

# Study on Pb-Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications

Part IV. Corrosion investigation of steels at 550 and 650°C after 800, 2,000 and 5,000 h of exposure to stagnant liquid Pb-Bi containing  $10^{-4}$  and  $10^{-5}$  wt% of oxygen

January, 2004



**Japan Nuclear Cycle Development Institute**  
**Forschungszentrum Karlsruhe GmbH**

本資料の全部または一部を複写・複製・転載する場合は、下記にお問い合わせください。

〒319-1184 茨城県那珂郡東海村村松4番地49  
核燃料サイクル開発機構  
技術展開部 技術協力課  
電話：029-282-1122 (代表)  
ファックス：029-282-7980  
電子メール：jserv@jnc.go.jp

Inquiries about copyright and reproduction should be addressed to :

Technical Cooperation Section,  
Technology Management Division,  
Japan Nuclear Cycle Development Institute  
4-49 Muramatsu, Tokai-mura, Naka-gun, Ibaraki, 319-1184  
Japan

©核燃料サイクル開発機構 (Japan Nuclear Cycle Development Institute)  
独国・カールスルーエ研究所 (Forschungszentrum Karlsruhe GmbH)  
2004

# Study on Pb-Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications

*Part IV. Corrosion investigation of steels at 550 and 650 °C after 800, 2, 000 and 5, 000 h of exposure to stagnant liquid Pb-Bi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen*

Georg Müller\*, Gustav Schumacher\*, Alfons Weisenburger\*,  
Annette Heinzl\*, Frank Zimmermann\*, Tomohiro Furukawa\*\*  
and Kazumi Aoto\*\*

## Abstract

This is the fourth report on the compatibility of structural and fuel cladding materials that has to be investigated for a possible advanced heavy metal cooled reactor system.

The first three reports considered the behavior of 316FR, P122 and ODS steels during 800, 2,000, 5,000 and 10,000 h in stagnant LBE between 500 and 650 °C containing  $10^{-6}$  wt% of oxygen. This report describes experiments of 800, 2,000 and 5,000 h duration in liquid Pb-Bi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen for 316FR, P122 and ODS steels at 550 and 650 °C.

1. No significant dissolution attack occurred on 316FR and P122 steels at 550 °C with  $10^{-4}$  wt% oxygen in LBE. They have protective oxide layers at the surface, like in the experiments with  $10^{-6}$  wt% oxygen. At the high oxygen concentration ( $10^{-4}$  wt%) thick oxide multilayers develop on 316FR instead of thin spinel layers at  $10^{-6}$  wt%, in both experiments LBE is enclosed in the oxide layer. With  $10^{-8}$  at% oxygen in LBE, however, there is no protective scale formation but strong dissolution attack (up to 120  $\mu\text{m}$ ) occurs at the 316FR specimen. At the P122 only very little dissolution attack (<2  $\mu\text{m}$ ) is observed at the surface.
2. Oxide scale formation of 5 – 8  $\mu\text{m}$  on ODS at 650 °C with  $10^{-4}$  wt% oxygen, thin scale with  $10^{-8}$  wt%. At  $10^{-4}$  wt% oxygen samples are attacked at the surface like in LBE with  $10^{-6}$  wt% oxygen. After 5,000 h of exposure, like with the P122, some spots with a flat dissolution attack < 3  $\mu\text{m}$  can be observed. Dissolution attack is less than in samples exposed to higher oxygen concentrations of  $10^{-6}$  and  $10^{-4}$  wt%.
3. No attack on GESA alloyed ODS at  $10^{-4}$  wt% oxygen. For the  $10^{-8}$  wt% specimen no conclusion can be drawn because of failures in the alloying process.

---

\* Institute for Pulsed Power and Microwave Technology, Forschungszentrum Karlsruhe GmbH

\*\* Advanced Material Research Group, Advanced Technology Division, O-arai Engineering Center, Japan Nuclear Cycle Development Institute

## 原子炉構造材料及び燃料材料の鉛ビスマス中腐食に関する研究

第4報:  $10^{-4}$ wt%および $10^{-8}$ wt%の酸素を含有した550°Cおよび650°Cの停留鉛ビスマス中における800、2,000および5,000時間浸漬材の腐食評価

Georg Müller\*, Gustav Schumacher\*, Alfons Weisenburger\*,  
Annette Heinzl\*, Frank Zimmermann\*, 古川 智弘\*\*, 青砥 紀身\*\*

### 要 旨

本報告書は、重金属冷却炉への適用が検討されている炉心・構造材料の鉛ビスマス中における耐食性評価に関する第4報である。

第1報から第3報では、 $10^{-6}$ wt%の酸素を含有する500°Cから650°Cの停留鉛ビスマス中における316FR、P122(12Cr鋼)およびODS-M鋼の800、2,000、5,000および10,000時間浸漬後の腐食挙動について報告した。本報告書では、これら3鋼種の $10^{-4}$ wt%および $10^{-8}$ wt%の酸素を含有した550°Cおよび650°Cの停留鉛ビスマス中における800、2,000および5,000時間浸漬材の腐食挙動について報告する。

本研究により得られた主な知見は以下のとおり。

1. 550°C、酸素濃度 $10^{-4}$ wt%の鉛ビスマス中において、316FRおよびP122鋼にはDissolution attackは観察されなかった。これらの試験片表面には、酸素濃度 $10^{-6}$ wt%の試験結果と同様に、酸化(保護)皮膜が形成されていた。 $10^{-6}$ wt%の酸素濃度条件において、316FR表面には薄いスピネル層が形成されていたが、本高酸素濃度条件( $10^{-4}$ wt%)の同材上には、複数の層からなる厚い酸化層が形成されていた。なお、両ケースにおいて、酸化層内にLBEは侵入している。 $10^{-8}$ wt%の鉛ビスマス中酸素濃度条件下では、試験片表面には酸化(保護)皮膜は観察されず、316FR試験片では120 $\mu$ mに達するDissolution attackが観察された。P122では、ほとんど鉛ビスマスによる腐食が観察されていない(2 $\mu$ m以下)。
2. 650°CにおけるODS鋼の酸化皮膜は、酸素濃度 $10^{-4}$ wt%の鉛ビスマス中では5~8 $\mu$ mであり、 $10^{-8}$ wt%条件下では極わずかであった。 $10^{-4}$ wt%条件下の試験材表面には、 $10^{-6}$ wt%条件下試験材と同様な損傷を生じていた。 $10^{-8}$ wt%下の5,000時間浸漬後には、P122のように3 $\mu$ m以下のわずかな腐食が複数の観察位置で認められた。 $10^{-8}$ wt%条件下でのDissolution attackの程度は、 $10^{-4}$ wt%や $10^{-6}$ wt%試験材のそれらに比べて少なかった。
3.  $10^{-4}$ wt%の酸素濃度条件下で浸漬したODS-GESA(アルミニウム表面改質材)には腐食が認められなかった。 $10^{-8}$ wt%試験材については、表面改質(製作)過程での不具合が発生していたため、結論を得るには至らなかった。

\* 独国・カールスルーエ研究所、Institute for Pulsed Power and Microwave Technology

\*\* 核燃料サイクル開発機構 大洗工学センター 要素技術開発部 新材料研究グループ

## Content

1	Introduction .....	1
2	Oxygen control .....	3
3	Results after 800, 2000 and 5000 h of exposure to LBE with $10^{-4}$ wt% of oxygen	6
3.1	316FR steel, 550 °C .....	6
3.2	P122 steel, 550 °C .....	8
3.3	ODS steel 650 °C .....	10
3.3.1	ODS original .....	10
3.3.2	ODS steel GESA alloyed 650 °C .....	13
4	Results after 800, 2000 and 5000 h of exposure to LBE with $10^{-8}$ wt% of oxygen	14
4.1	316FR steel, 550 °C .....	14
4.2	P122 steel, 550 °C .....	16
4.3	ODS steel 650 °C .....	17
4.3.1	ODS original .....	17
4.3.2	ODS GESA alloyed .....	19
5	X-ray diffractometry of samples exposed to LBE .....	20
5.1	oxygen content $10^{-4}$ wt%, 550 °C .....	21
5.1.1	316FR steel .....	21
5.1.2	P122 steel .....	22
5.2	oxygen content $10^{-4}$ wt%, 650 °C .....	23
5.2.1	ODS steel .....	23
5.3	oxygen content $10^{-8}$ wt%, 550 °C .....	24
5.3.1	316FR steel .....	24
5.3.2	P122 steel .....	25
5.4	oxygen content $10^{-8}$ wt% .....	26
5.4.1	ODS steel .....	26
6	Results after exposure to furnace atmosphere .....	27
6.1	316FR steel .....	27
6.2	P122 steel .....	28
6.3	ODS steel .....	29
6.4	X-ray diffractometry of samples exposed to air .....	30
6.4.1	316FR at 550 °C, $10^{-4}$ and $10^{-8}$ wt% .....	30
6.4.2	P122 at 550 °C, $10^{-4}$ and $10^{-8}$ wt% .....	31
6.4.3	ODS at 550 °C, $10^{-8}$ wt% .....	32
7	Summary .....	33
7.1	Experiments with $10^{-4}$ wt% oxygen .....	33
7.2	Experiments with $10^{-8}$ wt% oxygen .....	33
7.3	Experiments in furnace atmosphere .....	34
8	Annex1: Longitudinal section of P122 and 316 at 550°C at $10^{-4}$ wt% .....	35

## 1 Introduction

This is the fourth report on the work started in October 2001 according to the research agreement between Japan Nuclear Cycle Development Institute (JNC) and Forschungszentrum Karlsruhe GmbH (FZK) entitled: "Cooperation regarding Study on Lead-Bismuth Corrosion Studies of the Structural and the Fuel Cladding Materials for Nuclear Application". The parts 1 to 4 of the "Study on Pb/Bi Corrosion of structural and fuel cladding materials for nuclear applications" describe corrosion investigation of steels after 800, 2,000, 5,000 and 10,000 hours of exposure to stagnant liquid Pb/Bi at temperatures of 500 to 650 °C in the COSTA device<sup>1</sup>. The concentration of oxygen in Pb/Bi was controlled at  $10^{-6}$  wt%. The first part of the report contained also a description of the principles of oxygen control through the gas phase and of the experimental devices and methods employed for the corrosion investigations.

The major results of the three reports concerning experiments in LBE containing  $10^{-6}$  wt% oxygen are:

- (1) At 500 °C after 5000 h of exposure all steels still show satisfying behavior. After 10,000 h the austenitic 316FR shows partly deep dissolution attack. No dissolution attack takes place on martensitic ODS and P122 steel. Maximum oxide layer thickness is 40 – 70 µm.
- (2) At 550 °C up to 2,000 h all steels have still protective oxide layers. After 10,000 h all steels show dissolution attack. The 316FR is attacked down to 200 µm, the ODS and P122 is attacked continuously to a depth of 20 µm only. The observed result for the martensitic steel is in contradiction to investigations of the same samples close below the surface of LBE. There no dissolution attack can be observed. Ongoing experiments will solve this discrepancy. Most probably the oxide layer spalls off, covers the LBE surface and than slows down the oxygen transport into the LBE. As a result the oxygen concentration drops with increasing distance from the LBE surface.
- (3) At 600 °C already after 2,000 h all steels show at least partly dissolution attack. After 10,000 h a complete massive surface attack occurs on all of the steels up to a depth of 200 µm.

---

<sup>1</sup> JNC report TY 9400 2002-016 -023, Study on Pb/Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications, June 2002, Japan

(4) At 650 °C after 800 h the 316FR show attacks at some spots up to 30 µm in depth. After 5,000 h all of the original steel specimens are completely attacked with partly deep LBE penetration.

After alloying Al into the surface by GESA, materials show good corrosion resistance without any attack at all temperatures up to 10,000 h of exposure. Although, a few structural defects are observed on the surface, no dissolution attack occurs. The defect spots (small cracks) are closed with a Cr-Al spinel compound and sealed by this process. If too less Al exist in the steel surface formation of thick oxide layers occur like on original steels. As opposed to the original steels this oxide layers do not spall off during the whole exposure time of 10,000 h.

The present report describes the results obtained by conducting experiments up to 5,000 h of exposure to the LBE melt with 10<sup>-4</sup> and 10<sup>-8</sup> wt% of oxygen. Table 1 given below indicates the experiments planned and carried out. The dashed region depicts materials and parameters investigated for the reports 1,2 and 4 while the grey areas show those for the present fifth report. The third report was an intermediate report containing preliminary results of exposure to 10<sup>-4</sup> and 10<sup>-8</sup> wt% oxygen containing LBE and was presented to JNC in April 2003.

Material (amount)	T [°C]	O <sub>2</sub> content 10 <sup>-4</sup> w[%]				O <sub>2</sub> content 10 <sup>-8</sup> w[%]				O <sub>2</sub> content 10 <sup>-4</sup> - 10 <sup>-8</sup> w[%]*			
		800 h	2000 h	5000 h	10000 h	800 h	2000 h	5000 h	10000 h	800 h	2000 h	5000 h	10000 h
316FR original (15')	500					X	X	X	X				
	550	X	X	X		X	X	X	X	X	X	X	
	600					X	X	X	X				
316FR GESA (3)	500					X	X	X	X				
	550					X	X	X	X				
	600					X	X	X	X				
P122 Original (15')	500					X	X	X	X				
	550	X	X	X		X	X	X	X	X	X	X	
	600					X	X	X	X				
P122 GESA (3)	500					X	X	X	X				
	550					X	X	X	X				
	600					X	X	X	X				
ODS Original (18')	500					X	X	X	X				
	550					X	X	X	X				
	600					X	X	X	X				
	650	X	X	X		X	X	X	X	X	X	X	
ODS GESA (6)	500					X	X	X	X				
	550					X	X	X	X				
	600					X	X	X	X				
	650	X	X	X		X	X	X	X	X	X	X	

Table 1: Parameter set for corrosion investigation in COSTA

## 2 Oxygen control

A scheme of the technical realization of the oxygen control for the 4 furnaces (5,6,7,8) of the COSTA device for oxygen concentrations of  $10^{-4}$  and  $10^{-8}$  wt% is drawn in Fig. 1.

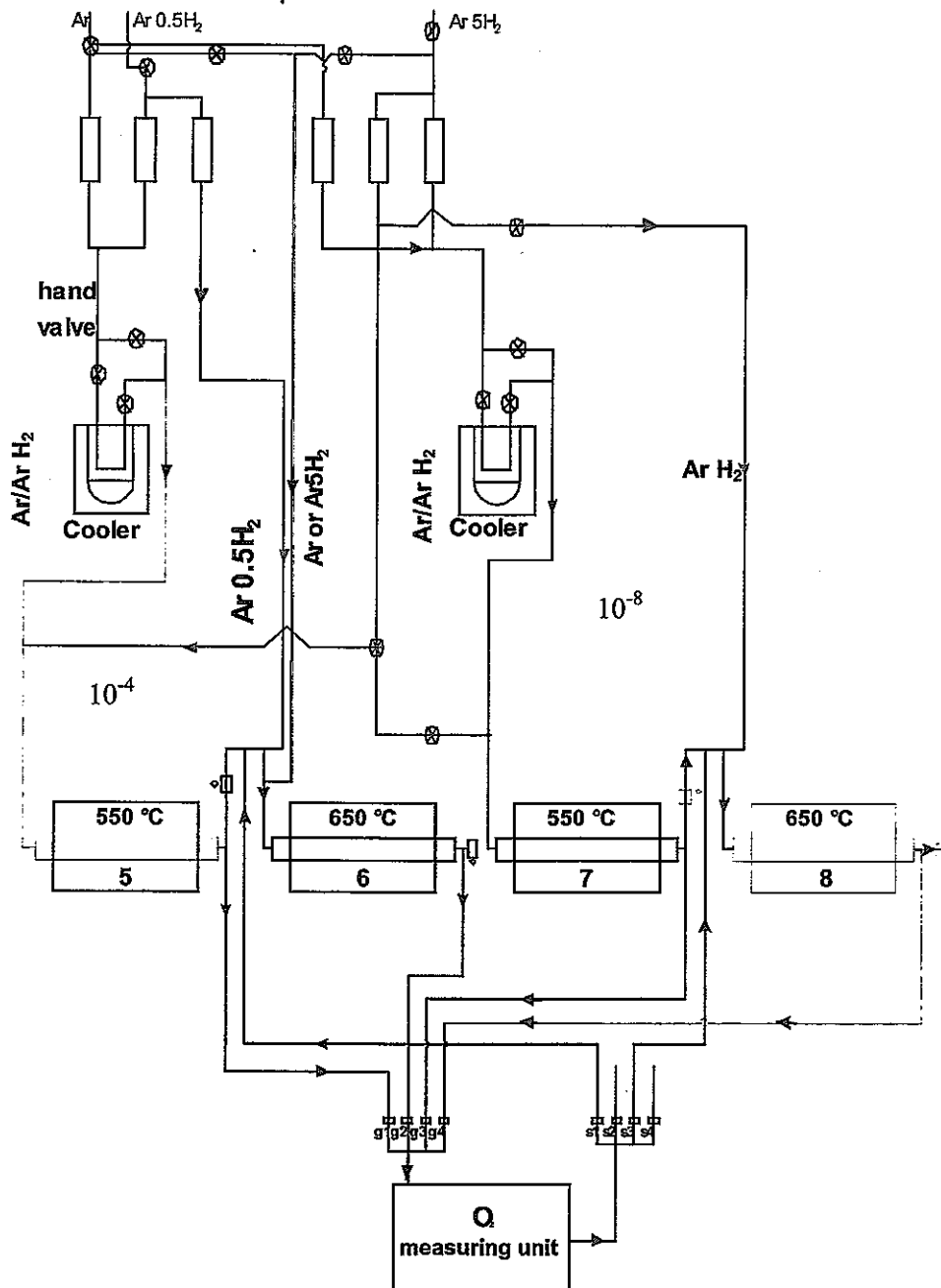


Fig. 1: Scheme of the technical realization of the oxygen control for the 4 furnaces

Also here, one Ar and one Ar 5% H<sub>2</sub> and one Ar 0.5% H<sub>2</sub> bottle (50 l, 200 bar) provide the gas for the experiment. The gas mixing system is designed such that 2



thermostats are sufficient for the gas conditioning. The gas mixture in the first line passes the thermostat and feeds into furnace 5 with 550 °C to keep the oxygen concentration at  $10^{-4}$  wt%. After it left the furnace just a little more  $H_2$  has to be added to reach this condition for the higher temperature, 650 °C, in furnace 6. From there it is released to the atmosphere. We remember, the oxygen concentration curves have a negative slope with temperature in the Ellingham diagram. Therefore, we need a higher  $H_2/H_2O$  ratio for the constant concentration at higher temperatures. The next 2 furnaces No. 7 and 8 are served in the same way. We did not consider the connections to the oxygen and moisture meter yet for reasons of simplifying. Each furnace exit is connected one after another for  $\frac{1}{2}$  h to the measurement station. When gas of furnace 5 is to be measured, the automatic valve at its exit is shut and the ones signed g1 and also s1 (Fig. 1) at the station are opened. Now the gas passes the measurement station before it comes back to the position behind the valve at the exit of furnace 5. From there the gas enters furnace 6. After  $\frac{1}{2}$  h of measurement the exit valve at furnace 5 is opened and valves g1 and s1 at the measurement station are shut while g2 and s2 are opened and the exit valve at furnace 6 is closed. Now the gas leaving furnace 6 is measured. After another  $\frac{1}{2}$  h g2 and s2 are shut and exit valve 6 opened. Now the same procedure as before starts for furnace 7 and 8. Note, that during measuring the gas of furnace 6 and 8 the gas is released after passing the measurement station to the atmosphere via valves s2 and s4, respectively.

Now the only question not answered is about the function of the hand valves in the flow meter region and before the thermostats. These valves are used to sweep dry Ar 5%  $H_2$  through the system for cleaning of the pipes or reduction of the liquid metal in oxygen if necessary. To increase the flow rate for reduction and cleaning a direct connection between a flow controller with high flow rate of Ar 5% $H_2$  (500 cm<sup>3</sup>/min) and furnace 5 and 7 is established. One has to remark that Furnace 6 can not be attached to the exchange glove box. To guarantee the controlled gas atmosphere during the exchange of specimens in this furnace a high flow rate of Ar or Ar 5% $H_2$  (> 2l/min) can be established via a separate gas-line using a regulator valve instead of a flow-controller.

The third series of experiments is carried out with 2 orders of magnitude higher oxygen concentration,  $10^{-4}$  wt%, and also 2 orders of magnitude lower oxygen concentration,  $10^{-8}$  wt%, compared to the first experiments which all were carried out with LBE containing  $10^{-6}$  wt% of oxygen. Table 2 shows the parameters of the third

series of experiments. The last 2 rows show the real oxygen partial pressures in the respective reaction tubes and the actual readings of the oxygen partial pressure meters from which they are calculated.

oxygen concentration [wt%]	$10^{-4}$		$10^{-8}$	
Temperature [°C]	550	650	550	650
H <sub>2</sub> /H <sub>2</sub> O ratio	$1.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	1.84	12.3
P <sub>O<sub>2</sub></sub> [bar]	$5.9 \cdot 10^{-19}$	$3.2 \cdot 10^{-17}$	$5.8 \cdot 10^{-27}$	$3.2 \cdot 10^{-25}$
P <sub>O<sub>2</sub></sub> [bar] at oxygen meter	$7.3 \cdot 10^{-13}$	$1.65 \cdot 10^{-14}$	$7.3 \cdot 10^{-21}$	$1.65 \cdot 10^{-22}$

Table 2: Parameter set of third experiment

We should note that the oxygen meters work at 750 °C, a temperature which is higher than that in the furnaces.

### 3 Results after 800, 2,000 and 5,000 h of exposure to LBE with $10^{-4}$ wt% of oxygen

#### 3.1 316FR steel, 550 °C

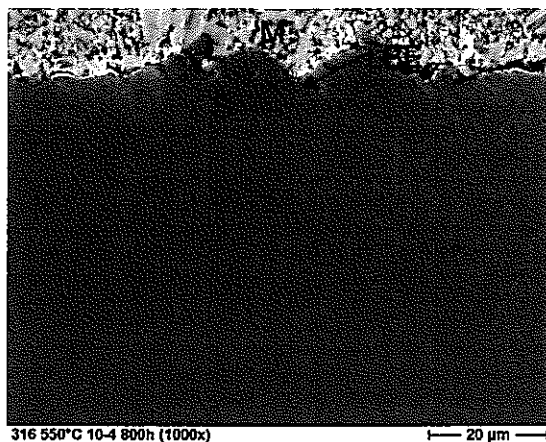


Fig. 2: Original 316FR after 800 h

Specimen 316FR without surface treatment, after 800 h of exposure, shows partially thick multilayered nodes consisting of a magnetite(M) and spinel(S) zone (Fig. 2). LBE is penetrated into the spinel layer and some dissolution of Ni takes place. Mn is enriched inside the spinel zone up to 3.9 wt% and on top of the magnetite zone up to 0.7 wt%. The main part of the surface is covered by a thin protective spinel layer. Compared to the respective specimen exposed to LBE with  $10^{-6}$  wt% we see no difference in oxidation behavior up to 800 h of exposure. In both cases we have no strong dissolution attack.

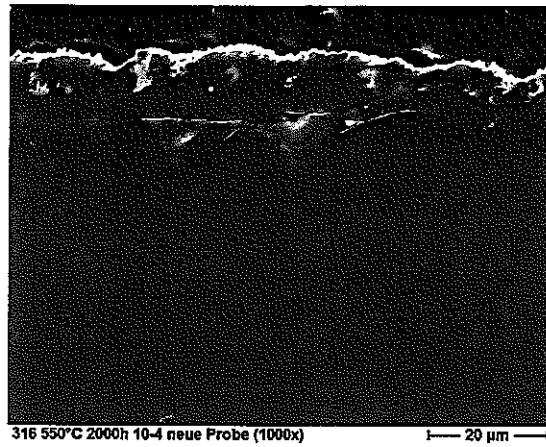


Fig. 3: Original 316FR after 2000 h

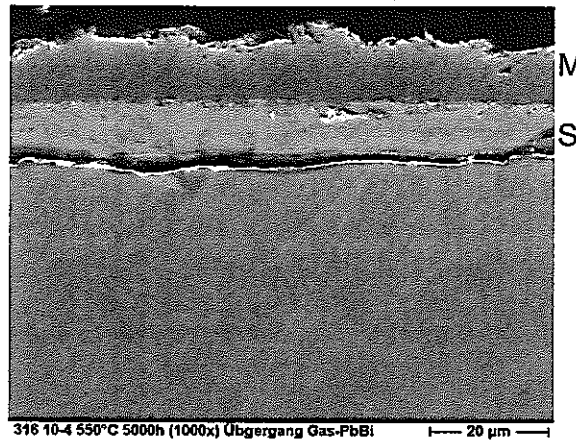


Fig. 4: Original 316FR after 5000 h

After 2,000 h of exposure up to 20 µm thick multilayered oxide scales appear. LBE is enclosed in this oxide layer. This does not change after 5,000 h of exposure. The thick oxide layer grows to about 30 µm. LBE penetrates the spinel layer and dissolution attack below the oxide scale can be observed at single spots. This attack can reach depths of 10 to 20 µm.

Compared to the respective specimen exposed to LBE with 10<sup>-6</sup> wt% we see no difference in oxidation behavior up to 5,000 h of exposure. In both cases we have oxide scales with some LBE enclosed and little dissolution beneath the scale.

### 3.2 P122 steel, 550 °C

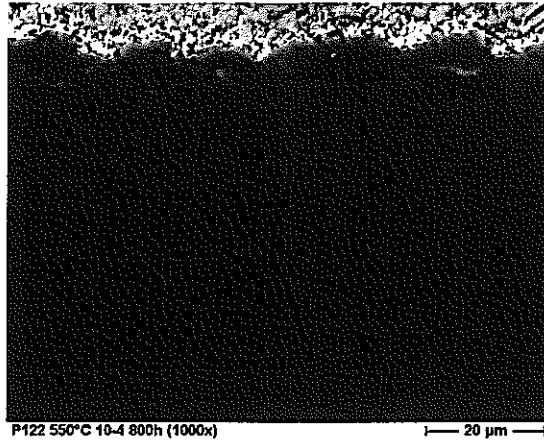


Fig. 5: Original P122 after 800 h of exposure

Original P122 show an irregular oxide formation similar to that on 316FR but with a closer coverage of the oxide nodes. On top there is a porous magnetite layer. PbBi penetrates partly into the space between magnetite and spinel layer (upper right node in Fig. 5). As in 316FR there is an enrichment of Mn in the spinel zone. The oxygen diffusion zone is very small. On the contrary, the oxide layers on the specimen exposed to LBE at  $10^{-6}$  wt% of oxygen are regular and homogenous. After 2,000 h, as expected from experiments at an oxygen concentration of  $10^{-6}$  wt% in LBE, regular and homogenous oxide scales with a thickness of about 22  $\mu\text{m}$  are observed. The magnetite layer already spalls off significantly. At some places only the diffusion zone remains on the surface of the specimen. A pore belt develops below the diffusion zone.

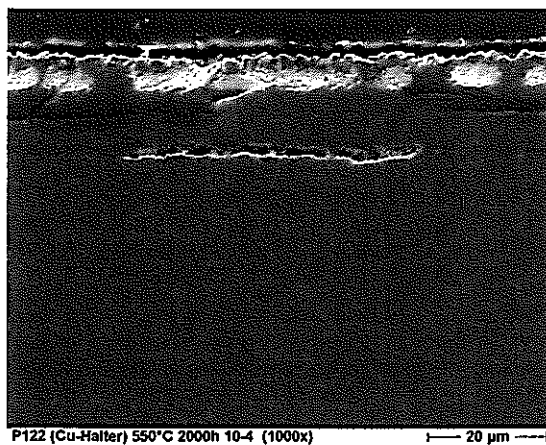


Fig. 6: Original P122 after 2000 h of exposure



Fig. 7: Original P122 after 5000 h

After 5,000 h the magnetite layer spalls off completely. The upper part of the oxide scale visible in Fig. 7 is a spinel layer. Beneath the diffusion zone formed after 2,000 h is converted to a spinel zone and underneath a new diffusion zone is growing. In comparison to the exposure in LBE containing  $10^{-6}$  wt% oxygen the oxide scale beside the magnetite is still on top of the sample and prevents the steel from dissolution attack. In addition after 5,000 h a covering of the LBE surface by spalled off magnetite layer was observed like in the  $10^{-6}$  wt% experiments. But at an oxygen concentration of  $10^{-4}$  wt% still enough oxygen will be available to oxidize the steel and prevent it from dissolution attack.

### 3.3 ODS steel 650 °C

#### 3.3.1 ODS original

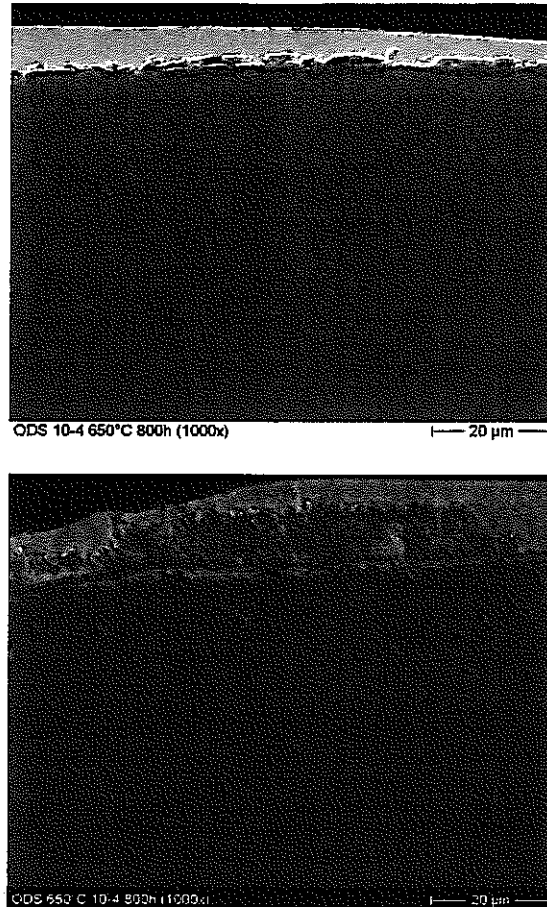


Fig. 8: Original ODS steel after 800 h, 2 typical corrosion phenomena.

ODS steel without surface treatment after 800 h exposure depicts a 5-6 µm thick oxide multilayer of magnetite and spinel which partly starts to break away (Fig. 8 upper part). This behavior differs from that in LBE with  $10^{-6}$  wt% oxygen where a thin oxide scale only protects the specimen from dissolution attack. It is a clear effect of the higher oxygen concentration. The high concentration enhances the driving force for Fe ion diffusion and leads to formation of a magnetite layer on top of the spinel zone. With  $10^{-6}$  wt% of oxygen the thin spinel layer is not penetrated by  $\text{Fe}^{+}$ .

The corrosion phenomenon shown in the lower part of Fig. 8 is observed at single spots at  $10^{-4}$  and as well of  $10^{-6}$  wt%. It is characterized by a thin almost pure  $\text{Cr}_2\text{O}_3$  layer on top and a porous structure underneath. This structure is strongly depleted in Cr, down to 1 wt%, besides of the oxide scale formation, obviously by precipitation of

sulfides and carbides of Cr which brake away in preparation. This is the reason for the appearance of pores.

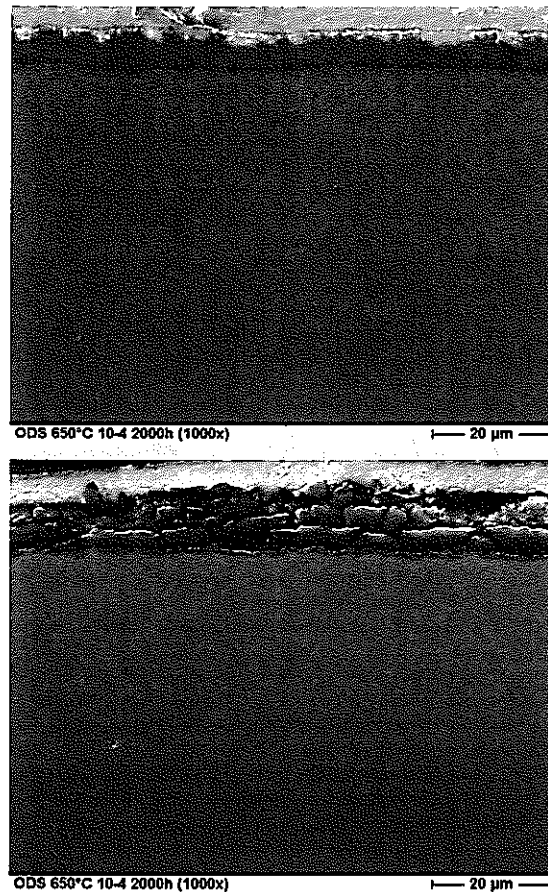


Fig. 9: Different features on ODS steel after 2000 h

After 2,000 h of exposure the oxide multilayer on the original ODS steel rod surface increased to 7-8  $\mu\text{m}$  (Fig. 9 upper part). The magnetite layer is lost at some places by break away which leads to a dissolution attack in a single place on the prepared cross section that is not shown here. The break away occurs at a position where Cr is depleted by sulfide and carbide formation as already observed in the tests with  $10^{-6}$  wt% oxygen.

Another type of oxide covering is observed on a surface produced by cutting of the rod into the specimen shapes used in the experiments (Fig. 9, lower part). The fresh surface which does not have a thin oxide layer at begin of the experiments depicts a heavily fractured magnetite and spinel layer with a thin protective spinel layer underneath. No dissolution attack is observed with this structure.



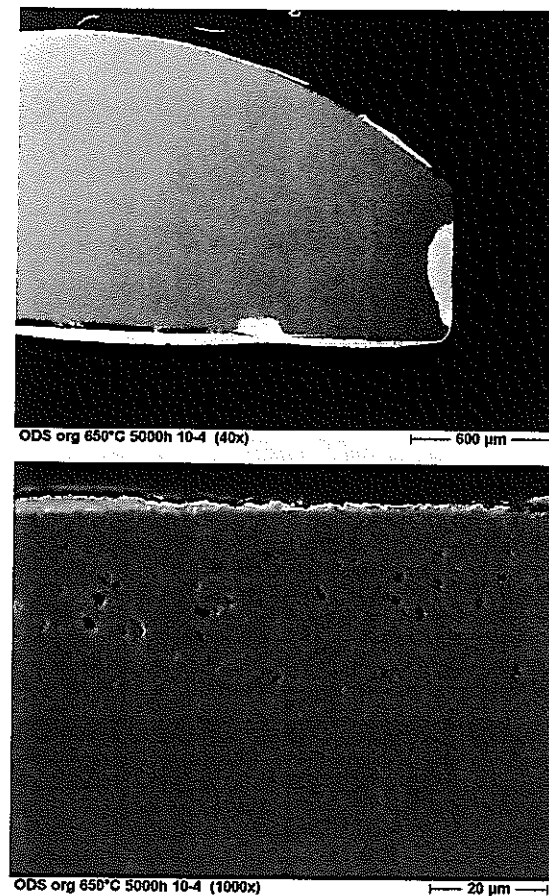


Fig. 10: Original ODS steel after 5000 h

After 5,000 h of exposure at some places strong dissolution attack up to 120 μm in depth occurs as shown in upper part of Fig. 10. The lower part of Fig. 10 shows a typical corrosion phenomena of the ODS-steels already described for the 800 h samples. The attack grows in size and depth according the longer exposure times. No significant difference can be observed in comparison with specimens exposed to LBE containing  $10^{-6}$  wt% of oxygen.

### 3.3.2 ODS steel GESA alloyed 650 °C

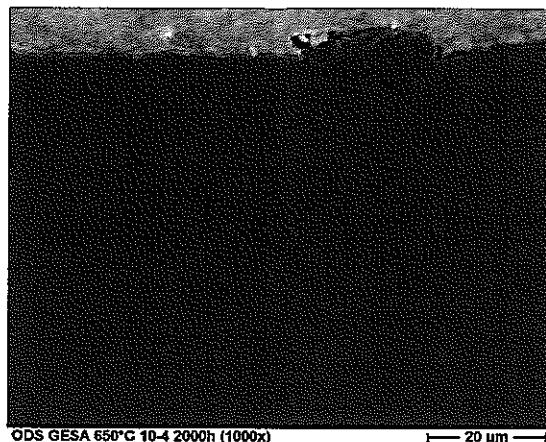


Fig. 11: GESA Al-alloyed ODS steel after 2000 h of exposure

There is no dissolution attack after 5,000 h to be observed on the GESA alloyed ODS steel. Because there was no homogenous Al concentration distribution at some spots we see single places with thick oxide nodes consisting of Al-Cr-Fe spinel. Their thickness amounts to about 12 μm. They appear already after 800 h. Normal homogenous Al alloying would prevent those phenomena. They were not observed with 10<sup>-6</sup> wt% oxygen. Like in all GESA alloyed specimens no precipitation of carbides and sulfides occurs.

Most parts > 95% of the sample do not show any sign of oxidation. Representative for most parts of the specimen after 5,000 h is Fig. 12, that has an appearance like before the exposure to LBE.

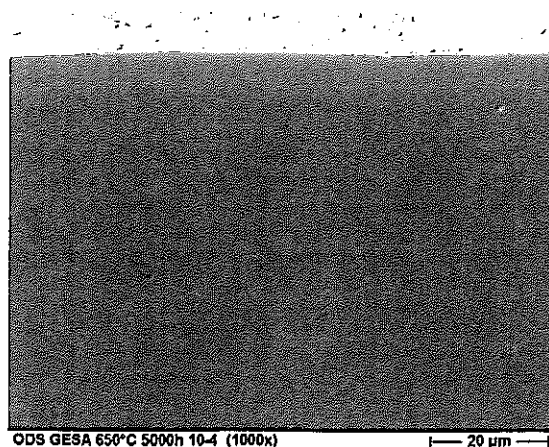


Fig. 12: GESA Al-alloyed ODS steel after 5000 h

## 4 Results after 800, 2,000 and 5,000 h of exposure to LBE with $10^{-8}$ wt% of oxygen

### 4.1 316FR steel, 550 °C

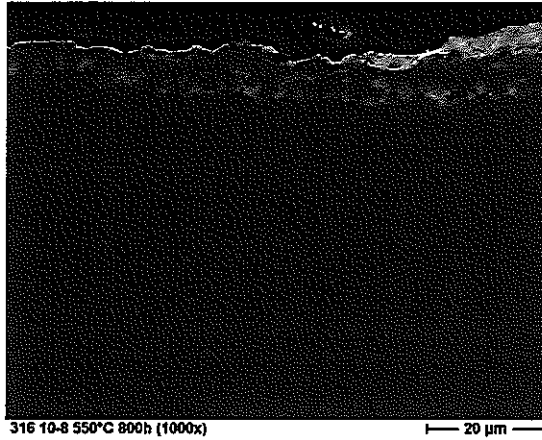


Fig. 13: Original 316FR steel after 800 h exposure

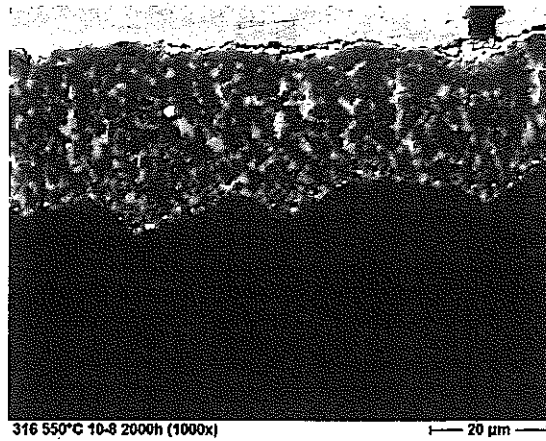


Fig. 14: Original 316FR steel after 2000 h of exposure

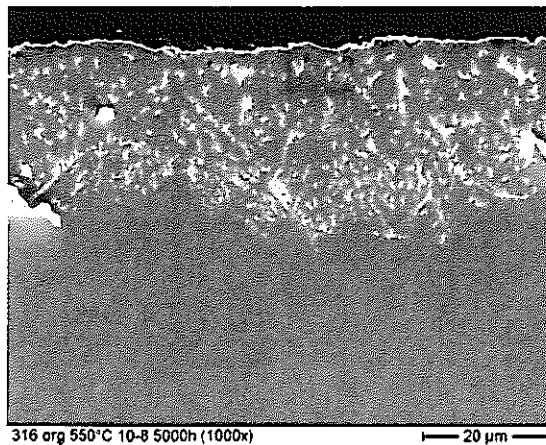


Fig. 15: Original 316FR steel after 5000 h of exposure

There is no protective oxide scale formation on original 316FR at  $10^{-8}$  wt% oxygen concentration in LBE (Fig. 13). Half of the surface is attacked by preferential dissolution of Ni and Cr. The concentration of Ni is 2-3 wt%, that of Cr 3-4 wt% in the surface region. LBE penetrates down to 25  $\mu\text{m}$  below the surface. The other half of the surface is still covered by a thin protective oxide scale which is originally on the steel.

The dissolution attack extends during 2,000 h of exposure to about 60% of the surface (Fig. 14) and up to 100  $\mu\text{m}$  maximal depth. After 5,000 h of exposure the dissolution attack is spread over the entire surface with no change in depth. This unchanging in corrosion depth can be a result of the increasing amount of Ni in LBE and therefore the reduction in dissolution potential of Ni in LBE. The structure changes from  $\gamma$ -Fe to  $\alpha$ -Fe because of the strong depletion of Ni. This is a very different behavior compared to the results of the tests at  $10^{-4}$  and  $10^{-6}$  wt% oxygen in which no dissolution attack could be observed after short time exposure.

## 4.2 P122 steel, 550 °C

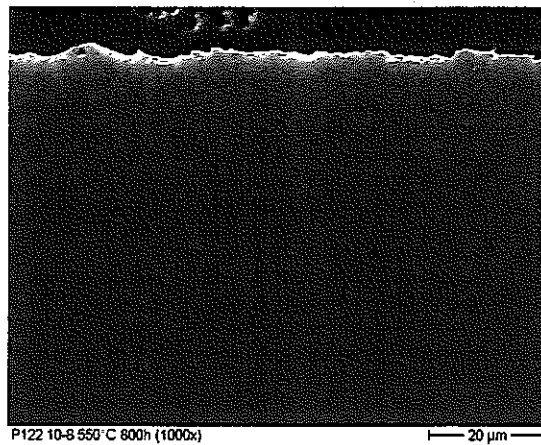


Fig. 16: Original P 122 steel after 800 h of exposure

There is no such oxide scale like in the experiment at 550 °C with 10<sup>-6</sup> and 10<sup>-4</sup> wt% oxygen. The whole surface is attacked only little by dissolution in a depth of about 1 μm. This situation proceeds during 2,000 and 5,000 h of exposure. Even after 5,000 h of exposure the dissolution attack is not significant. After 5000 h of exposure Cr<sub>2</sub>O<sub>3</sub> precipitates partly on grain boundaries close to the surface (Fig. 18a). The overall appearance of P122 exposed at 550 °C to LBE containing 10<sup>-8</sup> wt% oxygen is good.

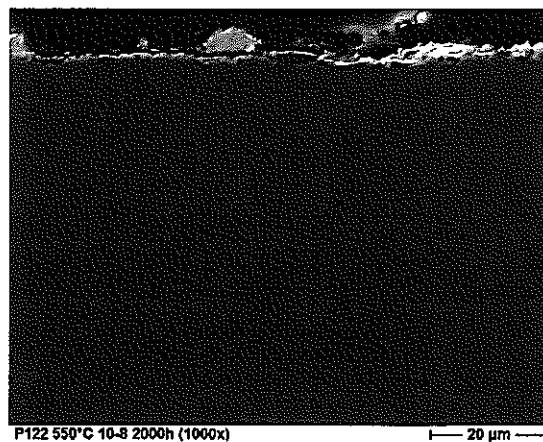


Fig. 17: Original P122 steel after 2000 h of exposure

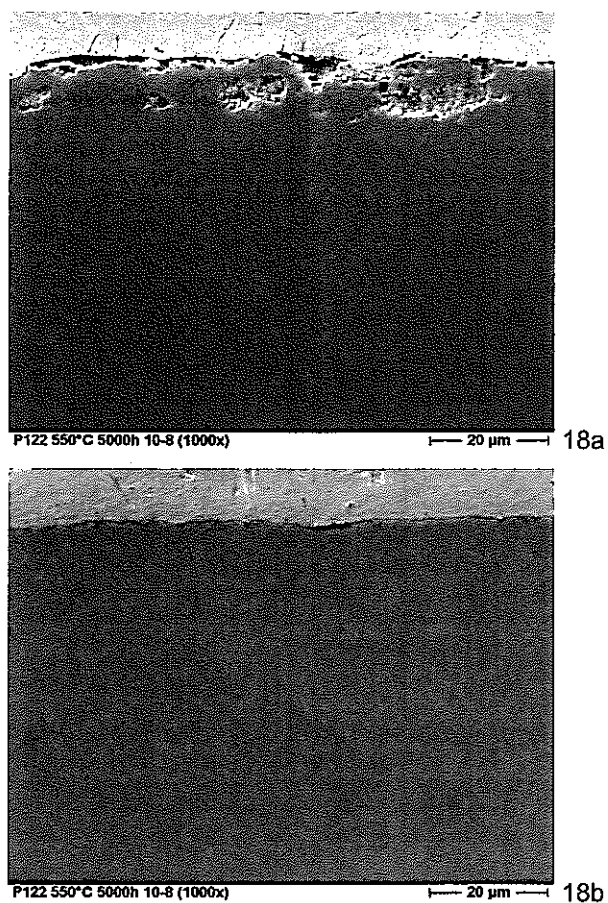


Fig. 18: Original P122 steel after 5000 h of exposure

### 4.3 ODS steel 650 °C

#### 4.3.1 ODS original

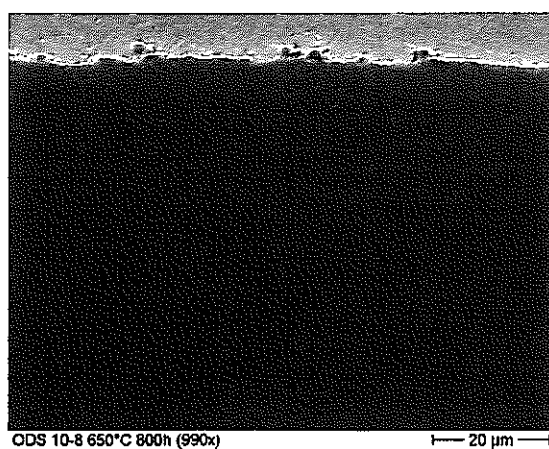


Fig. 19: Original ODS steel after 800 h of exposure

A thin protective oxide scale covers the surface like the one on the specimen exposed to LBE with  $10^{-6}$  wt% oxygen at 600 °C. No local attack could be found like it

was in the experiments with  $10^{-6}$  wt% oxygen. Like in former experiments some pores are observed underneath the surface. This region is depleted in Cr down to 5 wt% by precipitation and break away of sulphides or carbides of Cr during preparation. This behaviour does not change after 2,000 h of exposure (Fig. 20a). After 5,000 h of exposure some spots with a flat dissolution attack  $< 3 \mu\text{m}$  can be observed (Fig. 20b). Dissolution attack is less than in samples exposed to higher  $10^{-6}$  and  $10^{-4}$  wt% oxygen concentrations. Both martensitic steels show similar behaviour at an oxygen concentration of  $10^{-8}$  wt%.

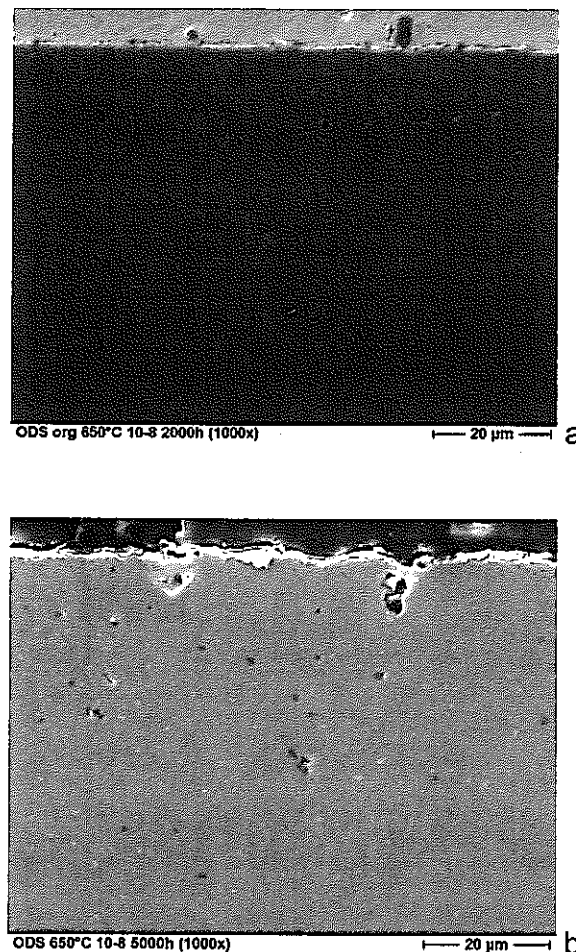


Fig. 20: Original ODS steel after 2000 (a) and 5000 h (B) of exposure

#### 4.3.2 ODS GESA alloyed

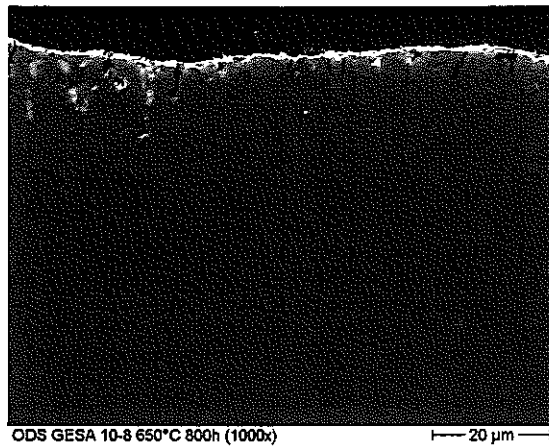


Fig. 21: GESA alloyed ODS after 800 h of exposure

The alloying process was obviously not successful because the Al-concentration in the bulk of the surface layer was < 3 wt%. Fissures developed on the surface contain LBE saturated with Al. Like in all other GESA alloyed specimens no precipitation of carbides and sulphides occurs. This experiment has to be repeated. The result of the repeated exposure is not yet available.

***All samples investigated so far were insufficient alloyed!***

***There will be a separate report concerning these experiments.***



## **5 X-ray diffractometry of samples exposed to LBE**

X-ray diffractograms are obtained from the specimen surface after removing LBE from the specimen. The specimen is immersed in oil of 180 °C temperature to allow wiping away of the LBE from the surface. After this the specimens are cleaned with acetone in an ultrasonic bath.

## 5.1 oxygen content $10^{-4}$ wt%, 550 °C

### 5.1.1 316FR steel

XRD patterns for the 316FR steel in original state and after exposure to LBE containing  $10^{-4}$  wt% oxygen at 550 °C for 800, 2,000 and 5,000 h are shown in Fig. 22. After 800 h the  $\alpha$ -Fe peak appears, which is not present in non exposed samples. Dissolution of Ni from the surface layer is indicated by this  $\alpha$ -peak. In addition PbO and  $\text{Fe}_3\text{O}_4$  peaks appear. This is in good agreement to the investigation with the SEM -Oxide nodes consisting of spinel with some LBE inclusions. After 2,000 and 5,000 h the magnetite peaks grow strongly indicating a homogenous oxide layer on the sample. This also is in good agreement with the results obtained by SEM. At lower oxygen concentration of  $10^{-6}$  wt% no continuous oxide scale can be observed after 5,000 h of exposure.

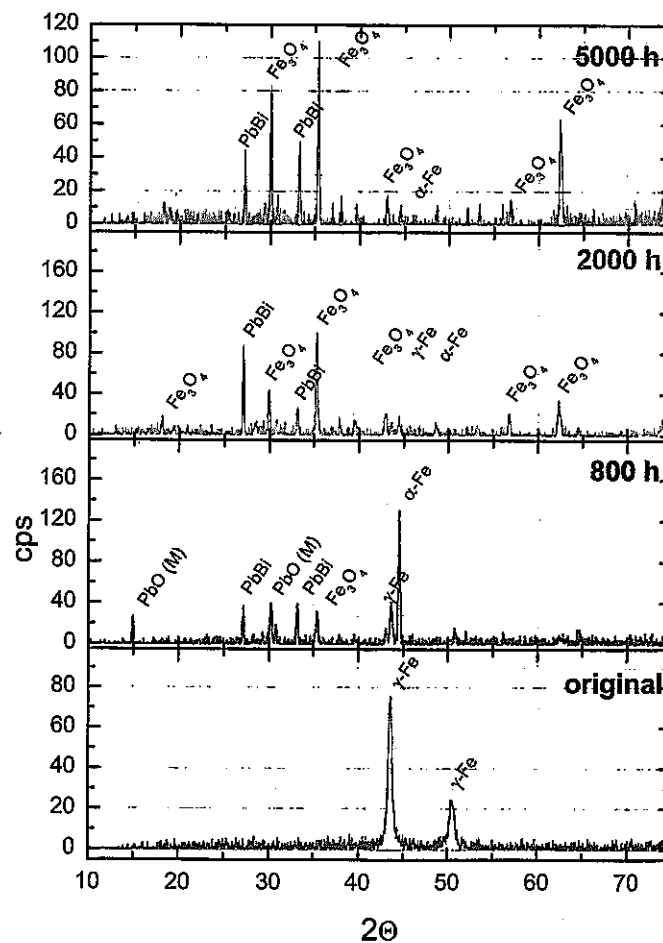


Fig. 22: 316FR at 550 °C, oxygen content  $10^{-4}$  wt%

**5.1.2 P122 steel**

After 800 h exposure of P122 to LBE at 550 °C containing  $10^{-4}$  wt% oxygen,  $Fe_3O_4$  (magnetite) - peaks appear. The metallic  $\alpha$ -Fe is still visible indicating that the oxide scale is not continuously covering the surface. After 2,000 h no  $\alpha$ -peaks are visible and the magnetite peaks are growing due to the now completely closed oxide scale. After 5,000 h of exposure the growing of the magnetite peaks is continued.

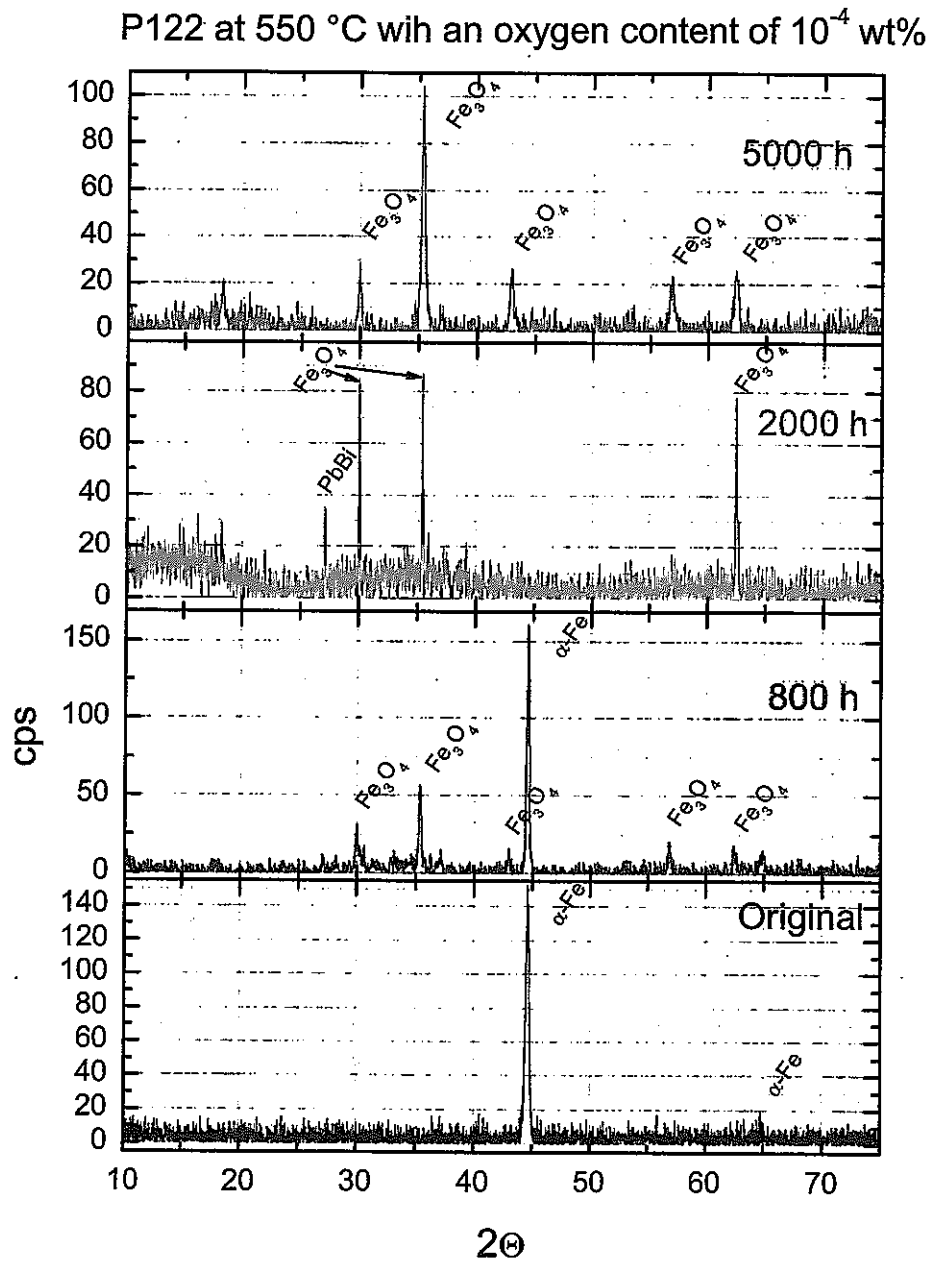


Fig. 23 P122 at 550 °C, oxygen content  $10^{-4}$  wt%

## 5.2 oxygen content $10^{-4}$ wt%, 650 °C

### 5.2.1 ODS steel

After 800 h exposure of ODS to LBE at 650 °C containing  $10^{-4}$  wt% oxygen  $\text{Fe}_3\text{O}_4$  (magnetite) and Cr rich spinel peaks appear. The metallic  $\alpha$ -Fe is very small indicating that most of the surface is covered by an oxide scale. After 2,000 h  $\alpha$ -peaks are growing and magnetite peaks are diminishing. Spallation of the oxide scale was visible in the SEM pictures (Fig. 9). After 5,000 h of exposure the growing of the  $\alpha$ -Fe peak is continued. The magnetite peak disappeared entirely. This is in good agreement with the observations using the SEM.

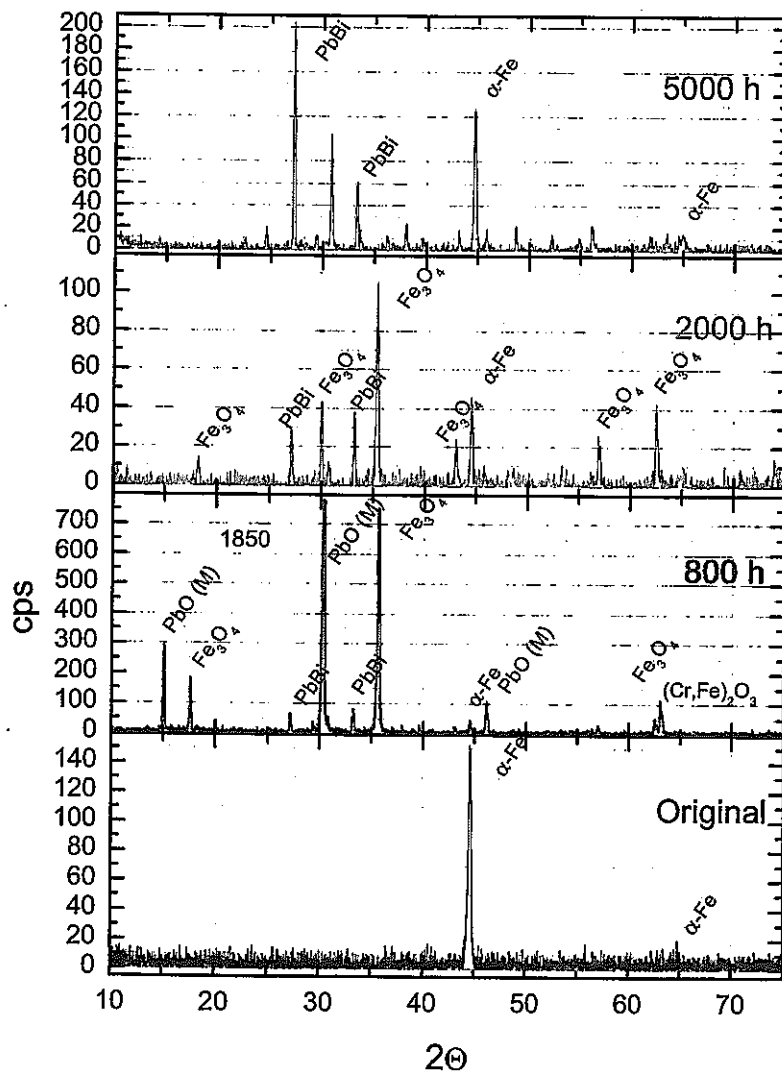


Fig. 24 ODS at 650 °C, oxygen content  $10^{-4}$  wt%

### 5.3 oxygen content $10^{-8}$ wt%, 550 °C

#### 5.3.1 316FR steel

XRD patterns for the 316FR steel in original state and after exposure to LBE containing  $10^{-8}$  wt% oxygen at 550 °C for 800, 2,000 and 5,000 h are shown in Fig. 25. After 800 h a small  $\alpha$ -Fe peak appears, which is not present in non exposed samples. Dissolution of Ni from the surface layer is indicated by this  $\alpha$ -peak, a ferritic surface layer starts to develop. No oxide peaks are visible. This is in good agreement to the investigation with the SEM. After 2,000 h the  $\alpha$ -Fe peak dominate the  $\gamma$ -Fe peak, and after 5,000 h the  $\gamma$ -Fe peak is no longer present. This again is in very good agreement with the SEM observations where we have a dissolution attack on the entire surface after 5,000 h of exposure.

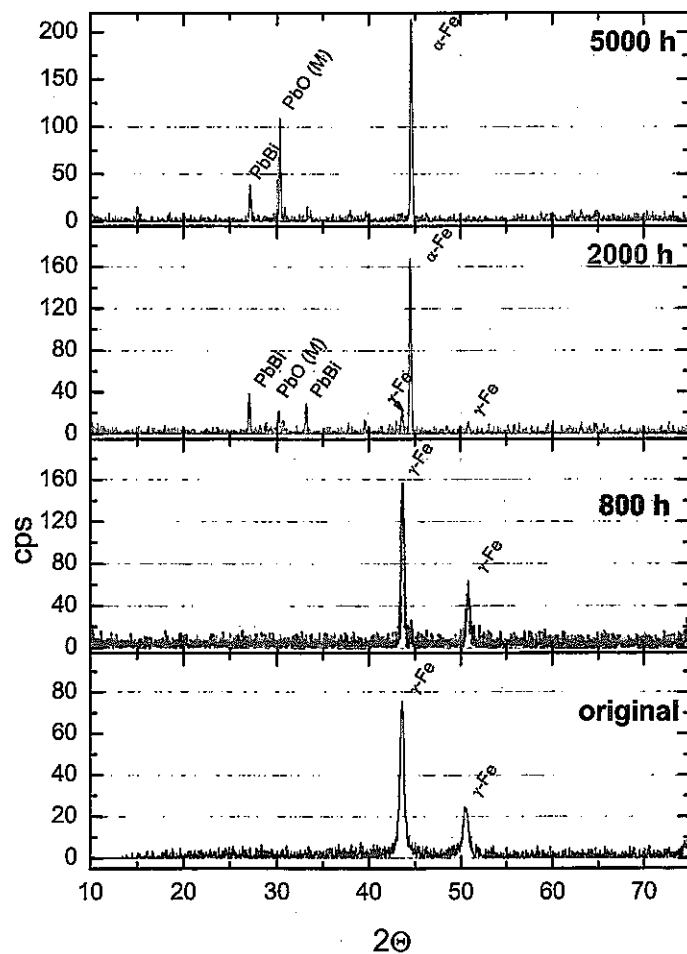


Fig. 25: 316FR at 550 °C, oxygen content  $10^{-8}$  wt%

### 5.3.2 P122 steel

After 800 h exposure of P122 to LBE at 550 °C containing  $10^{-8}$  wt% no oxide peaks are visible, only  $\alpha$ -Fe peaks appear. Small PbBi peaks due to dissolution attack appear already after 800 h. No changes after 5,000 h of exposure, beside some Pb-oxides appearing after 5,000 h take place. This is in good agreement with the observations using the SEM.

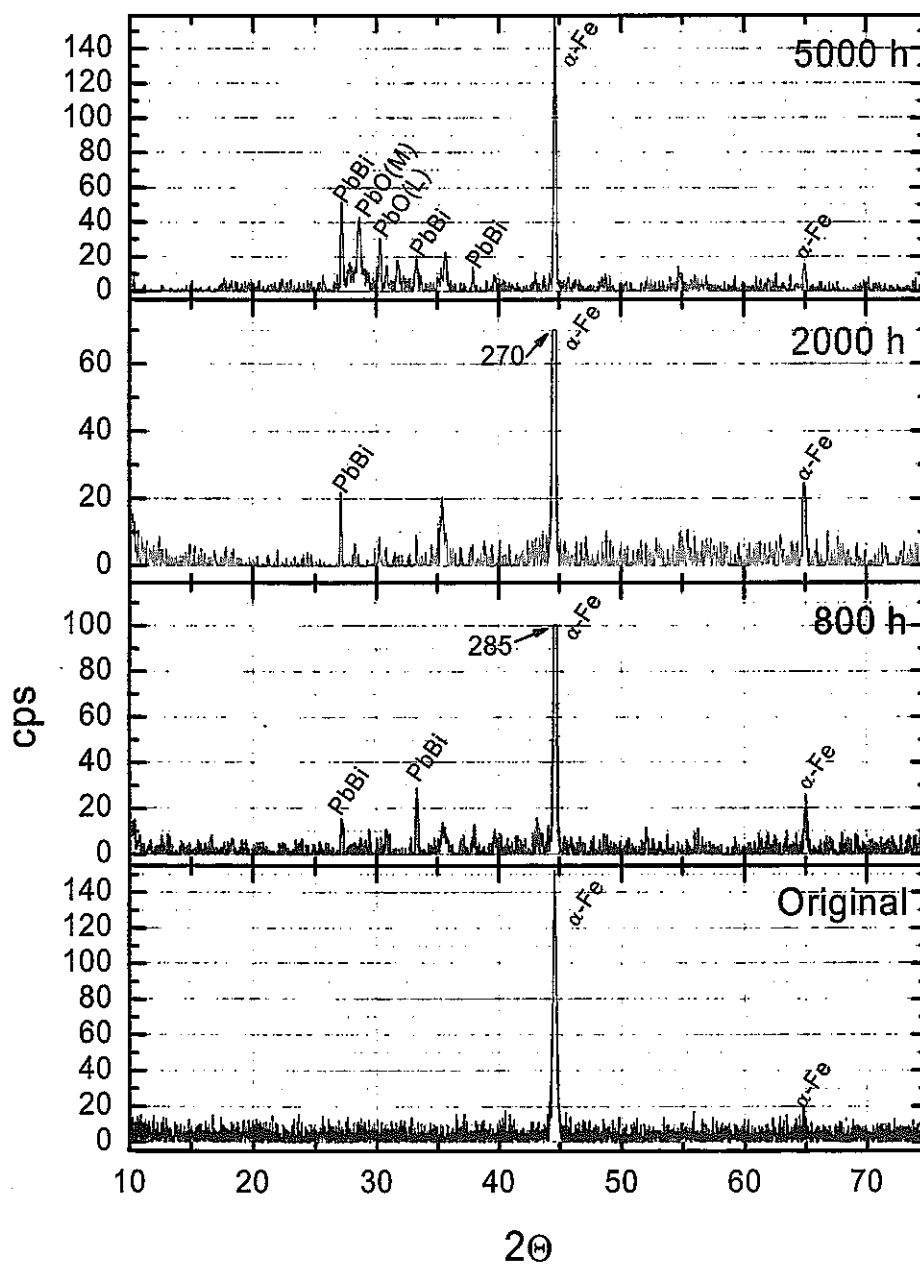


Fig. 26 : P122 at 550 °C, oxygen content  $10^{-8}$  wt%

## 5.4 oxygen content $10^{-8}$ wt%

### 5.4.1 ODS steel

After 800 h exposure of ODS to LBE at 650 °C containing  $10^{-8}$  wt% no oxide peaks are visible, only  $\alpha$ -Fe peaks appear. Small PbBi peaks due LBE adherent to the surface appear already after 800 h. No changes after 5,000 h of exposure, beside some Pb-oxide, due to not totally removed LBE before XRD-examination appearing after 5,000 h, take place. This is in good agreement with the observations using the SEM, where only little attack at the surface was observed.

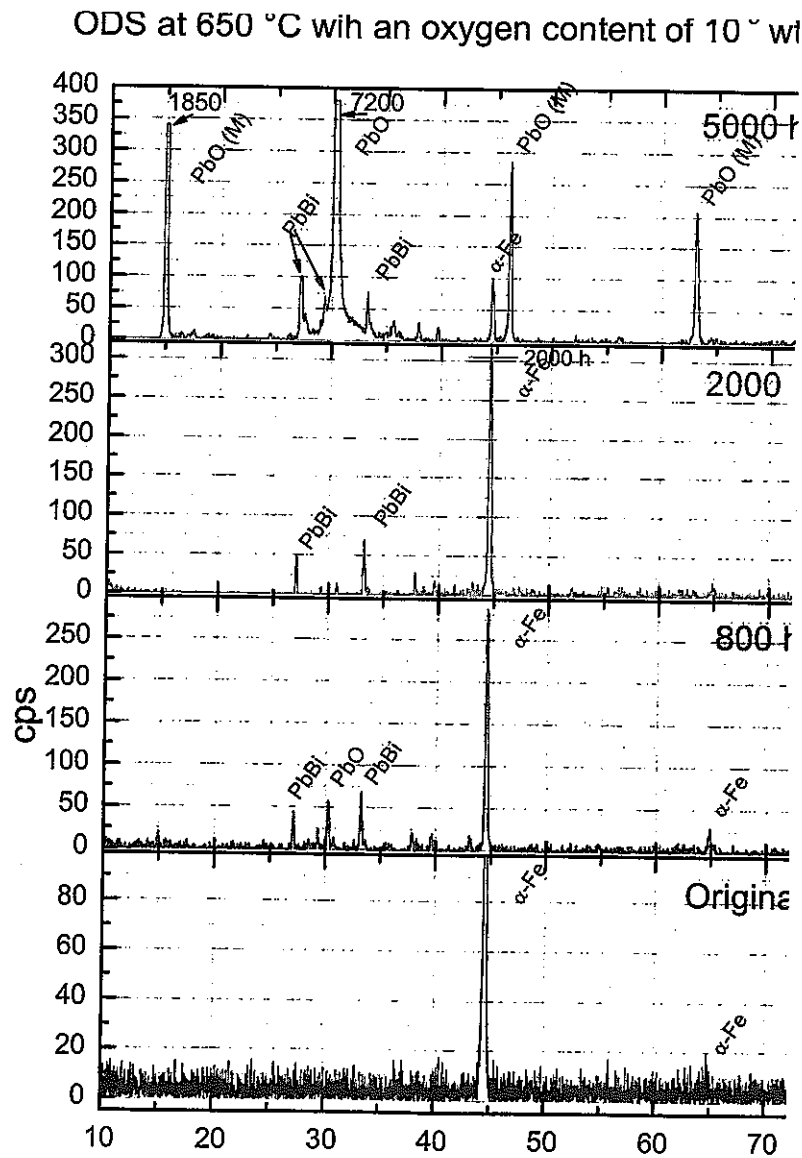


Fig. 27 ODS at 650 °C, oxygen content  $10^{-8}$  wt%

## 6 Results after exposure to furnace atmosphere

### 6.1 316FR steel

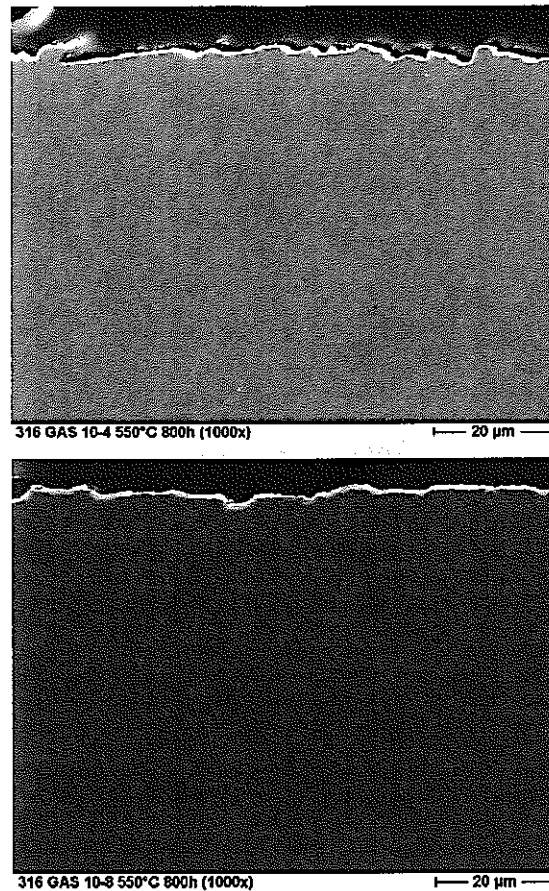


Fig. 28: Original 316FR in furnace atmosphere at 550 °C equilibrated with  $10^{-4}$  wt% (above) and  $10^{-8}$  wt% (below) oxygen concentration in LBE after 800 h of exposure

There is no visible oxide layer on the surface of both specimens. On both specimens exposed to the atmosphere in the furnace with  $10^{-4}$  and  $10^{-8}$  wt% oxygen in LBE, however, there is a thin oxide scale detected, consisting of Cr-oxide and Cr-Fe spinel (EDX).



## 6.2 P122 steel

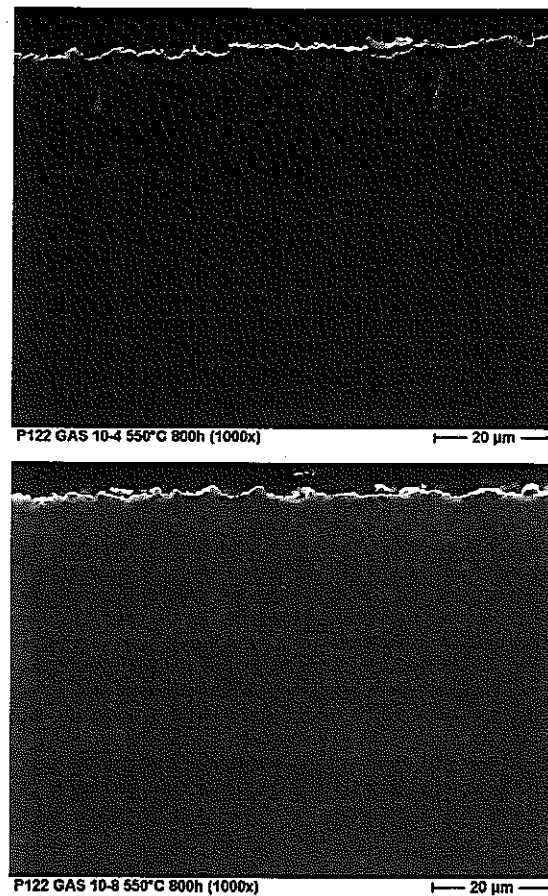


Fig. 29: Original P122 in furnace atmosphere at 550 °C equilibrated with  $10^{-4}$  wt% (above) and  $10^{-8}$  wt% (below) oxygen concentration in LBE after 800 h of exposure

A thick oxide scale stratified as usual appears on the sample placed in the furnace atmosphere with  $10^{-4}$  wt% oxygen in LBE while there is only a very thin scale consisting of Cr oxide and Cr-Fe spinel on the specimen in the furnace atmosphere for  $10^{-8}$  wt% oxygen in LBE.

### 6.3 ODS steel

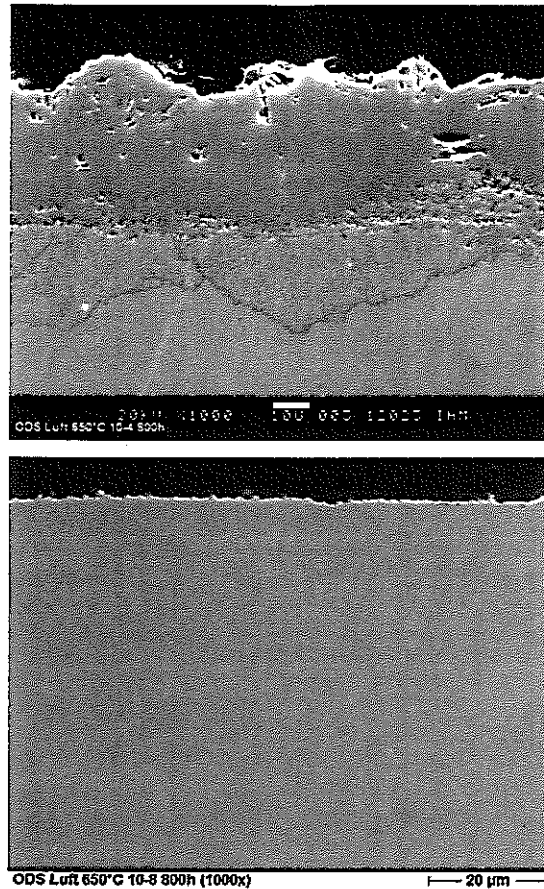


Fig. 30: Original ODS in furnace atmosphere at 650 °C equilibrated with  $10^{-4}$  wt% (above) and  $10^{-8}$  wt% (below) oxygen concentration in LBE after 800 h of exposure

Similar to P122 a thick oxide scale appears in the furnace atmosphere with  $10^{-4}$  wt% oxygen in LBE while there is only a very thin scale consisting of Cr oxide and Cr-Fe spinel on the specimen in the furnace atmosphere for  $10^{-8}$  wt% oxygen in LBE.

### 6.4 X-ray diffractometry of samples exposed to air

#### 6.4.1 316FR at 550 °C, 10<sup>-4</sup> and 10<sup>-8</sup> wt%

On both specimens exposed to furnace atmosphere only metallic Fe peaks appear.

This is in excellent agreement with the SEM observations.

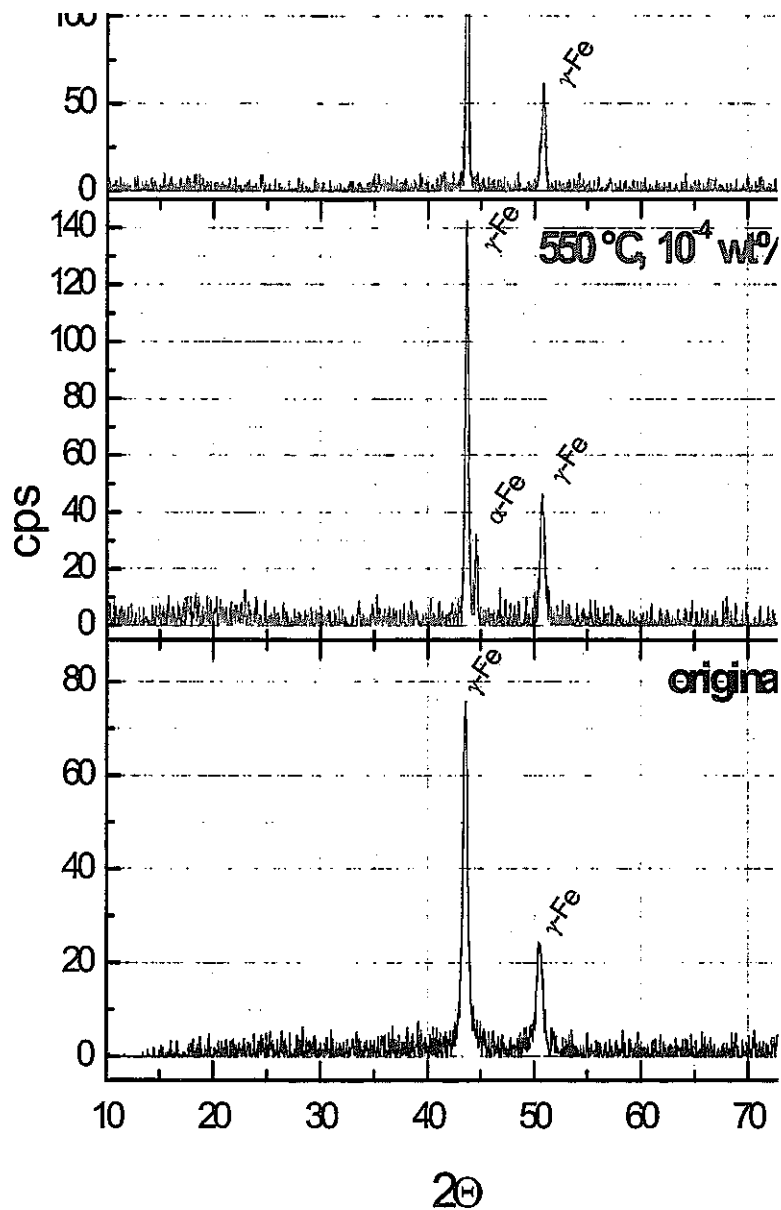


Fig. 31: 316FR at 550 °C exposure to furnace atmosphere, oxygen content 10<sup>-4</sup> and 10<sup>-8</sup> wt%

### 6.4.2 P122 at 550 °C, $10^{-4}$ and $10^{-8}$ wt%

At an oxygen concentration of  $10^{-4}$  wt% only magnetite peaks are measured by XRD. This is a result due to a closed oxide scale on top of the sample. At  $10^{-8}$  wt% the magnetite peak is significantly smaller than the  $\alpha$ -Fe peak. Almost no oxide is formed on the surface. The XRD results are in good agreement with the SEM observations.

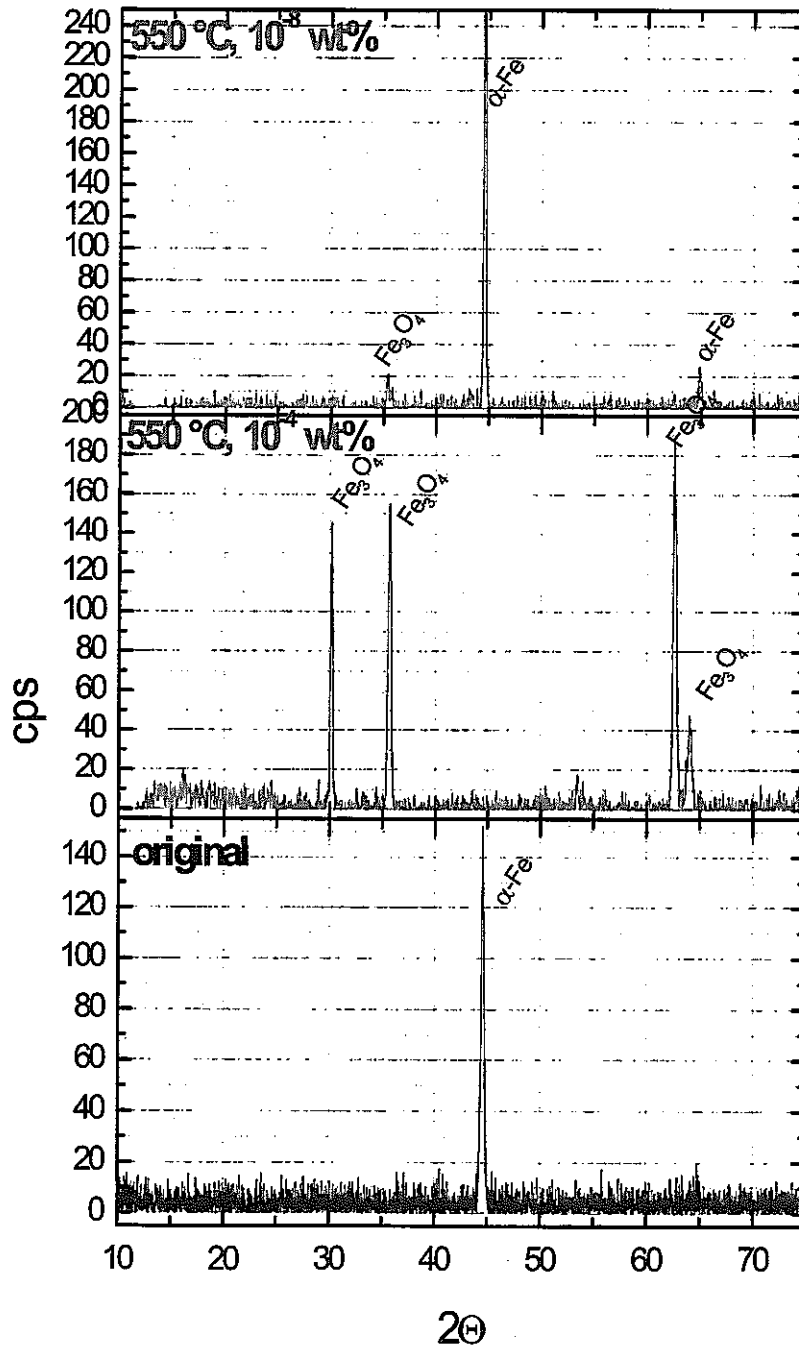


Fig. 32: P122 at 550 °C exposure to furnace atmosphere, oxygen content  $10^{-4}$  and  $10^{-8}$  wt%

### 6.4.3 ODS at 550 °C, $10^{-8}$ wt%

No oxides formed on the surface of the ODS steel exposed to furnace atmosphere at  $10^{-8}$  wt%, only metallic Fe peaks are detected. The SEM observations presented ahead show the same result.

*No sample at  $10^{-4}$  wt% was examined by XRD*

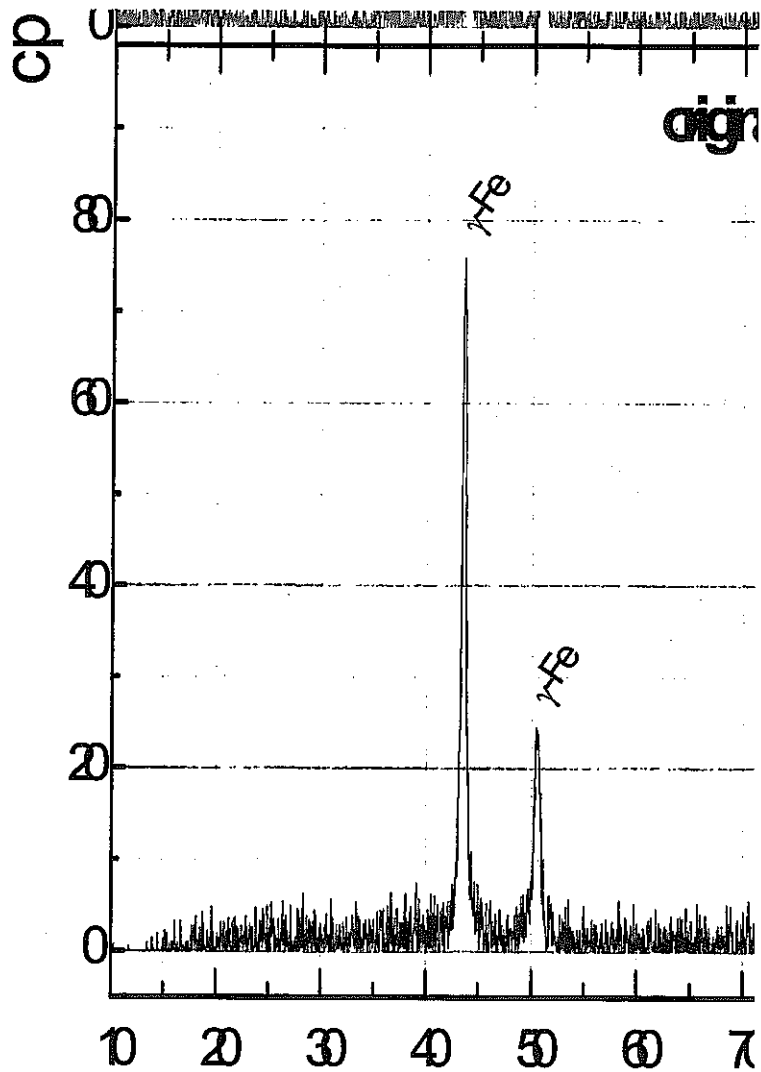


Fig. 33: ODS at 550 °C exposure to furnace atmosphere, oxygen content  $10^{-8}$  wt%

## 7 Summary

### 7.1 Experiments with $10^{-4}$ wt% oxygen

- 316FR at 550 °C is protected over the whole period of 5,000 h. Although LBE penetrates the oxide-scale, only very little dissolution attack below the oxide scale is observed at single spots
- P122 at 550 °C lost the magnetite scale but is still protected by a continuously growing spinel-layer covering the entire surface. No dissolution attack can be observed.
- Most parts of the ODS at 650 °C are protected by an oxide scale. At single spots after 5,000 h of exposure severe dissolution attack up to 120 µm in depth occurs. In addition Cr depletion occurs in areas of carbide and sulfide precipitation.
- GESA alloyed ODS steel shows at 650 °C no dissolution attack and no carbide and sulfide precipitations like in the original steel specimens.

### 7.2 Experiments with $10^{-8}$ wt% oxygen

- There is no protective scale on 316FR at 550 °C. 316FR is attacked on the whole surface to a depth of about 100 µm. This results in structure transition from  $\gamma$ -Fe to  $\alpha$ -Fe, observed by XRD, because of severe losses of Ni.
- On P122 beside some Cr<sub>2</sub>O<sub>3</sub> precipitations on grain boundaries no thick oxide scales could be observed. Even after 5,000 h of exposure only partly non significant dissolution attack (<2 µm) occurs.
- Like the P122 sample only little dissolution attack is observed. Dissolution attack is less than in samples exposed to higher  $10^{-6}$  and  $10^{-4}$  wt% oxygen concentrations. Both martensitic steels show similar good behaviour at an oxygen concentration of  $10^{-8}$  wt%.
- The GESA alloyed ODS specimen are not presented here due to failures during the alloying process that resulted in inhomogeneous Al concentrations. The experiment has to be repeated. ***There will be a separate report concerning these experiments.***

### **7.3 Experiments in furnace atmosphere**

- Only on martensitic steels P122 and ODS a thick (20 - 35  $\mu\text{m}$ ) multilayered oxide scale develops in the  $10^{-4}$  wt% atmosphere. In the  $10^{-8}$  wt% oxygen atmosphere and in general on 316FR only thin scales are present.

## **8 Annex1: Longitudinal section of P122 and 316 at 550°C at 10<sup>-4</sup> wt%**

Samples were cut along the axis to investigate the existence of oxygen concentration gradient from the surface of LBE down to the bottom of the crucible.

### **Annex 1: Longitudinal Section**

Samples were cut along the axis to investigate the existence of oxygen concentration gradient from the surface of LBE down to the bottom of the crucible.

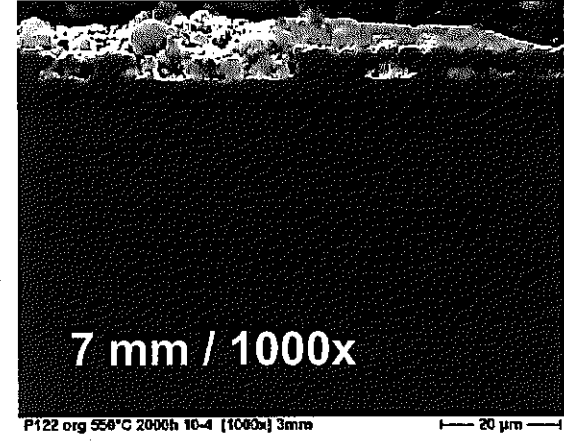
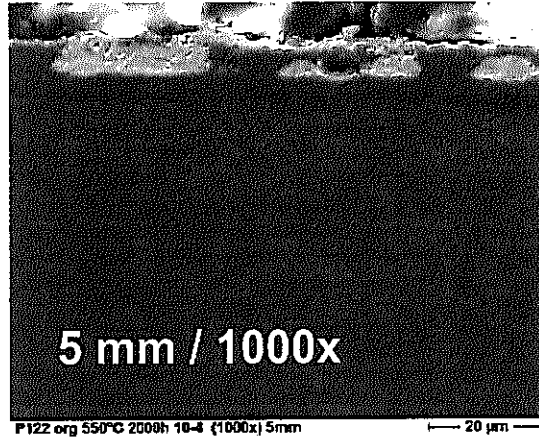
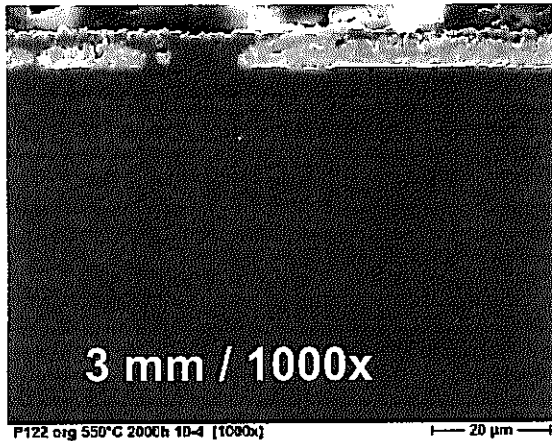
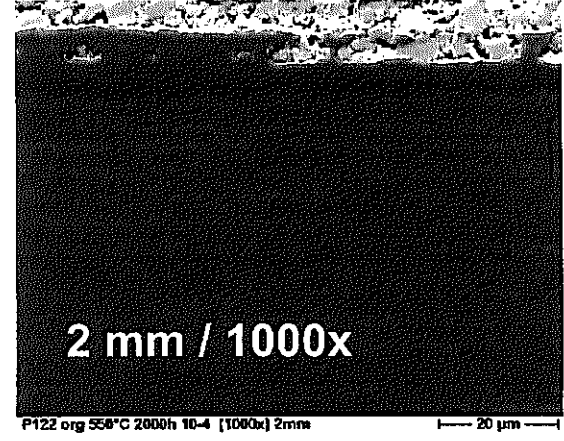
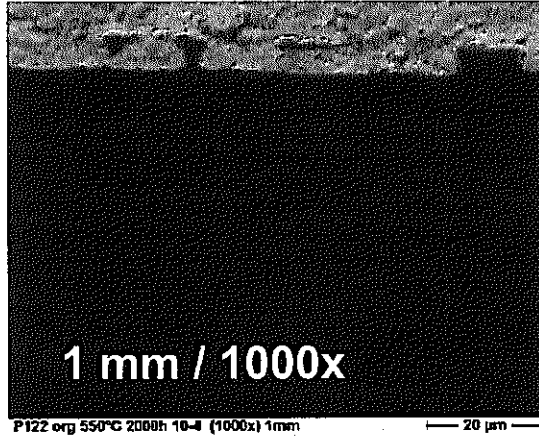
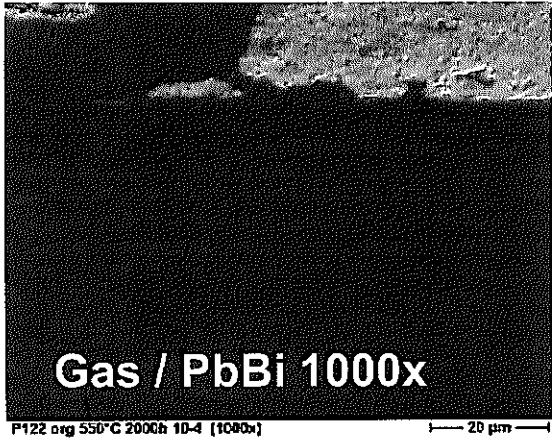
After 5,000 h of exposure in case of P122 and ODS at 550 °C exposed to LBE containing 10<sup>-6</sup> wt% oxygen significant differences in corrosion and oxidation depending on the distance to the surface are found. Most probably the oxide layer spalls off, covers the LBE surface and than slows down the oxygen transport into the LBE. As a result the oxygen concentration drops with increasing distance from the LBE surface. We know from previous experiments that at a concentration of 1\*10<sup>-7</sup> wt% corrosion starts at the temperatures of exposure.

With a preset oxygen concentration of 10<sup>-4</sup> wt% no such change in corrosion or oxidation depending on the distance from the LBE surface could be found in samples after 2,000 h of exposure (Fig.1 and 2). Even after 5,000 h we do not observe any difference in oxidation or corrosion depending on distance from LBE surface (Fig. 3 and 4). If an oxide scale covers the entire surface of the LBE in the crucible at an oxygen concentration of 10<sup>-4</sup> wt% still enough oxygen will penetrate into the LBE to guarantee a concentration > 10<sup>-6</sup> wt% at the bottom of the crucible. This concentration would be high enough to ensure proper oxidation and to prevent the steel from dissolution.

Therefore we believe that all investigations and results presented in report No. 5 show how the steels behave at the preset temperature and oxygen concentration in LBE



P122: 550°C 10<sup>-4</sup> wt% 2000 h



Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen, FZK/IHM report, September 2003

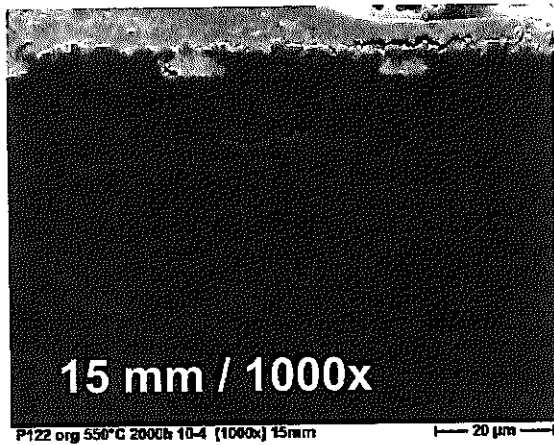
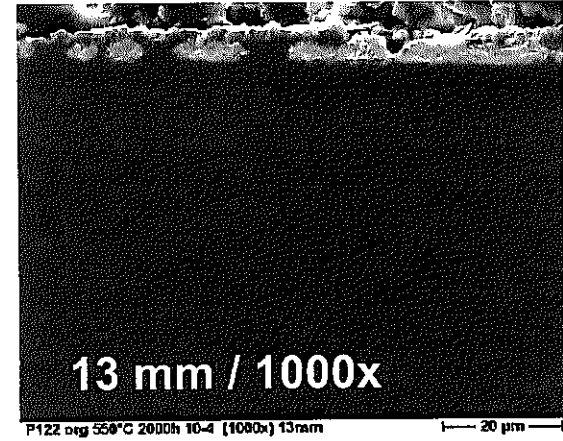
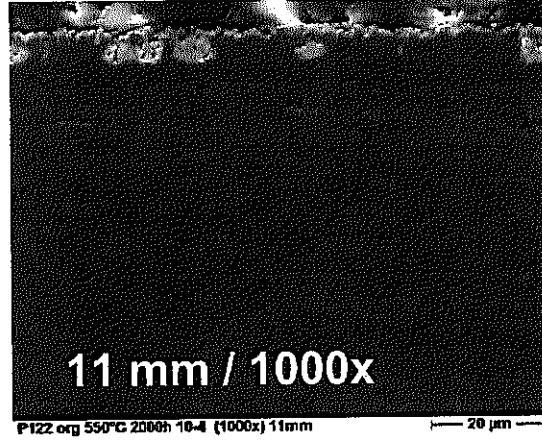
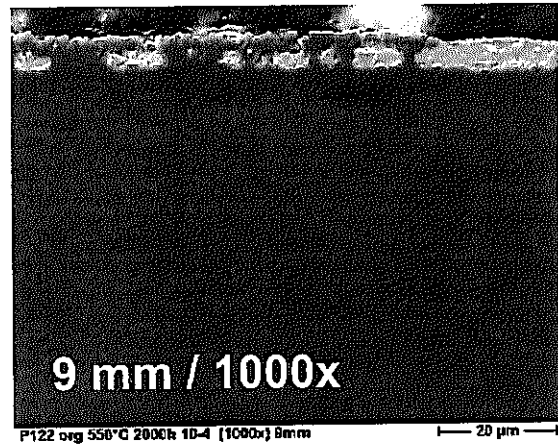
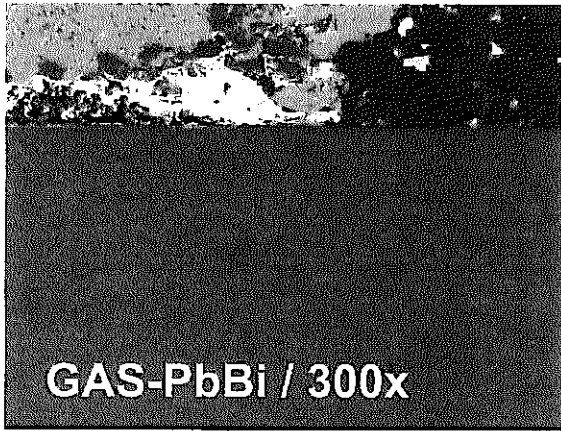


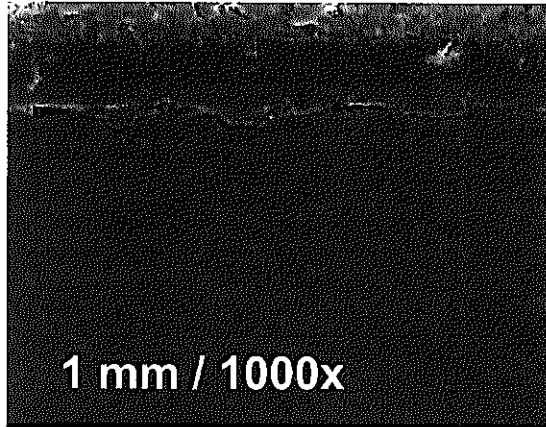
Fig. 1 : Longitudinal section of P122 at 550°C  $10^{-4}$  wt% 2000 h

Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen, FZK/IHM report, September 2003

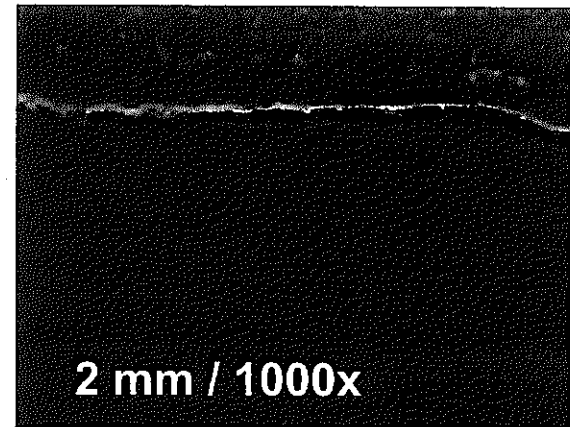
**316FR 550°C  $10^{-4}$  wt% 2000 h**



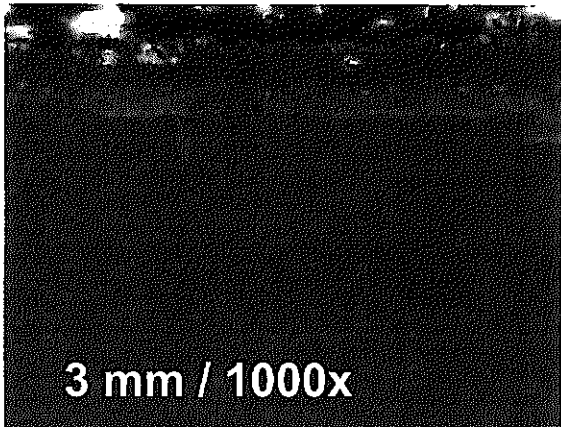
316 550°C 10-4 2000h (300x) Übergang Gasatm.-PbBi 70 µm



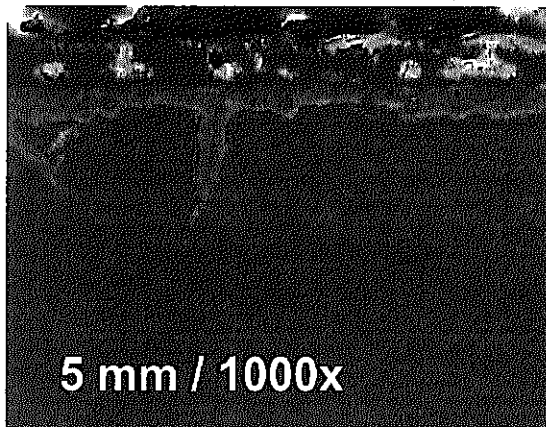
316 550°C 10-4 2000h (1000x) 1mm 20 µm



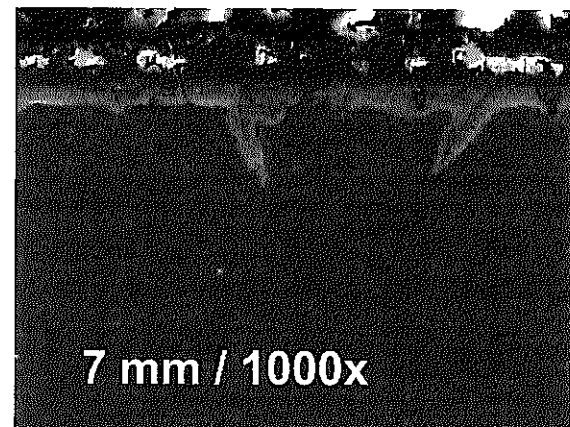
316 550°C 10-4 2000h (1000x) 2mm 20 µm



316 550°C 10-4 2000h (1000x) 3mm 20 µm



316 550°C 10-4 2000h (1000x) 5mm 20 µm



316 550°C 10-4 2000h (1000x) 7mm 20 µm

Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen, FZK/IHM report, September 2003

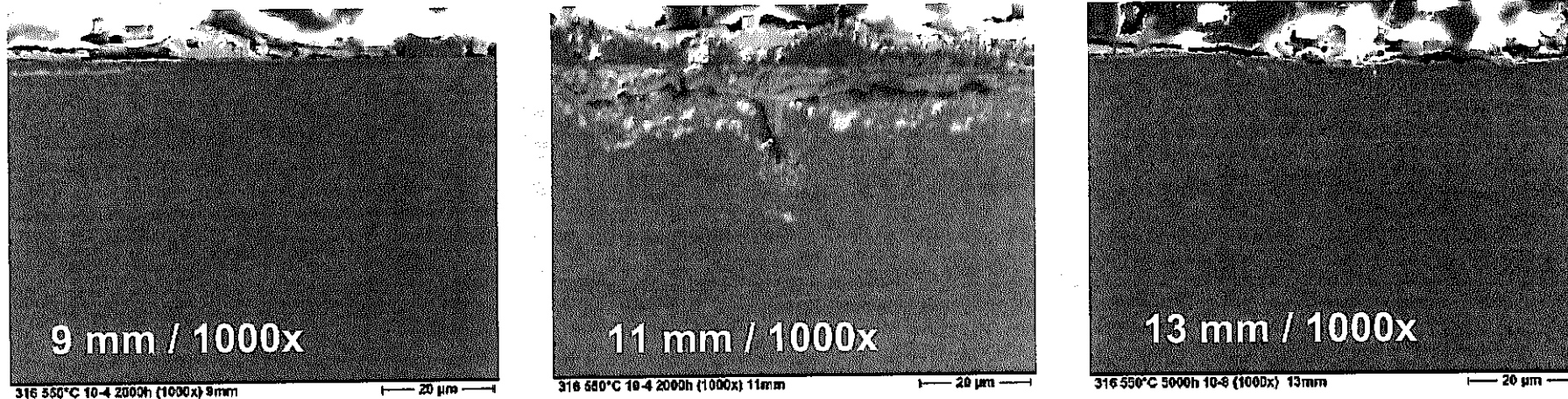
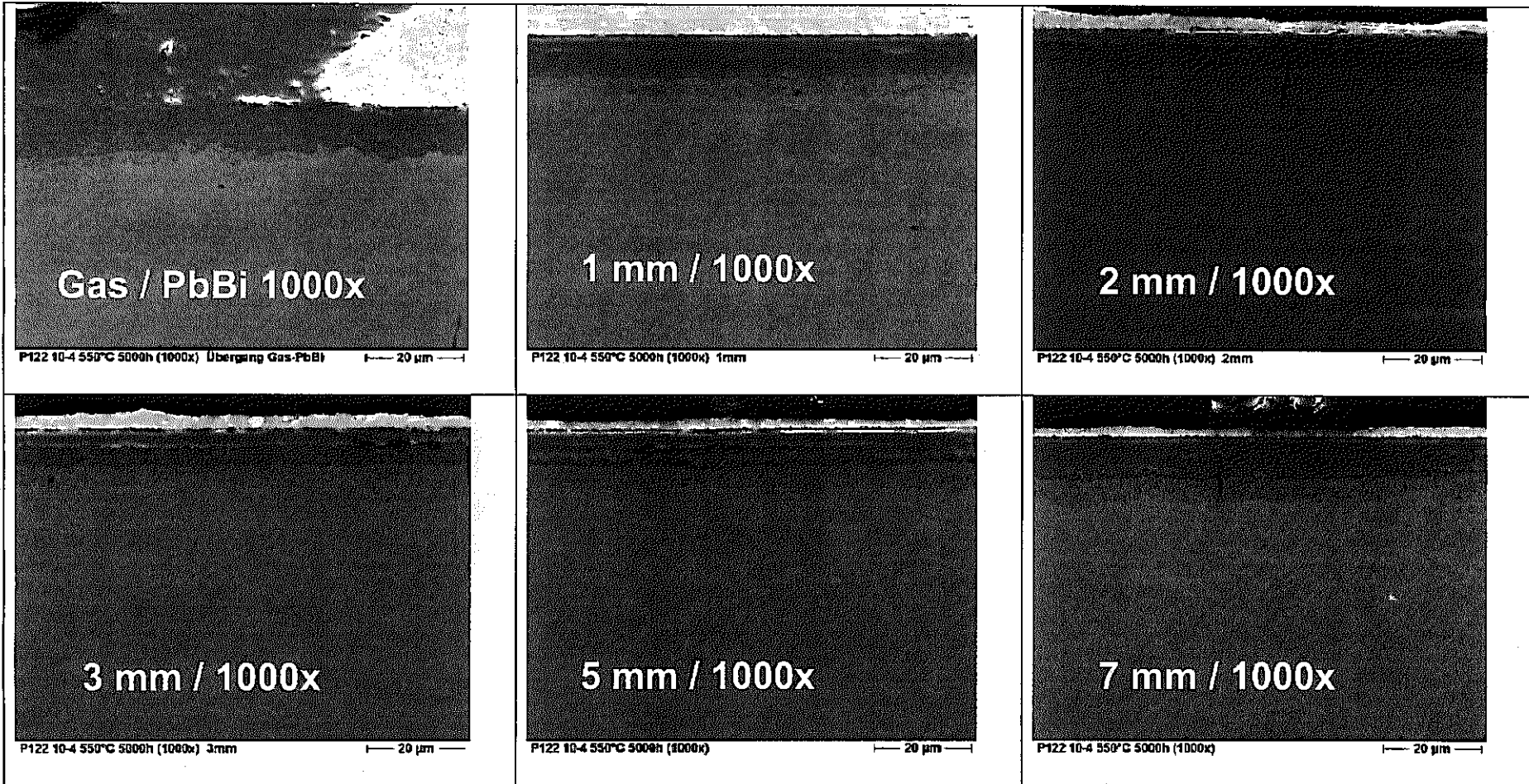


Fig. 2 : Longitudinal section of 316FR at 550°C  $10^{-4}$  wt% 2000 h

Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing  $10^{-4}$  and  $10^{-5}$  wt% of oxygen, FZK/IHM report, September 2003

**P122: 550°C  $10^{-4}$  wt% 5000 h**

— 40 —



Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing  $10^{-4}$  and  $10^{-8}$  wt% of oxygen, FZK/IHM report, September 2003

JNC TY9400 2003-028

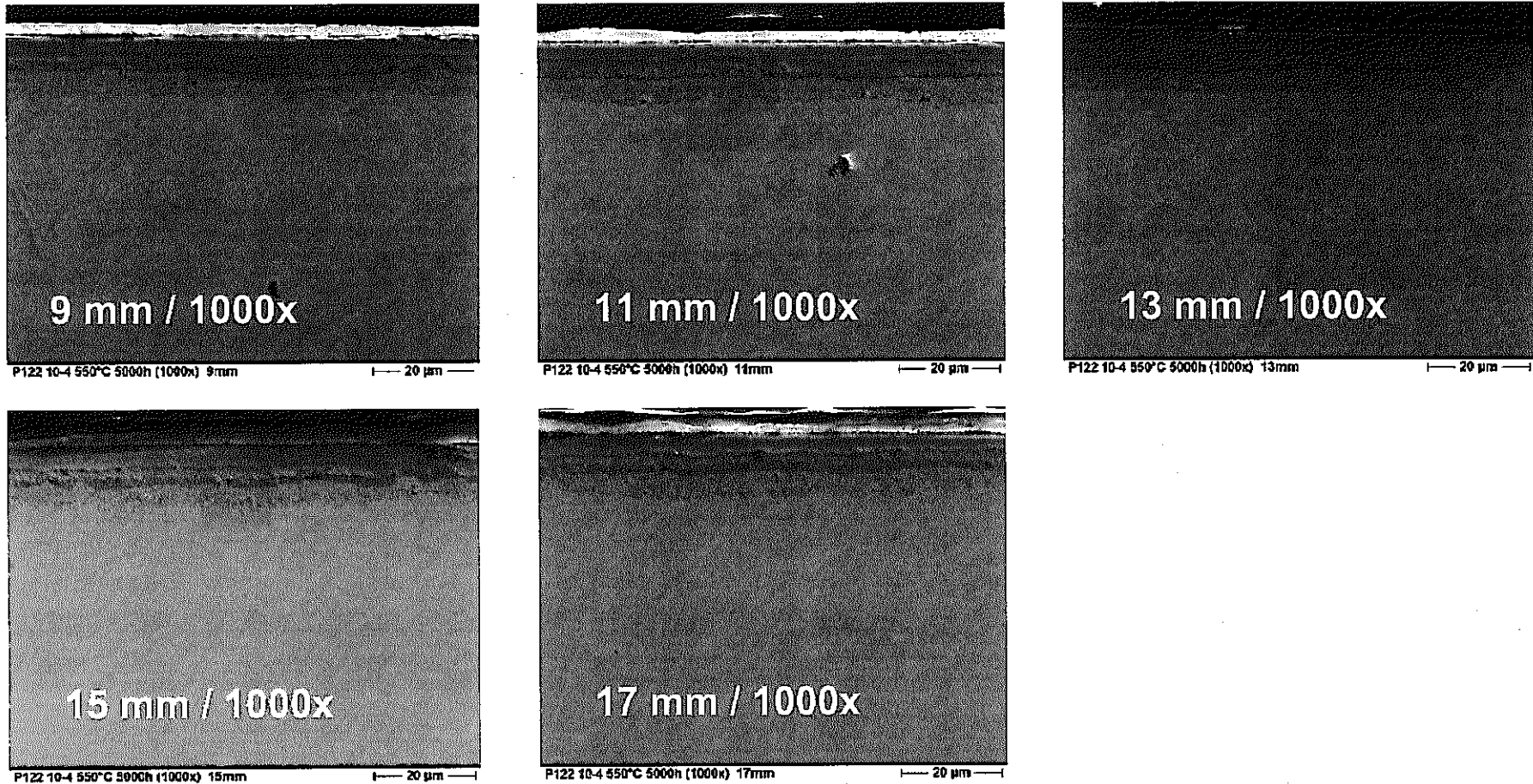
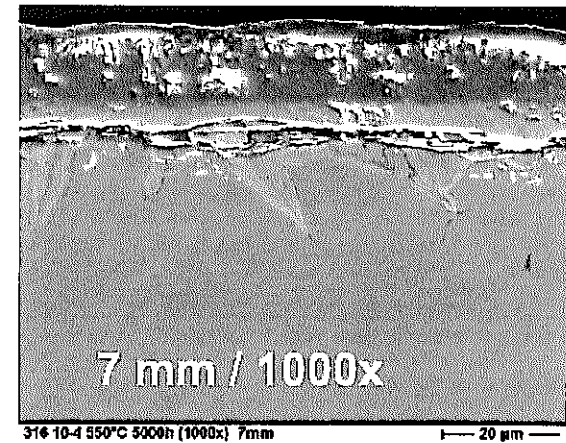
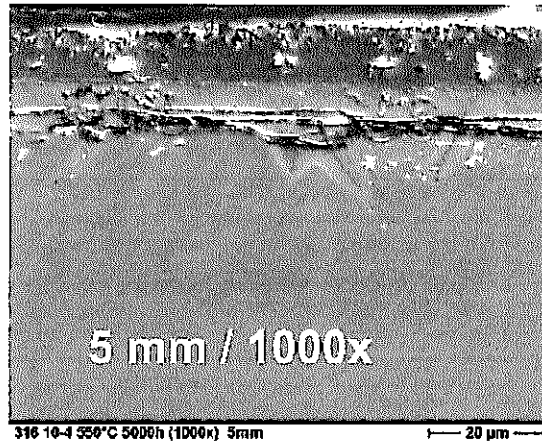
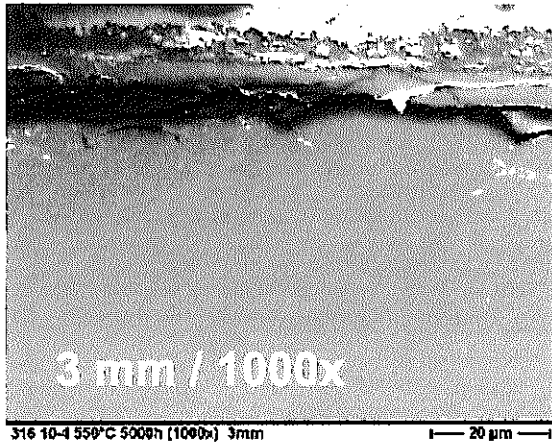
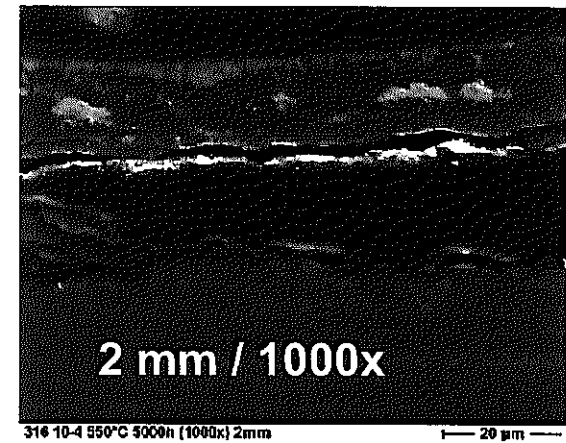
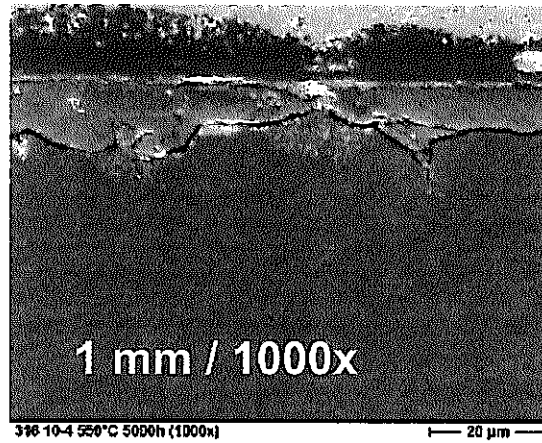
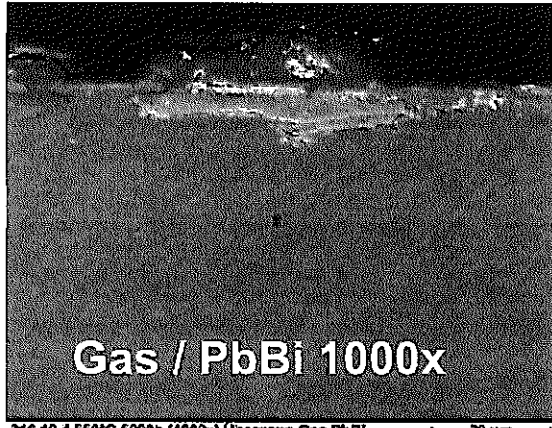


Fig. 3 : Longitudinal section of P122 at 550°C  $10^{-4}$  wt% 5000 h

Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing 10<sup>-1</sup> and 10<sup>-4</sup> wt% of oxygen, FZK/IHM report, September 2003

**316FR: 550°C 10<sup>-4</sup> wt% 5000 h**



Corrosion investigation of steels at 500 and 650 °C after 800, 2000 and 5000 h of exposure to stagnant liquid PbBi containing 10<sup>-4</sup> and 10<sup>-6</sup> wt% of oxygen, FZK/IHM report, September 2003

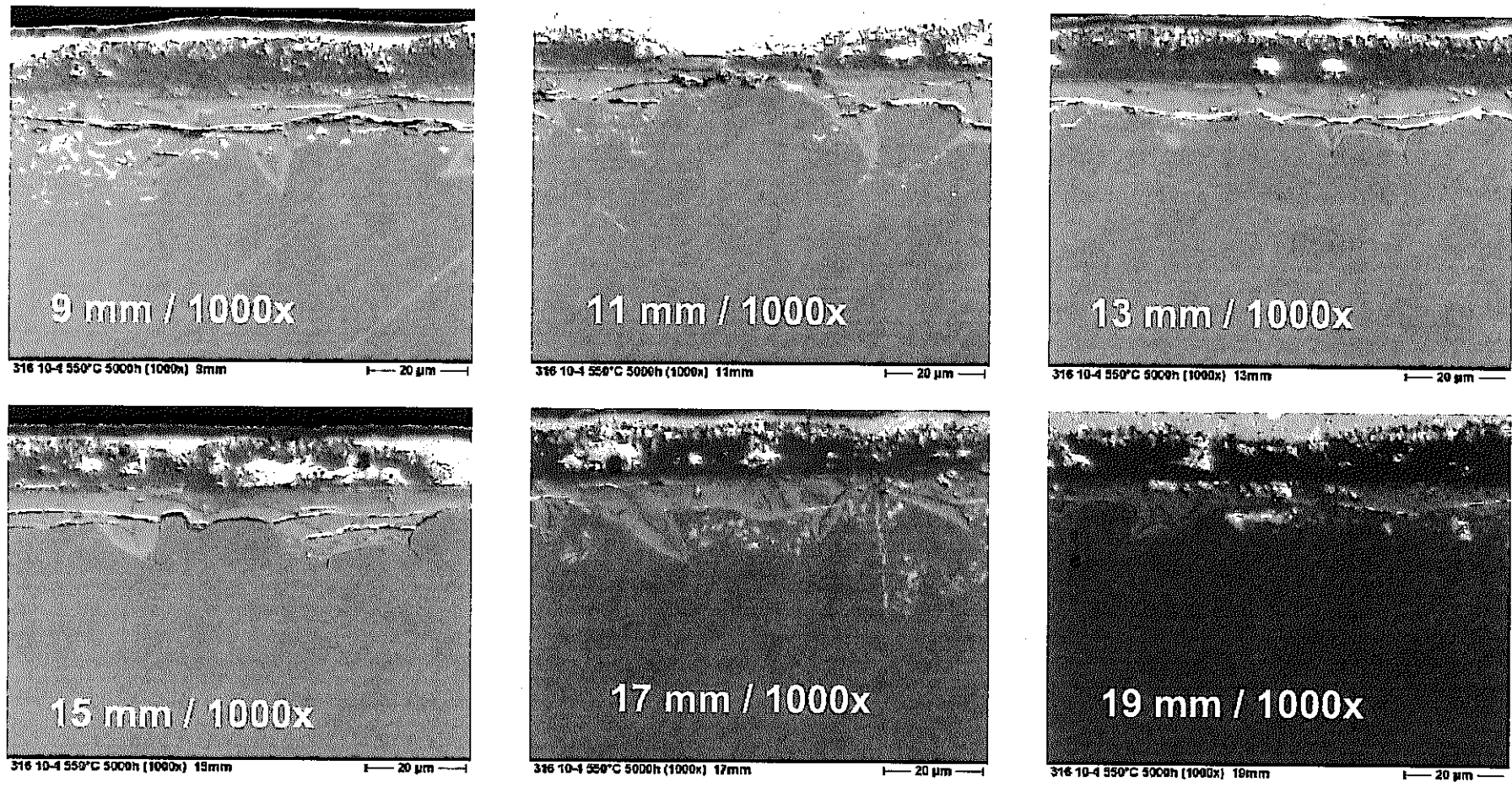


Fig. 4 : Longitudinal section of 316FR at 550°C 10<sup>-4</sup> wt% 5000 h