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Deoxidation of stainless steels during vacuum brazing

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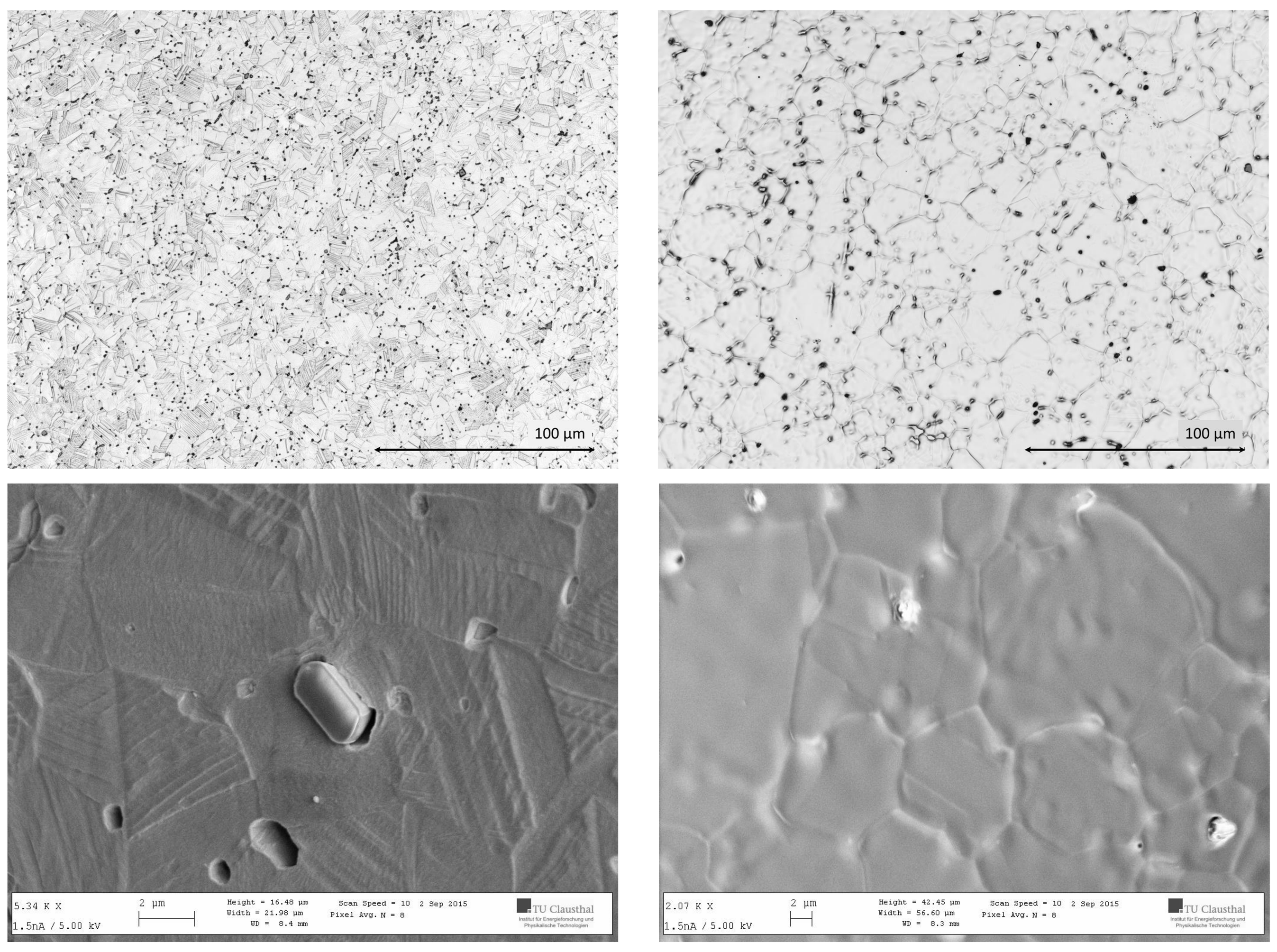
Introduction

Stainless steels are in widespread use due to their excellent mechanical and corrosion-proof properties. Corrosion resistance stems from native oxide layers formed on the surface of stainless steels, a few nanometers thick and consisting of a mixture of chromium and iron oxides and hydroxides.
This oxide layer is the main inhibitor of wetting the surface with molten braze, a critical procedural 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. Deoxidation of two stainless steels is studied, easily brazed austenitic AISI 304 and procedurally demanding ferritic AISI 446. Effect of heat treatment is recreated in laboratory scale by electron impact heating. Chemical analysis before and after heat treatment is carried out by XPS, AES and EDX/ WDX, optical and topographical properties are studied by CLSM. Due to different information depths of XPS/ AES and EDX/ WDX, bulk changes can be separated from surface changes.

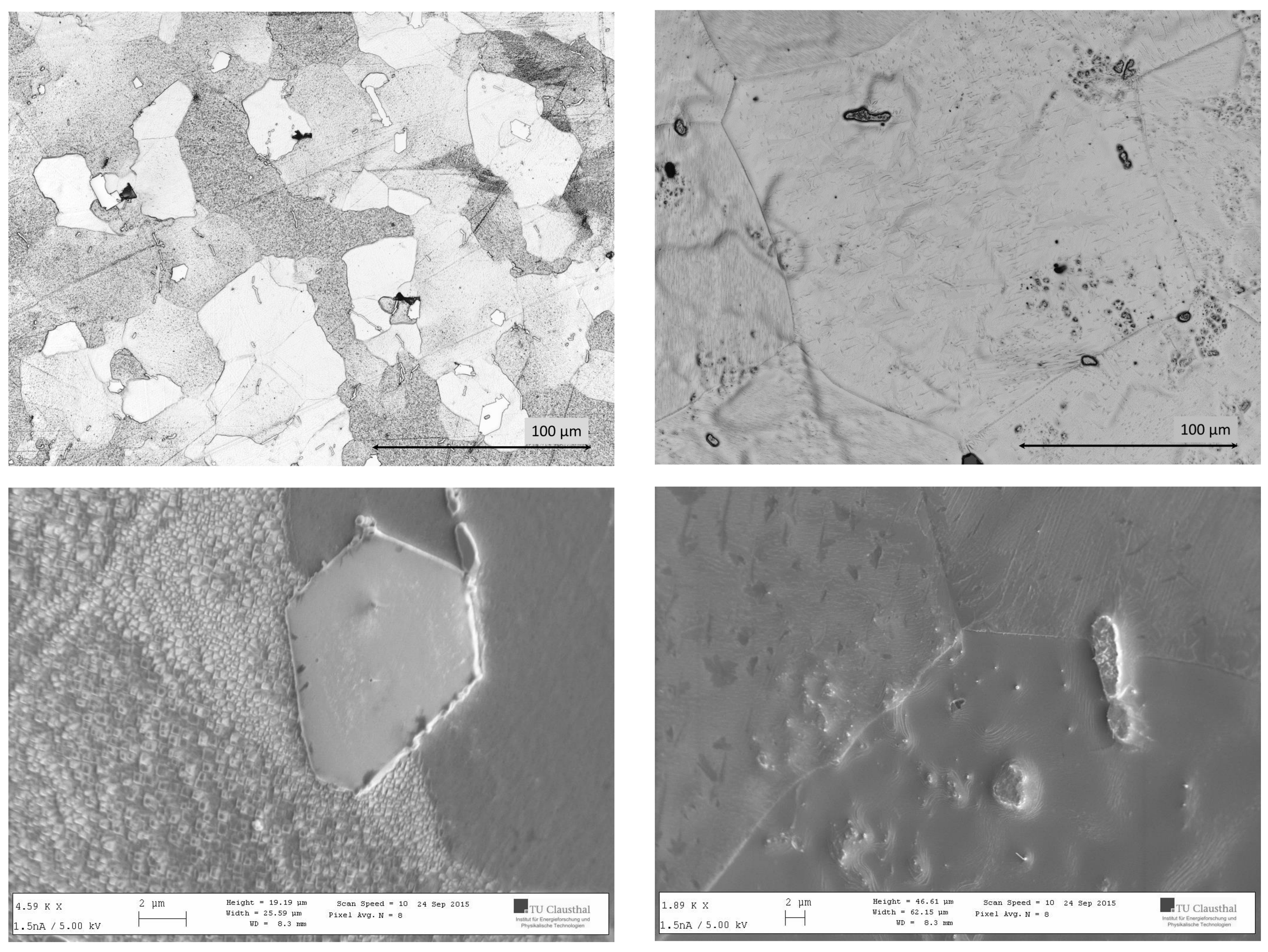
AISI 304



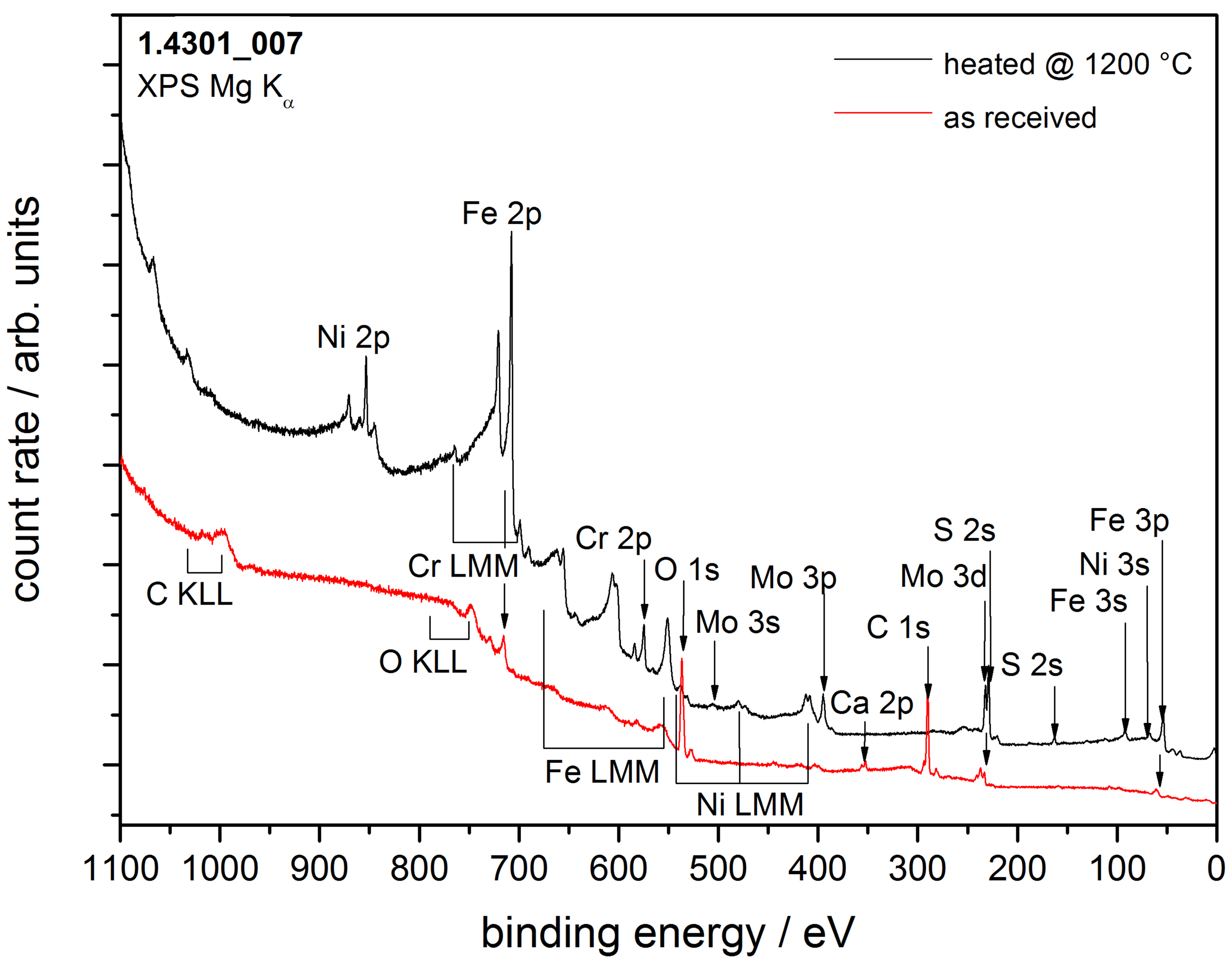
CLSM and SEM images of etched steels AISI 304 (1.4301, on the left) and AISI 446 (1.4762, on the right).

Etching is done to visualize grain structure. Effect of heat treatment on grain structure can be studied and compared on both steels.

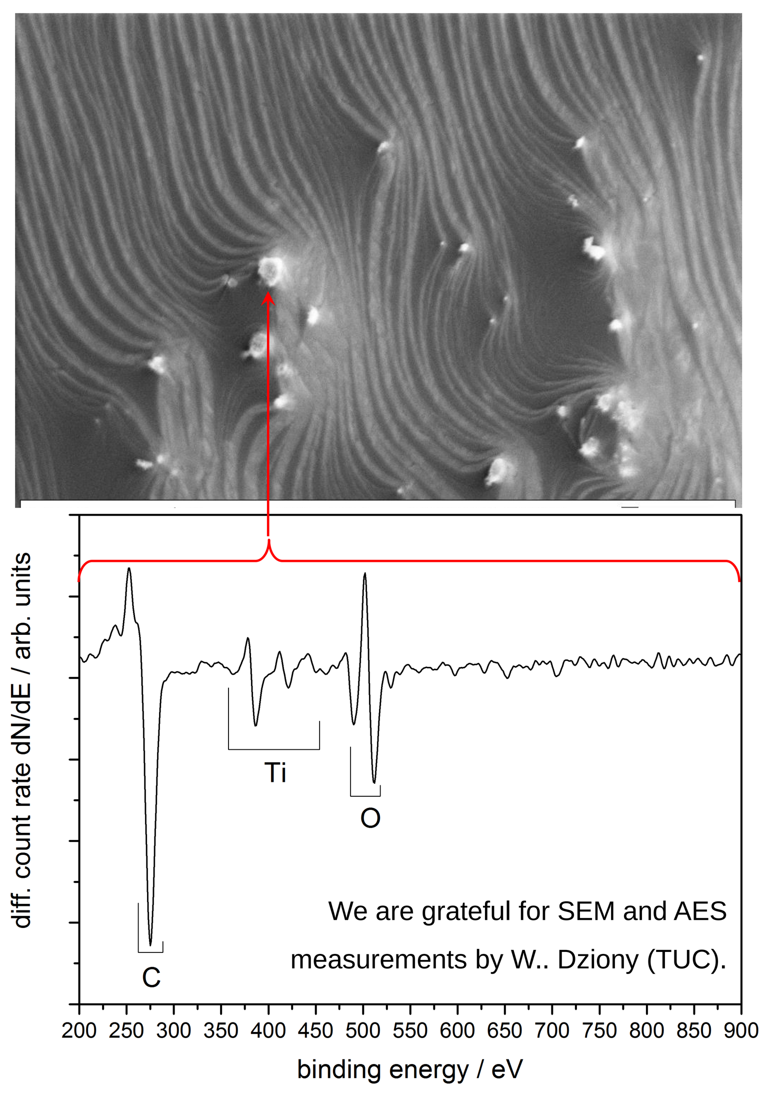
AISI 446

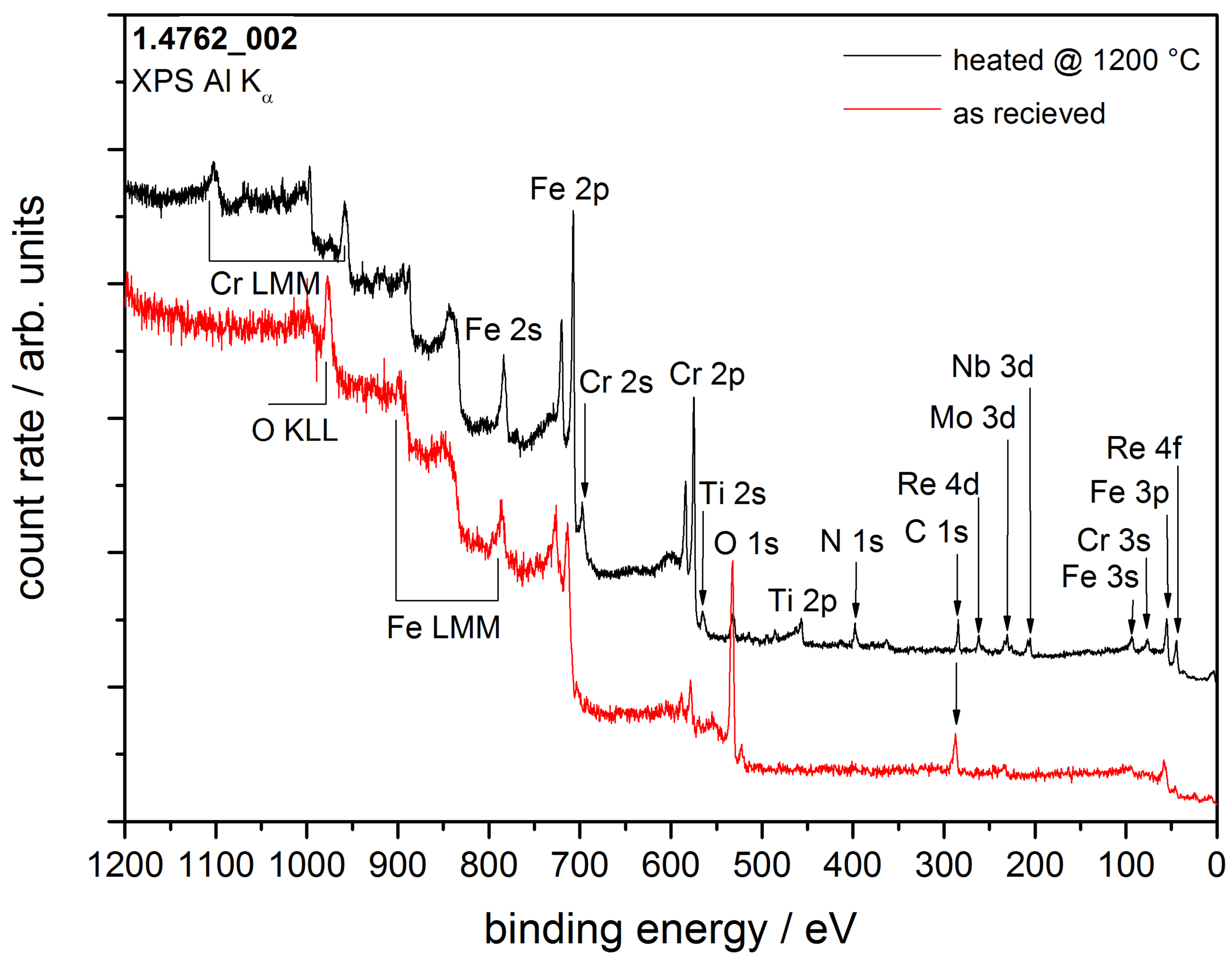


Surface composition



X-Ray Photoelectron Spectra on polished steels AISI 304 (1.4301, on the left) and AISI 446 (1.4762, on the right).
Measurements were carried out before and after heating to 1200 °C.





Element	Change after heating to 1200 °C
O	**- 27,8 %** from **29,3 %**
C	**- 62,7 %** from **62,7 %**
Fe	**+ 62,3 %** from **3,0 %**
Cr	**+ 9,0 %** from **0,9 %**
Mo	**+ 2,1 %** from **2,4 %**
Ca	**- 1,8 %** from **1,8 %**
Ni	**+11,9 %** from **0 %**
S	**+ 6,9 %** from **0 %**

- On easily brazed AISI 304, both metal oxides and organic contamination are gone after heating. Carbon fraction is reduced to zero, oxygen only remains as trace.
- On AISI 446 however, substantial amounts of both carbon and oxygen remain. A shift of the C 1s signal seems to indicate the presence of stable carbides. Several (alloying) elements show surface enrichment, especially titanium seems to form oxide phases on the surface as shown in the SEM image (chemical analysis by AES).

Element	Change after heating to 1200 °C
O	**- 43,8 %** from **54,7 %**
C	**- 12,9 %** from **31,2 %**
Fe	**+ 13,6 %** from **11,3 %**
Cr	**+ 22,3 %** from **2,8 %**
N	**+ 10,9 %** from **0 %**
Ti	**+ 3,8 %** from **0 %**
Mo	**+ 2,8 %** from **0 %**
Nb	**+ 2,5 %** from **0 %**
Re	**+ 0,8 %** from **0 %**

Bulk composition

- AISI 304 (1.4301): EDX measurements show decreasing chromium and oxygen amounts and increasing iron content. Nickle content depends strongly of the measured phase, varying from grain to grain in the unheated sample. Other elements, both alloying elements and contaminants like magnesium, aluminum, silicon and titanium, show constant concentrations independent from heat treatment.
- AISI 446 (1.4762): In contrast, chromium content increases or remains constant, while iron content decreases. Enrichment of (alloying) elements can only be observed in precipitations like aluminum nitride or zirconia of constant composition before and after heat treatment. Oxygen amount in the heated specimen still accounts for up to 8 at.% of total composition.

Element	Fe	Cr	Ni	Mn	Si	C	N
Content (%)	66,7	20,8	9,9	2,0	2,0	0,3	0,4

We are grateful for SEM and EDX measurements by K. Hermann (TUC).

Compositions according to spec sheet in at.%

Element	Fe	Cr	Al	Si	Mn	C
Content (%)	66,1	26,5	3,3	2,6	1,0	0,5

Summary

- AISI 446 shows significant element enrichment on the surface, as shown by XPS and AES. Especially titanium seems to segregate and form oxide inclusions undissolved by heat treatment. Neither carbon nor oxygen can be completely removed, from both bulk and surface. Possibly AISI 446 undergoes phase transformations that leaves the surface saturated (e.g. with thermodynamically stable titanium oxide), thus inhibiting wetting with molten braze.
- AISI 304 on the other hand has no residual oxygen or carbon on the surface and bulk oxygen decreases substantially. Removal of oxygen and carbon possibly leaves the surface unsaturated, promoting wetting due to higher surface energy. No new stable phases seem to be formed.