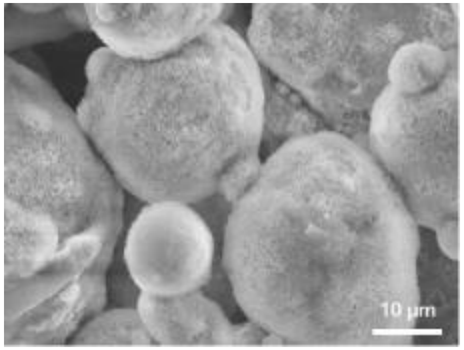
- AlSi10Mg reacts with ambient moisture
- Hydroxide layers are formed on the surface:

$$2\,Al + 3\,H_2O \longrightarrow \underset{\textit{alumina}}{Al_2O_3} + 3\,H_2$$

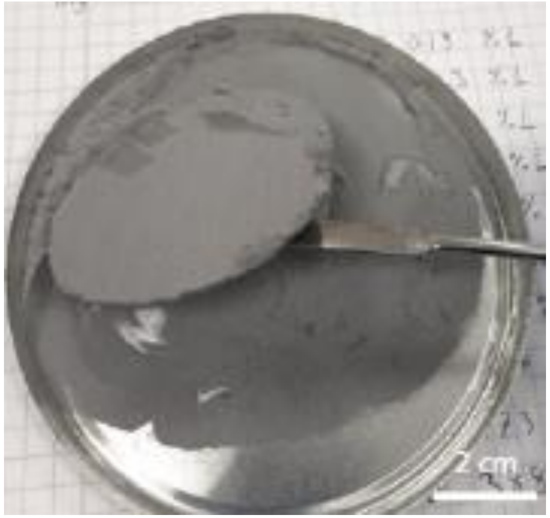
$$2\,Al + 4\,H_2O \longrightarrow \underset{\textit{boehmite}}{AlO(OH)} + 3\,H_2$$

$$2\,Al + 6\,H_2O \longrightarrow \underset{\textit{bayerite}}{2\,Al(OH)_3} + 3\,H_2$$

Hydroxide layer formation
on AlSi10Mg (verified by FTIR)



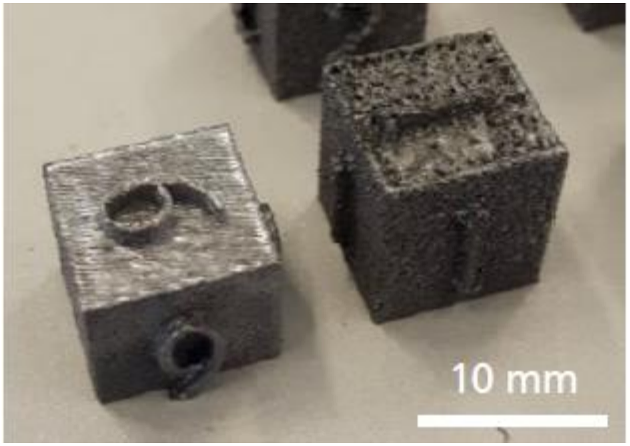
"Caking" on AlSi10Mg powder due to crystal connection of neighboring particles



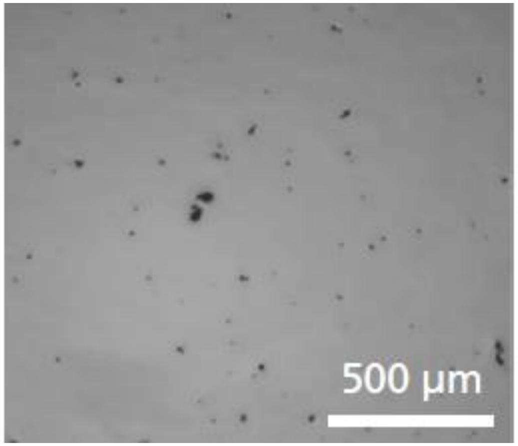
# Relevance of Oxygen & Hydrogen Effect on LBM Process and Quality

- New powder (A)
- Powder (B) aged: storage at high humidity and elevated temperatures
- Note: Powder (B) still shows unchanged fluidity

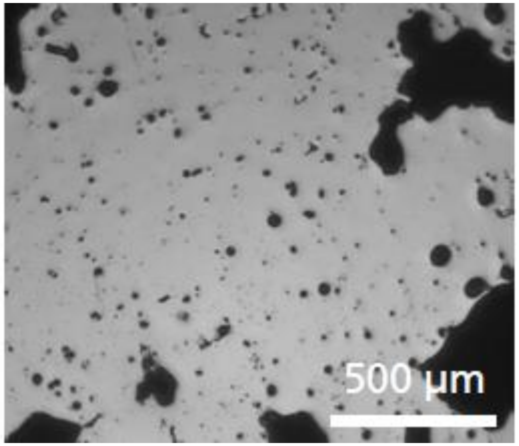
Sample specimen:
A (left), B (right)



**A**: Density 99.5%



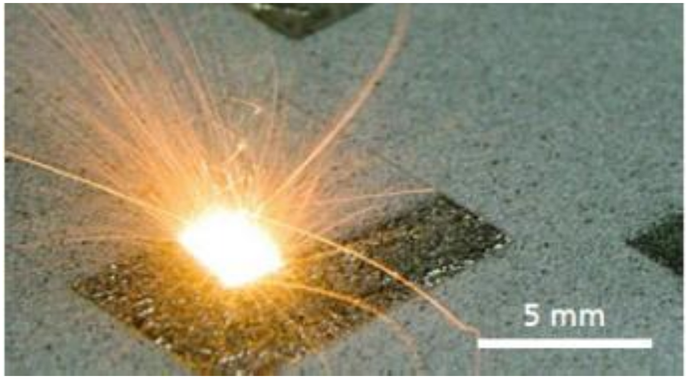
**B**: Density 96.5%

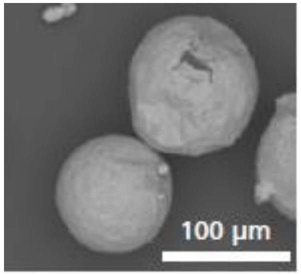


# Relevance of Oxygen & Hydrogen Example: Spatter Formation

## Origin

- 7.5 mg spatter material per g material fused
- Spatter end-up in powder bed

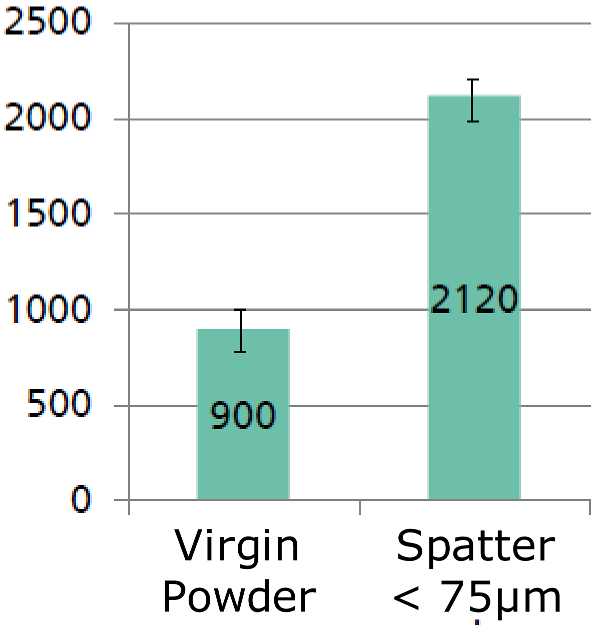




Spherical spatter, solidified in flight

## Oxygen Content [ppm]

IGF, *n*=5



## Oxide Layer Thickness

(XPS-measurement as $Al_2O_3$)
Virgin powder: 27 nm
Spatter: 35 nm

# Relevance of Oxygen & Hydrogen
# How to determine O, N, H (and Ar)?

Graphite crucible on lower electrode

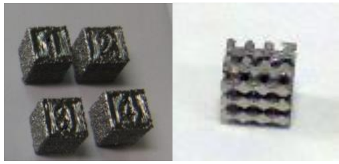
- Techniques like WD-XRF and OES cannot determine O, H, N or Ar
- Inert gas fusion (**IGF**) was applied in this study
  - A sample of any shape (powder, pieces, drillings, etc.) is weighed
  - The sample is fused inside a graphite crucible (up to 3000 dC) in a flow of high purity inert gas

$$\mathbf{M}_n\{\mathbf{O}_x,\mathbf{N}_y,\mathbf{H}_z\}_m \xrightarrow[\text{inert gas atm.}]{T \gg \text{m.p.}} n\,\mathbf{M} + m\{x/2\,\mathbf{O_2} + y/2\,\mathbf{N_2} + z/2\,\mathbf{H_2}\}$$

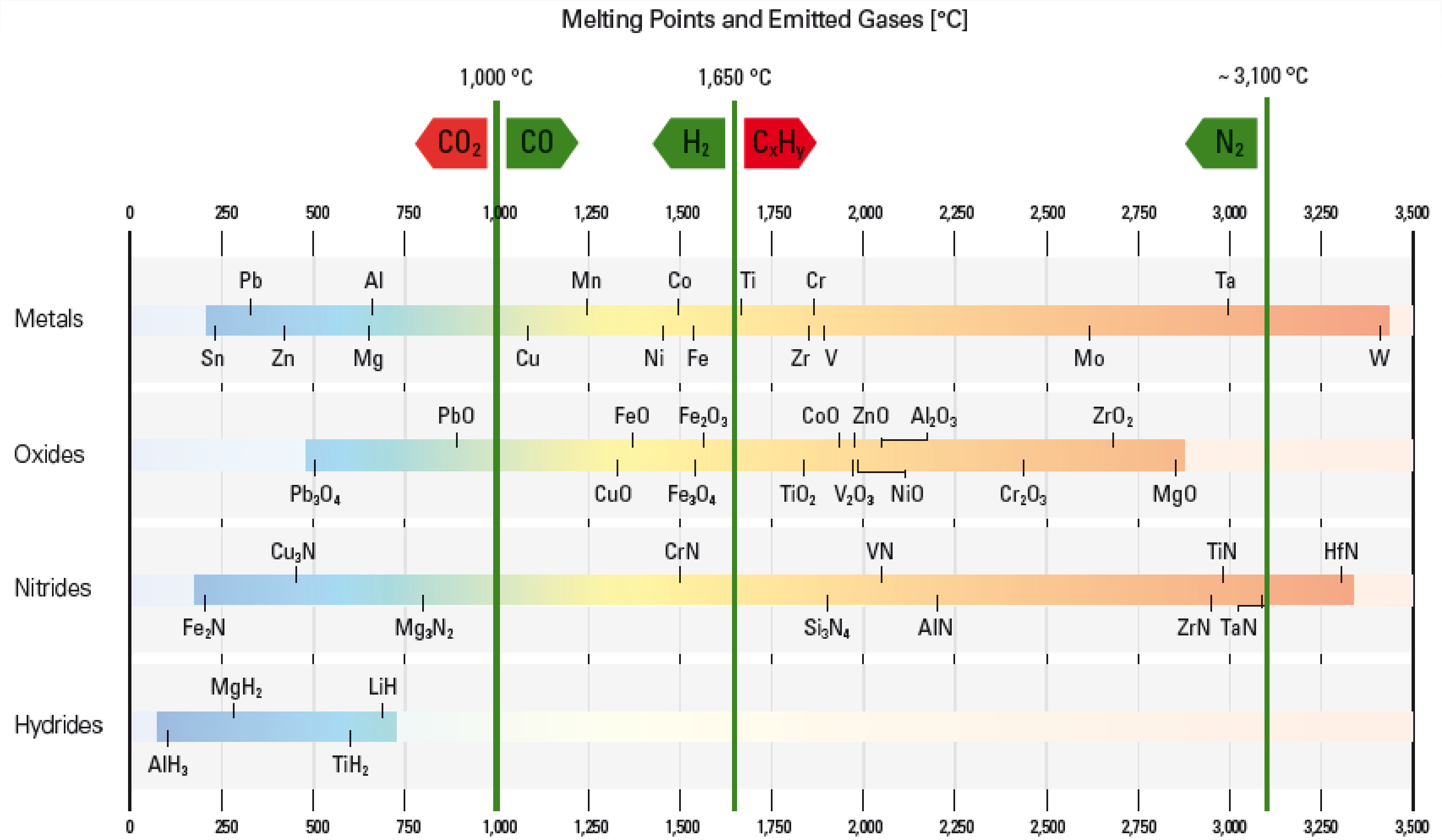
$$\mathbf{O_2} + \{\mathbf{C}\} \xrightarrow[\text{inert gas atm.}]{T > 1800\ °\text{C}} 2\,\mathbf{CO}\ \ (+\ \mathbf{CO_2})$$

$$\mathbf{CO_2} + \{\mathbf{C}\} \overset{T > 1000\ °\text{C}}{\rightleftharpoons} 2\,\mathbf{CO} \qquad (\textit{Boudouard}\ \text{Equilibrium})$$

Ti6Al4V test specimen produced by LBM



# Relevance of Oxygen & Hydrogen IGF: Temperature matters



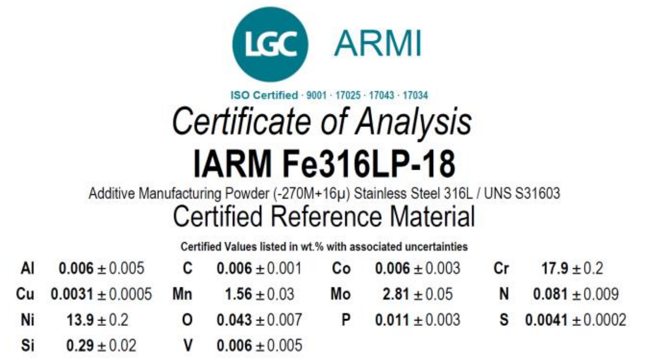
Melting Points and Emitted Gases [°C]

# Relevance of Oxygen & Hydrogen Characteristics of IGF

**Inert gas fusion is:**

- a volumetric method (entire specimen is analyzed)
- a relative method that requires calibration (CRM or gas dosing) ⇒ result traceability
- not limited in concentration ranges: high-ppb to 100%
- Fast (30s pre-cleaning of crucible, 60-90s measuring time)
- applicable to all inorganic solids (must be dry!)
- flexible by coupling a MS: Ar determination or isotopic tracers
- able to deliver kinetic information by applying heating rates (e.g. separation of oxides)

# Relevance of Oxygen & Hydrogen CRMs for AM



LGC ARMI

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*Certificate of Analysis*

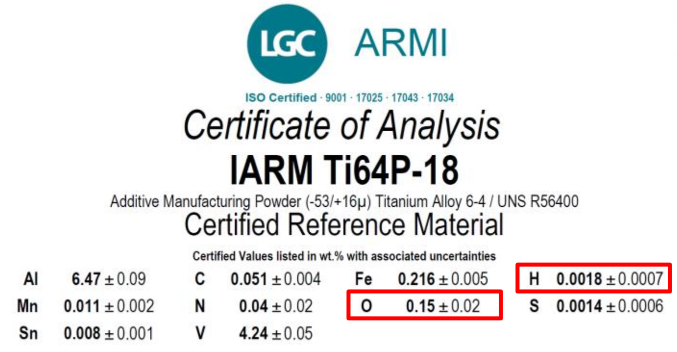
**IARM Fe316LP-18**

Additive Manufacturing Powder (-270M+16µ) Stainless Steel 316L / UNS S31603

Certified Reference Material

**Certified Values listed in wt.% with associated uncertainties**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Al** | **0.006** ± 0.005 | **C** | **0.006** ± 0.001 | **Co** | **0.006** ± 0.003 | **Cr** | **17.9** ± 0.2 |
| **Cu** | **0.0031** ± 0.0005 | **Mn** | **1.56** ± 0.03 | **Mo** | **2.81** ± 0.05 | **N** | **0.081** ± 0.009 |
| **Ni** | **13.9** ± 0.2 | **O** | **0.043** ± 0.007 | **P** | **0.011** ± 0.003 | **S** | **0.0041** ± 0.0002 |
| **Si** | **0.29** ± 0.02 | **V** | **0.006** ± 0.005 | | | | |



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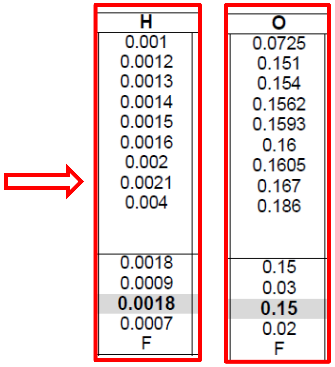
**IARM Ti64P-18**

Additive Manufacturing Powder (-53/+16µ) Titanium Alloy 6-4 / UNS R56400

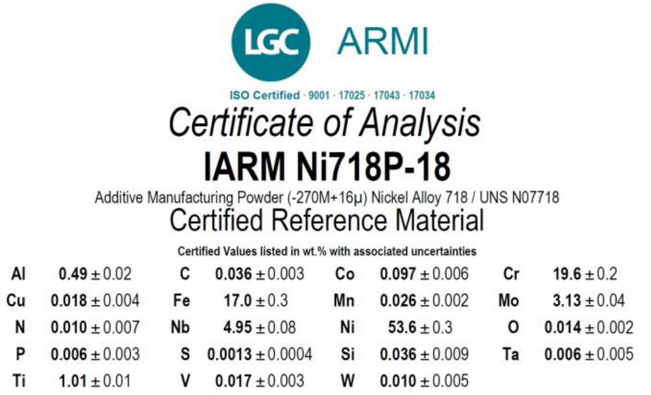
Certified Reference Material

**Certified Values listed in wt.% with associated uncertainties**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Al** | **6.47** ± 0.09 | **C** | **0.051** ± 0.004 | **Fe** | **0.216** ± 0.005 | **H** | **0.0018** ± 0.0007 |
| **Mn** | **0.011** ± 0.002 | **N** | **0.04** ± 0.02 | **O** | **0.15** ± 0.02 | **S** | **0.0014** ± 0.0006 |
| **Sn** | **0.008** ± 0.001 | **V** | **4.24** ± 0.05 | | | | |



| H | O |
|---|---|
| 0.001 | 0.0725 |
| 0.0012 | 0.151 |
| 0.0013 | 0.154 |
| 0.0014 | 0.1562 |
| 0.0015 | 0.1593 |
| 0.0016 | 0.16 |
| 0.002 | 0.1605 |
| 0.0021 | 0.167 |
| 0.004 | 0.186 |
| 0.0018 | 0.15 |
| 0.0009 | 0.03 |
| **0.0018** | **0.15** |
| 0.0007 | 0.02 |
| F | F |



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*Certificate of Analysis*

**IARM Ni718P-18**

Additive Manufacturing Powder (-270M+16µ) Nickel Alloy 718 / UNS N07718

Certified Reference Material

**Certified Values listed in wt.% with associated uncertainties**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Al** | **0.49** ± 0.02 | **C** | **0.036** ± 0.003 | **Co** | **0.097** ± 0.006 | **Cr** | **19.6** ± 0.2 |
| **Cu** | **0.018** ± 0.004 | **Fe** | **17.0** ± 0.3 | **Mn** | **0.026** ± 0.002 | **Mo** | **3.13** ± 0.04 |
| **N** | **0.010** ± 0.007 | **Nb** | **4.95** ± 0.08 | **Ni** | **53.6** ± 0.3 | **O** | **0.014** ± 0.002 |
| **P** | **0.006** ± 0.003 | **S** | **0.0013** ± 0.0004 | **Si** | **0.036** ± 0.009 | **Ta** | **0.006** ± 0.005 |
| **Ti** | **1.01** ± 0.01 | **V** | **0.017** ± 0.003 | **W** | **0.010** ± 0.005 | | |

Jernkontoret swerea | KIMAB

**Certified Reference Material**

**Jernkontoret**

**JK 47A**

**Iron powder**

Materials supplier: Höganäs Sweden AB

**CERTIFIED VALUES - Mass content in %**

| | O | N | C |
|---|---|---|---|
| $M_M$ | **0.69** | **0.0062** | **0.370** |
| C(95%) | 0.02 | 0.0002 | 0.003 |

# Relevance of Oxygen & Hydrogen Ar? ⇒ Process Gases Inclusions

- During the gas atomization, liquid metal is hit/"nebulized" by a jet of a process gas (argon or nitrogen)
- Impurities in the gas like moisture, oxygen, etc. can react
- Additionally, traces of the process gas remain in the particles:
  - Ti, Al, Mg and other reactive alloys react with nitrogen ⇒ argon is used as atomizing gas
  - **Ar** does not react but stays in the powder in form of **entrapped closed porosity**
  - Pores filled with Ar cause similar embrittlement like hydrogen but starting at much smaller levels: <100 pp**b** [1, 3]
  - Micro CT (µCT) can't tell whether pore is filled with Ar
  - Post-processing cannot remove a pore filled with gas [4]
- IGF coupled to a mass spectrometer allows ppb detection limits of argon

# Relevance of Oxygen & Hydrogen Motivation

From the AM user perspective the powder metal market is complex and non-transparent:

- Manufacturers of AM machines offer their own powder
- Premium powder manufacturers
- Smaller primary metal manufacturers starting own powder productions

Concerning the chemical composition

- Alloying elements and material grade is given and specified (and often verified multiple times – although that is invariant during the process)
- Very seldom light elements like C, S and O, H are listed
- Hydrogen and Argon are ignored (except: NADCAP)
- No quality threshold values are defined

**A lack of knowledge currently prevails regarding initial O,N,H contents of commercially available powders for powder bed fusion processes**

# Relevance of Oxygen & Hydrogen AlSi10Mg – Series I

- Five **different lots** of AlSi10Mg - from 2 years
- Same supplier/manufacturer of LBM-machine
- Identical specification (but no O,N,H given in certificate)
- Fresh powder
- *n*=5, one STD in brackets as measure for homogeneity

| Lot (year) | Oxygen / ppm | Nitrogen / ppm | Hydrogen / ppm |
|---|---|---|---|
| A (2016) | 1323 (187) | 55 (6) | 56 (4) |
| B (2016) | 1730 (45) | 42 (14) | 57 (3) |
| C (2017) | 1074 (71) | 66 (24) | 56 (6) |
| D (2017) | 1378 (100) | 55 (9) | 64 (3) |
| E (2017) | 937 (18) | 48 (14) | 46 (3) |

# Relevance of Oxygen & Hydrogen AlSi10Mg – Series II

- Identical specification - but no O,N,H given
- Five **different suppliers**, same year
- Fresh powder
- *n*=5, one STD in brackets as measure for homogeneity

| Supplier | Oxygen / ppm | Nitrogen / ppm | Hydrogen / ppm | Comment |
|---|---|---|---|---|
| 1 | 1378 (100) | 55 (9) | 64 (3) | |
| 2 | 1106 (79) | 25 (9) | 69 (4) | |
| 3 | 2594 (119) | 41 (9) | 94 (6) | obtrusive in AM |
| 4 | 1004 (135) | 28 (9) | 47 (2) | |
| 5 | 1328 (43) | 17 (6) | 62 (5) | |

Best quality AlSi10Mg ⇒ O: ≤1000 ppm, H: ~50 ppm

# Relevance of Oxygen & Hydrogen Series III – Other Metals

- *n*=5, one STD in brackets as measure for homogeneity

| Material | Description | O / ppm | N / ppm | H / ppm | Questions… |
|---|---|---|---|---|---|
| Steel 1.7131 16MnCr5 | low alloyed steel | 1474 (133) | 92 (3) | 12 (1) | |
| SS316L | 316L low carbon stainless steel | 476 (46) | **112** (5) | 10 (1) | Ar atomized? |
| SS316L | 316L low carbon stainless steel | 543 (43) | **675** (6) | 11 (1) | $N_2$ atomized? |
| 1.2709 | Tool steel, highly alloyed | 504 (16) | 83 (2) | 14 (3) | |
| Inconel 718 | | 358 (29) | 330 (6) | 59 (4) | ??? |
| Inconel 718 | | 175 (11) | 191 (3) | 4.7 (0.2) | |
| Ni-Base Pwd. | comparable to Inconel | 267 (19) | 78 (3) | 14 (1) | |
| 18Ni300 | Steel with high Ni | 403 (23) | 212 (1) | 18 (3) | |
| CuCr1Zr | 90%Cu, "Zr aged" | 2072 (123) | 24 (3) | 13 (1) | green Laser req. |

# Relevance of Oxygen & Hydrogen Series IV: Ti-6Al-4V

Typical values for Ti6Al4V analyzed so far (fresh powder)

- **O**: 950 – 1250 ppm (but up to 3600 ppm in specimen)
  ASTM limit grade 1: <1800 ppm
- **N**: 150 – 350 ppm
- **H**: 13 – 220 ppm
- **Ar**: 0.3 – 1.3 ppm (limit in HIP-AM: 0.1 ppm)

# Relevance of Oxygen & Hydrogen Conclusions

- Oxygen and Hydrogen are the most critical elements for quality and costs (e.g. recycling)
- To optimize the process and find the best compromise, Process- and Quality-Control of these elements is indicated
- Metal powder produced by gas atomization infiltrates process gases. Wish: The contaminants shall be specified and also tested in the final product (until experience values for AM are set)
- A high level of care concerning the used process gases and especially their impurities, like **moisture**, is required to run a robust AM process with highest quality
- Inert gas fusion is a fast, effective and readily available analytical method for process and quality control in powder metallurgical processes

# Relevance of Oxygen & Hydrogen

## Thank you for your attention!

**References**

[1] B. Hofer, F. Bigolin, M. Hamentgen, H. Stremming, C. Zühlke, "Measuring the gas content in HIP components and impurities in the argon- and chemical reacted gas used to compacting near net shape parts and castings. Presentation of the measurement technique", Session 215, HIP 2014 conference (Stockholm, Sweden)

[2] P. J. Mohr, B. N. Taylor, D. B. Newell; "CODATA recommended values of the fundamental physical constants - 2010"; National Institute of Standards and Technology, USA, http://physics.nist.gov/constants

[3] P. Mellin, M. Östlund, W. Fredriksson, C. Pellegrini, H. Blom, O. Björnberg, A. Strondl; „Detecting Argon Trapped In Reference Samples Made By Hot Isostatic Pressing", WorldPM 2016 (Hamburg, Germany), WP1603294934

[4] C. Schaak,W. Tillmann, M. Schaper, M. E. Aydinöz; "Process Gas Infiltration in Inconel 718 Samples during SLM Processing", RTeJournal - Fachforum für Rapid Technologie, Vol. 2016 (2016), Germany