Surface development of a brazing alloy during heat treatment

- A comparison between UHV and APXPS

L Rullik¹, N Johansson¹, F Bertram², J Evertsson¹,
T Stenqvist³ and E Lundgren¹

¹ Division of Synchrotron Radiation Research, Department of Physics,
Lund University, Box 118, 221 00 Lund, Sweden

² DESY Photon Science, Notkestr. 85, 226 07 Hamburg, Germany

³ Gränges Research and Innovation, 612 81 Finspång, Sweden

E-mail: lisa.rullik@sljus.lu.se

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Abstract. In an attempt to bridge the pressure gap, APXPS was used to follow the surface development of an aluminum brazing sheet during heating in an ambient oxygen-pressure mimicking the environment of an industrial brazing furnace. The studied aluminum alloy brazing sheet is a composite material consisting of two aluminum alloy standards whose surface is covered with a native aluminum oxide film. To emphasize the necessity of studies of this system in ambient sample environments it is compared to measurements in UHV. Changes in thickness and composition of the surface oxide were followed after heating to 300°C, 400°C, and 500°C. The two sets presented in this paper show that the surface development strongly depends on the environment the sample is heated in.

Keywords: brazing, aluminum alloy, APXPS, oxide thickness

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1. Introduction

Aluminum alloys are one of the most commonly used lightweight metallic materials. This is due to their characteristic properties: low density, high strength, good thermal conductivity, and high corrosion resistance. The good corrosion resistance of aluminum alloys is based on the rapid formation of a stable and surface covering aluminum oxide layer. The thickness of this native aluminum oxide layer is widely dependent on the underlying substrate[1] and its formation and composition has been subject of previous studies[2, 3, 4, 5].

For their various industrial applications, compounds made out of aluminum alloys are often required to be permanently joined which is in the case of the here investigated composite aluminum alloy designed for automotive heat exchangers realized by brazing. Brazing is a hot joining process in which temperatures above 450°C but below the solidus of the parent material are used. This allows for selective melting of the outer alloy, the braze cladding, as shown in figure 1. The molten braze cladding wets the surface and is drawn between the work pieces by capillary forces to form the joint upon cooling.

A major obstacle during the industrial brazing process is the removal of the surface oxide and the prevention of re-oxidation since the predominant surface oxide made of alumina has a high melting range, which is from 2040°C to 2050°C. Therefore, vacuum, protective atmosphere, or flux brazing are commonly used for the manufacturing of aluminum heat exchangers. The major advantage of vacuum brazing over flux brazing is the absence of fluxes, which impose a hazard for workers and environment, resulting in a clean surface, and the possibility to use age hardenable alloys alloyed with magnesium. Vacuum brazing for automotive heat exchangers is typically performed at pressures ranging from 0.5 mbar[6] down to the high vacuum regime. The realization of UHV in brazing furnaces is not cost effective.

The changes occurring at the surface during brazing have been of research interest for several decades using a range of experimental techniques[7, 8]. Previous studies have

Figure 1. Model of aluminum brazing sheet. In this study an AA3003 is used as core material and AA4104 as braze cladding. The surface of the composite material is covered by an aluminum oxide layer.

been performed under strict UHV conditions and/or with *ex situ* preparations[9, 10]. To understand the chemical changes occurring during the industrial process both approaches can be deceptive since they only depict extreme cases, either a dearth or excess of oxygen in the sample environment.

In this study we compare the surface development after heat treatment of an industrial brazing alloy designed for heat exchanger applications in UHV and *in situ* employing an oxygen atmosphere similar to the industrial process. This was achieved by using ambient pressure x-ray photoemission spectroscopy (APXPS), which allowed us to follow the chemical changes, variations in the oxide thickness as well as oxide composition. The differences seen between the UHV and ambient pressure data demonstrate the importance of studying applied materials in industrial like conditions since the chemical composition of the surface near region is highly dependent on the surrounding atmosphere.

2. Experimental Procedure

The APXPS measurements were performed at the MAX-II storage ring at the Swedish National Synchrotron Radiation facility, MAX IV laboratory, Sweden. Its beamline I511 is an undulator beamline that provides photons in the energy range of 30-1500 eV[11]. The APXPS branch[12] of the SPECIES beamline[13] is equipped with a SPECS Phoibos 150 NAP hemispherical analyzer. The experimental endstation's vacuum system has a background pressure in the low 10^{-10} mbar range. To allow *in situ* experiments in pressures up to 25 mbar a reaction cell inside the analysis chamber can be attached to the analyzer. The sample is irradiated with photons incoming at an angle of 45° and the XP spectra were collected in normal emission geometry.

Prior to the experiments the samples were degreased with acetone and ethanol in an ultrasonic bath. The brazing alloy samples were spot welded into small envelopes of Ta-foil with a 6 mm wide opening to prevent the possible spilling of molten alloy within the UHV chamber. The encased samples were mounted on a transferable stainless steel sample plate. The temperatures were measured with a chromel-alumel thermocouple (type K) which was spot welded onto the sample holder since spot welding onto the alumina surface was not possible. Due to the position of thermocouple an error in the measured temperature is estimated to be $\pm 15\%$, where it is more likely that actual temperature is higher than the measured temperature since elemental silicon and bismuth were detected after heating to 500°C in UHV indicating the onset of partial melting. Measurements with a pyrometer were not applicable since the reaction cell obscures the line-of-sight onto the sample.

The measurements were performed in two sets using two samples since it is not possible to recover the sample after heating. The first set was obtained under UHV conditions whereas the second set was measured in an atmosphere of maximum 0.01 mbar oxygen to mimic a partial oxygen pressure similar to the actual industrial process, where a maximum total pressure of 0.5 mbar is used [6]. The pressure in the

reaction cell is created by flowing 0.2 SCCM (Standard Cubic Centimeters per Minute, where standard refers to 25°C and 1 bar) of oxygen into the reaction cell. The pressure was measured by a commercial Ceravac (CTR100) full range pressure gauge situated at the exhaust pipe of the reaction cell which through a feedback loop to a valve ensures constant pressure. The gas flow was controlled by commercial flow controllers (Brooks Instruments GF125 Analog I/O).

For both measurement sets, overview spectra and Al 2p spectra were obtained at a photon energy of 1100 eV. At a photon energy of 650 eV XP spectra were measured for O 1s, Al 2p, Si 2p, Mg 2p, and C 1s core levels. Additionally, Al 2p, Si 2p, and Mg 2p XP spectra were recorded at a photon energy of 400 eV. All spectra were collected at room temperature, and after heating to 300°C, 400°C, and 500°C. Further, after heating to 500°C Bi 4f XP spectra were obtained at photon energies of 400 eV and 650 eV.

All spectra were calibrated towards the Fermi edge, when calibration to the Fermi edge was not possible the metallic peak of the Al 2p line was used as reference since its binding energy is well-known [3]. The data were further normalized with respect to beam current and photoionization cross-section. No correction for the attenuation by the oxygen-gas environment was made. Due to the compositional range of the alloy each peak is composed of an unknown number of individual contributions. This results in an overall wide peak. Hence, asymmetric Voigt functions were curve fitted to the O 1s, Al 2p, and Si 2p lines to obtain values for the chemical shift and the integrated intensity. For the Mg 2p peaks a Gaussian line shape was used as the large amount of non-stoichiometric oxides completely covers the natural line width. Linear backgrounds were subtracted from the O 1s, Al 2p, and Mg 2p spectra whereas polynomial backgrounds were used for the Si 2p data. The background shapes were chosen as to represent the acquired data outside the near-peak region. The figures showing derived values, thickness and integrated intensities, consistently use light blue for quantities of the UHV measurements and red for the ones performed in an ambient oxygen environment. Further, the same markers are used for the same photon energy.

Gränges Research and Innovation provided a cold rolled aluminium sheet that was commercially produced. The core material is the non-heat treatable aluminum-manganese alloy AA3003. The aluminum-silicon alloy AA4104 was used as braze cladding. The chemical composition of the sample is given in Table 1. The total thickness of the brazing sheet is 0.42 mm whereof the outer 7.5% on both sides consist of the braze cladding. To ensure maximum comparability between the two samples, they were cut from one sheet and therefore both samples contain on average the same amount of alloying and trace elements. This also implies that they were exposed to the same production environment, i.e. temperature, humidity, contaminants from rolling, etc. However, local inhomogeneities within the samples cannot be avoided for these industrial material.

Table 1. Melt composition of the brazing alloy. Quantities given in wt. %.

part	alloy	Si	Fe	Cu	Mn	Mg	Bi	others
core	AA3003	0.13	0.50	0.11	1.13	0.03	0.00	< 0.01
clad	AA4104	10.16	0.17	0.002	0.00	1.34	0.12	< 0.015

3. Results and Discussion

To compare the changes in surface development in UHV to an oxygen environment two samples were measured. The overall surface composition is illustrated by the overview spectra acquired at a photon energy of 1100eV, see figure 2 a) for the UHV case and b) for the ambient oxygen atmosphere, respectively. For both samples, the main elements present in the surface near region are aluminum, oxygen, magnesium, silicon, and carbon. Additionally, in the UHV case bismuth was detected after heating to 500°C. Even though the braze cladding and core alloy contain a significant amount of iron, see table 1, none was detected at the surface-near region. Further, no manganese or copper from the core alloy were observed. These observations from the overview scan were confirmed by detailed regional scans for the respective core levels. Therefore, the analysis of the surface development focuses on aluminum, silicon, magnesium, and oxygen.

To ensure that the samples used for the measurements are similar despite their local inhomogeneity XP spectra of the sample used for the measurements in the oxygen were recorded before the prior to oxygen exposure. Comparing the XP overview spectrum of the second sample before the filling of the reaction chamber at room temperature, see figure A1, with the overview spectrum of the UHV sample at room temperature shows that the pristine surface compositions are similar. Hence, changes occurring during the heat treatment are originating from the different atmospheres and not from differences within the samples.

The influence of the ambient oxygen environment at room temperature was investigated by comparing the APXP spectra with the XP spectra obtained prior to insertion of oxygen into the reaction cell, see figure 2 a). Only a minor change was observed in the C 1s line, see figure A1. Detailed XP spectra on the carbon contamination can be found in the Supporting Information, figure A3.

The corresponding APXP spectra development in the oxygen atmosphere are shown in figure 2 b), where also a small amount of nitrogen was observed after heating to 300°C. The exact origin of the nitrogen is unclear.

Further, new peaks appear after heating to 500°C at binding energies of 687 eV, 447 eV, and 30 eV. These peaks are assigned to F 1s, F KLL, F 2s, respectively. The fluorine signals do not originate from the sample itself but rather from the viton gaskets used in the experimental setup. Viton is a fluoropolymer that can release fluorine at elevated temperatures which explains the sudden occurrence at 500°C. Since the photoionization cross-section of F is very high at a photon energy of 1100 eV[14] the

Figure 2. Overview spectra at 1100 eV in a) UHV and b) ambient oxygen pressure at RT and after heating to 300°C, 400°C, and 500°C showing the composition in the surface near region.

actual amount of F containing compounds in the reaction cell is still minor and no significant influence on the alloy surface development is expected.

3.1. Aluminum

The recorded Al 2p spectra provide information on several properties of the sample. Chemical shift were used to distinguish between the metallic and different aluminum oxides species. Recording XP spectra at different photon energies also gave insight into the chemical composition at different probing depths. Here, detailed Al 2p spectra were recorded at three different photon energies: 400 eV, 650 eV, and 1100 eV. Further, they can be used to estimate the surface oxide thickness through which the photoelectrons are attenuated.

The Al 2p spectra measured at 1100 eV show a great similarity between the UHV and the ambient pressure set with oxygen, see figure A2. There are no major chemical shift during the heat treatment, which suggests that the chemical environment of the bulk oxide remains unchanged. The only major change occurs after heating to 500°C for the sample heated in an ambient pressure of oxygen, where no aluminum signal was

Figure 3. XP spectra for Al 2p measured at a photon energy of 650 eV in a) UHV and b) 0.01 mbar oxygen. d) and e) were collected at a photon energy of 400 eV also for UHV and the oxygen atmosphere respectively. The oxide thicknesses calculated according to (1) are shown as a function of temperature in c). The continues line indicates the average thickness. The "above Δ " represents the estimate that the surface oxide thickness in the ambient oxygen pressure after heating to 500°C is greater than 8.8 nm as explained in section 3.3.

detected.

The more surface sensitive Al 2p spectra obtained at photon energies of 650 eV and 400 eV, see figure 3, show, however, variations in the oxide peak position and intensity component during heat treatment. To deconvolute the oxide peak into different components by curve fitting is not applicable in the case of this sample since the composition of the alloy allows for the formation of a wide range of non-stoichiometric oxides whose binding energy gradually changes with composition[15]. To follow the shifts in binding energy of the oxide component their relative position towards the metallic aluminum peak is listed in table 2. The minimal range of compounds that need to be addressed to understand the changes in the surface near region and their resulting binding energy shifts are non-stoichiometric aluminum oxide ($\text{Al}_{2-x}\text{O}_3$)[16], aluminum oxide (Al_2O_3)[17], magnesium aluminate (MgAl_2O_4)[18], and aluminum silicate[19], metallic aluminum, here named in the order of decreasing binding energy.

In the Al 2p spectra for the UHV case, see figure 3 a) and d), large binding energy shifts in the oxide component were observed after heating. The changes in binding energy are especially pronounced at the more surface sensitive photon energy of 400 eV as shown in table 2. At RT the oxide component in the UHV case has a relative shift of 2.63 eV at a photon energy of 400 eV and 2.57 eV at a photon energy of 650 eV, which is 0.18 eV and 0.3 eV higher, respectively than for the measurements in ambient

Table 2. Binding energy shifts of aluminum oxide peak relative to the metallic peak at a binding energy of 73 eV. Values were obtained by curve fitting asymmetric Voigt functions with a linear background to both peaks.

Al 2p	RT	300°C	400°C	500°C
UHV, 650 eV	2.57	2.84	2.82	2.58
UHV, 400 eV	2.63	3.01	2.68	2.34
O ₂ , 650 eV	2.39	2.40	2.92	–
O ₂ , 400 eV	2.33	2.31	2.83	–

oxygen conditions. This indicates that more magnesium aluminate is present closer to the surface and more pronounced in the ambient oxygen environment[15, 18, 16]. This interpretation is supported by the Mg 2p spectra shown in figure 5 where the RT peaks also have a higher binding energy for the UHV case related to magnesium oxide than for the ambient oxygen case for which lower binding energies suggests the presence of magnesium aluminate[16]. By heating to 300°C in UHV the oxide component in figure 3 d) shifts to higher binding energies implying increased formation of aluminum oxide and non-stoichiometric aluminum oxide. Through further heating the oxide components decreases in binding energy again, which can be related to the development of more stoichiometric aluminum oxide, magnesium aluminate, and aluminum silicate. Again the formation of magnesium aluminate is also seen in a decrease in binding energy in the Mg 2p line, especially at a photon energy of 400 eV as shown in figure 5 d).

For the measurements in ambient oxygen pressure a major shift in binding energy for the oxide peak was observed at a temperature of 400°C for both photon energies as shown in figure 3. The lower relative binding energy of the oxide components at RT and 300°C can be assigned to magnesium aluminate[15, 18, 16]. This designation is supported by the binding energy of the Mg 2p line at the same temperatures, see figure 5 b) and d). By heating to 400°C a shift to higher binding energies was observed, hence the magnesium aluminate transforms into aluminum oxide and magnesium oxide. The variations in the binding energies of the oxide peaks relative to the metallic peaks at different photon energies as shown in table 2 can be explained by the change in ratio between magnesium aluminate and aluminum oxide.

In an effort to determine the surface oxide thickness, two asymmetric Voigt functions, one for the metallic and one for the oxide component, were fitted with a linear background. The calculated integrated signals are summarized in table A2,A3 and A4 for the spectra acquired at three different photon energies for the UHV and the oxygen atmosphere case.

The aluminum oxide thickness, d , was calculated according to (1)[20] ,

$$d = \lambda_{OX} \sin(\theta) \ln \left(\frac{N_{ME} \lambda_{ME} I_{OX}}{N_{OX} \lambda_{OX} I_{ME}} + 1 \right) \quad (1)$$

in which λ is the photoelectrons inelastic mean free path (IMFP), N is the volume density,

where the ratio of the volume densities calculated from the densities given in table A1 is $N_{ME}/N_{OX} = 1.4$ [21], and I is the integrated signal for the aluminum oxide (OX) and the metallic aluminum (ME). Further, θ is the photoelectron emission angle, which in this case was 90° due to the normal photoelectron emission geometry. The IMPF was calculated using the software QUASES-IMFP-TPP2M [22] based on [23, 24], where a binding energy of 72 eV for the metallic aluminum and 75 eV for the aluminum oxide were used to calculate the electron kinetic energy. An overview of the values for λ is given in table A1.

The development of the oxide thickness as a function of heating temperature is shown in figure 3 c). It can be seen that the oxide thickness is very similar for the UHV and the oxygen environment at RT and 300°C . After heating to 400°C the oxide thickness increases for both cases but in the oxygen atmosphere case the increase is about 1.8 nm whereas the increase in the UHV case is less than a 1 nm. In the UHV case after heating to 500°C the oxide thickness reduces to less than the initial thickness, whereas in the oxygen environment the oxide thickness continues to increase to such an extent that at 500°C neither a metallic aluminum nor aluminum oxide signal could be observed at any of the employed photon energies. Hence, the oxide thickness could not be calculated. The lack of any aluminum signal in the APXP spectra taken after heating to 500°C indicates that the surface is no longer covered by aluminum oxide but rather by an oxide compound including one of the other alloying elements.

3.2. Silicon

Even though about 10 wt.% of silicon is added to the alloy, it does not exhibit a high abundance in the surface near region when considering the integrated intensities after normalization to the photoionization cross-section. This low abundance of silicon in the surface near region was observed at RT in UHV and in the ambient oxygen environment as shown in figure 4. Asymmetric Voigt functions were curve fitted to the Si 2p data for the set measured at a photon energy of 650 eV and 400 eV for both sample environments in order to follow the development of the elemental and silicon oxide component.

As shown in figure 4 c), heat treatment in UHV leads to an increase in silicon with a large increment of about 100 times between heating to 400°C and 500°C at a photon energy of 650 eV. However, at a photon energy of 400 eV the elemental silicon signal is observed to diminish significantly after heating to 400°C before the pronounced increase after heating to 500°C as illustrated in figure 4 f). The silicon oxide amount increases from RT to 300°C and slightly decreases at 400°C for both excitation energies. Per contra, the development after heating to 500°C differs between the photon energies. The silicon oxide continues to decrease at the more surface sensitive measurement at a photon energy of 400 eV, whereas it increases at a photon energy of 650 eV. Hence, the silicon oxide is less prevalent at the surface. This also leads to a steeper increase of the total silicon amount at the slightly deeper probing depth. The presence of elemental silicon indicates the onset of the partial melting of the braze cladding.

Figure 4. XP spectra of Si 2p obtained at 650 eV in a) UHV conditions and b) in ambient oxygen pressure, d) and e) measured at 400 eV. c) and f) depict the development of silicon, silicon oxide, and the total sum of all integrated silicon intensity versus the heating temperature.

In the ambient case, the silicon behavior differs from that described above. During heating in an oxygen atmosphere, the development of the elemental silicon shows a similar decreasing trend for both excitation energies, see figure 4. At a photon energy of 400 eV the elemental silicon amount is reduced by 50% when heating from RT to 500°C, whereas at 650 eV the elemental silicon amount at RT is twice compared to the amount after heating to 400 eV but no silicon signal was detected at 500°C, see figure 4 b). The absence of the silicon signal at 650 eV can be explained when considering that the photoionization cross-section at 650 eV is about a fourth of the one at 400 eV[14]. Hence, the silicon intensity at 650 eV is lost in the background noise. The silicon oxide amount is only marginally varying between RT and 300°C to slightly increase at 400°C. After heating to 500°C only minute amounts of silicon oxide were detected at a photon energy of 400 eV. Due to the small amount of elemental silicon the total silicon development is governed by the silicon oxide contribution.

The contribution of silicon to the surface composition is in general very little except for heating up to 500°C in UHV. The observation of elemental silicon is under such conditions entirely induced by the UHV environment since the formation of silicon oxide is thermodynamically favored even at elevated temperatures[25].

Table 3. Binding energies of the magnesium oxide peaks. Values were obtained by curve fitting asymmetric Gaussian functions with a linear background.

Mg 2p	RT	300°C	400°C	500°C
UHV, 650 eV	51.80	51.74	51.88	51.78
UHV, 400 eV	51.75	51.95	51.76	51.55
O ₂ , 650 eV	51.62	51.46	52.08	52.21
O ₂ , 400 eV	51.57	51.42	52.05	52.05

3.3. Magnesium

The development of the Mg 2p line was followed at two photon energies, 650 eV and 400 eV, for both sample environments as shown in figure 5. For both cases only different magnesium oxide species and no metallic magnesium were observed in the surface near region. The single oxide peaks are convoluted peaks of magnesium oxide, hydroxide and magnesium aluminate in varying stoichiometries, where lower binding energies indicate the presence of magnesium aluminate[18, 16], as discussed in section 3.1. Table 3 summarizes the During the heating in UHV the amount of magnesium oxides increases up to 400°C and then marginally decreases after heating to 500°C for both photon energies. In the data set measured in ambient oxygen pressure the amount of magnesium oxide at before heating is already about five times higher than the amount observed at UHV at a photon energy of 400 eV, and at 650 eV it is more than three times the amount found in UHV. Further, the magnesium oxide content continues to increases throughout the heating process in the ambient pressure case in contrast to the UHV situation. This immense growth of magnesium oxide at the surface also explains why no aluminum signal could be detected after heating to 500°C, see figure 2 and figure 3. This absence of the aluminum signal together with the fact that the surface is covered by magnesium oxide can be used to estimate the minimum thickness of the surface oxide. The probing depth in normal emission geometry, $\theta=90^\circ$, is governed by the attenuation through the material, which can be described in a first approximation by,

$$I(d) = I(d=0)\exp\left(\frac{-d}{\lambda}\right) \quad (2)$$

where I is the intensity, d is the thickness and λ is the IMFP for a specific material at certain excitation energy. By assuming a thickness of 4λ only 1.8% of the photoelectrons will be emitted. Since the resulting intensity in the XP spectrum will be in the level of the background noise, we can assume that the attenuating surface layer is thicker than or equal 4λ as no signal could be separated from the noise. Therefore, we conclude that the magnesium oxide is thicker than 8.8 nm since $\lambda(\text{MgO}, 1025\text{eV})=2.2 \text{ nm}$ [22] because no aluminum signal was observed at an excitation energy of 1100 eV.

Figure 5. XP spectra of Mg 2p measured at 650 eV in a) UHV conditions and b) in ambient oxygen pressure, d) and e) were obtained at 400 eV. c) shows the amount of the magnesium oxide developing during the heat treatments in UHV (blue) and ambient oxygen pressure (red) in a log-scale. The continuous line indicated the averaged signal from both photon energies.

3.4. Oxygen

The thickness and composition of the surface oxide of the brazing alloy are paramount to understand the disruption of the oxide layer necessary for joint formation. In figure 6 the development of the O1 s line during the heating process is shown in a) UHV conditions and b) ambient oxygen environment. In the UHV case, the oxygen signal increases until a temperature of 400°C and then slightly decreases during further heating. For the measurements in the ambient oxygen environment peaks assigned to gas phase oxygen are observed in the binding energy range of 539-541 eV, see figure 6 b). The oxygen signal increases in this case first when heating from RT to 300°C, while decreasing after further heating. After heating to 500°C two distinct components are observed at binding energy of 532.2 eV, assigned to magnesium oxide, and 534.3 eV. This is an indication for the formation of magnesium hydroxide[26, 27, 28]. The formation of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) can be explained by the background pressure of water in the oxygen gas used to create the ambient conditions. Another assignment for the peak at 534.3 eV could be magnesium peroxide (MgO_2)[29], which is difficult to distinguish from magnesium hydroxide by its binding energy position, but thermodynamic calculations and XRD experiments suggest the formation at GPa-pressures of oxygen[30, 31]. Hence, the formation of magnesium hydroxide is more likely.

To estimate the relative composition of the surface oxide it was assumed that the integrated intensity, I , of the oxygen signal should be equal to the sum of the integrated

Figure 6. XP spectra for O1 s at 650 eV measured a) in UHV and b) in ambient oxygen environment. c) and d) shows the integrated oxygen intensity and the relative contribution of the different alloying element oxide components according to (3) in UHV and ambient conditions displayed in log-scale. The total integrated intensity of oxygen is shown in black and the relative contributions of aluminum oxides, magnesium oxide, and silicon oxide are shown in blue, green, and purple respectively.

oxide signals from the alloying elements present at the surface, see (3). Prefactors for the different stoichiometries of the oxides were used. If several oxide components can form the prevalent oxide species was used to assign the prefactor. To accommodate for errors in the total sum a correction factor, k , was introduced.

$$I(O1s) = k \left[\frac{3}{2} I(Al2p)_{OX} + 2 I(Si2p)_{OX} + I(Mg2p)_{OX} \right] \quad (3)$$

By using (3) the relative composition of the surface oxide was estimated. In the UHV case the surface oxide is mainly composed of alumina and even though the relative amount of magnesium and silicon oxide increases during the heat treatment the amount of non aluminum oxide does not exceed 5.5% of the total amount of oxide on the surface, figure 6 c). In contrast, the surface oxide at low temperatures mainly consists of alumina and at higher temperatures transforms into a magnesium oxide and magnesium hydroxide film in the case of the ambient oxygen atmosphere as shown in figure 6 d). This also leads to work function shift, which is reflected by the binding energy shift of the gas phase peaks[32]. After heating to 500°C using the ratio between the magnesium oxide and magnesium hydroxide peak, we can conclude that about 40% of the magnesium oxide is hydroxylated. The contribution of silicon oxide is in the same order of magnitude as for the UHV case but after heating to a temperature of 500°C no silicon contribution

could be observed.

3.5. Other alloying elements

Throughout the measurements no XP signal for iron, copper, or manganese was observed in the surface near region in both measurements set. Only in the case of the UHV heat treatment bismuth was observed after heating to 500°C, see figure A4. The integrated intensity of bismuth at a photon energy of 400 eV is about twice of the integrated intensity at a photon energy of 650 eV indicating that bismuth is situated rather close to the surface. The ability to detect bismuth already after heating to only 500°C can be explained by the increased photoionization cross-section of the Bi 4f line at here employed photon energies. The difference in photoionization cross-section is about one order of magnitude between an excitation with photons from an Al-K α and 650 eV photons[14], making it possible to detect bismuth before its typical occurrence close to the melting temperature of the brazing alloy. In the ambient oxygen environment no bismuth was observed during the measurements.

3.6. Surface development in UHV vs ambient oxygen-pressure

The initial surface oxide thickness is about 5 nm for both samples, indicating that the pristine samples are not heavily affected by the different environment at room temperature. The main difference between heating in UHV and heating in 0.01 mbar oxygen can be found in the thickness compositional development of the surface oxide. In the UHV case the heating leads to a maximum oxide thickness of 6.4 nm after heating to 400°C and a prominent drop in thickness after further heating to 500°C, see figure 3 c), whereas the surface oxide in the ambient oxygen pressure continues to grow throughout the entire heating process reaching a thickness of at least 8.8 nm after heating to 500°C. Further, the composition of the surface oxide in ambient oxygen pressure transforms from a mainly aluminum oxide to a complete magnesium oxide throughout heating to 500°C as shown in figure 6 d). In contrast, the surface oxide in the UHV case remains mainly as an aluminum oxide, where the largest amount of non-aluminum oxide is reached at 500°C of about 5.5% being composed of magnesium and silicon oxides. Two other features only occurred at 500°C in the UHV case: The significant increase in elemental silicon, figure 4 a) and d), and the appearance of bismuth in the surface near region, figure A4. Figure 7 is an attempt to summarize these changes graphically by illustrating the pristine surface composition and after heating to 500°C in UHV and an ambient oxygen environment.

The strong influence of the sample environment is in agreement with thermodynamic expectations, which can be derived from a standard Ellingham diagram[33]. It shows that the standard Gibbs free energy for the formation of magnesium oxide is energetically favored over the formation of aluminum oxide in the presence of oxygen. However, the observed thermodynamic behavior occurs at temperatures lower than expected, which could be due to either uncertainties in the

Figure 7. Graphical summary of a) the pristine surface composition of the brazing alloy and after heating to 500°C b) in UHV and c) in an ambient oxygen pressure.

present temperature measurements or related to a difference in the thermodynamics at the surface compared to the bulk. Finally, the various contaminations observed in the present study such as fluorine, carbon, and water may also affect the measurements, resulting in a temperature deviation from the expected thermodynamic behavior.

4. Conclusions

We have studied the surface development of an aluminum brazing sheet during heat treatment in two sample environments, UHV and 0.01 mbar oxygen, the later mimicking the expected environment in an industrial brazing oven. The study highlights the differences in surface oxide thickness and composition for the two different environments. The XPS analysis shows that in the ambient oxygen environment, the surface oxide transforms completely from a mainly aluminum oxide into magnesium oxide and magnesium hydroxide film upon heating to 500°C whereas the surface oxide in the UHV case remains as aluminum oxide with a slightly increased amount of other oxides, which do not exceed 5.5% of the total surface oxide. The thickness calculations show the continuous growth throughout the heating process in ambient oxygen pressure and the stagnation and decrease in the UHV case.

The present study demonstrates the potential strength of applying in situ APXPS on industrial materials. The environment in the real application, the vacuum brazing oven, can be mimicked in the APXPS set-up, providing a realistic environment to convincingly describe the surface development during the industrial process. We believe that APXPS has the potential to mimic a number of other applied processes, such as aging, quenching and other heat treatments of applied metal alloys in a realistic gas environments, to follow the development of various surface phases and structures. Obviously, the resulting surface structure and composition from thermal treatments in a realistic environment is of significant importance for the production process and the corrosion protection, and therefore the durability of the material.

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Supporting Information

To calculate the surface oxide thickness according to 1 the values shown in A1 were used. The densities for pure aluminum and 92-96% pure alumina can be found in [34, 35], respectively, resulting in a volume number density ratio ($\frac{N_{ME}}{N_{OX}}$) of 1.4. The IMPF was calculated using the software QUASES-IMFP-TPP2M [22] based on [23, 24], where a binding energy of 72 eV for the metallic aluminum and 75 eV for the aluminum oxide were used to calculate the electron kinetic energy.

Table A1. Values used for the calculation of the oxide layer thickness.

	ρ [g cm ⁻³]	$\lambda(400\text{eV})$ [Å]	$\lambda(650\text{eV})$ [Å]	$\lambda(1100\text{eV})$ [Å]
Al	2.7	10.42	15.60	24.18
Al ₂ O ₃	3.6	11.53	16.79	25.62

Additional XP spectra are shown in figure A1-A3 to support the conclusions drawn in the main article. Figure A1 shows that the sample's surface is not significantly altered by filling the reaction chamber with an ambient oxygen pressure at RT. In figure A2 the development of the Al 2p core-level at a photon energy of 1100 eV is shown. It shows that the more bulk like layer is not largely affected by the heating process. Only in the ambient oxygen pressure case at 500°C major change occurs since no aluminum signal could be observed. XP spectra for C 1s were obtained to control the C contamination of the alloy surface, see figure A3.

Figure A1. Overview spectra at 1100 eV comparing changes occurring through filling the reaction chamber with an ambient oxygen pressure at RT.

Figure A2. XP spectra for Al 2p measured at a photon energy of 1100 eV in a) UHV and b) 0.01 mbar oxygen for RT, 300°C, 400°C, and 500°C.

Figure A3. XP spectra for C 1s measured at a photon energy of 650 eV in a) UHV and b) 0.01 mbar oxygen for RT, 300°C, 400°C, and 500°C. The additional high energy peak in the ambient oxygen environment at around 290 eV can be assigned to carbonates. The presence of C at the alloy surface is of minor concern since it is a contaminant from the production and sample preparation. The reduced intensity of the C signal at higher temperature can be explained by desorption.

Bi 4f

Figure A4. Bi 4f XP spectrum obtained at photon energy of a) 650 eV and b) 400 eV after heating to 500°C in UHV. The $4f_{7/2}$ and $4f_{5/2}$ lines can be assigned to the peaks at 157 eV and at 162 eV respectively. The peak at 150 eV is originating from Si 2s.

Tables A2-A9 provide the values for the integrated intensities in arbitrary units for the respective core level peak, photon energy, sample environment, and temperature resulting from curve fitting asymmetric Voigt functions for O 1s, Al 2p, and Si 2p and Gaussians for Mg 2p to the data. Linear background were subtracted for O 1s, Al 2p, and Mg 2p lines and polynomial backgrounds were used for Si 2p data. Table A2-A4 also include the calculated thicknesses of the surface oxide.

Table A2. Integrated intensities and their corresponding standard deviations for the metal and oxide component of the Al 2p line respectively measured at a photon energy of 1100 eV and their resulting oxide thicknesses calculated according to (1) and table A1.

Al 2p 1100 eV	RT	300°C	400°C	500°C
UHV metal	445.4±26.1	282.9±27.5	344.49±27.1	491.6±40.9
UHV oxide	1904.9±95.4	1605.9±105.0	2714.7±94.0	2054.3±157.2
O ₂ metal	1469.5±71.6	954.9±76.4	574.6±61.6	–
O ₂ oxide	7713.4±276.2	5905.2±304.9	7590.6±213.3	–
UHV thickness [nm]	4.9	5.5	6.2	4.8
O ₂ thickness [nm]	5.3	5.7	7.5	

Table A3. Integrated intensities and their corresponding standard deviations for the metal and oxide component of the Al 2p line respectively measured at a photon energy of 650 eV and their resulting oxide thicknesses calculated according to (1) and table A1.

Al 2p 650 eV	RT	300°C	400°C	500°C
UHV metal	429.3±15.1	817.2±38.4	437.2±40.8	1845.1±58.6
UHV oxide	6418.7±55.0	14918±97.9	14783±109.1	11457±240.7
O ₂ metal	20384.0±1003.1	1306.5±82.5	440.4±82.6	–
O ₂ oxide	332450±3188.8	30798±234.9	34360±212.2	–
UHV thickness [nm]	5.1	5.4	6.4	3.7
O ₂ thickness [nm]	5.2	5.8	7.8	–

Table A4. Integrated intensities and their corresponding standard deviations for the metal and oxide component of the Al 2p line respectively measured at a photon energy of 400 eV and their resulting oxide thicknesses calculated according to (1) and table A1.

Al 2p 400 eV	RT	300°C	400°C	500°C
UHV metal	89.9±11.3	243.8±26.1	139.8±19.7	2091.3±71.0
UHV oxide	5160.5±34.8	18191±71.2	18578±52.2	12724 ±307.5
O ₂ metal	742.8±48.0	441.1±45.7	114.7±49.1	–
O ₂ oxide	35935 ±144.0	30605 ±119.2	34682±98.3	–
UHV thickness [nm]	5.0	5.3	5.9	2.5
O ₂ thickness [nm]	4.8	5.2	6.9	–

Table A5. Integrated intensities and their corresponding standard deviations for the elemental and oxide component of the Si 2p line respectively measured at a photon energy of 650 eV. The entry for the elemental silicon peak at 500°C is the sum of the area of two Voigt functions since a clear spin-orbit splitting was visible.

Si 2p 650 eV	RT	300°C	400°C	500°C
UHV elemental	25.5±6.5	26.8±9.8	54.0±15.0	510.0±5.6
UHV oxide	46.5±6.4	129.2±4.5	94.4±4.3	139.7±22.2
O ₂ elemental	89.9±18.0	56.0±15.5	46.0±20.7	–
O ₂ oxide	167.2±8.0	147.2±9.1	179.0±9.7	–

Table A6. Integrated intensities and their corresponding standard deviations for the elemental and oxide component of the Si 2p line respectively measured at a photon energy of 400 eV. The entry for the elemental silicon peak at 500°C is the sum of the area of two Voigt functions since a clear spin-orbit splitting was visible.

Si 2p 400 eV	RT	300°C	400°C	500°C
UHV elemental	7.2±2.7	25.2±5.8	20.1±4.0	468.2±22.6
UHV oxide	37.1±3.1	226.2±6.4	158.0±4.4	99.9±13.3
O ₂ elemental	41.0±6.3	39.1±7.1	30.7±14.5	23.7±8.4
O ₂ oxide	186.1±3.0	201.8±2.9	252.9±4.9	35.7±2.5

Table A7. Integrated intensities and their corresponding standard deviations for the oxide component of the Mg 2p line measured at a photon energy of 650 eV.

Mg 2p 650 eV	RT	300°C	400°C	500°C
UHV	77.2±2.5	377.3±5.6	770.6±5.2	701.9±5.3
O ₂	287.4±7.7	719.9±8.3	3430.2±14.6	9242.3±27.6

Table A8. Integrated intensities and their corresponding standard deviations for the oxide component of the Mg 2p line measured at a photon energy of 400 eV.

Mg 2p 400 eV	RT	300°C	400°C	500°C
UHV	64.8±1.4	420.4±2.6	1088±2.8	900.5±2.3
O ₂	324.3±2.6	779.9±3.3	4884.6±10.6	17208±35.4

Table A9. Integrated intensities and their corresponding standard deviations of the O 1s line measured at a photon energy of 650 eV. The entry for the oxygen peak in ambient gas pressure at 500°C is the sum of the area of two Voigt functions since a the signal of a second component became distinguishable.

O 1s 650 eV	RT	300°C	400°C	500°C
UHV	598.5±12.7	1635.7±16.7	2373.6±17.6	2068.3±23.6
O ₂	6846.7±193.4	4395.6±217.1	6302.8±164.8	3257.72±49.144

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