Application Note [2621]

V-L 450-600/10-1G HV & GPCMA 11/37

Optimizing the atmosphere for stress relief annealing of L-PBF samples by SEM-EDX method

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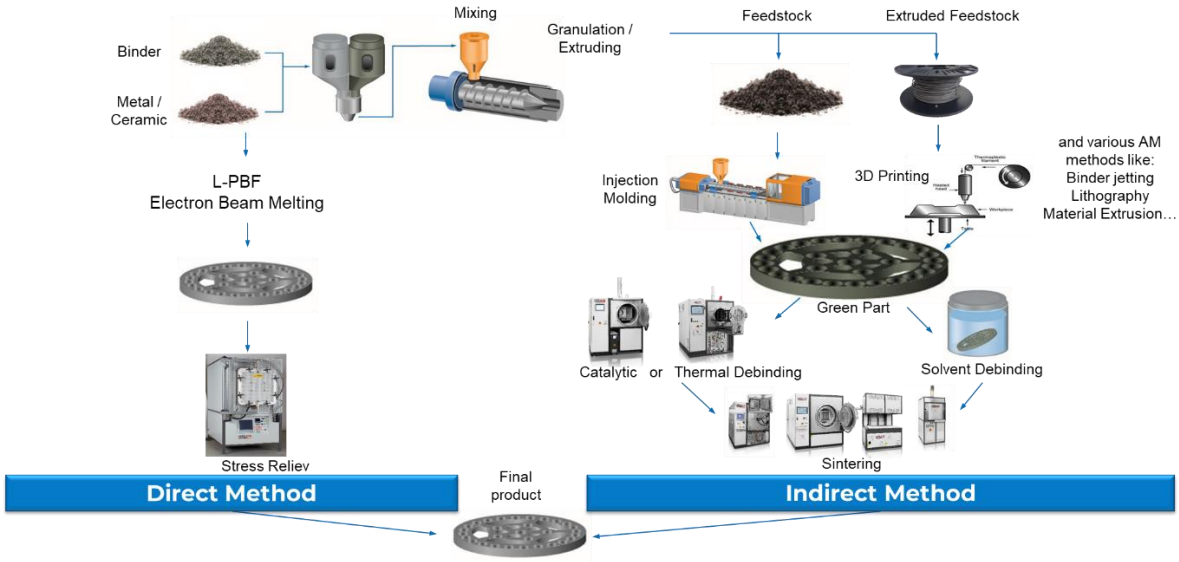
Abstract:
This study reports on the oxygen content measured by EDX analysis of samples which were heat treated in either atmospheric pressure or in high vacuum. The samples were manufactured by Laser-Powder-Bed Fusion (L-PBF) technology, where and subsequent heat treatment is required. In theory and in practice, it could be shown, that oxygen in high vacuum is always lower than at atmospheric pressure. This results in a reduction in oxidation by 38% on the titanium (Ti-6Al-4V) samples used in this report.

1. Indirect methods in additive manufacturing – L-PBF

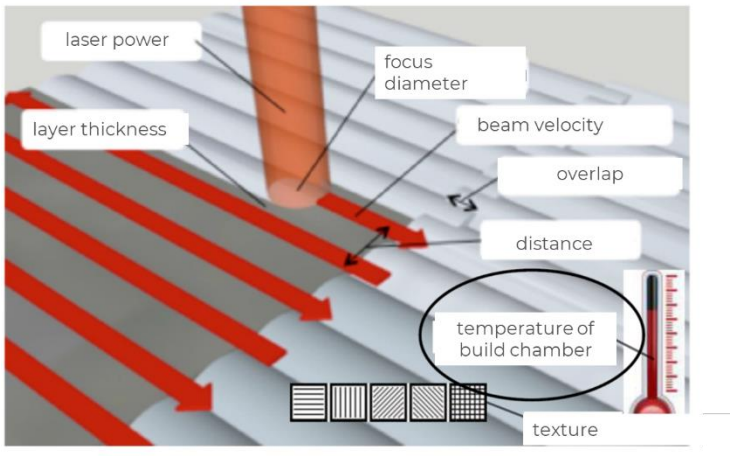
Heat treatment is inevitable when post-processing additive manufactured (AM) parts. This is true for all the indirect- and for all the direct methods in AM. The heat treatment for the indirect route of AM is more demanding, since here a debinding step is followed by a rest- debinding and sintering step. Depending on the binder type and the powder material, debinding can be done catalytically, thermally or by a solvent. The subsequent rest- debinding and sintering is a complex step, both for ceramic and metal powders. For ceramics, rest- debinding in air is a safety related process, since any off gases must not exceed a lower explosion limit. For metals most widely hydrogen partial pressure debinding and sintering is applied.

However, the requirements for heat treating samples manufactured in a direct way are often underestimated. Due to the nature of the L-PBF process, the laser is focused on the powder bed. This local exposure causes stresses for the entire sample in each layer. Therefore, samples need to be heat treated after L-PBF. Since Ti-6Al-4V alloy completely oxidizes at a temperature of 427°C, this heat treatment needs to place in an inert atmosphere. Although, this process is exactly defined in DIN65084, commonly and widely used process is treating up to 700°C (with a dwell time of 1 hour per inch) in a high purity Argon atmosphere at standard atmospheric pressure.

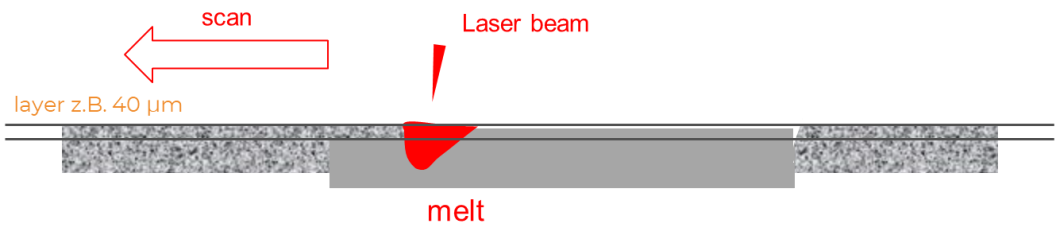
This article aims to qualify the difference between heat treatment in an Argon atmosphere and the heat treatment in a high vacuum environment. Therefore, two different furnace models are used: The GPCMA for the Argon atmosphere and the VL for high vacuum. The samples are manufactured identically by L-PBF and are heat treated in the GPCMA or in the VL afterwards. Those samples were then measured with respect to their oxygen content using the EDX method.



Direct and Indirect methods in Additive Manufacturing



Principle of Laser-Powder-Bed Fusion (L-PBF). A focused laser beam builds up the final part layer by layer.

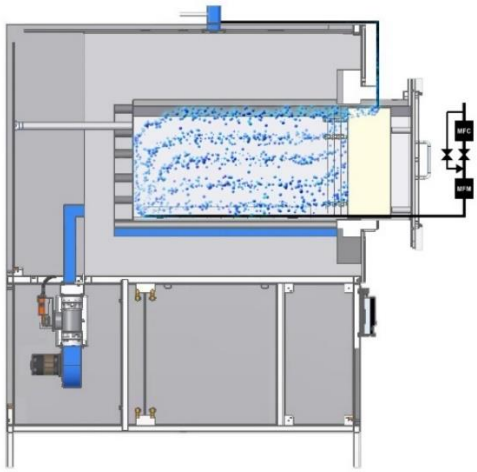


For L-PBF the powder bed is locally focused and melted by the laser beam, which leads to material tensions in the final part.

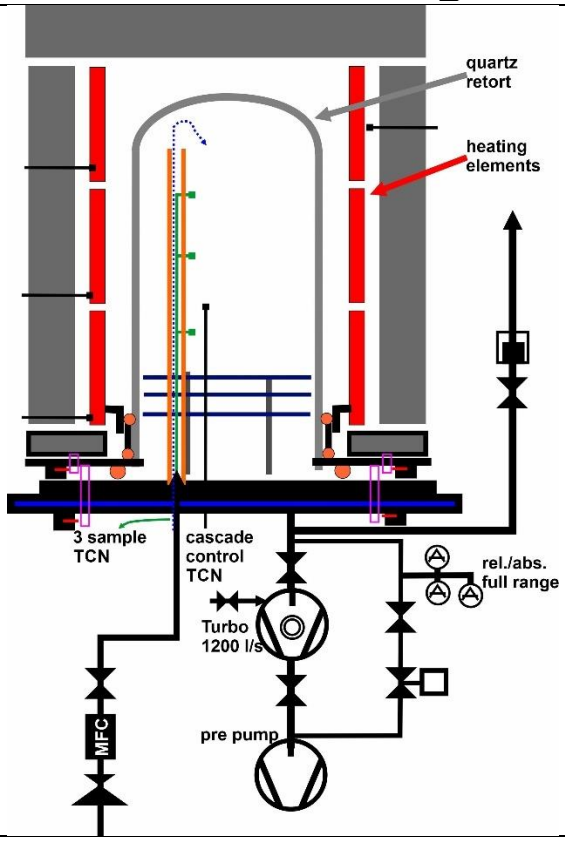
2. Stress relieving of L-PBF samples in the GPCMA and in the V-L

The heat treatment was carried out at Carbolite Gero GmbH in Neuhausen, Germany. Carbolite Gero possesses a laboratory for various heat treatment processes, which are carried out for internal R&Ds as well as for customers trials. Carbolite Gero is equipped with a GPCMA/174 for heat treatment in atmospheric pressure of Argon up to 1000°C. Additionally a V-L 450-600/10-1G HV is available for heat treatment in high vacuum (HV) up to 1050°C.

	
Picture of the GPCMA/174	Picture of the V-L 450-600/10-1G HV



Schematic drawing of the GPCMA/174: The metallic retort is heated from a two-zoned chamber furnace.



Schematic drawing of the V-L 450-600/10-1G HV: The quartz retort is heated from outside by means of 3-zoned heating elements

General specifications GPCMA/174

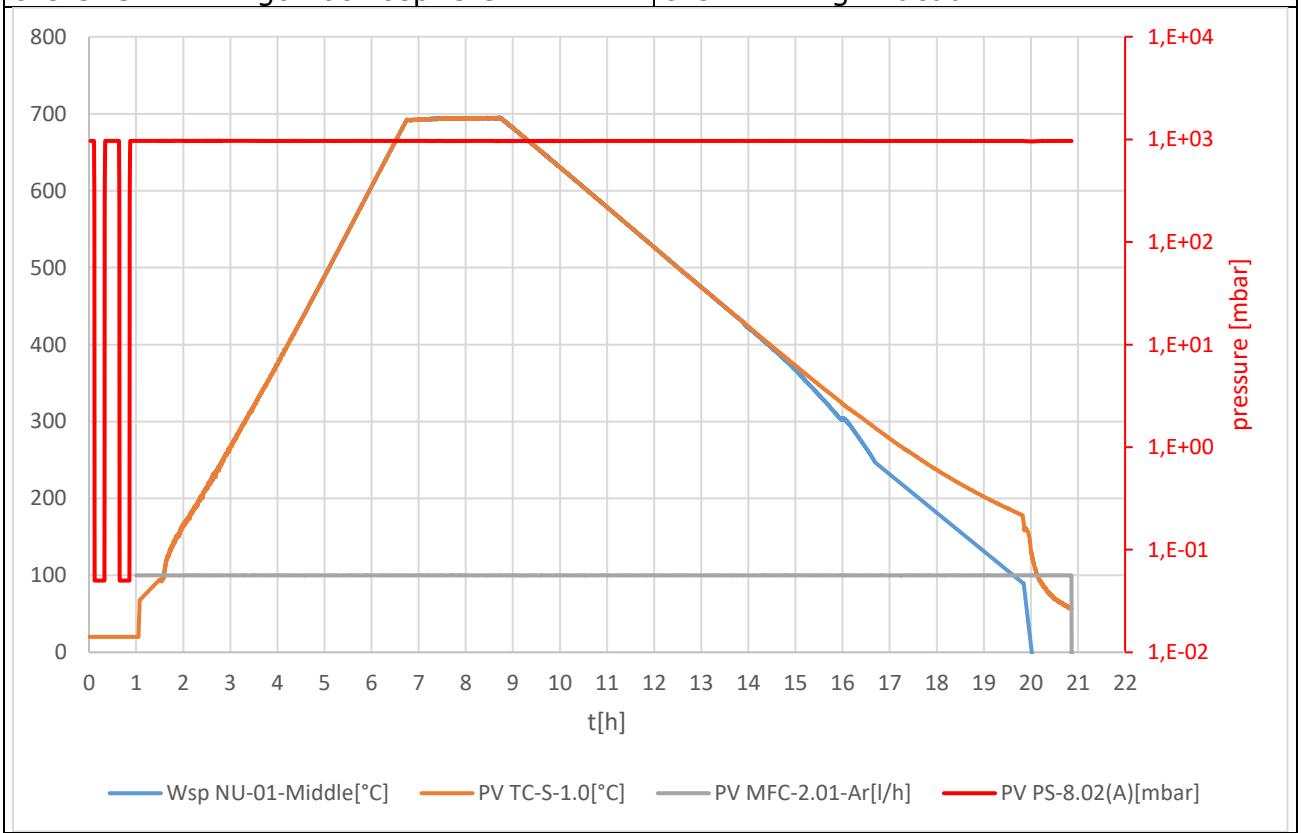
Item	Value	unit
T_{max}	1000	°C
Working pressure	1000	mbar
Usable volume	174	L
Maximum temperature under vacuum	20	°C
Lowest Oxygen level	<50	ppm
Number of heating zones	2	
Leakage rate	<5x10E-1	mbar l/s
Power	17	kW
weight	220	kg

General specifications V-L 450-600/10-1G HV

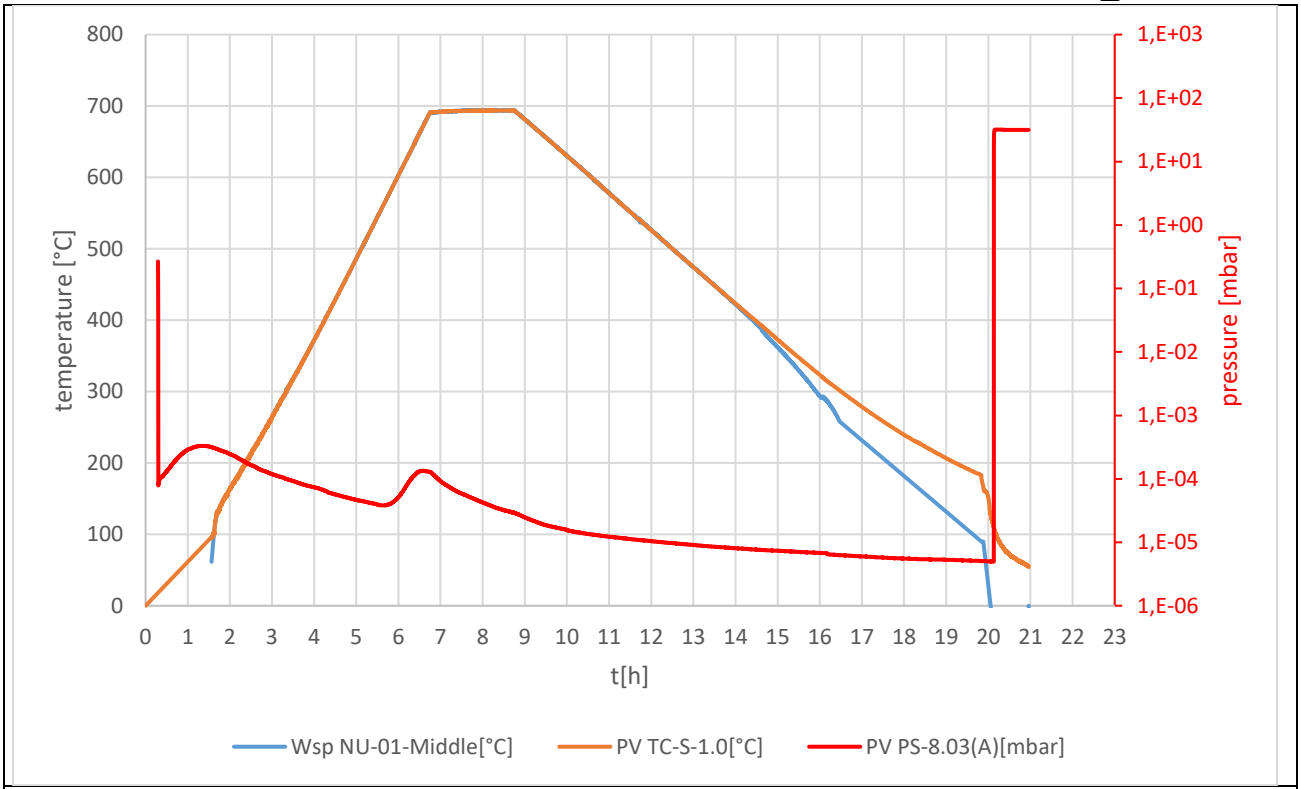
Item	Value	unit
T_{max}	1050	°C
Working pressure	10E-6 - 1000	mbar
Usable volume	100	l
Maximum temperature under vacuum	1050	°C
Lowest Oxygen level	2,1 x 10E-4	ppm
Number of heating zones	3	
Leakage rate	<5x10E-3	mbar l/s
Power	58	kW
weight	1800	kg

"Sample_GPCMA"
Titanium samples after heat treatment in the GPCMA in Argon atmosphere

"Sample_VL"
Titanium samples after heat treatment in the VL in high vacuum



Heat treatment in the GPCMA in Argon with a flow of 100 l/h at atmospheric pressure.
WSP NU-01-Middle[°C]: work set point of the master heating zone [°C]
PV TC-S-1.0[°C]: process value of the master heating zone [°C]
PV MFC-2.01-Ar[l/h]: mass flow of Argon inside the chamber [l/h]
PV PS-8.02(A)[mbar]: process value of the absolute vacuum pressure gauge shown on the secondary (red) axis [mbar]. Prior to the heat tretment the furnace was evacuated twice down to 5x10E-2 mbar.



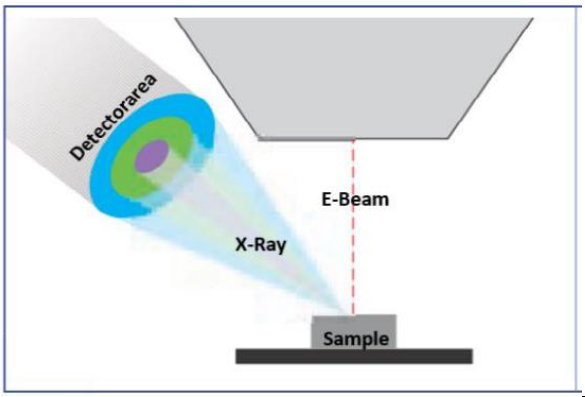
Heat treatment in the VL in vacuum
WSP NU-01-Middle[°C]: work set point of the master heating zone [°C]
PV TC-S-1.0[°C]: process value of the master heating zone [°C]
PV PS-8.02(A)[mbar]: process value of the absolute vacuum pressure gauge [mbar] shown on the secondary (red) axis

3. EDX analysis of the samples after heat treatment

EDX spectra were recorded at the university of Pforzheim at the Institute of Precious and Technology Metals. Their facility has a Scanning Electron Microscope (SEM) manufactured by FEI. The focused energy of the primary electrons on the sample, is adjustable and can be 30keV at most.
The SEM includes an energy dispersive EDX detector for the X-rays escaping from the sample.

Even the lowest remaining content of oxygen (O_2) inside the furnace chamber, reacts with titanium samples immediately, especially at elevated temperatures. Hence, there is an oxygen layer on the surface of the samples after heat treatment. To quantify this layer, the samples were examined by means of EDX analysis. Since the Kα line of oxygen is 0,526 keV, the energy of the primary electron beam was reduced to 5 keV. This increases the efficiency of the signal, as it is optimal to have 3 times the energy of the X-ray as primary electron beam energy. On the other hand, the penetration depth of the primary electrons is reduced for lowered energies ($\sim E^{2/3}$). A reduction from 30keV down to 5keV reduces the penetration depth by a factor of 3,3. Simultaneously, the lateral resolution is degraded by lower primary beam energy, due to increased lens aberrations and increased coulomb effects between the electrons traveling at reduced speed. Since the lateral resolution is not the main focus for this study,

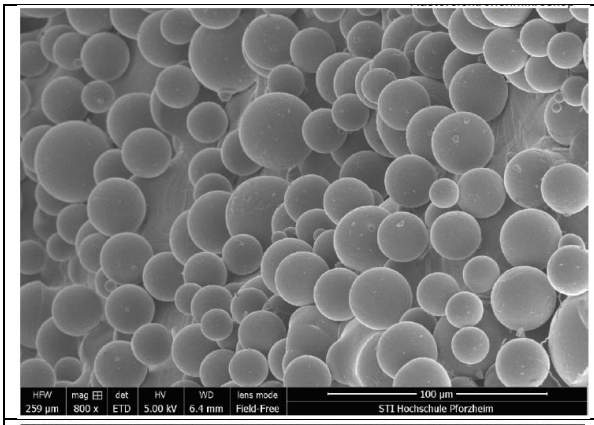
this effect can be accepted. As the oxygen layer is on the surface of the samples anyway, this is advantageous as oxygen X-ray lines should be able to be detected and quantified.

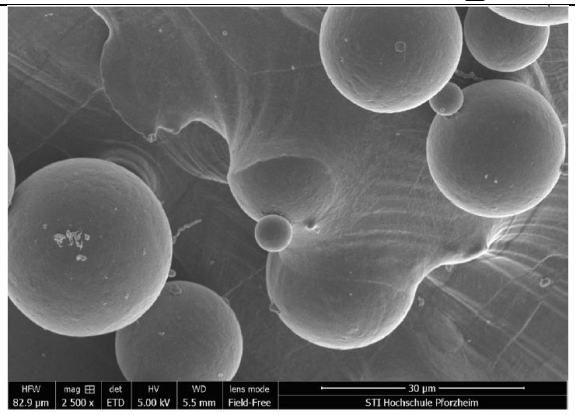


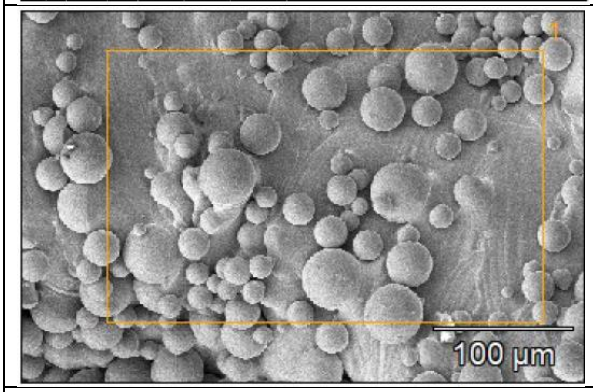
Schematic drawing of the SEM with the electron beam (E-Beam) generating X-rays.

Picture of FEIs Scanning Electron Microscope at the university of Pforzheim. The EDX detector is adapted from the left side to the chamber

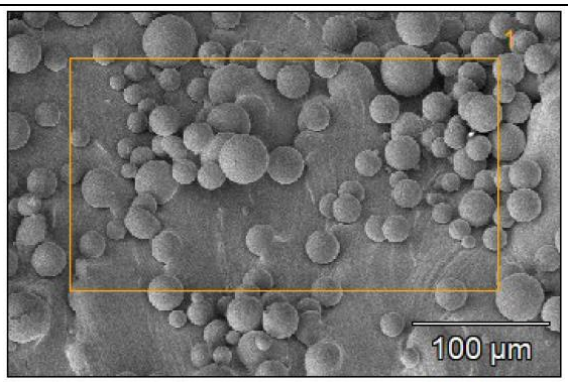
Samples recorded with the internal camera inside the chamber of the SEM







Spot area for EDX measurements for Sample_GPCMA



Spot area for EDX measurements for Sample_VL

Secondary electron microscope picture of the samples. Interesting to note, that there are still powder particles on the surface of the samples. This is why further post processing steps are needed, depending on the application.

Typical EDX spectrum of the sample_VL with a primary electron energy of 5keV.

sample	<O_2>	STABW	Average absolute pressure during the heat treatment <p> [mbar]
Sample_VL	5,1	0,5	5,5 x 10E-5 mbar
Sample_GPCMA	8,2	1,7	1000 mbar

EDX spectra of the samples. From each sample three points were focused and the EDX spectra recorded. In the table above, the average of the oxygen signal (<O_2>) and its standard deviation (STABW) was evaluated.

4. Purity of atmospheres a general consideration

To compare oxygen levels at atmospheric pressure and in vacuum, the following considerations were made: In air, at atmospheric pressure of 1000 mbar, the oxygen partial pressure is 210 mbar, i.e. 210.000 ppm. A high vacuum pump now reduces the pressure and consequently the total number of gas molecules inside the furnace. However, the oxygen level is still 210.000 ppm. As a "thought experiment" the furnace can be back flooded with 100% pure Argon. Now, the partial pressure of oxygen goes down, depending on the vacuum level, which was achieved previously, since the total number of molecules increases, while the number of oxygen molecules remains low (as they were reduced by the vacuum pump). This gives an idea of the purity in vacuum.

Partial pressure after backflooding from 5 x 10E-2 mbar					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	10,5	39	0,5	999950
Partial pressure after backflooding from 5 x 10E-3 mbar					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	1,05	3,9	0,05	999995
Partial pressure after backflooding from 5 x 10E-4 mbar					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	0,105	0,39	0,005	999999,5
Partial pressure after backflooding from 5 x 10E-5 mbar					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	0,0105	0,039	0,0005	999999,95
Partial pressure after backflooding from 5 x 10E-6 mbar					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	0,00105	0,0039	0,00005	999999,995

The table shows the concentration [ppm] of oxygen (O_2), nitrogen (N_2), water (H_2O) and Argon (Ar) after backflooding the furnace from an initial vacuum of 5x10E$^{-2,3,4,5,6}$ mbar to atmospheric pressure again. The concentration of water in the air atmosphere is assumed to be 1%.

Purity of an Argon quality of 4.6					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	<4	<10	<5	rest
Purity of an Argon quality of 4.8					
	Total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	<3	<10	<5	rest
Purity of an Argon quality of 5.0					
	total	p_{O2}	p_{N2}	p_{H2O}	p_{Ar}
[ppm]	1.000.000	<2	<5	<3	Rest

The table shows the concentration [ppm] of oxygen (O2), nitrogen (N_2), water (H_2O) and Argon (Ar) of Argon gas with a purity of 4.6,4.8 and 5.0.

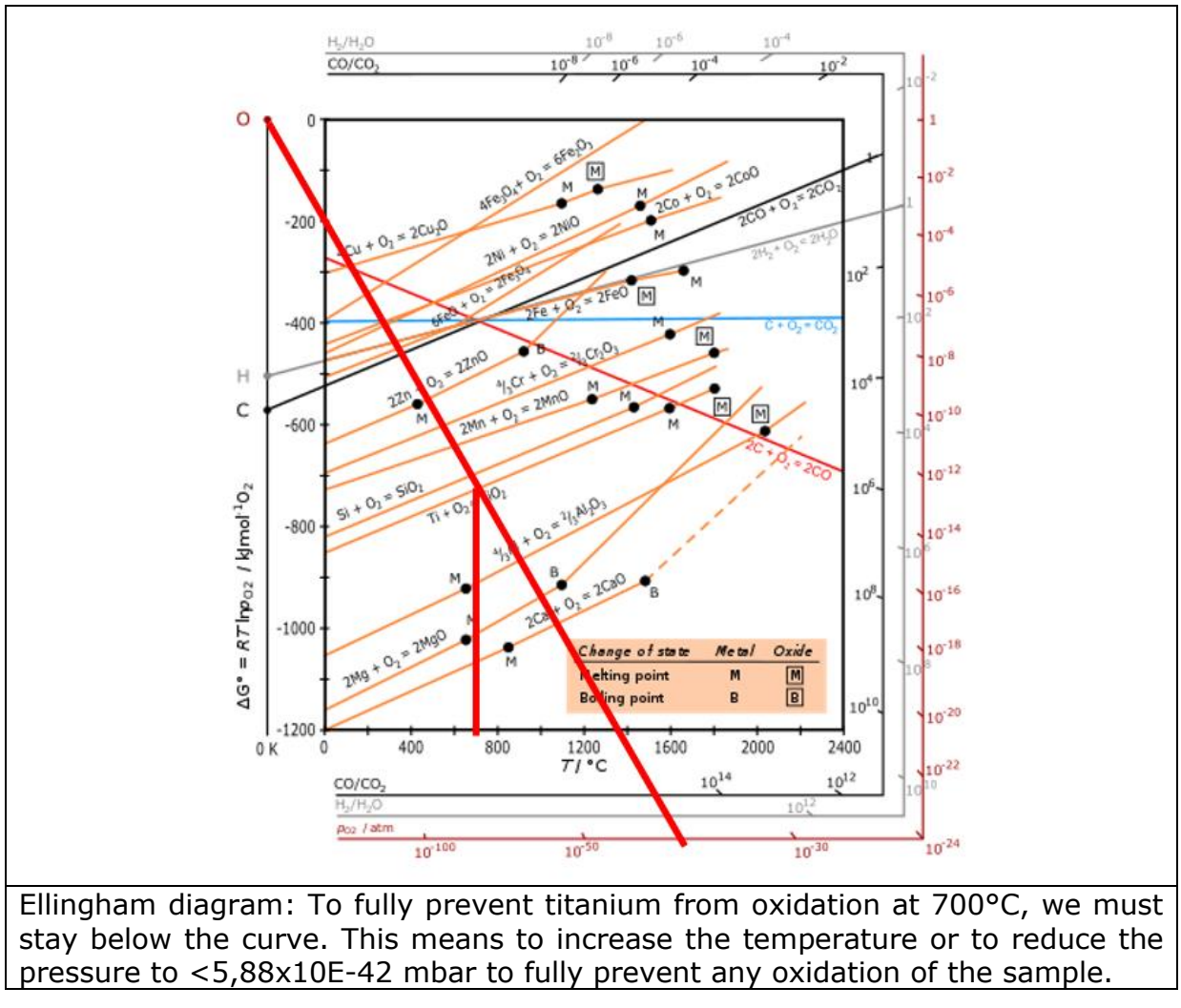
	Argon purity		
p_{O2}vac|p_{O2}Ar [ppm]	**4.6**	**4.8**	**5.0**
5,00 x 10E-2 mbar	10,5|**4**	10,5|**3**	10,5|**2**
1,67 x 10E-2 mbar	**3,5**|4	3,5|**3**	3,5|**2**
1,19 x 10E-2 mbar	**2,5**|4	**2,5**|3	2,5|**2**
1,00 x 10E-3 mbar	**1,05**|4	**1,05**|3	**1,05**|2

The table shows the remaining oxygen content in ppm, both in vacuum (p_{O2}vac) and for high purity Argon (p_{O2}Ar) for different vacuum pressures. Example how to read the tabel: A vacuum of 5x10E-2 mbar leads to a remaining oxygen content of 10,5 ppm, compared to 4 ppm, 3 ppm and 2 ppm oxygen of Argon 4.6,4.8, and 5.0 respectively.

Starting from a pressure below 1,90 x 10E-2 mbar, vacuum becomes better than Argon 4.6. Below 10E-3 mbar, even high purity Argon 5.0 has a remaining oxygen content, which is higher compared to vacuum. Starting from a vacuum level of ≤9,52 x 10E-2 mbar, the purity of the vacuum atmosphere is consistently better than the purity of the gases itself. In addition, the highest purity gases of quality 5.0 exhibit an oxygen content which is poorer than the oxygen content in the vacuum atmosphere. Usually, the average vacuum during heat treatment is better than 5x10E-5 mbar. This results in an oxygen concentration of <0,01 ppm. From this theoretical point of view, it is clear, that the high vacuum environment must always lead to better results than an atmospheric Argon environment, even if the highest possible purity of the gas is used.

5. Ellingham-Richardson Diagram

The Ellingham diagram is a graph showing the temperature dependence of the stability of compounds and shows the sensitivity of metals to oxidation. This analysis is usually used to evaluate the ease of reduction of metal oxides and sulfides. These diagrams were first constructed by Harold Ellingham in 1944.



Ellingham diagram: To fully prevent titanium from oxidation at 700°C, we must stay below the curve. This means to increase the temperature or to reduce the pressure to <5,88x10E-42 mbar to fully prevent any oxidation of the sample.

6. Conclusion

The samples heat treated at atmospheric pressure in Argon show an average oxygen content with a EDX peak intensity of 8,5 ±1,7.

The samples heat treated in high vacuum atmosphere of around 5x10E-5 mbar, show an average oxygen content with a peak intensity of 5,1 ± 0,5.

Therefore, the heat treatment to stress relief of those particular titanium samples shows a reduced oxidation by 38% when using high vacuum.

From a theoretical aspect, it was shown, that even the highest purity of Argon gases cannot provide oxygen levels better than those in high vacuum.
However, the benefit of a reduction in oxidation is 38%, comes along with a huge change in the heat treatment technology, when changing from an atmosphere system to a vacuum furnace. For day to day work the application and final requirements of the samples decide, if high vacuum is needed or not. The Ellingham Diagram shows this tendency of oxidation or reduction of different materials. It shows additionally that oxidation cannot be fully prevented during heat treatment. The well-known effect of hydrogen embrittlement in titanium forbids the use of hydrogen during the heat treatment and a pure atmosphere or a high vacuum is the only choice to optimize the atmosphere for stress relief annealing of L-PBF samples.

For stress relief heat treatment Carbolite Gero offers three product lines: The GPCMA, GLO and VL type furnaces. Attached an overview on the most important properties.

	Atmospheric pressure stress relieving in the GPCMA product line					
						
Item	**GPCMA/37**	**GPCMA/56**	**GPCMA/117**	**GPCMA/174**	**GPCMA/208**	**GPCMA/245**
T_{max}	1000°C	1000	1000	1000	1000	1000
Working pressure	1000 mbar	1000	1000	1000	1000	1000
Usable volume	37 l	56	117	174	208	245
Maximum temperature under vacuum	20°C	20	20	20	20	20
Lowest Oxygen level	<50 ppm	50	50	50	50	50
Number of heating zones	2	2	2	2	2	2
Leakage rate	<5x10E-1 mbar l/s	<5x10E-1	<5x10E-1	<5x10E-1	<5x10E-1	<5x10E-1
Power	17 kW	24	30	36	39	45
Weight	220 kg	485	608	705	800	950
Uniform volume	100x250x300 [mm]	150x275x300	200x400x550	350x400x550	350x400x800	400x500x500

	Vacuum stress relieving in high vacuum in the GLO product line					
						
Item	**GLO 10**	**GLO 40**	**GLO 75**	**GLO 120**	**GLO 260**	**GLO 400**
T_{max}	1100°C	1100	1100	1100	1100	1100
Working pressure	10E-5 – 10E-3 mbar	10E-5 – 10E-3 mbar	10E-5 – 10E-3 mbar	10E-5 – 10E-3 mbar	10E-5 – 10E-3 mbar	10E-5 – 10E-3 mbar
Usable volume	37 l	56	117	174	208	245
Maximum temperature under vacuum	1000°C	1000	900	800	750	750
Lowest Oxygen level	2,1x10E-3 – 2,1x10E-1 ppm	2,1x10E-3 – 2,1x10E-1 ppm	2,1x10E-3 – 2,1x10E-1 ppm	2,1x10E-3 – 2,1x10E-1 ppm	2,1x10E-3 – 2,1x10E-1 ppm	2,1x10E-3 – 2,1x10E-1 ppm
Number of heating zones	2	3	3	3	3	4
Leakage rate	<5x10E-3 mbar l/s	<5x10E-3	<5x10E-3	<5x10E-3	<5x10E-3	<5x10E-3
Power	14 kW	25	40	60	70	80
Weight	500 kg	1200	1500	2000	2500	3000
Uniform volume	150x150x400 [mm]	200x200x600	250x250x600	300x300x700	400x400x800	400x400x1200

	Vacuum stress relieving in high vacuum in the V-L product line		
			
Item	**V-L 180-300**	**V-L 300-400**	**V-L 450-600**
T_{max}	1100°C	1100	1100
Working pressure	10E-6 – 10E-4 mbar	10E-6 – 10E-4 mbar	10E-6 – 10E-4 mbar
Usable volume	7,6 l	28,2	95,4
Maximum temperature under vacuum	1050°C	1050	1050
Lowest Oxygen level	2,1x10E-4 – 2,1x10E-2 ppm	2,1x10E-4 – 2,1x10E-2 ppm	2,1x10E-4 – 2,1x10E-2 ppm
Number of heating zones	3	3	3
Leakage rate	<5x10E-3 mbar l/s	<5x10E-3	<5x10E-3
Power	14 kW	42	58
Weight	700 kg	1200	1800
Uniform volume	Ø180x300 [mm]	Ø300x400	Ø450x600

7. Acknowledgment

The author acknowledges the valuable support of the university of Pforzheim on this project. The EDX measurements were kindly made by U. Kiefner and M. Mungenast.