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Study on Pb-Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications (2)

Part I. Stability of Oxide Layer Formed on High-Chromium Steels in LBE under Oxygen Content and Temperature Fluctuation

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Study on Pb-Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications (2)

Part I. Stability of Oxide Layer Formed on High-Chromium Steels in LBE under Oxygen Content and Temperature Fluctuation

G. Müller*, G. Schumacher*, A. Heinzel*, A. Weisenburger*,
F.Zimmermann*, T. Furukawa**, K. Aoto**

Abstract

The behaviour of protective oxide layers on P122 and its welds and of ODS steel is examined under conditions of fluctuating temperatures and oxygen concentrations to simulate hot spot and loss of oxygen control.

P122 steel (12Cr) and its welded joints are exposed to LBE at 550°C for 4000h with oxygen concentrations changing between 10^{-6} and 10^{-8}wt% every 800h. It is found that like in case of constant oxygen concentration of 10^{-6}wt% a protective spinel layer was maintained on P122 and also on its welded joint.

Experiments with fluctuating temperatures from 550°C to 650°C and back every 800h yield satisfying corrosion protection up to 4800h only for the GESA treated ODS steel in LBE with 10^{-6}wt%. Original ODS steel in LBE with 10^{-6} and 10^{-8}wt% oxygen showed local strong dissolution attack after 4800h in agreement with the behaviour of ODS in LBE with a constant temperature of 650°C. GESA treated ODS steel does not form stable protective alumina layers under condition of fluctuating temperatures in LBE with 10^{-8}wt% oxygen.

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原子炉構造材料および燃料材料の鉛ビスマス中腐食に関する研究 (2)

第 1 報　溶存酸素濃度および温度変動鉛ビスマス中における高クロム系鋼上に形成された酸化皮膜の安定性

G. Müller*, G. Schumacher*, A. Heinzel*, A. Weisenburger*,
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要　旨

炉内燃料被覆管の Hot Spot および冷却系酸素濃度制御喪失条件をイメージした温度および溶存酸素濃度変動鉛ビスマス（LBE）条件下における P122（12Cr 鋼）とその溶接継手および ODS 鋼上に形成された保護性酸化層の挙動について調べた

酸素濃度変動試験では、800h 毎に溶存酸素濃度を 10^{-6} and 10^{-8}wt%に繰り返した 550°C の LBE 中 で、12Cr 鋼母材とその溶接継手を対象に 4,000h の浸漬を実施した。その結果、10^{-6}wt%一定酸素濃度条件下のケースと同様に、保護性スピネル層が 12Cr 鋼母材およびその溶接継手上に安定形成していることが確認された。

800h 毎に LBE 温度を 550°C と 650°C に繰り返した温度変動試験（～4,800h）では、10^{-6}wt%で実施した GESA 表面改質 ODS 鋼でのみ満足する腐食抑制効果観察された。10^{-6}wt%および 10^{-8}wt%の酸素濃度条件で実施した ODS 受入材の 4,800h の温度変動試験では、650°C 温度固定の同鋼の腐食試験結果と同様に、Dissolution Attack が観察された。10^{-8}wt%の酸素濃度条件で実施した GESA 表面改質材表面には安定なアルミナ層が形成できずに腐食が発生した。

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Content

1 Introduction

Lead bismuth eutectic (LBE) is a candidate material for the coolant of a fast breeder reactor (FBR). One of the main problems in the development of these systems is compatibility of the employed steels with LBE.

In 1998 experiments were reported in which oxide scales formed on the surface of steel were shown to protect the steel from dissolution attack by LBE [1]. For stabilization of these oxide scales a controlled concentration of dissolved oxygen in LBE has to be maintained. The concentration applied in the experiments was 10^{-6}wt%. Recent work on corrosion of austenitic and martensitic steels gives an overview on the corrosion effects and processes and its prevention in stagnant and flowing Pb and LBE [2-12]. However, few data only were presented on the processes taking place in LBE with different oxygen concentrations and also at temperatures above 550°C. Experiments with ODS exposed for 5000 h to LBE with 10^{-4} and 10^{-8}wt% showed no dissolution attack up to 650°C while at 10^{-6} wt% attack was observed [13]. Tests with aluminized coatings on 316L and T91 steel with oxygen concentrations $< 10^{-8}$wt% in LBE showed satisfying protection only up to 500°C but severe dissolution attack at 600°C already after 1000h [14].

The work reported so far deals with the steel behavior at different constant temperatures and oxygen concentrations. It is, however, important to know the behavior of steels under conditions of fluctuations of temperature and oxygen concentrations which can be expected during the course of reactor operation. The present paper describes the effect of temperature fluctuations at different constant oxygen concentrations in LBE for ODS steel which is a candidate material for the fuel cladding of a LBE cooled FBR. The influence of changing oxygen concentration, which can happen due to loss of oxygen situations, is examined on P122 steel and also on welded joints of this material.

2 Experimental

The experiments are conducted in the COSTA device in which the specimens are exposed to stagnant LBE [2] under conditions of temperature and oxygen concentration fluctuations. The control of oxygen concentrations is obtained in this device via the gas phase by establishing the corresponding H_2/H_2O ratio in the gas flowing through the furnace tubes [2]. Fluctuation of oxygen concentration is attained by changing the H_2/H_2O ratio in the flowing gas. Temperature fluctuations are done by changing the heating power in the furnace.

The influence of changes in the LBE temperature and of the oxygen potential in the gas phase and consequently on the oxygen concentration in LBE can be revealed by looking at the Ellingham diagram [15] in Fig. 1.

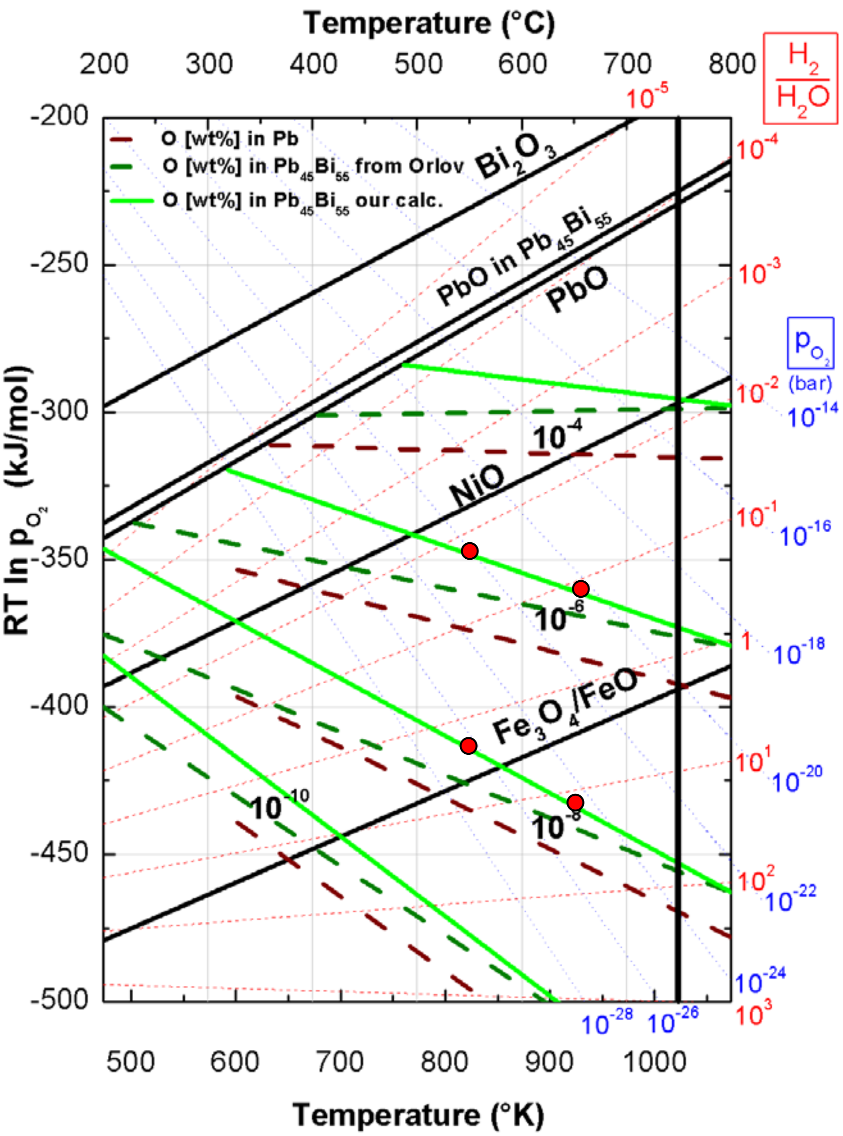

Fig. 1: The Ellingham diagram

H_2/H_2O equilibrium ratios are represented by dashed thin lines ascending with temperature and oxygen concentrations in LBE by solid and dashed thick lines descending with temperature. We refer in our considerations to the solid concentration lines which correspond to our calculations [15]. The points on the lines mark the conditions of the experiments described in the following chapters.

Fig. 2 illustrates the large decrease in oxygen activity during the temperature fluctuation from 550 to 650°C. The oxygen activity changes by a factor of 4.5 between the two temperatures.

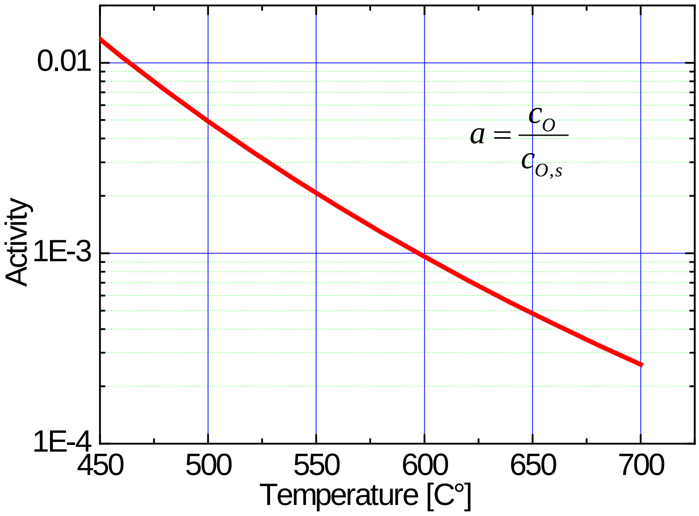

Fig. 2: Change of oxygen activity with temperature at an oxygen concentration of 10^{-6}wt%.

2.1 Specimens location in COSTA

A new crucible type was employed in the experiments with a diameter larger than before which offers a LBE-surface of 9.25cm^2 for the interaction with the oxygen controlled atmosphere. The former crucibles had a LBE surface of only 2cm^2. This measure provides a better access of the oxygen to the lower parts of the specimen immersed in LBE. Fig. 3 shows the new crucible type in comparison to the old one.

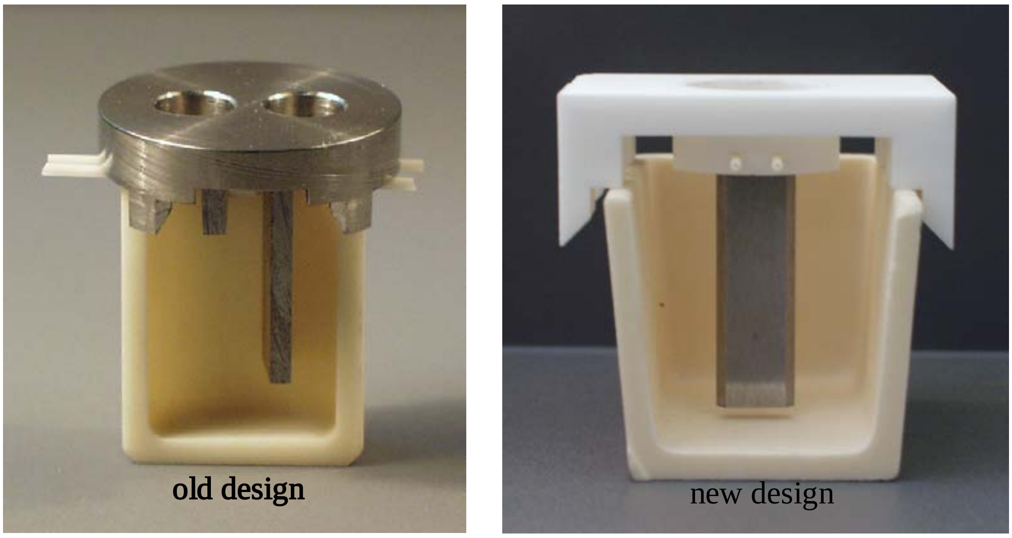

Fig. 3: New crucible type in comparison to the old one.

The specimen represented in Fig. 4 was used to look for the effect of the new crucible type employed for the first time in all the experiments described in this report. Cuts in different depth of the specimen below the LBE surface are examined and depicted in Fig. 4. The metallographically prepared sections at 2, 5, 7, 9, 11 and 13mm depth below the LBE surface show no difference in oxide scale formation and, thus, good access of the oxygen down to the depth of 13mm.

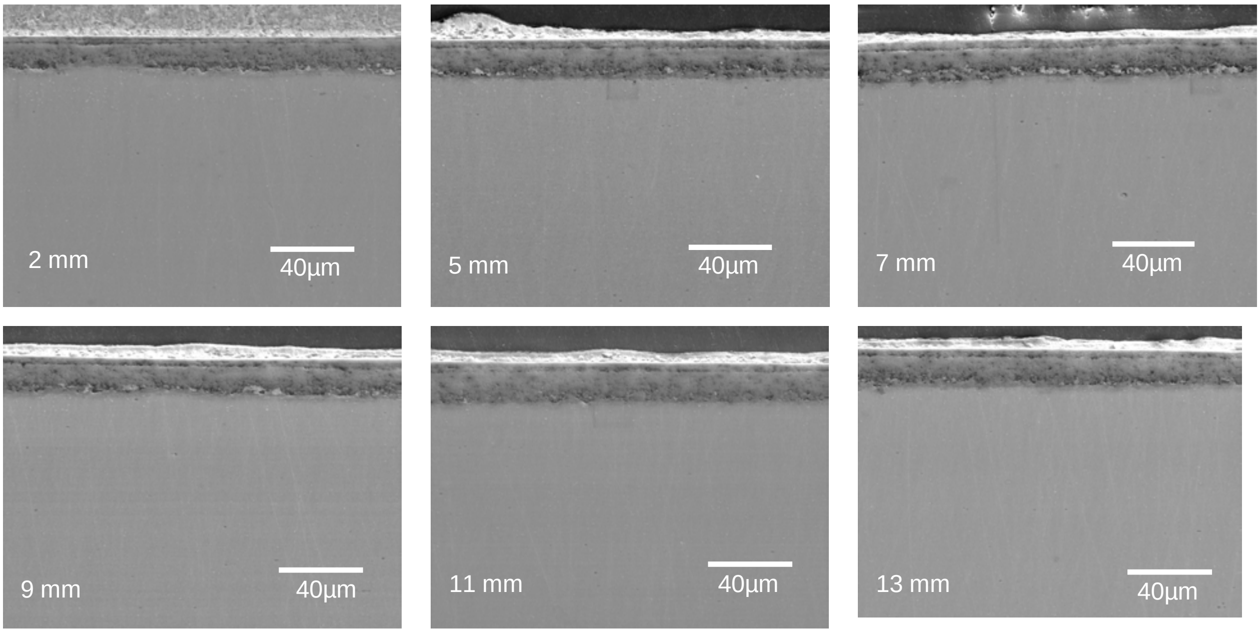

Fig. 4: SEM of cross sections at positions of 2, 5, 7, 9, 11 and 13mm depth below the LBE surface. Specimen same as in Fig. 10. Oxide scale does not change with depth.

The specimen locations in the COSTA device are represented in Fig. 5. It indicates on the left the positions of the specimen for the temperature fluctuation simulation at 10^{-8} and 10^{-6}wt % oxygen in LBE. ODSG stands for an ODS specimen which was surface alloyed with Al by GESA. To the right in Fig. 4 we see the positions of P122 specimens for the loss of oxygen simulation and those of the comparison test at constant oxygen concentration of 10^{-6}wt%. The added letter G again stands for the GESA surface alloyed specimen, the letter S for the welded joint.

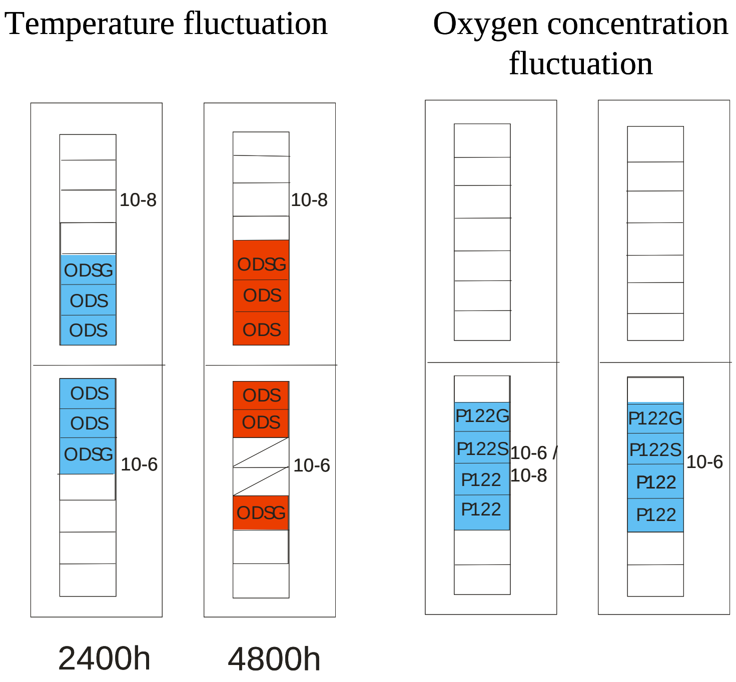

Fig. 5: Location of specimens in COSTA and their status of exposure.
Left: ODS specimens for hot spot simulation.
Right: specimens for loss of oxygen control test and comparison test at constant 10^{-6}wt% oxygen.
- G = Surface alloyed with Al by GESA
- S = Welded joint

2.2 Temperature fluctuation

Temperature fluctuations with original and GESA treated ODS specimens in LBE by changing the temperature from 550°C to 650°C and back after periods of 800h up to an exposure time of 4800h are shown in Fig. 6: The oxygen concentration was kept constant at 10^{-6} and 10^{-8}wt%, respectively, table 1.

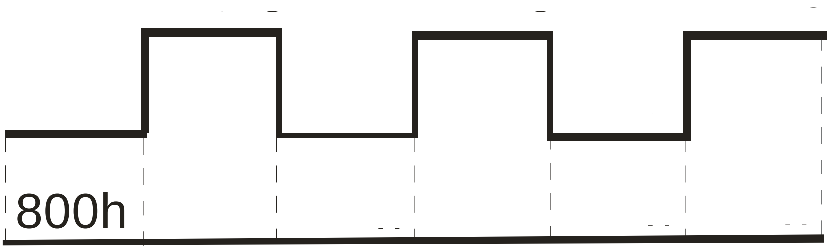

Fig.6: Temperature as a function of time for ODS in LBE

	550 °C		650 °C	
c_o [wt%]	H_2/H_2O	P_{O_2} [bar]	H_2/H_2O	P_{O_2} [bar]
10^{-6}	$1.84 \cdot 10^{-2}$	$5.83 \cdot 10^{-23}$	$1.25 \cdot 10^{-1}$	$3.17 \cdot 10^{-21}$
10^{-8}	1.84	$5.83 \cdot 10^{-27}$	12.25	$3.17 \cdot 10^{-25}$

Tab. 1: Oxygen concentrations in LBE and corresponding H_2/H_2O ratios and oxygen partial pressures in the gas phase at different temperatures

Looking at the points on the concentration lines for 10^{-6} and 10^{-8}wt% in the Ellingham diagram, Fig. 1, it follows that after increasing the temperature at constant oxygen concentration the oxygen potential RTln P_{O2} in LBE drops to lower values. Decreasing the temperature causes an increase in oxygen potential. A critical situation occurs with increasing the temperature on the 10^{-8} wt% line because Fe_3O_4 is not stable any more after this step. Tab. 1 lists the H_2/H_2O ratios and oxygen partial/pressures for 10^{-6} and 10^{-8}wt% oxygen concentration at 550 and 650°C.

2.3 Oxygen concentration fluctuation

Fluctuations in oxygen concentration of two original, one welded and one GESA treated specimens in LBE are simulated by changing the concentration from 10^{-6} to 10^{-8}wt% and back after periods of 800h up to an exposure time of 4000h, Fig. 7. In parallel to the fluctuation experiment the same number of specimens is exposed at constant oxygen concentration 10^{-6}wt% for comparison. The temperatures in the experiments are kept constant at 550°C.

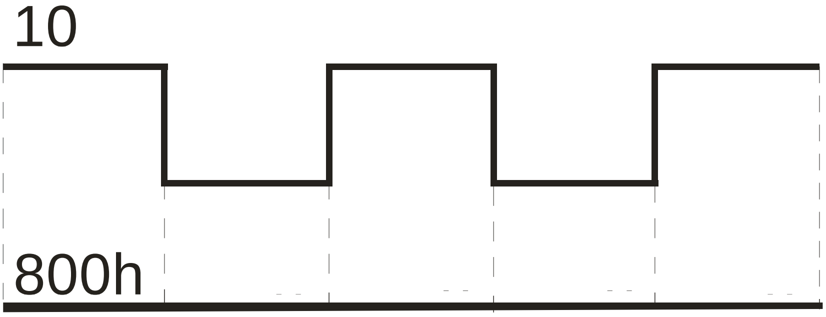

Fig. 7: Oxygen concentration in LBE as a function of time for P122 and its welded joints.

c_o [wt%]	H_2/H_2O	P_{O_2} [bar]
10^{-6}	$1.84 \cdot 10^{-2}$	$5.83 \cdot 10^{-23}$
10^{-8}	1.84	$5.83 \cdot 10^{-27}$

Tab. 2: Oxygen concentrations in LBE and corresponding H_2/H_2O ratios and oxygen partial pressures in the gas phase

The Ellingham diagram in Fig. 1 shows how the different oxygen concentrations in LBE are obtained. It needs a change of the H_2/H_2O ratio by 2 orders of magnitude to switch from 10^{-6} to 10^{-8}wt% and back. Table 2 lists the values of oxygen concentrations in LBE and the equilibrium H_2/H_2O ratios and oxygen partial pressures in the gas phase.

2.4 Evaluation

The specimens taken out of the COSTA device after 2400 and 4000h are cut with a diamond disk saw perpendicular to the exposed surface and are grinded and polished for the metallographic examinations. Light optical (LOM) and scanning electron (SEM) microscopy are employed for observation of the microstructure of the material surface and the oxide scale. The identification of the phases is supported by energy dispersive x-ray analysis (EDX).

2.5 Materials

The composition of ODS and P122 steels used in the experiments is given in table 3 and 4. The specimens are plates of 28 x 8 x 2 mm dimension.

Element [wt%]

C	Si	Mn	P	S	Ni	Cr	W	Ti	Y	O	N	Ar
0.13	<0.005	<0.01	0.001	0.003	0.01	8.85	1.94	0.2	0.27	0.17	0.011	0.005

Heat Treatment: 1050°C – 1h (AC), 800°C - 1h (AC)

Tab. 3: Composition of ODS steel

Element [wt%]

	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Nb+Ta	W	V	N
solder	0.09	0.3	0.52	0.005	0.002	1.51	1.04	10.5	0.26	0.05	1.43	0.2	0.0424
P122	0.11	0.27	0.64	0.016	0.002	1.0	0.33	10.54	0.34	0.048	1.76	0.19	0.071

Tab. 4: Composition of the P122 steel and its solder

The welded joints of P122 were obtained by using the TIG process using a solder the composition of which is very similar to that of P122. Fig. 8 shows the cross section of the joint and the structures that appear in and around the weld. The weld exhibits a coarse grained structure. It is separated from the joint steel by a heat affected fine-grained zone of 1.2cm thickness. No significant variation of the composition is found for the different zones.

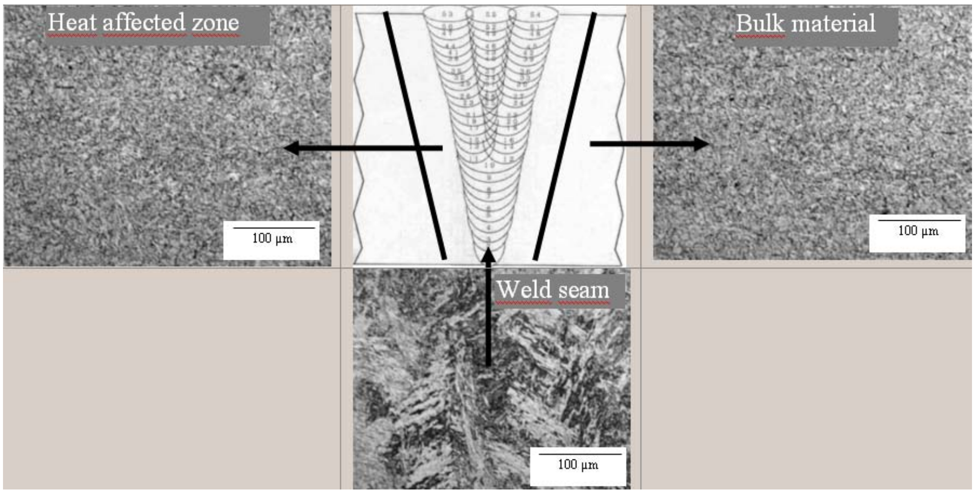

Fig. 8: Scheme of the welded joined and structures of the zones that appear

The P122 welded joint specimens are cut by wire erosion from the weld of two P122 sheets that is shown in Fig. 9a. Fig. 9b depicts the parts after cutting the welded zone out of the connected sheets. From the lower half of the weld in Fig. 9b cylindrical rods are cut out for experiments in the CORRIDA loop. The upper half of the weld is cut into 3 sheets parallel to the surface as shown in Fig. 9c. The lowermost sheet that represents the smallest part in the weld scheme depicted in Fig. 8 is employed as a specimen for the test with fluctuating oxygen concentration in LBE. The surface of the specimens after wire erosion is grinded and polished before the test.


a b c

Fig. 9: Welded joint specimens preparation
a) Welded joint between two P122 sheets
b) Cutted out weld zone with grooves left behind from wire erosion of small rod specimens
c) Scheme of cutted specimen sheets from the upper part of the weld in (b)

3 Results

3.1 Temperature fluctuation, 550 / 650°C, ODS steel

3.1.1 Original ODS exposed 2400h and 4800h at an oxygen concentration of 10^{-6}wt%

The oxide layer on the specimen constitutes of spinel, clearly indicated by the increased Cr concentration in the layer as shown in the concentration profile, Fig. 10. The spinel layer does not spall off during the temperature fluctuations up to 2400h exposure. No magnetite is found on the top of it. Small quantities of spalled off magnetite are found floating on the PbBi surface. A diffusion zone (internal oxidation) is not visible.

The formed spinel-layer is rather porous with inclusions of PbBi. Bigger pores are located mainly near the interface between spinel-layer and bulk material. The highest Cr concentration is measured near the interface in the bulk in about 15µm depth from the surface. The Cr concentration ranges between 19 and 30wt% and increases in direction to the interface, Fig. 10, right.

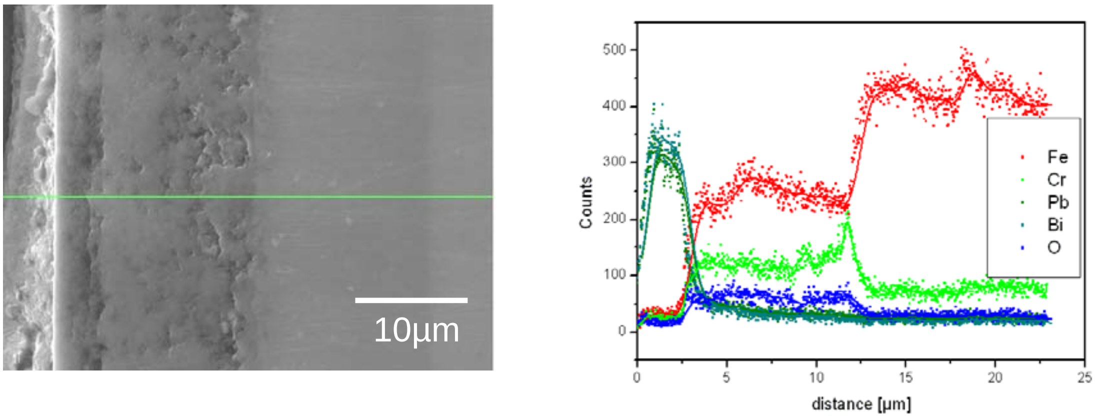

Fig. 10: SEM of ODS surface cross section after exposure to LBE with 10^{-6} wt% oxygen for 2400h at temperatures changing from 550 to 650°C and back every 800h (left), EDX line scan across surface region (right).

After 4800h, a similar structure and concentration distribution is observed along the cross section of the surface region in ODS steel, Fig. 11. However, the thickness of the spinel layer is by a factor of 2 smaller than that of the 2400h specimen. This may be explained by reduction of the older spinel layer due to partly spallation of sublayers that develop during the exposure at different temperatures.

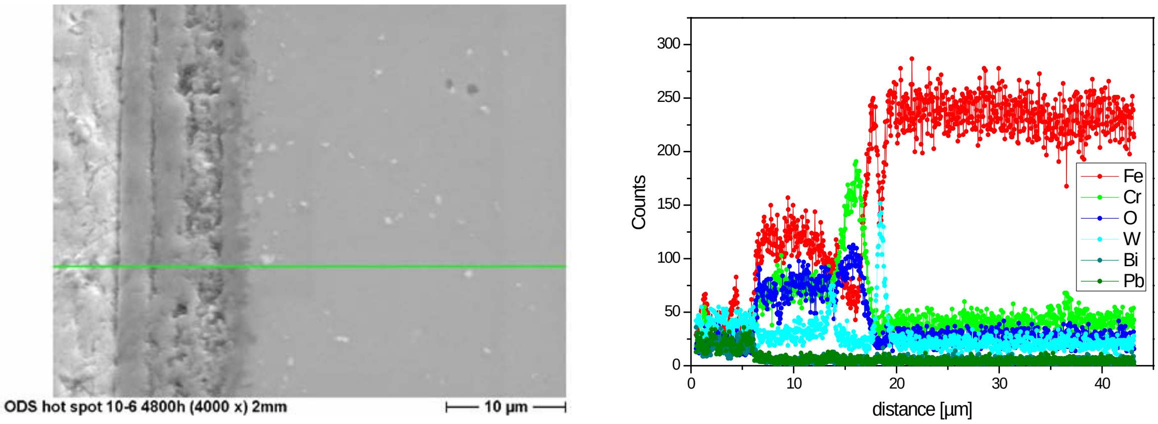

Fig. 11: SEM of ODS surface cross section after exposure to LBE with 10^{-6}wt% oxygen for 4800h at temperatures changing from 550 to 650°C and back every 800h (left), EDX line scan across surface region (right).

For comparison with corrosion tests at constant temperatures the result of tests conducted with 10^{-6}wt % oxygen at constant temperatures of 550°C and 650°C for 800h is depicted in Fig. 12. We see at 550°C a magnetite layer that starts to break and spall off but otherwise an intact spinel layer that protects the specimen from dissolution attack (left). At 650°C, however, there is strong dissolution attack in large parts of the specimen without protective oxide scales (middle). Compared to this, the steel specimen after temperature fluctuation shows a protective oxide scale (right).

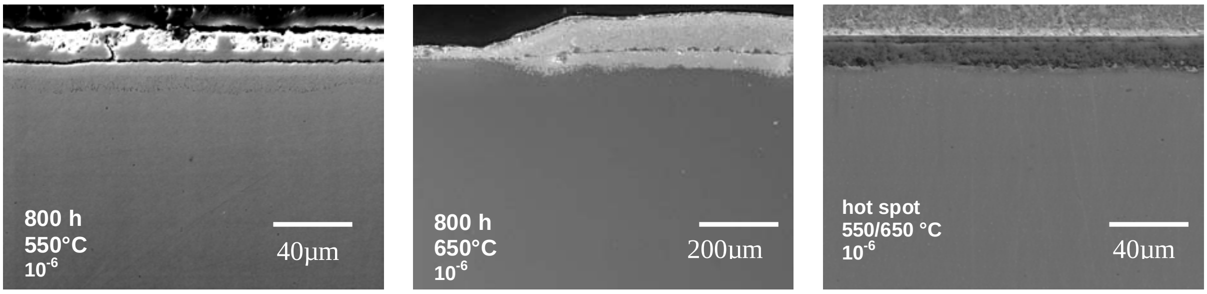

Fig. 12 Result of former COSTA experiments at constant temperatures of 550°C and 650°C [14] in the two figures to the left for comparison with the specimen in Fig. 10 (right).

There are however few spots with local dissolution attack on the surface of the specimen exposed for 2400h as well as on that exposed for 4800h with fluctuating tmperatures. This concerns 2 spots on one of 2 specimens examined after 2400h and 1 area on one of the 2 specimens exposed for 4800h. The left side of Fig. 13 shows an attacked spot of 300µm depth on the 2400h specimen. The enlarged edge of the attacked spot (lower left figure) shows clearly holes originated by brake out of Cr-oxycarbides during preparation. The oxycarbide formation is accompanied by diminishing of the Cr concentration that may result in a less resistant spinel layer. The dissolution attack on the 4800h specimen (Fig 13, right) which extends to almost 2mm in diameter and 600µm in depth is more severe and may be caused by a similar process as described above.

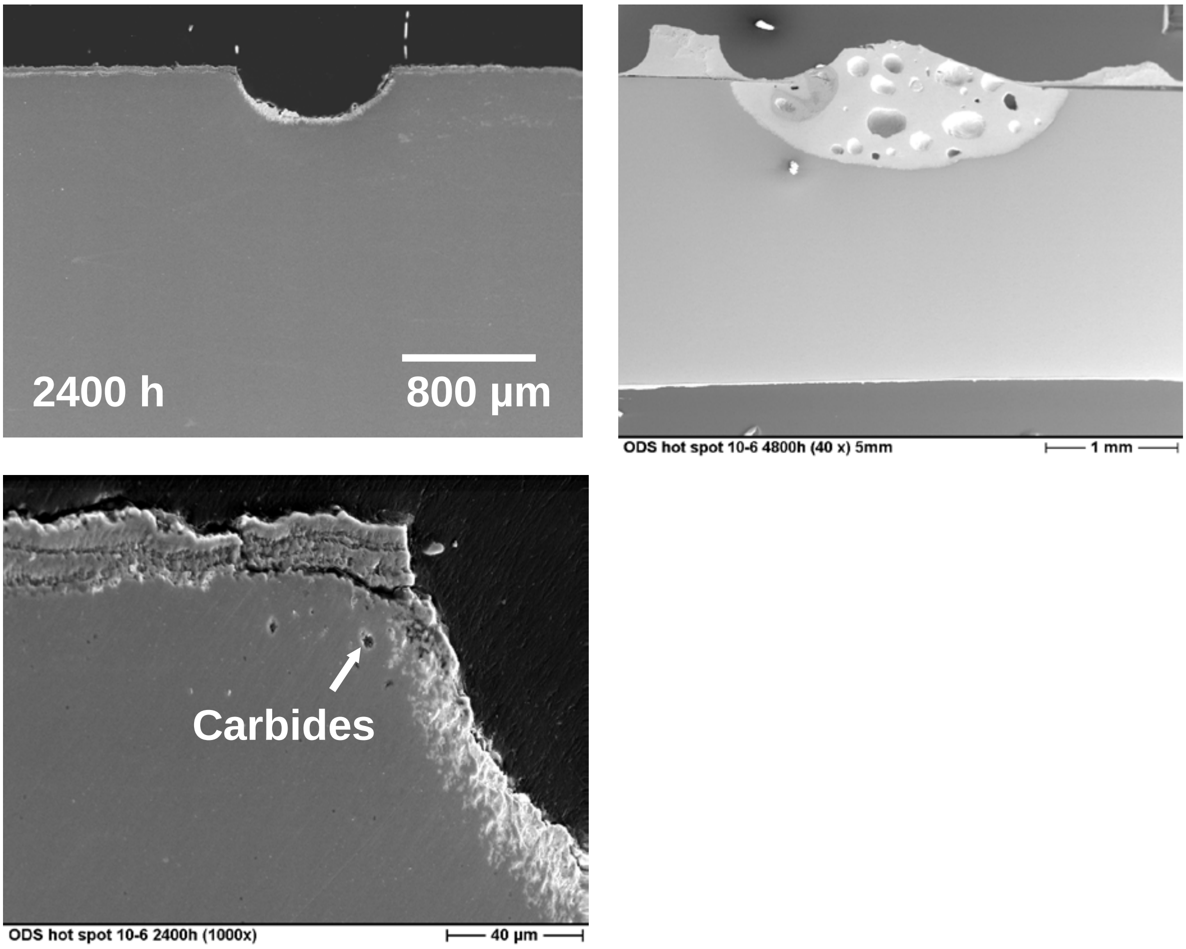

Fig. 13: Lokal corrosion phenomenon caused by dissolution attack on ODS in LBE with 10^{-6}wt% oxygen at temperatures changing from 550 to 650°C after 2400h (left) and after 4800h (right).

The XRD from the surface of ODS specimens exposed to LBE with 10^{-6}wt% oxygen at teperatures changing between 550 and 650°C agree with the phenomenon observed in Fig. 10-13 after 2400h and 4800h exposure, Fig. 14. The smaller spinel peaks of the 4800h specimen indicate the smaller spinel layer of this specimen. The XRD is obtained from the one specimen that has no dissolution attack.

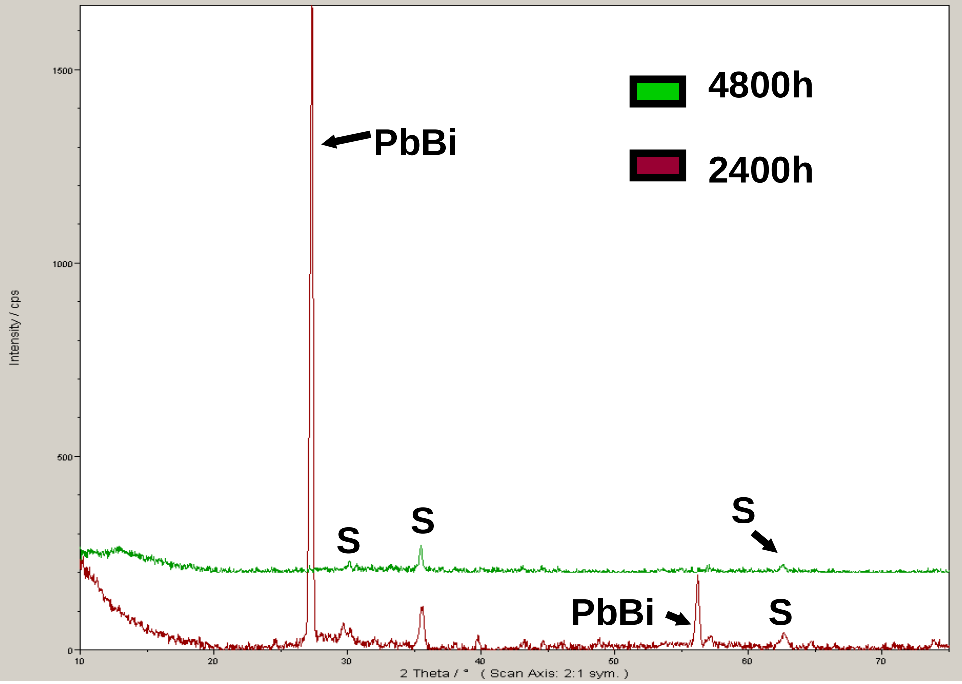

Fig. 14: XRD spectra of two specimens exposed to LBE with 10^{-6}wt% oxygen at temperatures changing between 550 and 650°C after exposure for 2400h and 4800h, respectively. (S=Spinel)

Therefore, a PbBi peak is only observed on the 2400h specimen, which had 2 areas of dissolution attack on the surface.

3.1.2 Surface alloyed ODS exposed 2400h and 4800h at an oxygen concentration of 10^{-6}wt %

There is no visible interaction in LBE with changing temperatures on the surface which is alloyed with Al by the GESA process after 2400h of exposure. This is in agreement with experiments on GESA alloyed ODS steel at a constant temperature of 650°C in COSTA and at 550°C in the CORRIDA loop with 7000h and 2018h exposure, respectively, as shown in Fig. 15.

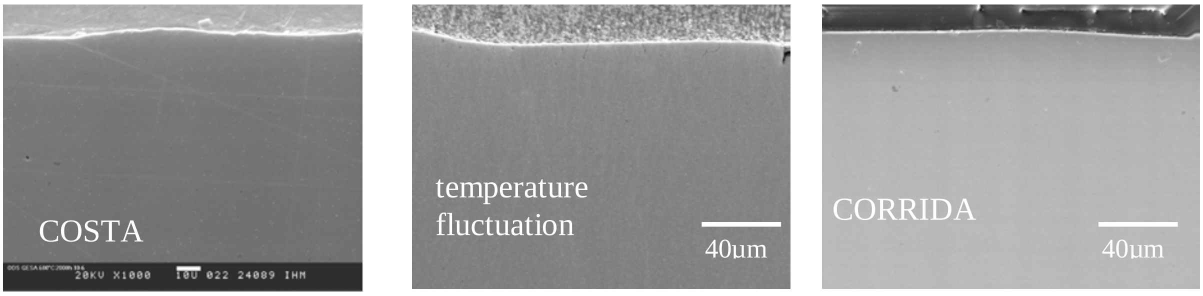

Fig. 15 SEM of surface cross section after exposure at fluctuating temperatures of 550°C / 650°C (middle) compared to that of 650°C, 7000h, in COSTA (left) and 550°C, 2018h, in the CORRIDA loop (right). All experiments with 10^{-6} wt % oxygen in LBE.

Also after 4800h, no interaction between LBE and surface alloyed ODS was visible after exposure to LBE with 10^{-6}wt% oxygen at temperatures changing from 550°C to 650°C and back, Fig. 16.

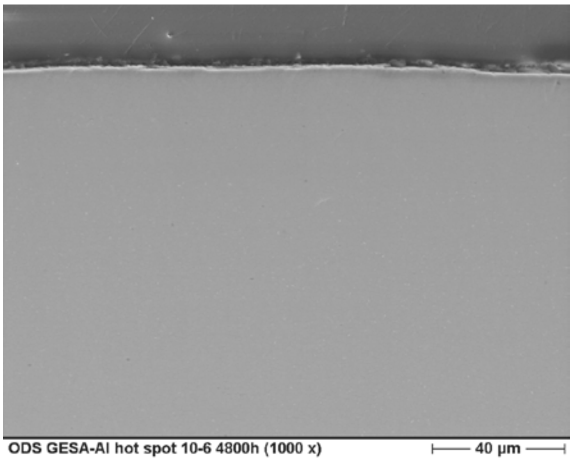

Fig. 16 Surface alloyed ODS after 4800h exposure at fluctuating temperatures of 550°C / 650°C with 10^{-6}wt % oxygen in LBE

The protective alumina scales on the specimens alloyed with Al by GESA are very thin, thus, they do not appear in the XRD spectra of the surface. Therefore, we see dominating α-Fe peaks and only in the 2400h specimen magnetite peaks which stem from some areas with too low Al concentration, Fig. 17.

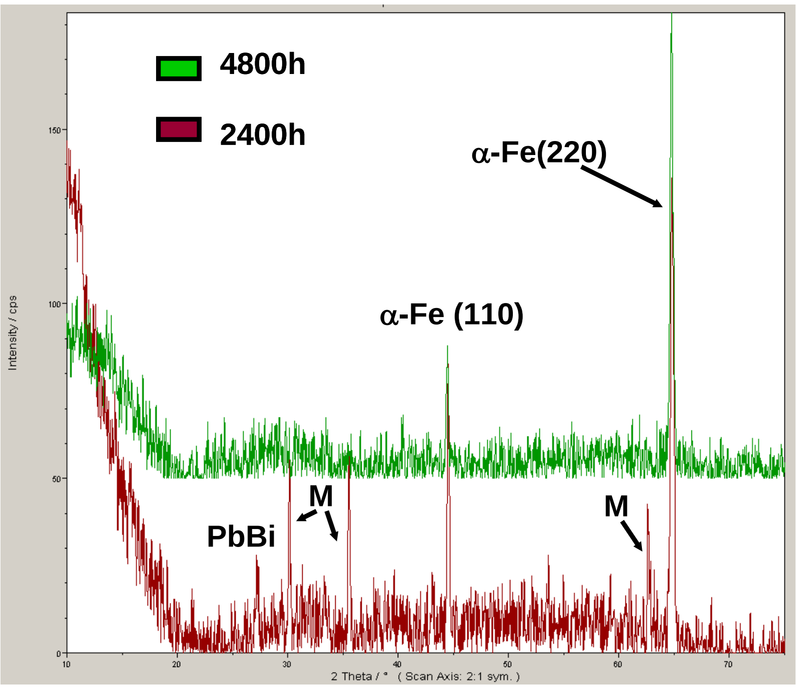

Fig. 17 XRD spectra of two specimens alloyed with Al by GESA after exposure to LBE with 10^{-6}wt% oxygen at temperatures changing between 550 and 650°C for 2400h and 4800h, respectively. (M=Magnetite)

3.1.3 Original ODS exposed 2400h and 4800h at an oxygen concentration of 10^{-8}wt%

ODS exposed at 10^{-8} wt% of oxygen shows no visible oxide scale. It is not clear from Fig. 13 if a very thin oxide layer prevents the specimen. There is also no indication of a real dissolution attack, which, if existent, should be very small. The holes below the surface are broken out during preparation and lay in a zone slightly depleted of Cr, Fig. 18 right.

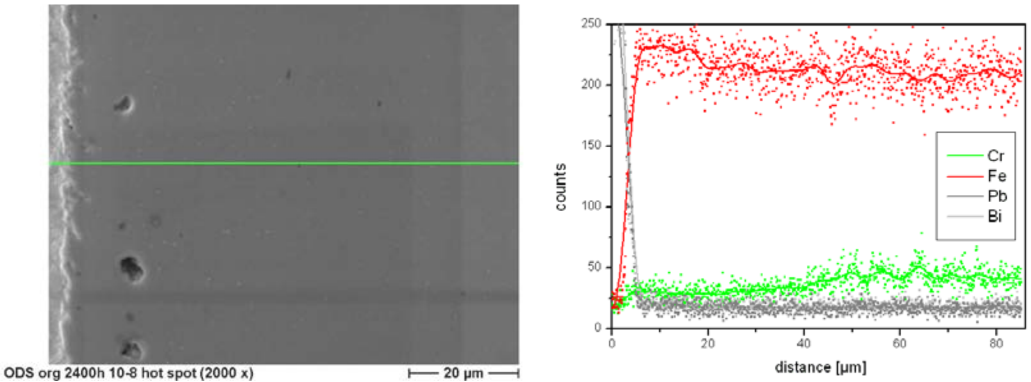

Fig. 18: SEM of ODS surface cross section after exposure to LBE with 10^{-8} wt% oxygen for 2400h at temperatures changing from 550 to 650°C and back every 800h (left), EDX across surface region (right).

The situation changes between 2400 and 4800h. Two kinds of corrosion phenomena are observed after exposure to LBE with 10^{-8}wt% oxygen and temperatures changing between 550°C and 650°C. Part of the surface exhibits dissolution attack with no visible oxide scale formation, Fig. 19 left. The other part formed a thin (<2µm) protective Cr spinel layer on top with an oxygen diffusion layer underneath which is sealed against the steel by a Cr-rich diffusion barrier, Fig. 19 right.

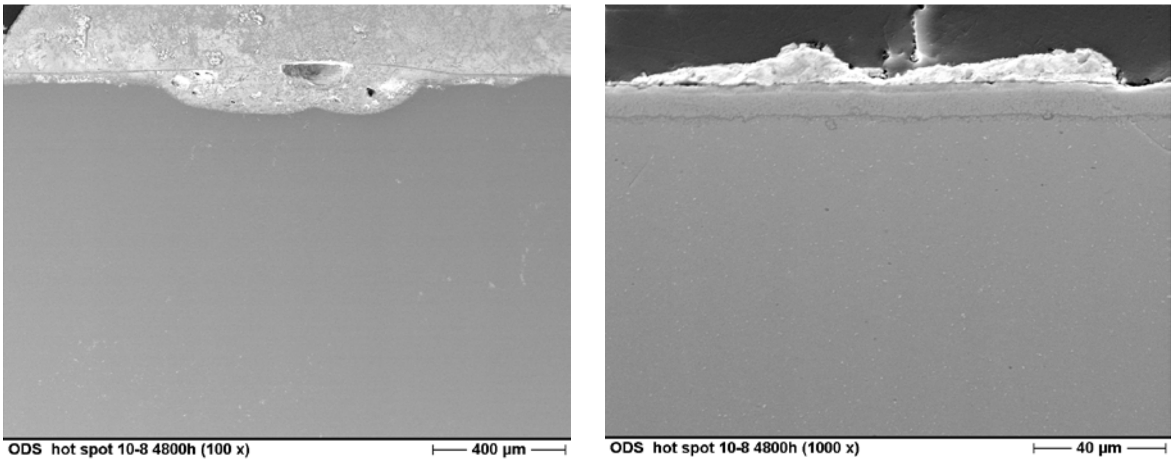

Fig. 19 Dissolution attack (left) and protective Cr-spinel layer (right) on ODS steel exposed to LBE with 10^{-8}wt% oxygen after 4800h exposure at temperatures changing between 550 to 650°C

For comparison with experiments on ODS at constant temperature of 650°C surface cross sections are presented in Fig. 20 which are obtained after 5000h exposure to LBE with 10^{-8}wt%. There is no dissolution attack visible. The specimen seems to be protected by a thin spinel layer, although there are some big holes present near the surface (Fig. 20 left). Some nodes which appear occasionally are observed in Fig. 20, right.

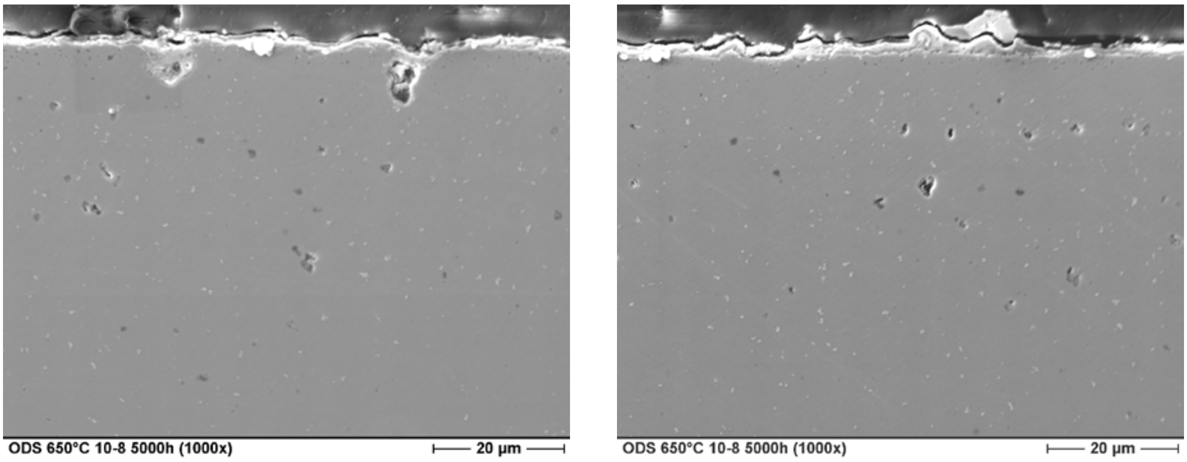

Fig. 20: ODS after exposure to LBE with 10^{-8}wt% oxygen at constant 650°C (COSTA) for 5000h, for comparison to Fig. 19

The XRD spectra of the two ODS specimens exposed to LBE with 10^{-8}wt% oxygen at temperatures changing between 550 and 650°C (Fig. 21) show mainly dominating α-Fe peaks and after 4800h also spinel peaks. This is in accordance with the respective micrographs in Fig. 18 and 19. It means, there is a very thin spinel layer after 2400 and an appreciable spinel layer after 4800h, which is visible on Fig. 19, right. The large α-Fe peaks on the 4800h specimen shows however that there are also areas with a very thin spinel layer. The PbBi peaks after 2400h may indicate some reaction or that LBE was not entirely removed.

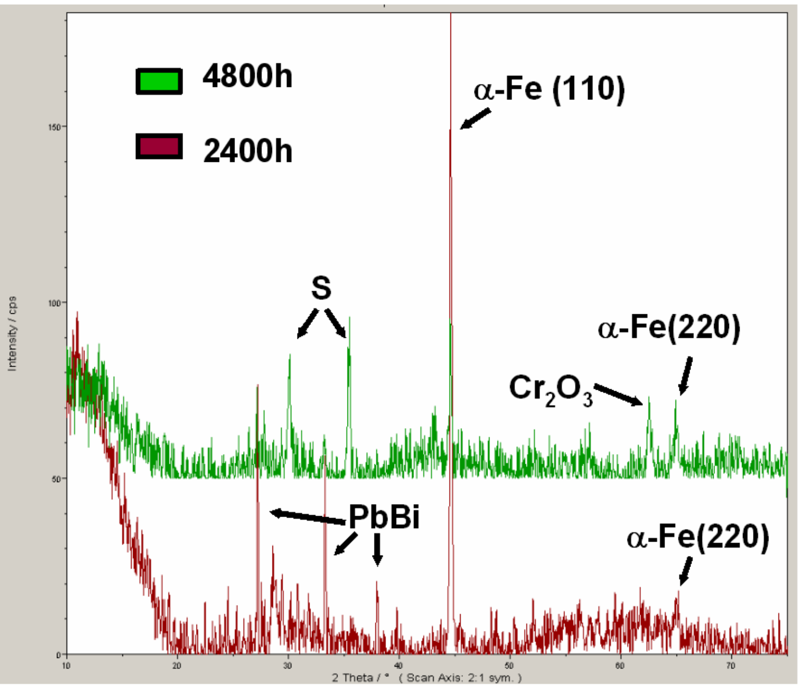

Fig. 21: XRD sprectra of two specimens after exposure to LBE with 10^{-8}wt% oxygen at temperatures changing between 550 and 600°C (S=Spinel)

3.1.4 Behaviour of Cr in experiments with temperatures fluctuating between 550 and 650°C

During spinel formation at the surface of original ODS steel changes in Cr concentration occur which depend on the temperature fluctuations and oxygen activity in LBE and also on the exposure time. The general observation is a more or less constant Cr concentration in the spinel zone which is above the mean concentration in the bulk. Furthermore a Cr enrichment takes place at the interface spinel/bulk which leads to a spinel formation with very high Cr concentrations. The Cr concentrations in the two zones that can be distinguished are listed in Tab.5.

Exposure time [h]	Spinel zone [wt%]	Interface spinel/bulk [wt%]	Extension of spinel zone [µm]
2400	19.9	27.8	18
4800	19	34.3	10 – 18

Tab. 5 Development of Cr-concentration on the ODS surface exposed to LBE with 10^{-6}wt% oxygen at temperatures changing between 550 and 650°C

The location of the small band of enhanced concentration at the interface can be recognized by looking at the Cr concentration curves presented in Fig. 10 and 11. The band is not broader than 1-2µm and the maximum concentration must be much higher than given in Tab. 5 if one considers the extension of the electron beam used for EDX analysis.

The step from 550°C to 650°C means also a step from higher to lower oxygen activity at constant oxygen concentration. Therefore it is worthwhile to look at the result of the CORRIDA experiment in which a strong fluctuation in the oxygen activity took place during the first exposure periods. The results are listed in Tab. 6.

Exposure time [h]	Spinel zone [wt%]	Interface spinel/bulk [wt%]	Extension of spinel zone [µm]
800	13.0	23.5	4.08
2000	18.9	31.2	8.19
5000	17.1	41.5	14 (original part on GESA treated sample)

Tab. 6 Development of Cr-concentration on the surface of ODS exposed to flowing LBE with changing oxygen activity at 550

We see that fluctuations in temperature and in oxygen activity, respectively, lead to similar results. After a short initial period the Cr content in spinel keeps constant while the Cr concentration at the interface increases to values above 50wt% if one takes into account that the electron beam of the EDX is by far too thick to produce a representative value of the peak maximum.

The high Cr-oxide layer on the interface constitutes an effective barrier against cation and anion diffusion with the consequence of no further oxidation of the bulk and prevention of the spinel layer growth. Looking at the spinel layer extension after 4800h we see partly a diminishing of the spinel by a factor of two but no growth. It seems that due to temperature changes the spinel layer spalls partially off in thin layers.

3.1.5 Surface alloyed ODS exposed 2400h and 4800h at an oxygen concentration of 10^{-8}wt %

At low oxygen concentration in LBE interaction of LBE with the steel surface takes place because Al-dissolution in LBE is fast enough to prevent protective Al_2O_3-formation on the surface, Fig. 22. The behaviour at positions with low Al-concentration is in agreement with results obtained at original ODS surfaces presented in Fig. 18.

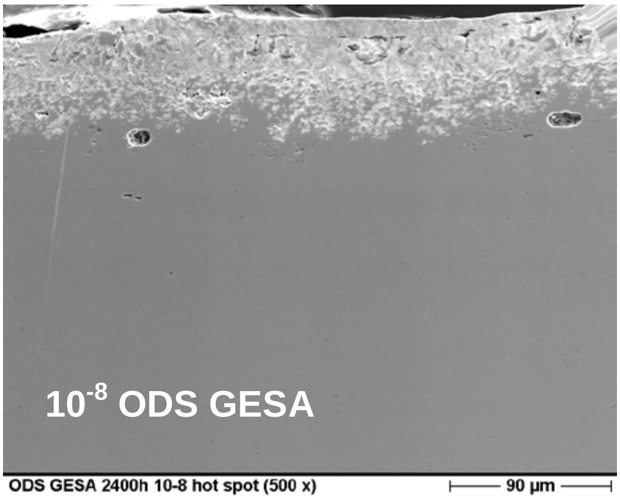

Fig. 22: SEM of ODS surface part alloyed with Al after exposure to LBE with 10^{-8}wt % oxygen for 2400h at temperatures fluctuating between 550°C and 650°C every 800h.

The GESA treated sample specimens also shows nearly overall dissolution attack after 4800h exposure to LBE with 10^{-8}wt% oxygen at temperatures changing between 550 and 650°C. This was to be expected already from the result after 2400h. Note, Fig. 23 has a magnification which is lower by one order of magnitude.

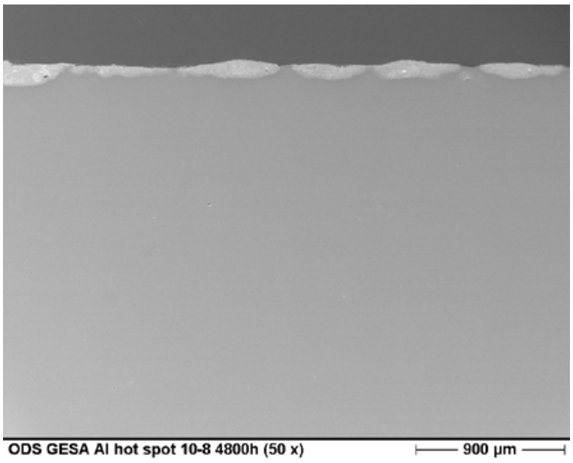

Fig. 23 SEM of ODS surface part alloyed with Al after exposure to LBE with 10^{-8}wt % oxygen for 4800h at temperatures fluctuating between 550°C and 650°C every 800h

The XRD of the specimen alloyed with Al by GESA shows only α-Fe peaks after exposure to LBE with 10^{-8}wt% oxygen at temperatures changing between 550 and 650°C. Scattering in the vicinity of the PbBi peak positions indicates that there is still some LBE remaining in the surface. Most of the LBE or reaction products are removed by washing the surface.

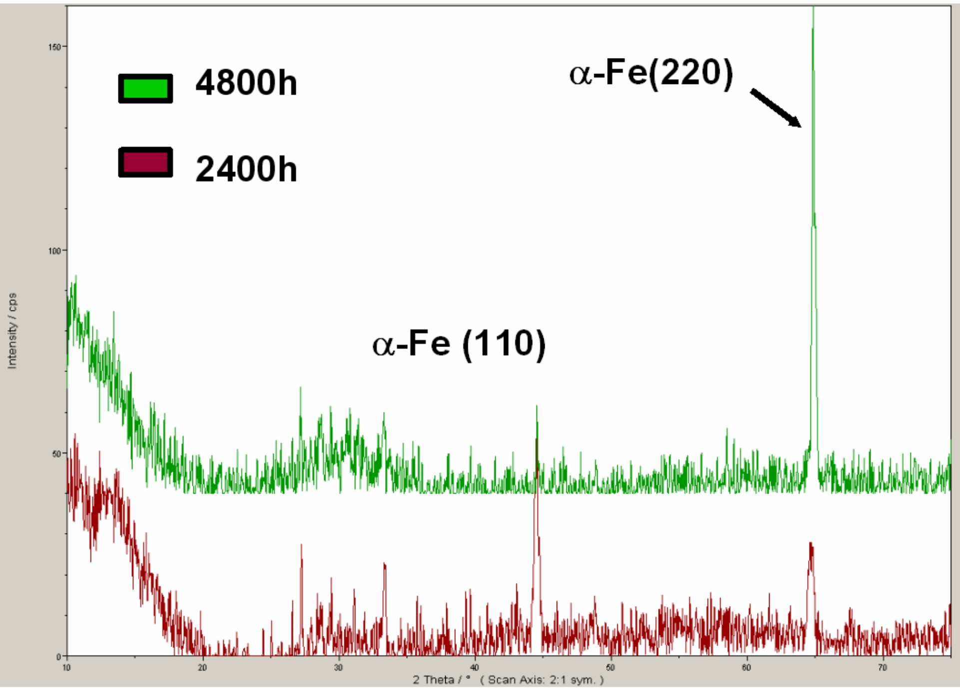

Fig. 24: XRD of two specimens alloyed with Al by GESA after exposure to LBE with 10^{-8}wt% oxygen at temperatures changing between 550 and 650°C for 2400 and 4800h exposure, respectively.

3.2 Fluctuation of oxygen concentration, 10^{-6} / 10^{-8}wt%, P122 steel

3.2.1 Bulk material and welded joint ODS exposed 4000h at 550°C

A dense magnetite and spinel layer develops on the P122 surface during the experiments with fluctuating oxygen concentration after 4000h of exposure, Fig. 25. On the bulk material and heat affected zone the layers are of almost constant thickness (14 µm) while on the weld seam the thickness scatters from place to place. The Cr content in the spinel layer reaches 20 wt%. LBE penetrated the magnetite layer and precipitated in the interface to the spinel layer, thus, separating the magnetite layer. This effect is largest in the heat affected zone, however, in any case the protective nature of the spinel zone is maintained.

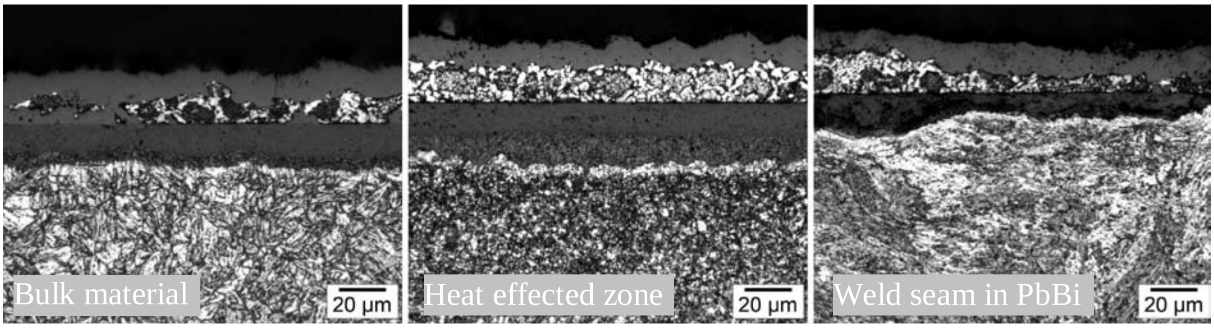

Fig. 25: LOM of the oxide scale and surface region on the different zones in the welded joint with oxygen concentrations of 10^{-6} / 10^{-8}wt% changing every 800h at 550°C.

Parallel to the experiment with changing oxygen concentration a second experiment with constant oxygen concentration at 10^{-6}wt% was conducted for comparison at the same temperature of 550°C. The result is shown in Fig. 26.

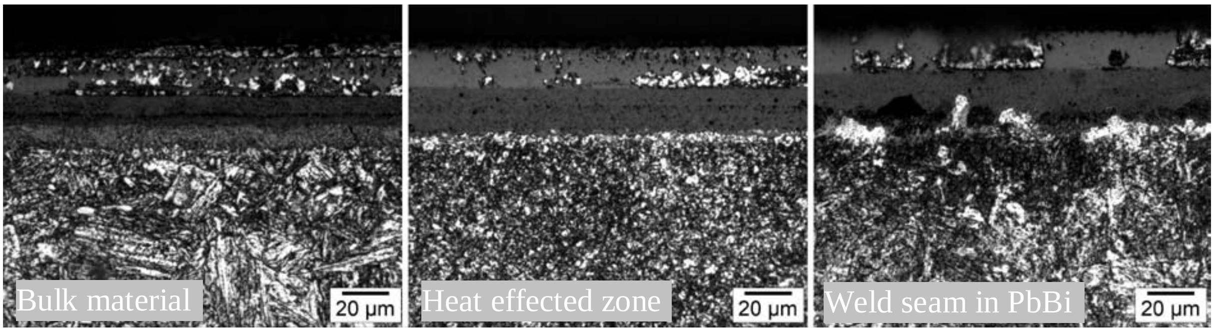

Fig. 26: LOM of the oxide scale and surface region on the different zones in the welded joint with constant oxygen concentration of 10^{-6}wt% at 550°C.

The appearance of the oxide scales formed with constant oxygen concentration is similar to that shown in Fig. 25. However, the scale in Fig. 26 seems to have higher porosity and is of larger thickness (24µm). Its spinel zone contains less Cr, about 16wt%. The magnetite layer is not separated but contains LBE in its pores, however, especially in the heat affected zone to a lesser extend than observed in Fig. 25.

The XRD of the bulk material of the welded joint P122 specimen exposed to LBE with oxygen concentrations changing between 10^{-6} and 10^{-8}wt% at 550°C for 4000h, Fig. 27 reflects the findings obtained in Fig. 25. Magnetite and spinel peaks are present together with that of PbBi. The spinel peaks may stem from the areas where the magnetite layer is removed. They are not visible on the specimen exposed to a constant oxygen concentration of 10^{-6}wt% in LBE.

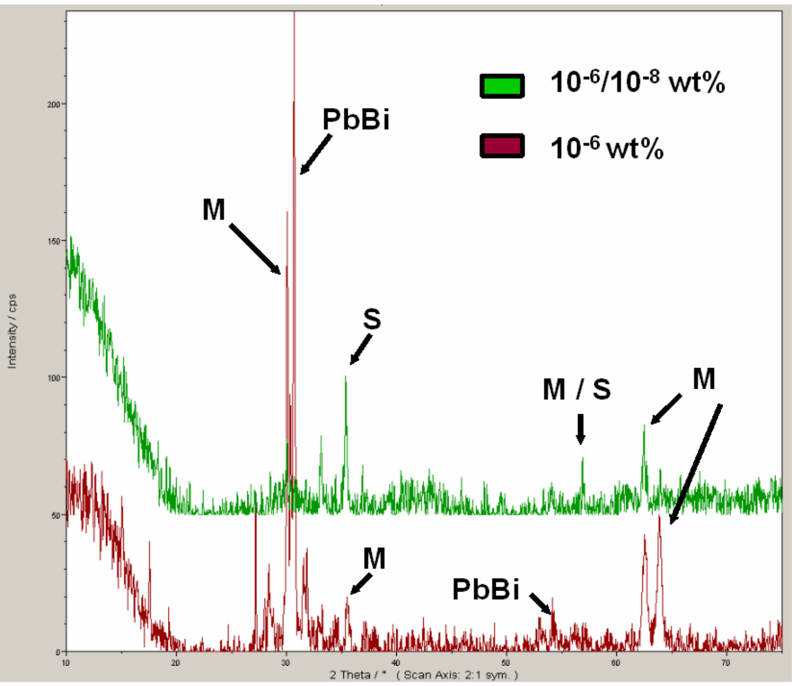

Fig. 27: XRD spectra of two specimens exposed for 4000h at 550°C to LBE with an oxygen concentrations that changes between 10^{-6} and 10^{-8}wt% and that is constant at 10^{-6}wt%, respectively.

3.2.2 *GESA treated bulk material exposed 4000h at 550° C*

Bulk material of P122 surface alloyed with Al by GESA does not show any corrosion by dissolution processes in LBE at 550°C with oxygen concentrations fluctuating between 10^{-6}wt % and 10^{-8}wt % as indicated by Fig. 28. For comparison Fig. 28 left shows GESA treated P122 steel after exposure to LBE with constant oxygen concentration of 10^{-6}wt %. In both cases a thin Al_2O_3 scale on the surface protects the steel specimen from dissolution attack by LBE.

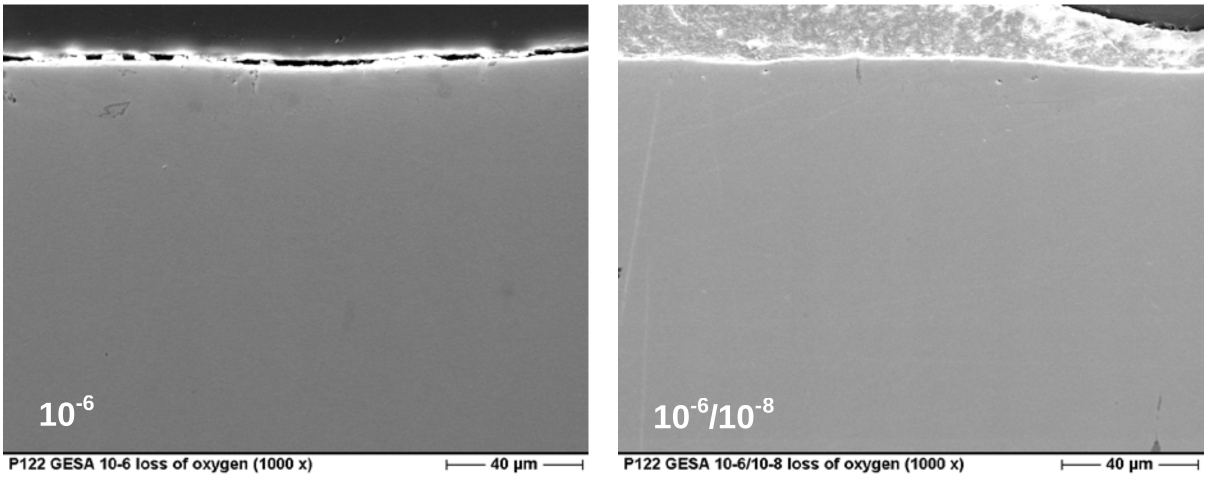

Fig. 28: SEM of cross section of P122, GESA treated, after exposure to LBE with fluctuating (right) and constant (left) oxygen concentration at 550°C.

As expected from the result of metallographic analysis the XRD spectra, Fig. 28, of the P122 specimen alloyed with Al by GESA exhibit no distinct oxide peaks but only α-Fe peaks, Fig 29. The alumina scale is to thin for producing the respective peaks. The same is observed for the specimen exposed to 10^{-6}wt% oxygen and otherwise under the same conditions. The PbO-peaks may stem from PbO remained of the surface after wasting off the LBE.

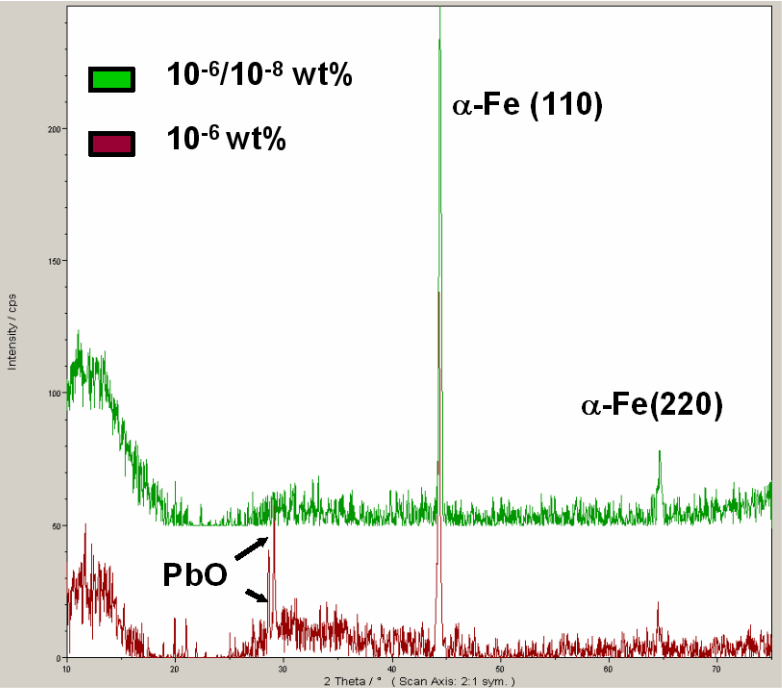

Fig. 29: XRD spectra of two P122 specimens alloyed with Al by GESA for 4000h at oxygen concentrations that change between 10^{-6} and 10^{-8}wt% and that is constant at 10^{-6}wt% respectively

3.3 *Summary of experimental data*

The results obtained in the corrosion experiments are listed in Tab. 7.

The temperature fluctuation experiments with temperatures changing from 550°C to 650°C and back every 800h yield satisfying corrosion resistance only for the GESA alloyed surface of ODS exposed to LBE with 10^{-6}wt% oxygen. Original ODS was protected in LBE with 10^{-6}wt% and 10^{-8}wt% of oxygen at fluctuating temperatures only up to 2400h. After 4800h severe local dissolution attack was observed for 10^{-6}wt% and 10^{-8}wt% oxygen as well. GESA alloyed ODS in LBE with 10^{-8}wt% oxygen showed dissolution attack already after 2400h.

Oxygen concentration fluctuations from 10^{-6} to 10^{-8}wt% oxygen and back every 800h did not lead to a dissolution attack on P122 steel and its welded joints as well as on P122 with a surface Al alloyed by GESA. The original P122 steel and its welded joints have protective spinel layers covered by magnetite which is penetrated by LBE. The penetration is more extended in the heat affected zone of the welded specimen exposed under fluctuating temperatures. In these specimens the penetrated LBE is accumulated at the interface between the dense magnetite layer and the spinel. As opposed to this, in the welded specimen exposed at a constant temperature of 550°C, the LBE is precipitated in the porous magnetite layer itself. Nevertheless, the spinel layer is protective in any way.

The GESA treated P122 steel is protected by a thin alumina scale against oxidation and dissolution attack.

Temperature fluctuations 550°C-650°C

	ODS original		ODS +GESA	
Experiment	10^{-6}wt%	10^{-8}wt%	10^{-6}wt%	10^{-8}wt%
2400h	Protective oxide scale, attack at 2 spots with Cr depletion	No interaction, thin spinel layer	No interaction, thin alumina scale	Dissolution attack
4800h	Local dissolution attack, partly Cr depletion	Local dissolution attack, Cr depletion	No interaction, thin alumina scale	Dissolution attack

Oxygen concentration fluctuations 10^{-6} – 10^{-8}wt%, 550°C

Experiment	P122 original	P122 welded joint	P122 + GESA
4000h	No interaction, protective spinel, LBE penetrated magnetite, partly separated	No interaction, protective spinel, LBE penetrated magnetite, partly separated	No interaction, thin protective alumina scale

Tab. 7 Summary of experimental data

4 Discussion

In the following a detailed description is given of the corrosion phenomenon observed.

Spinel oxide scales without magnetite develop on ODS under conditions of temperatures fluctuating between 550 and 650°C every 800h. At an oxygen concentration of 10^{-6}wt% the spinel layer is relatively thick, while at 10^{-8} wt% only a thin spinel layer is formed. The spinel layer prevents the ODS steel in the first period up to 2400h from dissolution attack with the exception of two spots on one of two specimens exposed to LBE with 10^{-6}wt% oxygen. This agrees also with former experiments with ODS at a constant temperature of 550°C and 10^{-6} wt% oxygen concentration up to 2000h of exposure [13]. However, strong local dissolution attack occurred on ODS steel after the exposure for 4800h at temperatures changing between 550 and 650°C. The attack starts in areas of depleted Cr concentration in which protective spinel formation does not take place any more after the prolonged exposure time. This agrees with the observation of the behavior of ODS during exposure to LBE with 10^{-6}wt% oxygen at a constant temperature of 650°C. The holes observed below the surface are originated by Cr-oxycarbide particles that break out during grinding. Defects in the spinel layer that may be caused by the temperature fluctuations can not be repaired because of the low Cr-concentrations in these places. In areas protected by an intact spinel layer a Cr enrichment at the spinel/bulk interface takes place which forms an effective diffusion barrier. Thus, further spinel growth and steel oxidation is prevented in these areas.

The positive result with GESA treated ODS steel under fluctuating temperatures in LBE with 10^{-6}wt% oxygen is obtained because of a stable alumina scale at the surface and the ability of self healing incase of a defect. This is possible because of migration of Al to the defect place and a sufficient supply of oxygen out of the LBE. In case of 10^{-8}wt% of oxygen the source of oxygen may be to low to ensure healing of defects. The high solubility of Al in LBE can prevent alumina scale formation at this low oxygen concentration. Therefore the GESA alloyed steel does not withstand the dissolution attack under condition of temperature fluctuations at 10^{-8}wt% oxygen.

The P122 specimen tested under loss of oxygen control conditions by fluctuation of the oxygen concentration every 800h (10^{-6} / 10^{-8}wt%) behaves in principal similar like the one tested at constant oxygen concentration of 10^{-6}wt% oxygen at 550°C. In both specimens Pb-Bi penetrates into the magnetite layer. However, a difference exists in the allocation of PbBi precipitates. In the constant 10^{-6}wt% specimen they distribute in more or less fine pores inside the magnetite, while in the specimen with fluctuating oxygen concentration they are located just between magnetite layer and spinel. In the loss of oxygen specimen the magnetite layer appears denser and does not allow formation of Pb-Bi inclusions in it. It is especially inside the heat affected zone, detached from the spinel layer by precipitated LBE. The spinel, however, keeps still its protective function.

Three different grain structures are observed in welded P122 joints. The finest grains appear in the transition zone between the welding and bulk material, the heat effected zone. The welded joint is a typical coarse-grained martensitic structure. The grain size of the bulk material is in between that of the both described structures. Despite this, the structures of the different oxide zones after exposure to LBE with fluctuating oxygen concentration are very similar with two exceptions. One is the thickness variation above the weld seam, which is caused by the coarse grains of this zone. The other is the more extended LBE infiltration into the spinel/magnetite interface which separates both layers. Nevertheless all parts of the weld are protected by a dense spinel layer.

There is no attack observed on GESA treated P122 for oxygen concentration fluctuations between 10^{-6} and 10^{-8}wt% at 550°C because of a thin protective Al_2O_3 scale on the surface. Due to the absence of temperature fluctuations it cannot be answered what would happen if the temperature changes during the period with 10^{-8}wt% oxygen in LBE.

5 Conclusion and summary

One goal of this work was to examine the behaviour of ODS steel in LBE with 10^{-6}wt% and 10^{-8}wt% oxygen under conditions of temperatures fluctuating between 550 and 650°C every 800h, to simulate its reaction to hot spots. The other goal was to examine the behaviour of P122 steel and its welded joint at 550°C in LBE with an oxygen concentration fluctuating between 10^{-6} and 10^{-8}wt% every 800h, to simulate loss of oxygen conditions.

The conclusions drawn from the experiments on ODS at temperatures fluctuating between 550 and 650°C are:

1. Original ODS at 10^{-6}wt% oxygen

- After 2400h oxide scales without magnetite develop in the hot spot experiments. The thickness of the oxide scale is around 15µm. After 4800h the oxide scale is similar but with reduced thickness, by a factor of 2. Probably a layer by layer spallation of the spinel takes place without further growth because of the diffusion barrier formed by migrating oxidized Cr at the spinel/bulk interface

- After both exposure times some local deep dissolution attack was observed (300µm deep after 2400h, two local points in one of two specimens; 600µm deep after 4800h.)
- Comparison with former experiments in PbBi with 10^{-6}wt% oxygen show no attack on ODS at 550°C but a large area dissolution attack at 650°C.
- The hot spot experiment shows that dissolution attack can not be prevented at 650°C, also if before at 550°C the formation of a protective oxide layer took place.

2. Original ODS at 10^{-8}wt% oxygen

- There is no dissolution and oxidation attack visible on ODS steel after exposure at 10^{-8}wt% oxygen under hot spot conditions (550–650 °C) for 2400h
- But after longer exposure for 4800h some local dissolution attack was observed, the major part of the surface is still protected by a thin spinel layer
- Pores accompanied by lowered Cr concentration near the surface are observed in both cases. They appear during grinding when Cr-oxy-carbides precipitated in grain boundaries break out of the surface.

3. GESA treated steel at 10^{-6}wt% oxygen

There is no dissolution attack at all in hot spot experiments (550–650°C) in PbBi with 10^{-6} wt% oxygen with GESA treated ODS. This agrees with former experiments on GESA treated ODS at 550°C and 650°C at 10^{-6}wt% oxygen.

4. GESA treated steel at 10^{-8}wt% oxygen

In contrary to the case at 10^{-6}wt% oxygen dissolution attack is observed. It looks like the low oxygen concentration hinders formation of a protective alumina scale because of the high solubility of aluminum in PbBi.

The conclusion drawn from experiments with oxygen concentrations fluctuating between 10^{-6} and 10^{-8}wt% oxygen at 550°C are:

- Normal P122 steel and its welded joints develop magnetite/spinel layers
- LBE penetrates the magnetite layer but not the spinel layer on P122 and its welded joint and is accumulated in the interface between spinel and magnetite

- The spinel layer prevents the P122 steel and its welded joint from dissolution attack
- The P122 steel and its welded joint have at constant 10^{-6}wt% oxygen and 550°C generally the same behaviour but with LBE precipitation in the porous magnetite layer and not into the interface magnetite/spinel.
- Welding does not impose a problem to the protection by surface oxide.
- GESA Al-alloyed specimens show for both conditions (10^{-6} and $10^{-6}/10^{-8}$) no dissolution and no visible steel oxidation.

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