

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

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Abstract Text: The measurement of argon gas in near net shape products and reaction gases in HIP components as a criterion of the enabling can be done with the most varied instruments. The combination of devices for the measuring the gas in the component, as in the HIP densification gas, which is used in high-quality castings is cost effective. Beginning of the powder production through atomization over bottling the powder in a capsule for the HIP-process, it may lead to reactions with the ambient gases (O₂, N₂, C_nH_m, H₂O). The problems during the hot or cold vacuum process will be described. The mechanical properties which are depending of different qualities of vacuum in the closed capsule filled with duplex steel were determined and compared with the gas content.

With high-performance scientific instruments and solutions for analytical and medical applications covering Mass Spectrometry (MS) and hot extraction application with the optional infrared furnace is the determination of diffusible hydrogen in welds and steel materials, especially in high strength steel possible. The high-end analyzer is designed for the automatic and precise determination of oxygen, nitrogen and hydrogen in solid materials.

Keywords: Argon, capsule, gas, vacuum, measuring Argon, hot extraction method, quadrupole mass spectrometer, oxygen, nitrogen and hydrogen concentration

Introduction

Highly-strained castings [1] for the plane-, medical- and gasturbine- industry require a homogeneous and flawless structure without any micropores. The surface must not feature any nitride- and oxide layers or other impurities. It is important to prevent any diffusion of reaction gases with the casting during the heat treatment process. For this reason all the gases used in the heat treatment process must contain a limited and clearly defined degree of impurities. In the heat treatment which is used to eliminate the pores, the carrier gas Argon must comply with these conditions. It is absolutely necessary to prevent any absorption of reaction gases during the process of atomization up to the densification in the HIP furnace.

Content

Reasons for impurities in the carrier gas

The degree of purity of Argon which is used to densify castings and powder metallurgical components is 99,999 %. This is necessary to prevent the HIP-Furnace from reactions with trace elements and consequently from premature wear. On the other hand the gas must not react with the casting. Nevertheless the impurities below (Table 1) are acceptable. However it may happen that the components to be treated, the castings or capsules filled with powder may have impure surfaces, which could lead to the contamination of the carrier gas. To prevent this, the components should be carefully cleaned and if necessary sandblasted before the HIP-procedure. The check of the gas purity is an indicator of the degree of the impurity and the further usability of the Argon gas. If the limiting value is exceeded, the gas should be released into the atmosphere.

Impurity	Maximum volume (%)	ppm (Vol)
Nitrogen	0.005	50
Hydrogen	0.0125	125
Oxygen	0.0025	25
Hydrocarbons (methane)	0.0025	25

Table 1: Impurity

Reasons for gas inclusions in HIP-components

To produce HIP-components it is necessary to have a capsule to transmit the pressure of the Argon gas. The capsule is usually made of low alloyed metal sheet. All the contact points must be welded gastight to prevent

any penetration of the Argon gas into the capsule during the HIP-process. To be on the safe side the capsules undergo a helium leakage test [2] before and after the powder is filled in. Nevertheless it may happen that the capsule becomes leaky and Argon gas gets in surrounding the powder grains (figure 1 + 2) thus preventing a complete diffusion of the chemical elements. If due to the effect of the heat and the lateral deformation pressure the penetration orifice is closed during the HIP-procedure, the capsule might swell and even burst when the external pressure is relieved during the cooling process. A short calculation (Table 2) according to the formula shows, without taking into account the adiabatic change of condition, the possible increase of the internal pressure in the capsule with the same penetration volume but a different penetration pressure. In the case of example A (table 2) a penetration pressure of 0.5 bar and a volume of 0,001 cm³ or 1 mm³ a final pressure of 5 bar with a volume of 0.1 mm³ is achieved. If with the change of condition the reduction of the volume is taken into account as well, the pressure is even higher. The exact calculation of the change of condition would take us too far in this paper. If 1 bar Argon gas penetrates (Example B: table 2) into the capsule the internal final pressure rises to 10 bar. Such incidents may damage the expensive HIP-furnace. To reduce the danger of injury for the stuff resulting from a swollen but not yet burst capsule it is advisable to perforate it slightly while using the appropriate measures of protection.

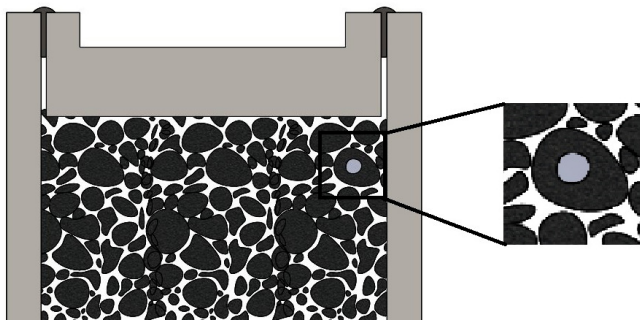


Figure 1: Argon assignment on the powder grain boundaries in the capsule

Figure 2: Argon in the powder grain

Technical errors may happen when atomizing the powder with Argon. Due to the surface tension, balls containing Argon might arise when atomizing the melt (Figure 2). Due to the Van-der-Waals [6] forces Argon becomes attached to the powder. Argon is used with alloys when the nitrogen atomization presents a high risk of the formation of nitride.

Assumption: initial volume V1 remains constant but the invading initial pressure increases							
		example	A	B	C	D	
V ₁	Initial volume of gas in the capsule at (assumption)	cm ³	0.001	0.001	0.001	0.001	
		°C	800	800	800	800	
p ₁	Initial pressure at 800 ° C	bar	0.5	1	2	4	
V ₂	Final volume at 20 ° after cooling (assumption)	cm ³	0.0001	0.0001	0.0001	0.0001	
		mm ³	0.1	0.1	0.1	0.1	
p ₂	Final pressure at 20 ° C	bar	= ?				
p ₂	=	$\frac{V_1 \cdot p_1}{V_2}$	bar	5	10	20	40
		$\frac{V_1 \cdot p_1}{V_2}$					

Table 2: Calculating the final pressure of argon in the capsule at 20 ° C.

Further errors are possible when evacuating the capsule. The capsule which is connected with an evacuation station in order to remove the air contained in it. With a bulk density of 72 % there remains a residual volume of air of 28 % consisting mainly of a small percentage of Argon and undesired nitrogen and oxygen (Table 3).

Gas	Formula	percent by volume	percent by weight
Nitrogen	N ₂	78.09	75.51
Oxygen	O ₂	20.95	23.15
Argon	Ar	0.93	1.28

Table 3: Main constituents air

Table 4 shows the calculation of the percentage of Argon in an open capsule \varnothing 6.2 x 68 cm. After filling the powder the bulk density is 70 %, the remaining 30 % are filled with air before the evacuation with an Argon volume percentage of 0.93 %. This volume is recalculated in weight percentages and finally related to the weight of the powder, the ratio being 3032 ng/g of Argon in the case of a non-evacuated capsule. If after the HIP-procedure the value is beyond this figure, it is obvious that Argon has penetrated into the capsule. The Argon content before the evacuation depends on the bulk density of the powder which is illustrated in diagram 1. The powder used was X2CrNiMoN22-5-3 (1.4462).

Calculation of argon content in the capsule		
description	unit	value
bulk density	%	68%
Density 1.4462	g/cm ³	7.8
\varnothing inside	cm	6.2
internal length	cm	68
volume capsule	cm ³	2053.0
Weight 1.4462 powder in the capsule	g	10888.9
argon content	%	0.93%
Density Argon	g/cm ³	0.001780
Volume of argon in the capsule	cm ³	19.1
Weight argon in the capsule	g	0.03398483
Weight argon in the capsule	ng	33984832
Proportion relative to the total weight		
Argon ratio weight / net weight (ng/g)	ng/g	3121

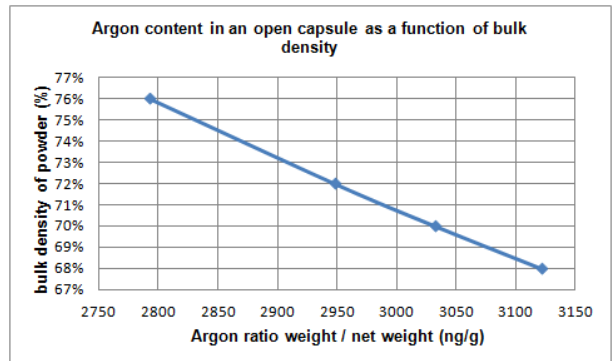


Table 4: Calculation argon content in a capsule before powder X2CrNiMoN22-5-3 (1.4462)

Diagram 1: Argon content in a open capsule as a function of the bulk density

Evacuating a capsule

The high percentage of air in the capsule must now be evacuated (Picture 3).

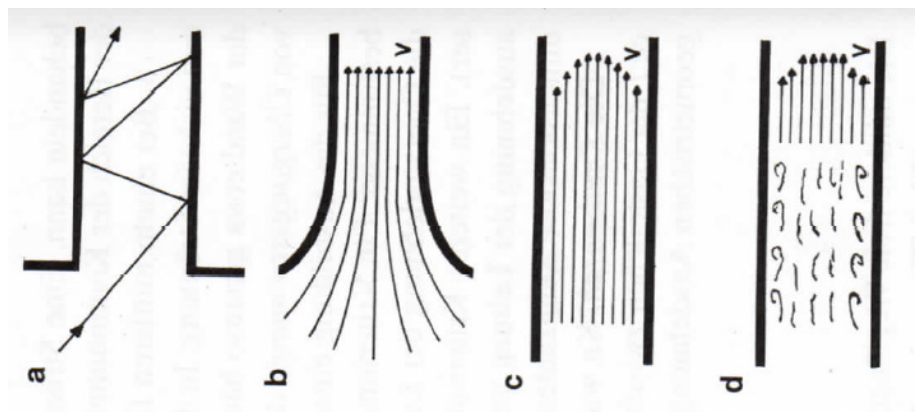
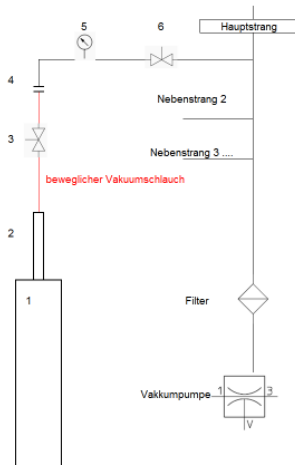


Figure 3: Evacuation station Figure 4: different types of gas flows [3, page 86]:

a) Molecular flow, viscous flows, **b)** Gas dynamic (in-coming flow), **c)** Laminar, **d)** Turbulent

The powder distribution and the grain size, the diameter of the evacuation pipe, the shape of the capsule and, of course, the power of the evacuation pump determine the duration of the evacuation procedure to achieve the desired pressure in the capsule. To determine the influence of the different flows capsules of the same dimension where evacuated for different timelengths and after closing the valve 6 (Picture 3 evacuation station) the pressure was measured after 10, 60 and 1800 seconds. (Diagram 2).

To prevent the powder from being sucked out and to optimize the following locking, the diameter of the evacuation valve is kept small. The smaller the diameter is, the longer the evacuation takes to reduce the air content to the desired minimum. The target pressure is < 4 mbar. This is roughly the mean value of 1 mbar to 10 mbar (or 10^2 Pa ... 10^3) which is used in the laboratories and procedures in the chemical industry [3]. For comparison, the indication of the pressures used in the vacuum used in the metallurgy 0.00001 mbar...10 mbar (or 10^{-3} Pa... 10^3 Pa).The HIP-Technology is not in the top range and even better results can be expected for special applications in the future!

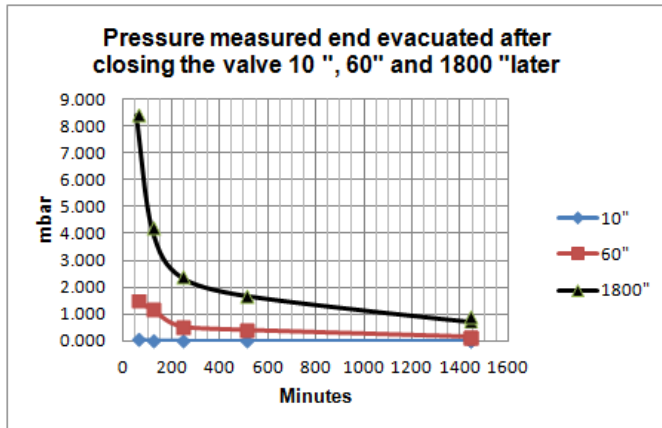


Diagram 2: Pressure measured end evacuated after closing the valve 10'', 60'' and 1800'' later

One should also consider the different types of flows (Picture 4: different types of gas flows) even in the case of low pressure. Powders in a capsule of a grain size of 10 – 500 μ produce different hollows and act as an obstacle. This slows down the process of evacuation and there are different gas pressures in the capsule. There is a clear pressure rise in the capsule after closing the valve at different evacuation times. It is not possible to achieve a complete pressure compensation in the capsule after an evacuation time of 8 hours after 30 minutes. Only after more than 8 hours of evacuation time there is a complete pressure compensation.

Argon gas content in a HIP-component

It is not possible to determine optically a small percentage of the penetrated Argon gas or the residual Argon gas due to a careless evacuation procedure. Only an expert analyzing a microsection can determine whether the sample is tight or leaky. The complete vacuum is based on the assumption that the hollows between the powder grains are void of air and that there is a physical nil. This is not possible with evacuated capsules.

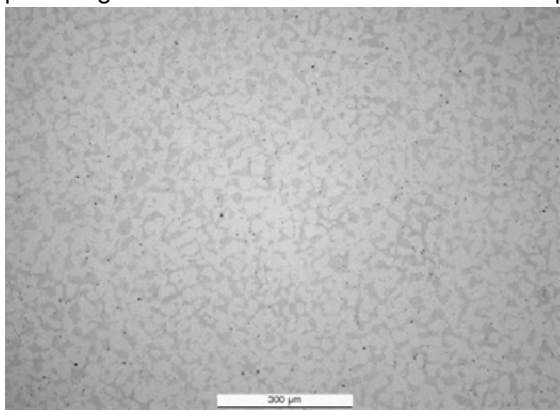


Figure 5: sample 1 without heat treatment. Argon content 40 ng/g

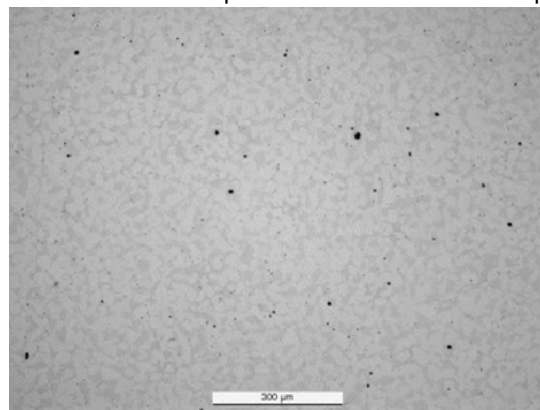


Figure 6: sample 1 without heat treatment. Argon content 16177 ng/g

There is always a residue of Argon in the capsule. Based on a simplified formula $p_1 \cdot V_1 = \text{constant}$ the theoretical Argon content at different low pressures was calculated. The capsules with different pressures were closed gastight and the hot isostatic pressed. The values of the Argon content were measured by

means of the carrier gas – hot extraction analysis at the top and at the bottom of the capsules (Table 6). The values calculated according to the Table 5 coincide up to 3 mbar with the measured values, because in the case of a pressure of 0,74 mbar a value <10 ng/g Argon cannot be measured anymore. It is interesting to notice the Argon values at a pressure of > 2,3 mbar. At the top there is a higher quantity of Argon than at the bottom and with a higher pressure the Argon content increases as well, but the theoretically calculated Argon content was not achieved. The argon content in the body is much higher than calculated. This goes back to the fact that because of the Van – der- Waals forces no pressure compensation had taken place in the capsule and the argon gas could move upwards because of the short evacuation time. The real low pressure in the capsule must have been higher than the one measured at the evacuation nozzle. Diagram 2 shows this quite clearly. The pressure rise after 40 minutes was highest in the short time evacuated capsules and would probably have risen in the case of a longer retention time. In theory the non evacuated capsule pressure = 1000mbar should feature a higher argon value. This is not the case and has to clear with further experiments.

Evacuated theoretical calculation of the argon content							
V ₁	in the capsule		cm ³	3121.0	3121.04	3121.04	3121.04
V ₂	Final volume at ? Mbar		cm ³	= ?			
p ₁	Anfangsdruck		bar	1	1	1	1
p ₂	Endruck		mbar	0.74	3	4.2	8.4
p ₂	Endruck		bar	0.00074	0.003	0.0042	0.0084
V ₂	=	$\frac{V_1 \cdot p_1}{p_2}$	cm ³	4217623	1040347	743105	371552
his volume has to the initial volume after expansion:			bar	0.00074	0.003	0.0042	0.0084
This number is divided by the initial volume at 1 bar. This gives the factor for the total gas volume in the xy bar in the vacuum							
V factor	=			1351	333	238	119
With this factor the existing ng / g are shared. This gives the			ng/g	2.3	9.4	13.1	26.2

Table 5: Evacuated theoretical calculation of the argon content

pressure	mean value: [ng/g]		mean value: [%]			
	Argon measurement		Nitrogen measurement		Oxygen measurement	
	top	bottom	top	bottom	top	bottom
1000	511	1559	0.211	0.187	0.0163	0.0161
8.40	489	1456	0.210	0.195	0.0170	0.0167
4.20	470	1441	0.208	0.195	0.0155	0.0164
2.40	436	1125	0.209	0.197	0.0158	0.0164
1.70	<10	<10	0.194	0.195	0.0187	0.0157
0.74	<10	<10	0.194	0.195	0.0173	0.0148
Powder	9		0.190		0.0117	

Table 6: Argon content in dependence on the pressure in the evacuated capsule

Apart from the pressure of 1000mb the measured nitrogen values are slightly above the measured value of the original powder. The slight increase of nitrogen may be due to the reaction of powder with the residual air in the capsule. A further explication could be that only one powder sample was measured and this is not sufficient for a statistically reliable distribution. However the measured values for oxygen were identical.

Comparison of the measured values with the guide line values for argon

The following Guideline Values are valid [2]:

- < 60 ng/g: The component can be used without any problem

- 60 – <150 ng/g: The part can be used depending on the application
- 150- ca. 400 ng/g: Customer authorisation is required or there exists values from past experience for the application (often statistical tension tests show no mechanical characteristics differences. Significant differences can be identified using an impact test)
- ca. 400 ng/g: The part is scrap.

Apart from the sample 0,74mbar and 1,7 mbar the measured values are above the indicated guideline values.

Measuring the argon content in argon-atomised nickel-base powder

Nickel-base alloys are mainly atomised with argon. Due to the Van-der – Waals forces argon becomes attached to the powder and increases massively the argon content. For example several samples of atomised nickel-base alloys feature values of 1050-1200 ng/g which are far beyond the permitted value of 400 ng/g as explained in the preceding passages.

Atomising with nitrogen entails the risk of the formation of undesired nitride which has a negative effect upon the toughness. The problem is to choose between two disadvantages, the formation of nitride or a higher argon content. A solution could be a hot evacuation over a longer time-period in case of an argon-atomised alloy.

Influence of the welded joints

As to their geometry welded joints (figures 7) can be subdivided into four types. Type A is the simple welding of sheet

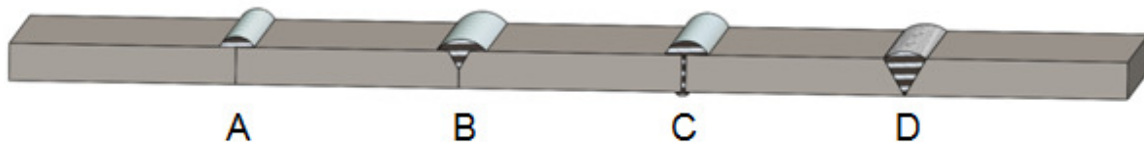


Figure 7: Possibilities of welded joints

metal fixed at right angles. Type B features a small V-weld followed by sheet metal adjoining in a right angle. With the new welding type C the sheet metal adjoining in a right angle is continuously welded. Type D is an old reliable method to weld continuously the V-groove. In the case of loads from above (figure 8) cracks might

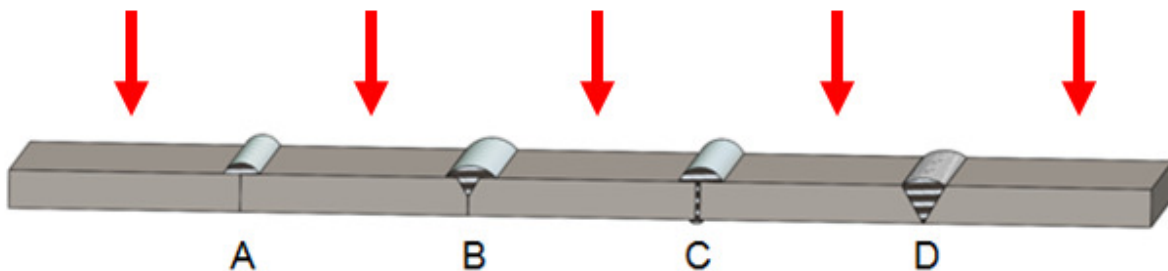


Figure 8: Loads from above

occur in the groove due to the expansion of the unwelded parts A + B. If the load comes from below (figure 9) the same grooves are affected again. In the case of a lateral pressure - or tension load (figure 10) A and B are impacted in the same way. The welding type A is risky at any type of load and should not be carried

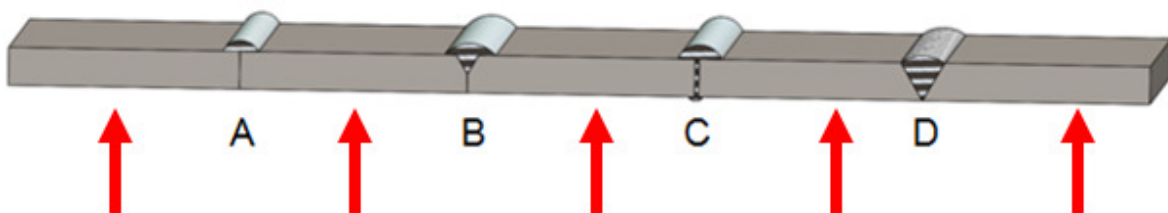


Figure 9: Load from below

out on HIP capsules (see the evaluation in table 7). The most highly rated welding technique requires enormous welding expertise of the operator and ultra-modern welding facilities. In the case of connections over the edge of the metal sheet the groove is even more heavily loaded and must be welded right down to the bottom. Figure 11 shows that all those conditions are complied with. Additionally as shown in picture b, the lengthening of the metal sheet at the welding point creates a pressure load during the HIP process preventing the risk of fracture when being deformed.

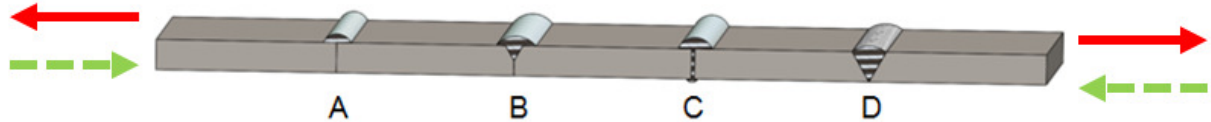


Figure 10: lateral load (pressure and tensile stress)

Type	groove	Welding in sheet metal (%)	Risk of fracture at a different load			
			top	bottom	lateral tensile stress	lateral pressure load
A	right angles 100%	0%	large	large	large	low
B	right angles 50%	50%	low	large	medium	low
C	right angles 100%	100%	the lowest	the lowest	medium	the lowest
D	V-groove	100%	low	the lowest	low	low

Table 7: Behavior of welded joints under different loads

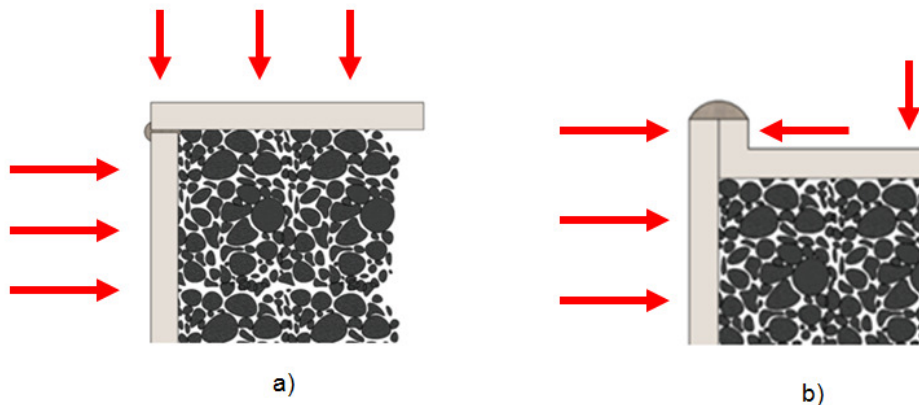


Figure 11: Design of a capsule, a) + b)

Effects of gas impurities in Duplex component

The solidity of a component depends on many facts, for example the argon content in the capsule, the HIP temperature and the heat treatment. In the case of Duplex steels the impact toughness at -46 degrees is of great importance. Table 8 shows the requirements according to Norsok standards. The aim of impact testing is to determine the toughness of a metal sample. The test bar of the material to be tested is notched at one side. In the present test the samples are tested according to the Charpy notch testing norms. In test [7] a Charpy hammer hits with a given kinetic energy the ungrooved back of the sample which undergoes a strong plastic deformation by absorbing a certain degree of the energy of the Charpy hammer. Depending on the material and the temperature the sample can break. Depending on the amount of energy absorbed by the sample, the Charpy hammer swings back to a certain height. The used impact power in Joule (J) and the impact toughness are the indicator of the resistance of the material to sudden impacts. If many samples of the same material are tested at different temperatures and impact testing is carried out via the temperature the cubic face - centered materials behave quite differently. Cubic body - centered materials such as high alloyed chromium steels are tough at high temperatures and brittle at low temperatures. In between there is a steep drop off with scattered values. The position of the steep drop off is indicated by the transitional temperature $T_{\bar{u}}$. This can be between the high and the low position. For steel it is usual to call the transitional temperature $T_{\bar{u}27}$, where a sample shows less than 27 impacts.

Moreover materials which are used in the off-shore industry are exposed to stress corrosion cracks. The field of the crack mechanics technology was established as a branch discipline of the mechanics at the beginning

of high technical developments in the 20th. century. Normally the development of the practical application of the crack mechanics [9] is linked with the name of Liberty ships of the American Navy in World War II. The sudden falling apart of these welded ships was a mystery for the engineers and finally led to the application of the basic findings of the crack mechanism from the 40ies of the 20th. Century. For more details about stress corrosion cracks consult [10].

	UNS	Test Temperature	Impact testing minimum (Charpy V-Notch): ASTM A 370		Test Temperature	Corrosion test (ASTM G 48 Methode A)
		°C	average (J)	single (J)	°C	
F60	S32205	-46	45	35
	S32505 ⁽¹⁾	-46	45	35	50	no pitting at 20X magnification; weight loss ≤ 4.0 g /m ²
NORSOK Standard M-65010.3.3 Additional testing section thickness/diameter > 50 mm						
	All	-46	27	20	50	no pitting at 20X magnification; weight loss ≤ 4.0 g /m ²

⁽¹⁾ based on the mechanical properties of UNS S32760

Table 8: Requirements according to NORSOK

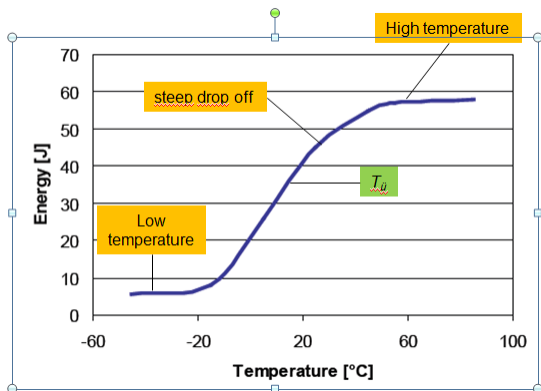


Figure 12: steep drop off



Figure 13: Liberty ship with brittle fracture

In order to determine the influence of the argon content the impact test samples with a defined argon content were heat treated and checked according to DIN EN ISO 148-1 processed and checked (Diagram 3 and Table 9). In comparison, the results influence of the argon content on the notched impact strength of the PM

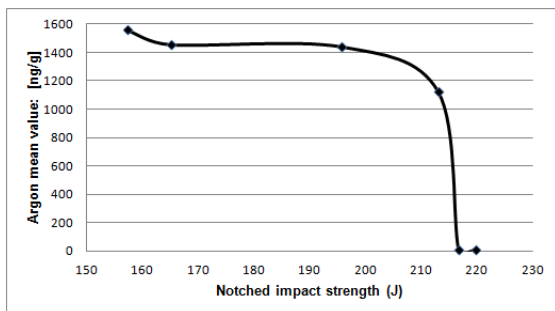


Diagram 3: decrease of the toughness with increasing argon content

Argon mean value: [ng/g]	Notched impact strength (J)
511	157
489	165
470	196
436	213
9	217
9	220

Table 9: Argon- und notched impact strength values

HIP duplex steel X2CrNiMoN22-5-3 (1.4462), heat treatment condition: solution annealed, notch shape (diagram4) from a study of Christopher Broeckmann [11] are shown. The values given in J/cm² were taken from the diagram translated and presented in J to the true cross section of 0.8 cm². A conversion from ppm to ng/g was calculated with a factor of 1000. The calculated values are listed in Table 10. Clearly, the influence

of the argon content in both studies greater than 520 ng/g is to see. The notched impact strength decreases rapidly but is still within the required values according to Table 8. The wall thickness dependence and thus the cooling rate of the sample remain undiscussed here and ask open-ended questions. Note the test temperature of 20 °C and not as required in the UNS Standard -46 °C. The values would fall more at the prescribed temperature.

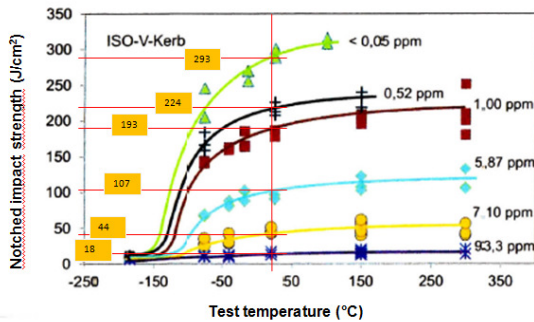


Diagram 4: Influence of the argon content [11]

Test temperature 20°C			
ppm	ng/g	J/cm ²	ISO-V (J)
0.05	50	293	234
0.52	520	224	179
1	1'000	193	154
5.87	5'870	107	86
7.1	7'100	44	35
93.3	93'300	18	14

Table 10: Conversion J/cm² from figure 17 [11] in J

Measuring Argon concentrations Argon content in steel (Carrier Gas – Hot Extraction Method)

Bruker Elemental offers a NEW possibility to combine two analytical measurements for the HIP process in one instrument combination. The connection of the quadrupole mass spectrometer with the G8 Galileo - Inert Gas Fusion instrument offers for the HIP process either to detect the impurities in the used Argon atmosphere or the Argon content in the final steel product.

Due to the need of measuring very low Argon concentrations in the HIP sample [12] material a sensitive and selective detection by a quadrupole mass spectrometer coupled to a commercially available ONH analyser was used.

The Bruker G8 GALILEO ON/H (figure 14) is a high-end instrument designed for the rapid and automatic 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 gas fusion analysis (GFA) principle is also commonly termed a melt extraction (ME) since the total oxygen, nitrogen and hydrogen composition is extracted via sample melting.

As a result of the applied high temperatures, the oxygen in the sample, which is generally in oxide form, reacts with the abundant carbon to form CO. Furthermore, nitrogen is released from nitrides through decomposition, as well as any hydrogen and Argon present in the sample.

The resulting sample gases CO, N₂, H₂ and Ar are transported with the carrier gas through a high stability detection system consisting of a selective NDIR detector for CO (optionally two) and -after removing interfering the gases by an oxidation/sorption process- through a thermostatically controlled thermal conductivity cell (TCD) for N₂ and H₂.

When combined with an external, infrared heated furnace, the G8 GALILEO can measure the diffusible hydrogen content in many sample materials, e.g. in welds according to ISO 3690 and AWS4 4.3 as well as in high strength steel.

Coupling a mass spectrometer to the G8 GALILEO analyzer leads to a substantially improved detection limits for the determination of ultra-low diffusible hydrogen concentrations e.g., in high strength steels as well as for the measurement of sub ppb concentrations of Argon in HIP sample materials.

Mass Spectrometric Detection Principle

Mass spectrometry (MS) is an analytical technique that measures the [mass-to-charge ratio](#) of charged compounds. The MS principle (figure 15) consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their [mass-to-charge ratio](#)).



Figure 14: G8 GALILEO ONH analyser with MS and infrared furnace for diffusible hydrogen

MS instruments consist of three modules:

- An *ion source*, which can convert gas molecules into ions
- A *mass analyzer*, which sorts the ions by their masses by applying electromagnetic fields
- A *detector*, which measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present

The quadrupole mass analyzer (figure 16) is one type of mass analyzer consisting of 4 circular rods, set parallel to each other. The *quadrupole* is the component of the instrument responsible for filtering sample ions, based on their *mass-to-charge ratio* (m/z). Ions are separated in a quadrupole based on the stability of their trajectories in the oscillating *electric fields* that are applied to the rods.

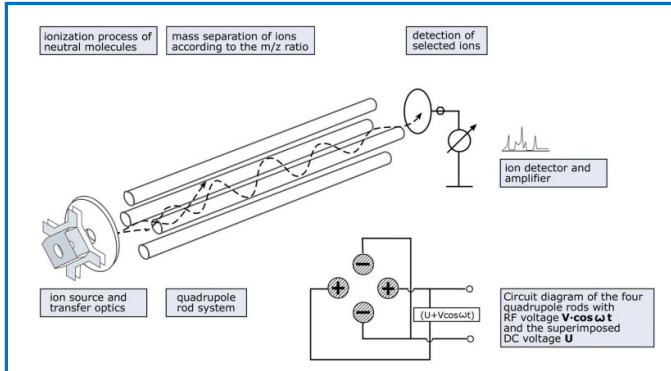


Figure 15: Principle of a quadrupole mass spectrometer

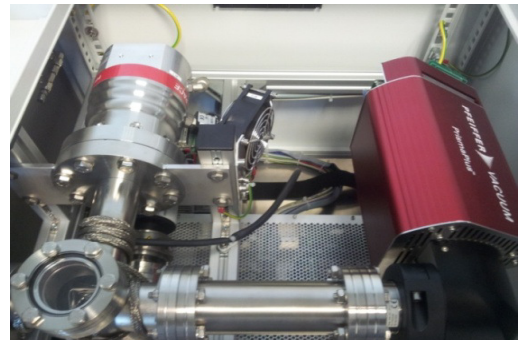


Figure 16: Insight into the mass spectrometer

The quadrupole consists of four parallel metal rods. Each opposing rod pair is connected together electrically, and a *radio frequency* (RF) voltage is applied between one pair of rods and the other. A direct current voltage is then superimposed on the RF voltage. Ions travel down the quadrupole between the rods. Only ions of a certain *mass-to-charge ratio* m/z will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods. This permits selection of an ion with a particular m/z or allows the operator to scan for a range of m/z -values by continuously varying the applied voltage.

The external quadrupole analyzer (Manufacturer: IPI InProcess Instruments, Bremen, Germany) which can be connected to the G8 GALILEO offers a mass range from 1 to 100 amu. The unit comprises a channeltron detector for improvement of sensitivity and sampling rate and an electrometer amplifier with quick switchover and auto ranging. It is operated with a turbo molecular pump, combined with a membrane pump. The ultra-high vacuum recipient is equipped with a total pressure measurement.

Argon Measuring Principle

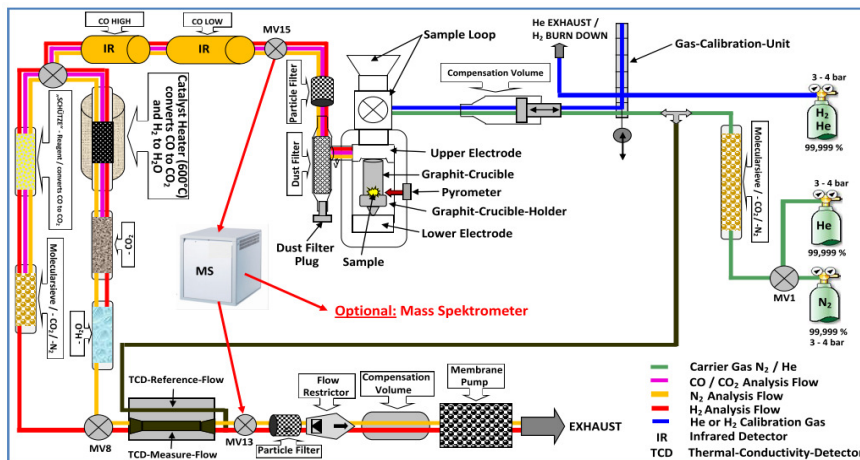


Figure 17 (left): Schematic gas flow G8 GALILEO ONH with MS; coupled with MS, enlarged detail: glowing graphite crucible



Figure 18 (right): ONH analyser

Experience has shown that pores at Ar levels below 400 ng/g cannot be identified by light microscopy. There is also the risk of mix-up between argon pores and nonmetallic inclusions. Therefore the carrier gas hot extraction is used for melting the sample at high temperatures and determining the released argon quantitatively by means of a coupled quadrupole mass spectrometer.

For the measurement of the Argon concentration in HIP sample material Helium 6.0 is used as carrier gas (figure 17 + 18). The sample is melted in a graphite crucible in the electrode furnace at temperatures of about 2.000°C. The sensitive quadrupole mass spectrometer, adjusted to the m/z ratio of 40 (Ar), is coupled via a special capillary gas inlet system to the standard G8 GALILEO. The extreme detection sensitivity of the MS allows a measurement of an Argon content in the range of 2 ng/g to 1000 µg/g, the detection threshold is about 0.5 ng/g.

Calibration Procedure

As there are no reference materials with defined Argon content on the market the calibration has to be carried out by dosing known volumes of Argon gas to the detection system.

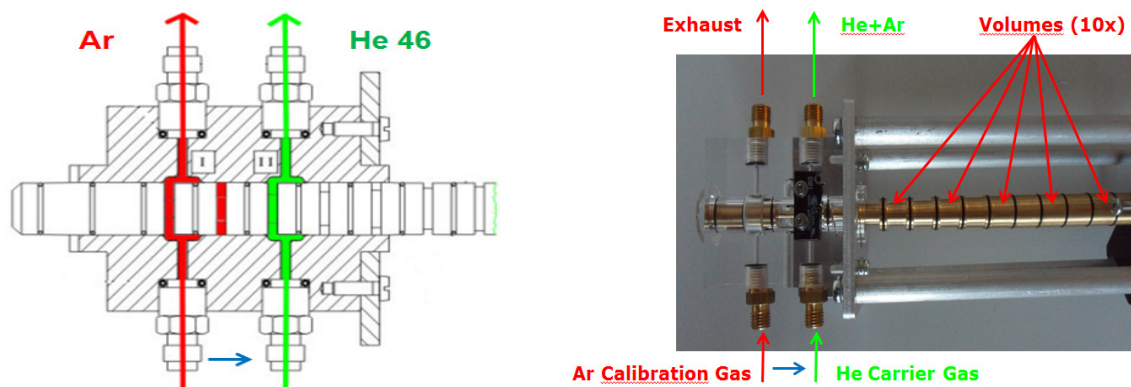


Fig. 19 and 20: Schematics and Function of Gas Calibration Unit (10 different volumes)

The optionally integrated, computer controlled gas calibration unit enables the dosing of exactly defined volumes of calibration gas. The gas calibration device is provided with 10 different volumes. The sequence of the desired volumes and the number of cycles are freely selectable from the software. Ambient temperature and atmospheric pressure are measured internally to enable the calculation of the mass of Argon gas in the particular volume.

Due to the expected Argon concentrations and the high detection sensitivity of the MS a certified calibration gas with 500 ppm Argon 6.0 in Helium 6.0 (Mixture „Saphir“) has been used for calibration applying up to ten different gas volumes (figure 19 + 20). The calculation of the calibration curve is made via a linear regression of the peak area (integrals). With this easy, cheap and long-term stable calibration a very low and wide ppb range can be covered (figures 21 – 26).

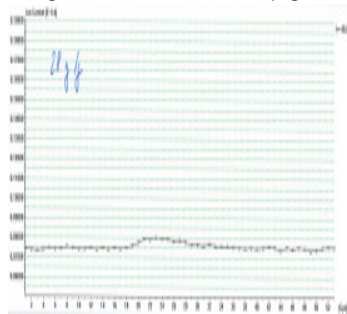


Figure 21: Vol 1 → 28 ng/g

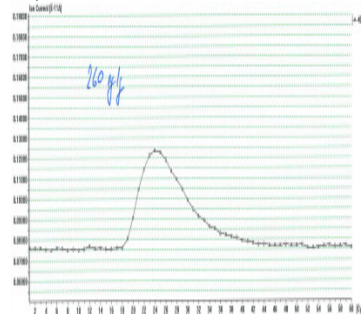


Figure 22: Vol 5 → 260 ng/g

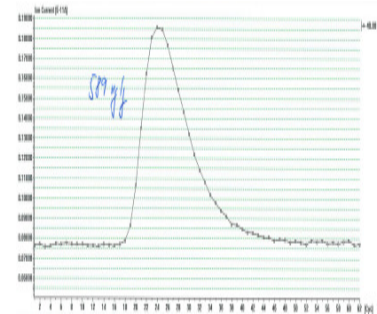


Figure 23: Vol 10 → 589 ng/g

Procedure of Argon measurement in steel

Sample preparation:

1. Separate larger moldings with water cooling
2. Shearing of the sample strips with hand lever shears with blades made of hardened steel (weight 0.7 - 1.0g)

3. Clean the sample in an ultrasonic bath with acetone for 10 min
4. Rinse the sample in acetone
5. Drying at 110 °C for about 10 min
6. Cool to room temperature
7. Sample weight (0.7 - 1.0g) to the analysis at 0.0001g exactly

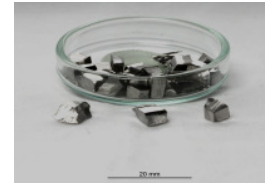


Figure 27: Sample shapes

Sample analysis in G8 Galileo

When the sample (figures 27) weight is transferred into the instrument software and the previously prepared sample is placed in the analyzer the measurement can be started. First the used graphite crucible is heated up to a higher temperature than needed for the actual analysis to remove all the blank from the crucible. After a baseline stabilization, the sample is dropping into the hot crucible for melting. After a defined analysis time and reassessment of the baseline, the analysis is automatically stopped and the raw data were saved. By means of a flexible peak integra algorithm the concentration of argon in the sample could be calculated. The following examples are steel samples which were loaded up with different argon contents in order to represent the wide measuring range.

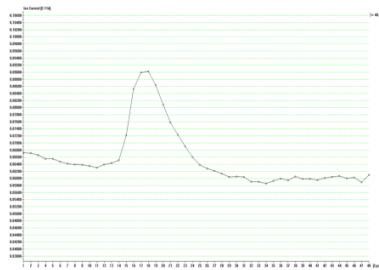


Fig. 24: Steel Sample 104 ng/g

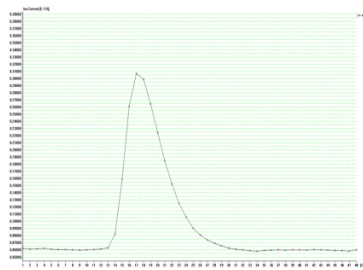


Fig. 25: Steel Sample 956 ng/g

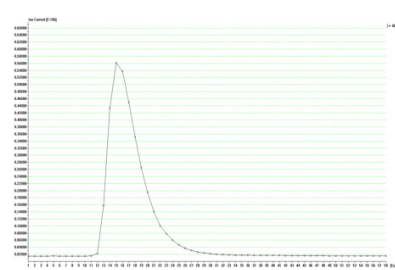


Fig. 26: Steel Sample 32945 ng/g

Impurities in used Argon atmosphere (Gas Analysis)

In the HIP process, the materials get in direct contact with the used argon purge gas during re-densification. In this case, the material may absorb impurities in forms of oxygen, nitrogen, hydrogen, hydrocarbons and moisture, which can then diffuse into the material.

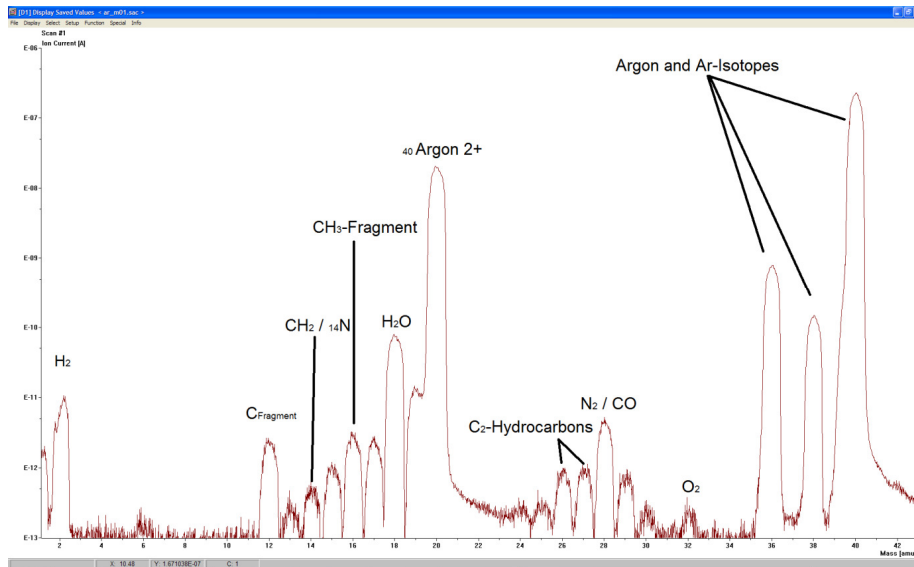


Figure 28: Impurity Analysis with Mass Spectrometer

This can force cracks, gas bubbles and degrades the quality of these highly stressed components. For this reason, the impurities (figure 28) in the argon gas should be limited and constantly monitored. This now provides the connected mass spectrometer, which can analyze these contaminants. In Addition an external

moisture sensor has been integrated in the instrument configuration which data are also transferred directly into the final protocol. During the entire HIP process, especially at the beginning, in the middle (highest temperature point) and at the end, control samples can be analyzed. The HIP system automatically sends samples to the mass spectrometer and in return receives a complete analysis report on the composition of the argon gas (figures 29). This is done via an additional valve (figure 30) circuit in the mass spectrometer and a predefined interface for data exchange and communication between the HIP system and the mass spectrometer.

Specification for the impurity analysis:

Oxygen: < 5 ppm
 Nitrogen: < 50 ppm
 Hydrogen: < 50 ppm
 Moisture: < 5 ppm

Hydrocarbons: not yet sufficiently specified...

Name	Minimum	Maximum	Mean	STD ABS	STD REL
N2	27.806ppm	28.459ppm	28.119ppm	1.617E-05	5.752E-03
O2	12.577ppm	12.993ppm	12.767ppm	8.496E-06	6.655E-03
Ar	99.9959%	99.9960%	99.9959%	1.916E-05	1.916E-07

Figure 29: Statistic for N2 and O2 Impurities

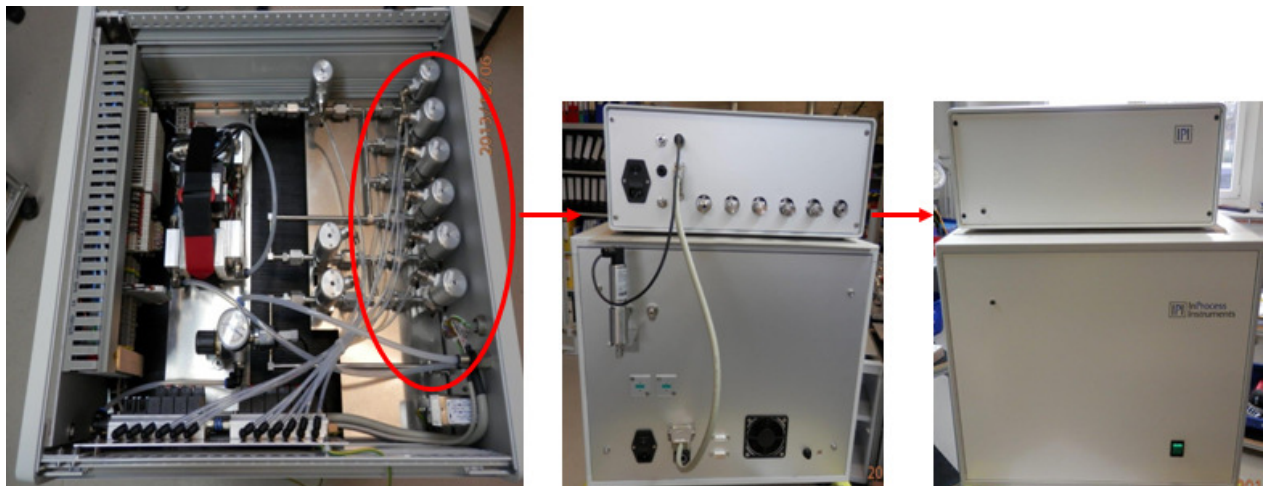


Figure 30: Additional Valve Box for Impurity Analysis, left: interior view, middle front side, right: back side

In the end, the customer receives a complete documentation of the production process, in order to exclude later complaints of components.

Summary

- G8 GALILEO ONH + Mass Spectrometer + Moisture Sensor = One instrument configuration to monitor the complete HIP process. Especially the Mass Spectrometer is a much more dynamic detector and safer.
- Qualitative and quantitative analysis of critical impurities in the used Argon gas.
- Measurement of the Argon concentration in the final solid product down to very low ppb range.
- Possibility to measure the oxygen, nitrogen and hydrogen concentration also in the final solid product down to very low ppm range.
- One interface between the HIP system and the Bruker instrument configuration for communication and data transfer.
- One final documentation/protocol of all conditions during the HIP process at every time.

- To control the oxygen content in the HIP furnace can also save cost because the molybdenum wire will brittle if it get in contact with oxygen.
- The G8 GALILEO is a user friendly instrument with low analysis cost, but offers the widest range of analytical performance.

Conclusions

The penetration of argon in the capsule as well as an incomplete evacuation process affect the solidity of steels. Flaws of any kind impair the toughness and the use of the tested Duplexsteel. Argon in a component increases the risk of failure due to the influence of different types of corrosion. The argon content is an important indicator for the behavior of the component in use. The same goes for components which were redensified with impure argon gas and featured surface impurities.

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