Mechanisms of surface deoxidation of stainless steels in vacuum brazing processes

C. Kunz, M. Marschewski, W. Maus-Friedrichs, Clausthal-Zellerfeld / D; S. Schöler, U. Holländer, and K. Möhwald, Hannover / D

Stainless steels are in widespread use due to their excellent mechanical properties. Their corrosion resistance stems from native oxide layers formed on the surfaces of stainless steels, only a few nanometers thick and mainly consisting of a mixture of iron and chromium oxides and hydroxides. This oxide layer is the main inhibitor of wetting the surface with molten braze, a critical step when choosing to join those steels by the means of vacuum brazing. For successful joining, the removal of those oxide layers is a necessity. While procedural knowledge is abundant, fundamental understanding of thermophysical and chemical processes is lacking.

The deoxidation of two stainless steels is studied, which differ drastically in terms of brazability: austenitic AISI 304 (1.4301) is easily brazed and ferritic AISI 446 (1.4762) is procedurally demanding. The effect of the heat treatment is reproduced on a laboratory scale. Chemical analysis before and after heat treatment is carried out by XPS and AES, optical and topographical properties are studied by CLSM and SEM. Due to the surface sensitivity of these methods, changes in the passivation layer can be detected.

1   Introduction

Deoxidation is a critical step when choosing to join parts by the means of brazing. Removing the oxide layer on the surface means that chemical bonds are broken, thus increasing the surface free energy. This is the origin of the driving force for wetting a surface with a droplet of molten braze, initiating metallurgical bonds between surface and braze. Those bonds are dependent on material combination and brazing temperature and can consist of two bonding types. The first bonding type is the formation of intermetallic phases, i.e. phases in which the constituent elements have different atomic arrangements than in solid form. This bonding type ususally, but not exclusively takes place during soldering, i.e. joining below 450 °C. The second bonding type is alloying, that is the formation of a solid solution of braze and parent material in which the constituent elements are mixed on an atomic level. Below 450 °C, this doesn't occur and is thus called brazing in contrast to soldering. It should be noted that this division isn't strict and is based on historic origins.

When using vacuum brazing, one cannot rely on the chemical removal of the oxide layer since fluxes are not being used. In this case, joining has to be carried out in an oxygen free atmosphere, which requires vacuum or inert gas. It is then assumed that the partial pressure of oxygen in the atmosphere is so low that the reduction of the oxide layer is energetically favoured. This originates from the variation of the Gibbs energy of the oxidation reaction. When a metal (denoted as M) reacts with oxygen to form the metal oxide $M_n O_m$, the variation of Gibbs energy ΔG per mole of produced oxide can be written as:

$$\Delta G_{\frac{m}{2} M_n O_m} = R \cdot T \cdot \ln(p_{O_2}^M), \tag{1}$$

where R denotes the universal gas constant ($R = 8{,}314$ J·mol⁻¹K⁻¹), T the absolute temperature in Kelvin and $p_{O_2}^M$ the dissociation pressure of the metal oxide. It is assumed that if the oxygen partial pressure is smaller than said dissociation pressure, reduction of the oxide layer will occur. The application of these facts is ususally done by using Ellingham diagrams [1].

These diagrams can't explain why stainless steels can indeed be joined by vacuum brazing, although chromium oxide, the main constituent of the steel's passivation layer, should not be reduced in the given atmospheres where oxygen partial pressures of about 10⁻⁶ mbar are common. This is why a thorough investigation of the thermophysical and chemical processes taking place during deoxidation is needed.

In very first investigations, two steels have been analysed. The first steel is easily brazed austenitic AISI 304. This steel is commonly used in sanitary environments. The second steel is ferritic AISI 446, which is much more demanding in regards of joining. Although its high temperature resistant properties would make this steel an ideal candidate for applications in e. g. solid oxide fuel cells, it has proven itself to be quite difficult to be joined due to bad wettability.

The two steels were heated up to 1000 °C in an ultra high vacuum chamber with a base pressure of 10⁻¹⁰ mbar. During the heat treatment, the change in oxygen amount on the surface was monitored by X-ray photoelectron spectroscopy (see section 2). The relative intensities are plotted as a function of temperature, **Fig. 1**. It is clearly visible that the surface of easily brazed AISI 304 is completely oxygen free beyond 750 °C, while this only happens for AISI 446 once 1000 °C is reached. This significant difference is an indicator for the fact that AISI 446 cannot be brazed in a vacuum furnace at about 800 °C: the oxide layer might not yet be completely removed from the surface and prevents wetting.

For further investigations, both steels underwent both chemical and optical analysis. Chemical analysis was split in two parts: surface sensitive X-ray photoelectron spectroscopy and Auger electron spectroscopy. Optical analysis was done by confocal laser scanning microscopy and scanning electron microscopy. Heat treatment during vacuum brazing is recreated on a laboratory scale.
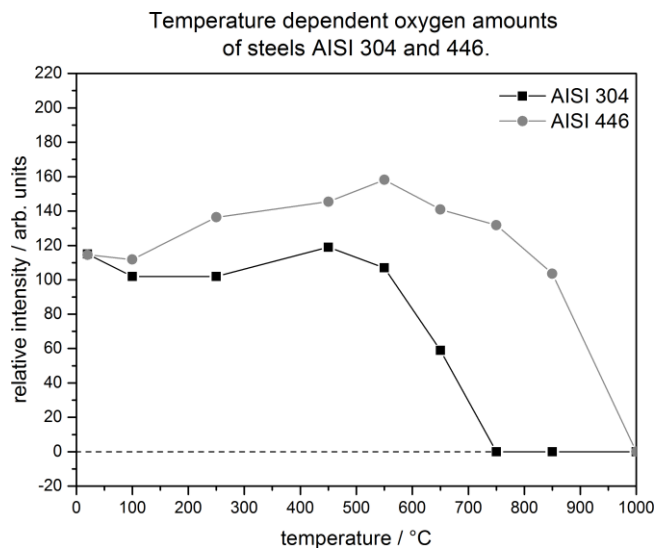
Fig. 1: Temperature dependent oxygen amounts of steels AISI 304 and 446 measured in situ during heat treatment.

2　Experimental

Chemical analysises were carried out by different methods explained below.

X-Ray Photoelectron Spectroscopy (referred to as XPS in the following) is a surface sensitive method, in which a material is illuminated by X-radiation of known energy. In this work, the Al K_α and Mg K_α lines were used, with energies of 1486.4 eV and 1253.6 eV respectively. Due to X-ray impact, electrons are released from the sample by the photoelectric effect. Those electrons posess kinetic energy that allows conclusions about the chemical state of the emitting atoms. In a XP spectrum, peaks that can be attributed to specific atomic orbitals are recorded – thus giving an element-specific fingerprint. Therefore, the chemical composition can be determined. Since electrons undergo inelastic scattering processes on their way out of the sample, only electrons out of the topmost atomic layers can be released into vacuum and be detected. This leads to an information depth of a few nanometers, thus to a very high surface sensitivity [2]. Electron energies are filtered by a hemispherical electron analyser operated at a pass energy of 44 eV which ensures a sufficient resolution. Several spectra are recorded and averaged to minimize noise. All measurements were carried out in an ultra high vacuum analysis chamber with a base pressure of $1 \cdot 10^{-10}$ mbar.

Auger Electron Spectroscopy (AES) is a highly surface sensitive analysis tool, in which electrons are released due to the Auger effect by impact of a primary electron beam. The primary electrons are accelerated to kinetic energies in the order of magnitude of 5-10 keV. The Auger effect takes place when an inner shell vacancy in an atom is filled by an electron of higher energy. The excess energy can be released as radiation (photon) or transmitted to another electron, the Auger electron, which is propulsed into vacuum. In analogy to XPS, the kinetic energy of the released electron is specific for the former chemical state of the emitting atom. Auger electrons are only emitted from the topmost atomic layers, providing an information depth of about 2 nm [2].

Auger spectroscopy was carried out with an Omicron NanoSAM (scanning Auger electron microscope) with a lateral resolution of 5 nm. Primary beam energy was 5 keV, beam current 1.5 nA.

Optical and topographical changes were studied by microscopy.

Confocal Laser Scanning Microscopy (CLSM) is a microscopy technique in which the sample is scanned with a laser beam. By detecting reflection maxima, the picture is built line by line. This technique combines classic wide field microscopy with topographical information. The resolution limit is significantly lower than with a conventional light microscope.
A Keyence VK-X210 with a laser wavelength of 408 nm was used.

Scanning Electron Microscopy (SEM) is frequently combined with AES and provides imaging of the measured sample. This way, specific areas can be measured, with a lateral resolution of a few nanometers for AES. An acceleration voltage of 5 keV was used.

Heat treatments were carried by a Tectra flange mounted boralectric stage heater in one apparatus, combined with Quadrupol Mass Spectrometry (QMS) in a Hositrad Multi Gas Analyser MGT with Thermal Desorption. Temperature measurement and regulation is ensured by a type K thermocouple.
In the other apparatus, i.e. the XPS vacuum chamber, electron impact heating is performed in a molybdenum sample holder, in which voltage is applied to a current-carrying filament. This accelerates electrons towards the sample on top of the filament, already heated by incandescence to up to 700 °C in the case of polished steel. Temperature is measured by an IMPAC 140 pyrometer.

The compositions of AISI 304 and 446 are given below in at.% and wt% respectively, **Table 1**. All values are maximum amounts.

Table 1: Compositions of AISI 304 and AISI 446 in wt.% and at.%. All values are maximum amounts.

Element	AISI 304 (1.4301)		AISI 446 (1.4762)	
	wt.%	at.%	wt.%	at.%
C	0,07	0,3	0,12	0,5
Si	1,0	2,0	1,4	2,6
Mn	2,0	2,0	1,0	1,0
P	0,045	0,08	0,04	0,07
S	0,03	0,05	0,015	0,02
Cr	19,5	20,8	26,0	26,5
Ni	10,5	9,9	-	-
N	0,1	0,39	-	-
Al	-	-	1,7	3,3
Fe	66,8	66,7	69,7	66,1

Chemical analysis of the surface by XPS was carried out on samples previously polished and cleaned in an ethanol ultrasonic bath. The samples were circular with a diameter of 10 mm. Those samples were electron impact heated to 1200 °C for 15 minutes and XPS studies were done before and afterwards.

For studying change in grain structure, samples were cut in half and etched, with V2A pickling solution and nitric acid for AISI 304 and 446 respectively. Those samples were studied by CLSM and AES/ SEM, one half of each underwent heat treatment by stage heating up to 1200 °C for 15 minutes accompanied by mass spectrometry, the other half was left as is to ensure comparability.

3   Results

Surface analysis of AISI 304 XP spectra of AISI 304 before and after heating to 1200 °C (grey and black line respectively) are shown, **Fig. 2**. The as-received sample shows organic surface contaminations, which is common for all surfaces in ambient conditions without any in situ cleaning procedure. Signals of iron and chromium, at about 710 eV and 577 eV respectively, can be attributed to oxide compounds and are indicators of a passivated steel surface. Molybdenum may originate from the sample holder and cannot be attributed to the steel surface with certainty. Calcium is most likely a contaminant in the steel and was also detected by energy dispersive X-ray spectroscopy in the bulk of another sample (these measurements are not presented in this work).

After heating to 1200 °C and holding for 15 minutes, another XP spectrum was recorded. With an amount of over 60 %, iron is now the main component of the annealed steel surface, with significant quantities of chromium, nickel and sulfur. Molybdenum could originate from the sample holder or result from segregation to the surface. Both metal oxides and organic contaminations have vanished. The carbon amount is reduced to 0 % from more than 60 % before heat treatment. Oxygen only remains as trace, reduced to an amount of 1.5 % compared to nearly 30 % before heating.

A SEM picture of the etched and unheated AISI 304 and the corresponding Auger spectrum are shown, **Fig. 3**. Etching reveals the grain structure that is visible in the picture, along with what seems to be a chromium rich carbidic segregation as suggested by the associated Auger spectrum.
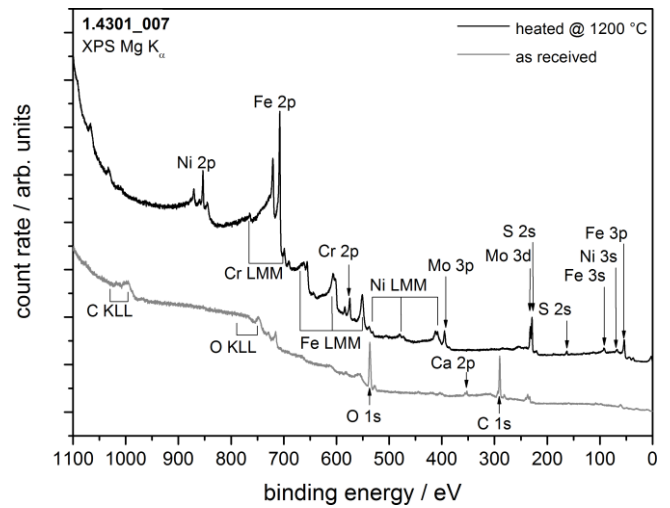

Fig. 2: XP spectra of a AISI 304 (1.4301) sample before (grey line) and after heating to 1200 °C (black line).
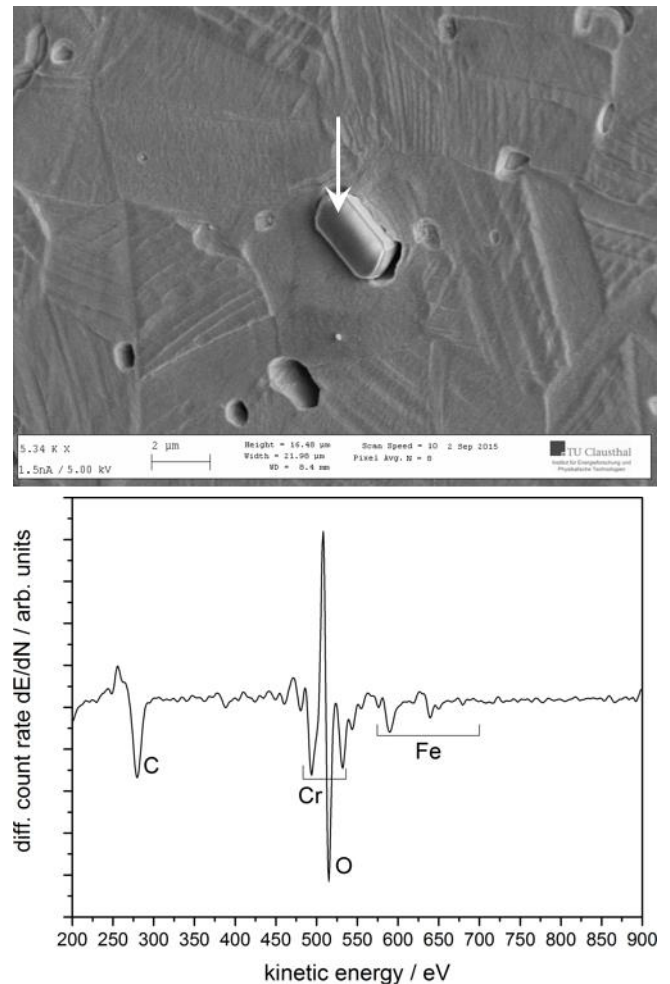

Fig. 3: SEM picture of etched AISI 304 before heating. The according Auger spectrum is recorded on the segregation marked by the arrow.

Surface analysis of AISI 446 XP spectra of AISI 446 before (grey line) and after heating to 1200 °C (black line) are shown, **Fig. 4**. The as-received sample shows organic surface contaminations like AISI 304, also along with iron and chromium being attributed to a passivated steel surface. After heating, several elements have enriched at the surface, mainly titanium, rhenium and niobium while iron and chromium are still present like before heating. It has to be noted that in contrast to AISI 304, substantial amounts of both carbon and oxygen remain after heating (18 % and 11 % respectively). A shift in binding energy in the carbon signal seems to indicate the presence of stable carbides, which posess a lower binding energy than e.g. organic compounds.
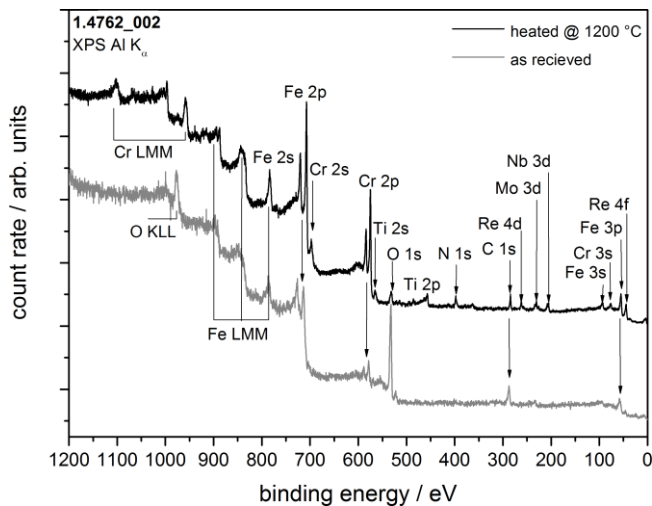

Fig. 4: XP spectra of an AISI 446 (1.4762) sample before (grey line) and after heating to 1200 °C (black line).

Auger spectra were recorded of etched and heated samples. A SEM picture shows a region on etched and heated AISI 446, **Fig. 5**. White segregations can be seen that were analysed by AES, the spectrum can be seen below the SEM picture. In the spectrum, neither iron nor chromium can be detected. Since the only components in this energy interval seem to be carbon, oxygen and titanium, it is safe to assume that the segregations consist of titanium oxide.
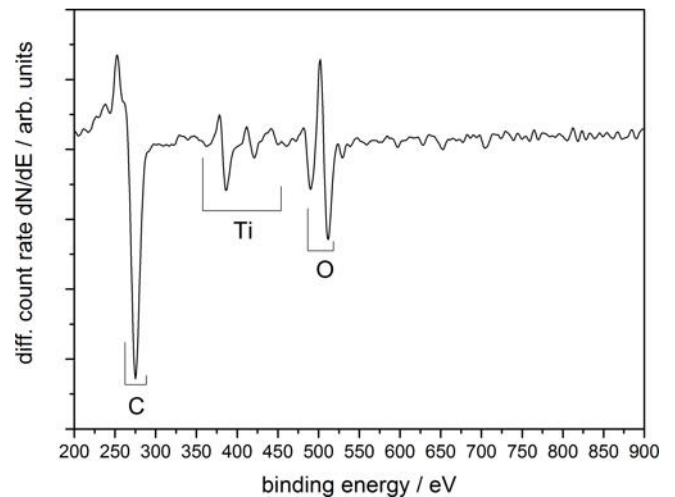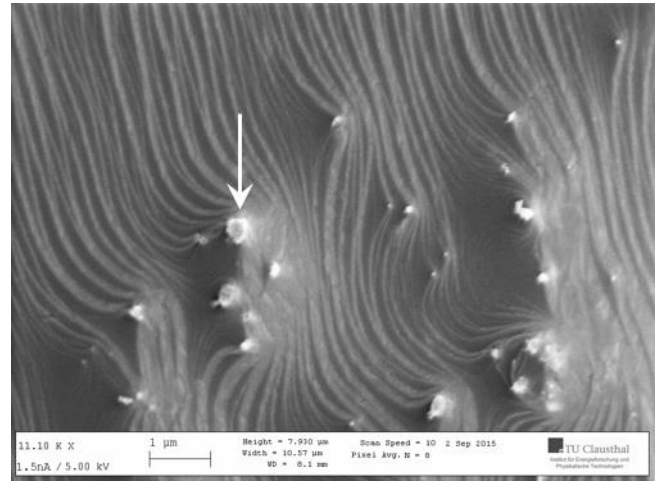

Fig. 5: SEM picture of etched and heated AISI 446. The white segregations (marked by white arrow) seem to consist of mainly titanium oxide as indicated by the recorded Auger spectrum also shown.

Confocal laser scanning microscopy
A compilation of CLSM pictures of etched and heated steels is shown, **Fig. 6**. On the top left, etched AISI 304 is seen, on the top right, etched and heated AISI 304. On the bottom left, etched AISI 446 is shown, on the bottom right, etched and heated AISI 446.
AISI 446 seems to have a much coarser grain structure than 304 both before and after heat treatment. The grain boundaries after heat treatment are much sharper. Coarse phases as seen in the middle of the picture on the bottom left are the result of etching and have the same composition as smooth regions as is shown by EDX measurements, which are not shown in this work.
Inclusions seen on AISI 304 seem to have dissolved after heating. The austenitic structure is clearly visible. After heating, the grain structure coarsens considerably, which is a known effect of heat treatment. Due to very small sample sizes, the cooling rate was very high after shutting down heating, which led to freezing of the grain structure.
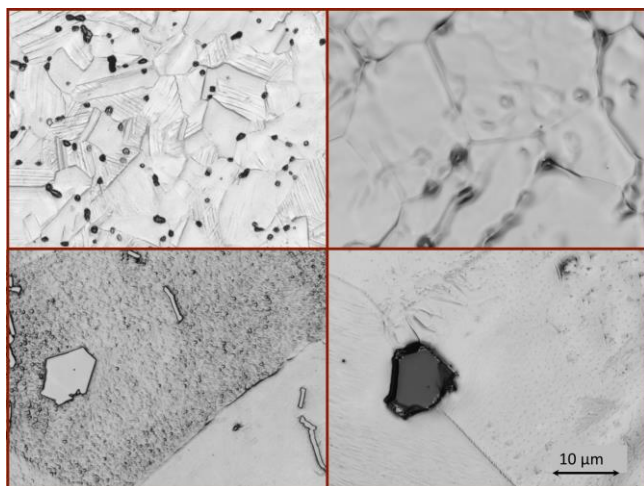
Fig. 6: : Compilation of CLSM pictures of etched and heated steels. Top left: etched AISI 304, top right: etched and heated AISI 304. Bottom left: etched AISI 446, bottom right: etched and heated AISI 446. All pictures show a 1500-fold magnification. The scale bar on the bottom right applies to all pictures.

Mass spectrometry/ thermal desorption Heat treatment by stage heating was accompanied by Quadrupol Mass spectrometry as explained above. Mass spectra were recorded for both steels, each recorded after holding 1200 °C for 15 minutes. The survey spectra are shown on top and a magnification of a smaller mass area below, **Fig. 7**. The grey lines denote AISI 446, the black lines AISI 304. The spectra mostly show similar features, like the peaks at 2 and 18 amu attributed to molecular hydrogen and water respectively.

Those peaks are very common, hydrogen desorption especially is a known phenomenon for stainless steels, studied extensively since it limits the best pressure achievable in ultra high vacuum analysis chambers [3]. Water absorbs on all surfaces and therefore dersorbs when heated. It has to be noted that water could also desorb from the chamber walls heated in the process as well. Two interesting features are both the peaks at 28 amu and 44 amu, attributed to nitrogen or carbon monoxide and carbon dioxide respectively. Since 28 amu can be attributed to both nitrogen and carbon monoxide, it is important to observe the peaks at 12 and 14 amu, attributed to atomic carbon and nitrogen respectively, hence the magnification of those peaks is shown. It is assumed that if there are peaks at 12 and 44 amu and none at 14 amu, then the peak at 28 amu has to be attributed to only carbon monoxide. Since this isn't the case for both steels, it has to be assumed that the 28 amu peak is a superposition of both nitrogen and carbon monoxide signals. In the case of AISI 304, the amount of nitrogen is presumably much higher then the amount of carbon monoxide.

AISI 446 on the other hand shows equal peak height of atomic carbon and nitrogen, meaning that the contribution of carbon monoxide in the 28 amu signal is higher then with AISI 304.
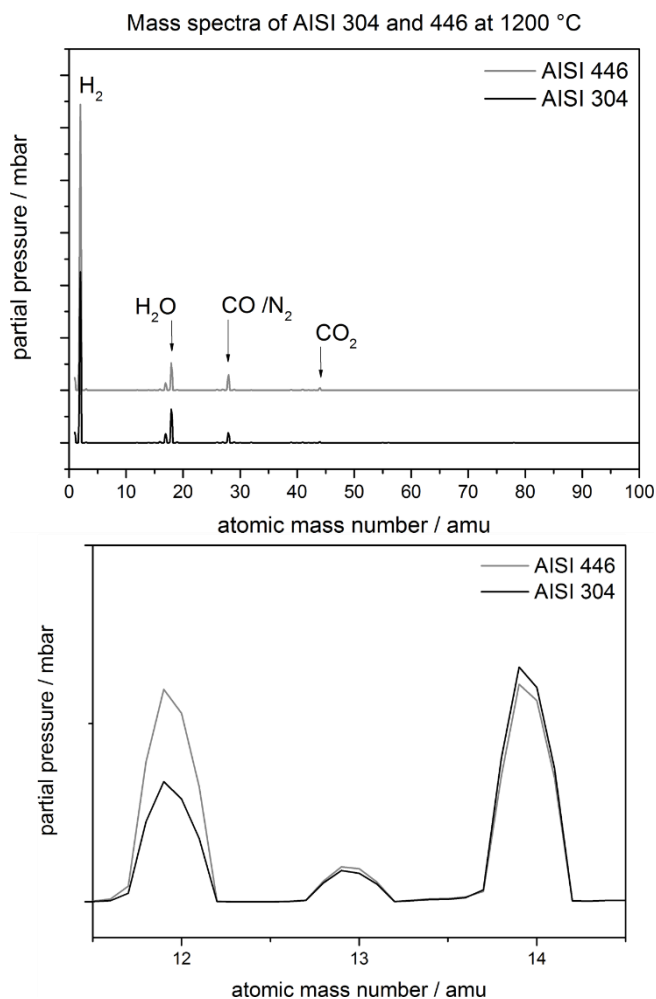

Fig. 7: Mass spectra of AISI 304 (grey line) and 446 (black line) recorded at 1200 °C. The graph below shows a magnification of the area between 12 and 14 amu.

Here, an interesting phenomenon could take place: carbon dissolved in the bulk of AISI 446 could diffuse to the surface and reduce oxide layers, resulting in bare metal and the desorption of carbon monoxide created in the process. (See the work of Kozlova et al. for a detailed study [4]). Whether or not this process takes place, and whether it takes place with AISI 304 too has to be investigated further.

4   Conclusion

AISI 446 shows significant enrichment of bulk elements on the surface, as shown by XPS and AES. Especially titanium seems to segregate and form oxide inclusions, which remain undissolved by heat treatment. Neither carbon nor oxygen can be completely removed from the surface. Possibly AISI 446 undergoes phase transformations that leaves the surface saturated (e. g. with thermodynamically titanium oxide), thus inhibiting wetting with molten braze.

AISI 304 on the other hand has no residual oxygen or carbon on the surface. Removal of carbon and oxygen possivly leaves the surface unsaturated, promoting

wetting due to higher surface energy. No new stable phases seem to be formed.

5 Acknowledgements

6 References

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