

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

**Part III. Corrosion investigation of steels between 500 and 650°C during
10,000 h of exposure to stagnant liquid Pb-Bi containing 10^{-6} wt% of oxygen**

January, 2004

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

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

Part III. Corrosion investigation of steels between 500 and 650°C during 10,000 h of exposure to stagnant liquid Pb-Bi containing 10^{-6} wt% of oxygen

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Abstract

This is the third 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 two reports considered the behavior of 316 FR, P122 and ODS steels during 800, 2,000 and 5,000 h in stagnant LBE at 500 – 650 °C containing 10^{-6} wt% of oxygen. This report describes the results of all experiments including that of 10,000 h duration.

Martensitic steels perform well at 500 and 550 °C up to the maximal exposure time of 10,000 h, while austenites fail after 5,000 h. At temperatures of 600 C and 650 °C all of the steels fail the earlier the higher the temperature is. Steels with Al – alloying at the surface by the GESA process withstand corrosion up to the maximal exposure time at all of the applied temperatures if it is ensured that the Al – concentration at the surface is in between 8 – 15 wt%.

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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3報: 10^{-6} wt%酸素含有停留鉛ビスマス中 550~650°C-10,000 時間
浸漬材の腐食評価

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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3報である。

第1報および第2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 および 5,000 時間浸漬後の腐食挙動について報告した。本報告書では、これらの試験結果を含め、10,000 時間までのこれら 3 鋼種の腐食挙動について報告する。

500°C および 550°C の鉛ビスマス中では、マルテンサイト鋼である P122 および ODS の受入材は 10,000 時間までの浸漬に対して、表面に形成された酸化(保護)皮膜による良好な耐食性を示した。一方、オーステナイト鋼である 316FR 受入材は 5,000 時間浸漬後にはその効果が認められなくなった。600°C および 650°C では全ての鋼種で酸化皮膜による保護効果が認められなかった。

これら 3 鋼種のアルミニウム表面改質材(GESA 材)については、表面のアルミニウム濃度が 8~15wt%に保たれた場合は、全ての試験ケースで耐食性は良好であった。

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1 Introduction

This is the third report on the first part of 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". This report deals only with the part of work under the contract above that concerns eutectic Pb/Bi (LBE) with 10^{-6} wt% of oxygen.

The first two parts of the "Study on Pb/Bi Corrosion of structural and fuel cladding materials for nuclear applications" describe corrosion investigation of steels after 800, 2000 and 5000 hours of exposure to stagnant liquid LBE at temperatures of 500 to 650 °C in the COSTA device¹. The concentration of oxygen in LBE is controlled at 10^{-6} wt%. The first part of the report contains 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 first two reports up to 5000 h of exposure are:

- (1) The steels 316 FR, P122 and ODS form protective layers on the surface up to 5000 h at 500 and 550 °C that prevent dissolution attack of the liquid LBE melt up to 2000 h of exposure.

At 550°C ODS and P122 lose their oxide layer completely in between 2000 and 5000 h of exposure. These oxide scales grow again and protect the steel in the upper part of the crucible from dissolution attack, while in the lower part dissolution attack occurs. The results of ODS and P122 exposed at 550 °C for 5000 h described in report 2 [2] do not show the real behavior at this conditions. Annex 1 will focus on this problem. On 316 FR, there are nodular magnetite-spinel scales, however, without dissolution attack.

- (2) Above 600 °C the oxidation behavior of the original materials changes, the oxide scales become very thin. There are attacks by LBE at singular spots at the surface of all of the three materials. The phenomena are observed after 800 h exposure for 316 FR and ODS, and after 2000 h for P122. After 5000 h of exposure a great part of 316 FR is still protected by a thin oxide layer. It is only partly attacked by LBE. ODS and P122 show completely, partly deep surface attack up to 60 µm depth.

- (3) At 650 °C all of the original steel specimens are completely attacked with partly deep LBE penetration of up to 60 µm after 5000 h of exposure.
- (4) After alloying Al into the surface by GESA, materials show good corrosion resistance without any attack at all temperatures up to 5000 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.

The present report describes the results of corrosion experiments in LBE with 10⁻⁶ wt% oxygen. It considers the results of the former experiments up to 5000 h exposure as well as the results of the continuation of these experiments to 10000 h. Table 1 given below shows the experimental parameters in the dashed region which includes the exposure times of 800, 2000, 5000 and 10000 h at temperatures of 500 – 650° C. The remaining part of the table concerns experiments at different oxygen concentrations in LBE, the results of which will be reported separately.

The experimental set up as well as the structure of starting materials and the shape of the specimen is comprehensively described in part 1 of the report issued in June 2002.

Material (amount)	T [°C]	O ₂ content 10 ⁻⁴ w[%]				O ₂ content 10 ⁻⁵ w[%]				O ₂ content 10 ⁻⁷ - 10 ⁻⁸ w[%]*			
		800h	2000h	5000h	10000h	800h	2000h	5000h	10000h	800h	2000h	5000h	10000h
316 FR original (15 ¹)	500					X	X	X	X				
	550	X	X	X		X	X	X	X	X	X	X	
	600					X	X	X	X				
316 FR GESA (3)	500					X	X	X	X				
	550					X	X	X	X				
	600					X	X	X	X				
P122 Original (15 ¹)	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 ¹)	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

It should be mentioned that the specimens after each test period are taken out of the LBE crucibles and not set back after cutting off the sample for metallographic examination. Thus each one of the specimens remains inside the test crucible in the furnace until the end of the exposure time is reached. It is agreed between the coopera-

¹ JNC report TY 9400 2002-016, Study on Pb/Bi Corrosion of Structural and Fuel Cladding Materials

tion partners that FZK takes a small sample of each specimen and after this sends the remaining specimen part to JNC for further examination.

The sample examined at FZK is always taken from the lower end of the specimens that is located in a depth of 1.5 cm below the LBE surface inside the test crucible. After a first examination at JNC it was ascertained that the corrosion behavior of the martensites varies with the distance from the LBE surface². Below an immersion depth of 1 cm dissolution attack occurs at 550 °C after 5000 h while in the upper specimen part still a protective oxide scale exists. The oxide scale broken away between 2000 and 5000 h covers the LBE surface and acts as an additional diffusion-barrier for oxygen. Therefore only the upper part of the samples located close to the surface receives the required oxygen and forms as expected thick multilayered oxide scales, while the lower part shows strong dissolution attack due to the reduced oxygen concentration. Such differences did not appear at 500 °C. In this case the lower end was also covered by a protective oxide scale, which did not spall off up to 5000 h of exposure. Therefore no differences have to be expected between the upper and lower part of the specimen immersed into LBE. There is also no influence of the immersion depth to be observed for temperatures of 600 °C and 650 °C. This is, because the oxide layers at these temperatures are generally very thin and the diffusion rate is higher than at 500 °C. Thus, only at 550 °C and for the martensitic materials the influence of the immersion depth has to be considered.

JNC TY9400 2003-026

² personal communication JNC, July 2003

2 Behaviour of steels in LBE

2.1 316 FR steel

2.1.1 Temperature 500 °C

The 316 FR steel has a thin protective spinel layer after 800 h of exposure which contains some oxide nodes of up to 6 µm thickness.

This appearance does not change up to 5000 h of exposure. Fig. 1 presents the cross section perpendicular through the surface region after 2000 h. The thin spinel layer in the left surface region is not visible but was detected by EDX technique with signals from the surface employing different electron energies.

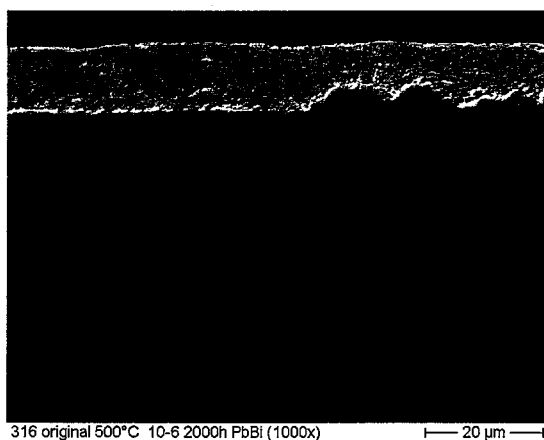


Fig. 1: Thin spinel layer partly with oxide nodes on the surface of 316 FR after 2000 h of exposure at 500 °C

After 10000 h of exposure a partly dissolution attack (up to 40 µm) was observed, Fig. 2. LBE obviously penetrates the spinel scale and migrates along grain boundaries to the interior of the specimen. This process is accompanied by depletion of Ni around the grain boundaries. Grain boundary attack occurs because the oxide layer has no complete coverage.



Fig. 2: Dissolution attack by grain boundary penetration in 316 FR after 10000 h of exposure at 500°C.

However, there are great parts of the surface area in which a thin and also thick oxide layer still protects the 316 FR steel from dissolution attack, Fig. 3.



Fig. 3: Surface part of 316 FR steel without dissolution attack after 10000 h exposure at 500 °C. Note the oxide scale observed at some places increased to 10 µm and more.

There are no signs of surface attack at the 316 FR specimens surface alloyed with Al by the GESA process. After all of the exposure times nothing changed at the surface which is still protected by a thin alumina layer. Fig. 4 shows the surface cross section of the specimen after 10000 h.

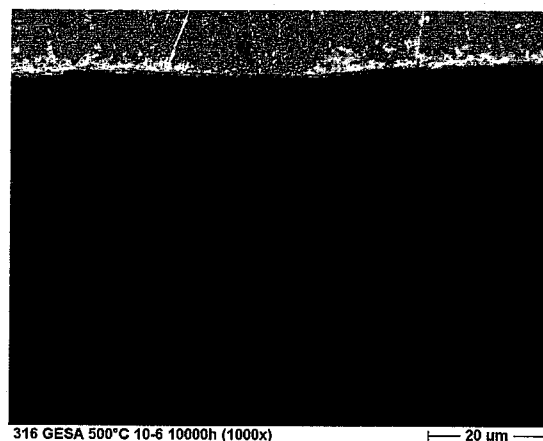


Fig. 4: Surface of the 316 FR steel specimen surface alloyed with Al by the GESA process after 10000 h of exposure at 500°C.

2.1.2 Temperature 550 °C

The surface behaviour of 316 FR up to 2000 h of exposure seems to be untypical because of the formation of a continuous magnetite and spinel layer of 10 – 20 µm instead of thin spinel layers with oxide nodes like observed at 500 °C. Fig. 5 shows the surface structure of the specimen after 2000 h of exposure.



Fig. 5: Continuous magnetite and spinel layer on 316 FR steel after 2000 h of exposure at 550 °C.

The reason for this untypical behaviour is assumed to be an accidental air intake during loading of these specimens. Thus, the oxygen concentration was higher for the 800 and 2000 h specimens during the first hours of exposure.

The specimen after 5000 h of exposure looks like expected for the 316 FR steel. Thin spinel layers and magnetite / spinel nodes cover the surface and protect it from dissolution attack. Compared to the 500 °C specimen the nodes are thicker and reach up to 15 μm. LBE penetrates the oxide nodes and precipitates at the border to the metallic phase.



Fig. 6: Magnetite and spinel layer nodes and spinel scale on 316 FR steel specimen after 5000 h of exposure at 550 °C.

After 10000 h of exposure strong dissolution attack occurs on a large part of the surface area. The maximal depth observed on the cross section was 200 μm. Fig. 7 shows this part of the surface area. The still existing oxide scale is penetrated by LBE which proceeds into the interior by migration along the grain boundaries.

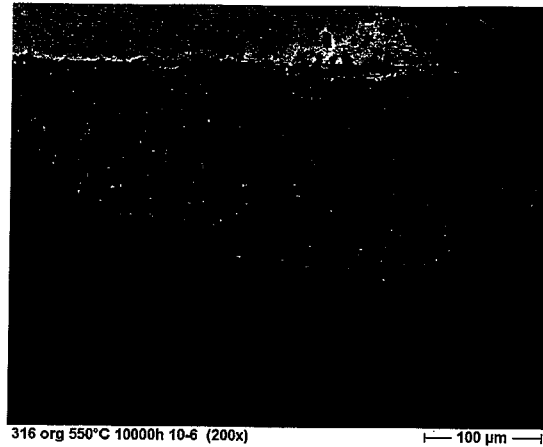


Fig. 7: Dissolution attack on 316 FR steel after 10000 h of exposure at 550 °C. Note the lower magnification!

All of the specimens Al – alloyed by GESA show no dissolution and oxidation attack like demonstrated in Fig 8 obtained from the 10000 h specimen.

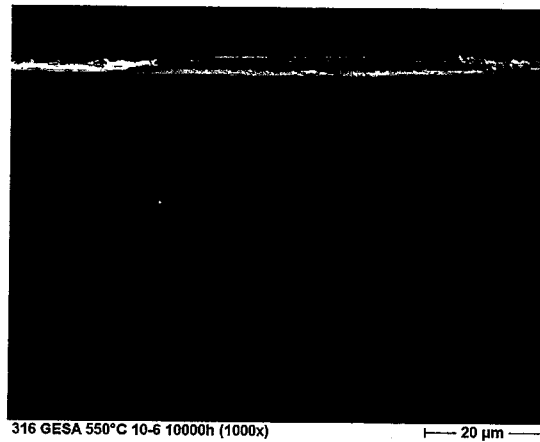
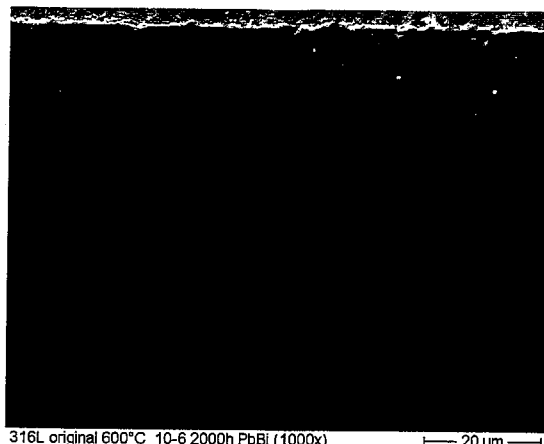


Fig. 8: 316 FR steel surface alloyed by GESA after 10000 h of exposure at 550 °C.

2.1.3 Temperature 600 °C

There is no magnetite layer observed on 316 FR steel at 600 °C. The surface is covered by a thin spinel layer like it is known to grow on ferritic steels at 600 °C. However, the spinel is penetrated by LBE after 800 h already to a depth of 5-10 μm. The dissolution attack increases in the cross sections observed to a depth of about 20 μm in the specimens exposed for 2000 and 5000 h. The effect on the 2000 h specimen is shown in Fig. 9.



316L original 600°C 10-6 2000h PbBi (1000x) 20 μm

Fig. 9: Grain boundary penetration of LBE in 316 FR after 2000 h of exposure at 600 °C.

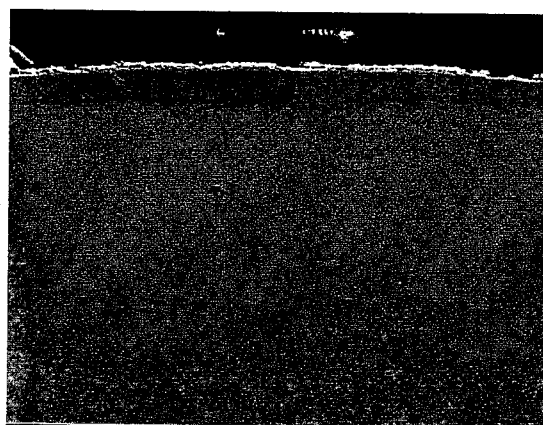
After 10000 h the dissolution attack along the grain boundaries spreads out to a depth of about 180 μm in the observed parts of the specimen, Fig. 10.



316 600°C 10-6 10000h (200x) 100 μm

Fig. 10: Deep grain boundary dissolution attack on 316 FR steel after 10000 h of exposure at 600°C. Nodes on top consist of Cr-spinel. Note the lower magnification!

No dissolution and oxidation attack occurs on the specimens surface alloyed with Al by GESA after all the exposure times. Fig. 11 shows the non affected surface of the 10000 h specimen.



316 GESA 600°C 10-6 10000h (1000x) 20 μm

Fig. 11: Non affected surface of the GESA alloyed 316 FR specimen after 10000 h at 600 °C.

2.2 ODS steel

2.2.1 Temperature 500 °C

A thick magnetite and spinel layer of 6 - 7 μm appears on the surface already after 800 h like it is typical for martensitic steels. After 5000 h this scale increases to about 20 μm as shown in Fig. 12. A pore belt appears below the spinel layer which is caused by migration of iron into the magnetite layer. It starts to develop after 2000 h. No dissolution attack is observed because this scale protects the surface.

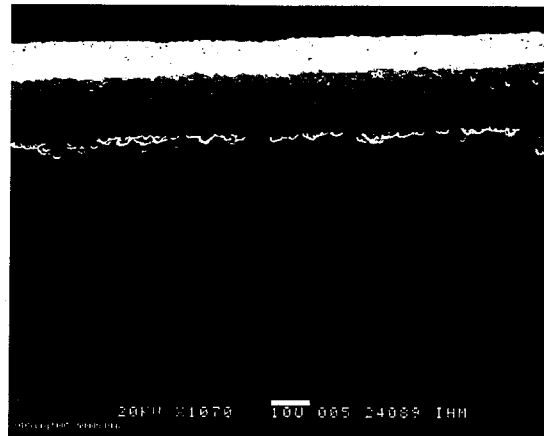


Fig. 12: Thick protective magnetite and spinel scale on ODS steel after 5000 h of exposure at 500 °C. A pore belt develops by iron migration into the magnetite layer.

After 10000 h the oxide layer grows to 40-50 μm thickness (Fig. 13) and starts to spall off at some places. No dissolution attack is observed.

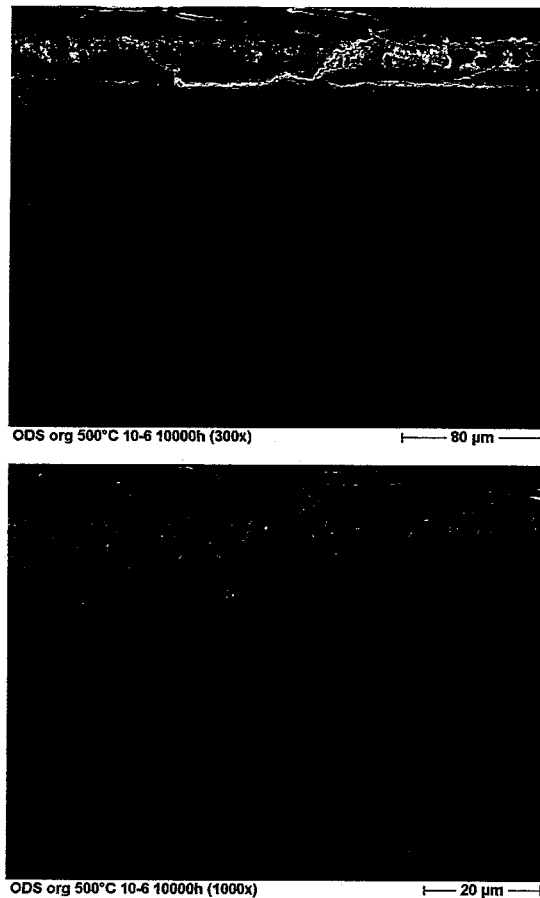


Fig. 13: Oxide layer grown to 30-40 μm on ODS steel after 10000 h of exposure at 500 °C. It starts to spall off at some places. Low magnification above, high below.

The growth of the three distinguished zones differs during the exposure time. The magnetite layer grows with a constant rate to a thickness of about 25 μm within 10000 h of exposure. The spinel layer grows during the first 2000 h to a thickness of about 8 μm with a constant rate. In the following 3000 h the thickness does not increase any further. From 5000 to 10000 h the spinel layer reaches a thickness of 20 μm . The diffusion zone grows parabolic to a thickness of about 15 μm after 5000 h. From 5000 to 10000h the thickness is reduced almost by half by extension of the spinel zone.

The growth of diffusion zone and spinel layer should be considered together. Doing so, a parabolic growth over the entire exposure time can be assumed.

If we plot the measured overall oxide layer thickness d , which is the sum of magnetite, spinel and diffusion zone thickness versus time like in the diagram of Fig. 14, we can fit the measured values using a parabolic curve $d = \sqrt{2kt}$, $k \equiv$ parabolic constant [$\mu\text{m}^2/\text{h}$],

$t \equiv$ exposure time [h]. The parabolic constant for 500 °C is $0.1 \mu\text{m}^2/\text{h}$. Thus we can describe the oxide layer thickness as a function of time of ODS at 500 °C by:

$$d = 0.447 \cdot \sqrt{t} \quad [\mu\text{m}] \quad (1)$$

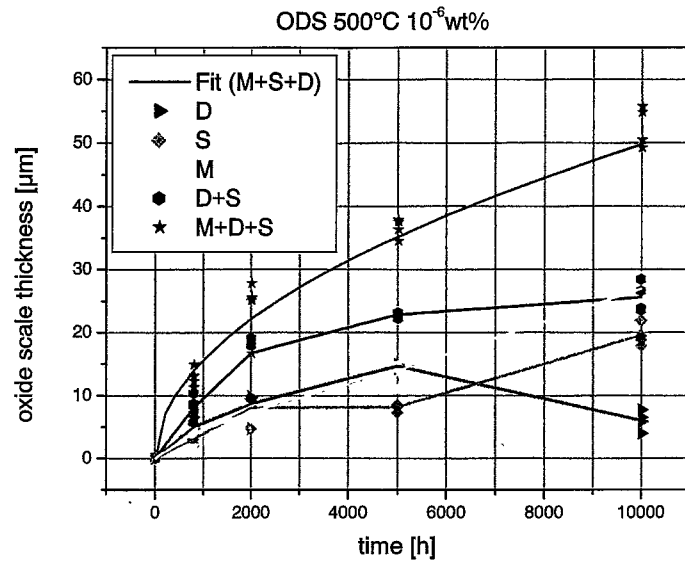


Fig. 14: Oxide scale thickness as function of exposure time for ODS at 500 °C

The specimen surface alloyed with Al by the GESA process did not show any signs of attack at all exposure times up to 10000 h. Fig. 15 shows the cross section through the 10000 h specimen. The lower part of the figure represents the normal surface appearance; however, oxide nodes appear at few spots of the specimen cross section, as shown in the upper part of Fig. 15. They are a consequence of two low Al concentrations at those spots. But, no dissolution attack is observed at those places

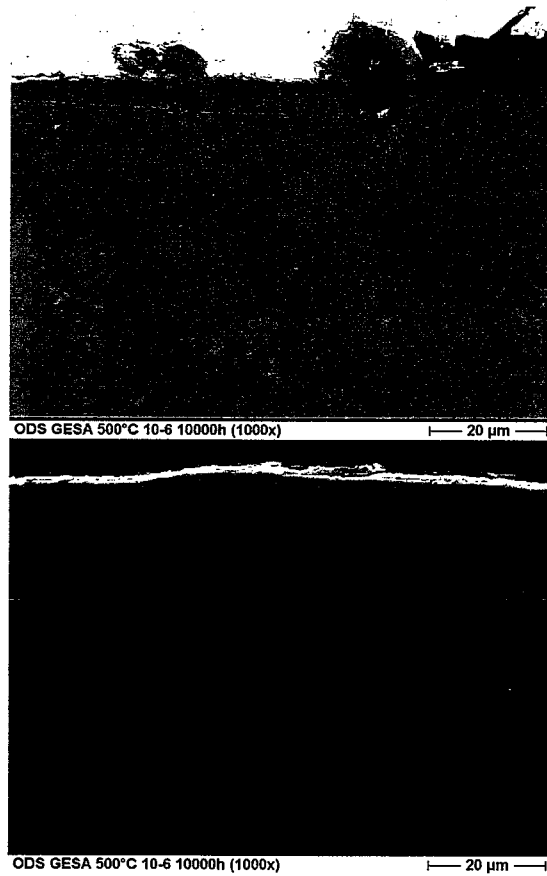


Fig. 15: No attack on GESA alloyed ODS specimen up to 10000 h of exposure at 500 °C. Above figure shows a surface part with oxide node.

2.2.2 Temperature 550 °C

The magnetite layer which was stable on the surface at 500° C starts to spall off after 800 h and 2000 already. After 5000 h the oxide layer grows again and protects the surface from dissolution attack, as shown in Fig. 16.

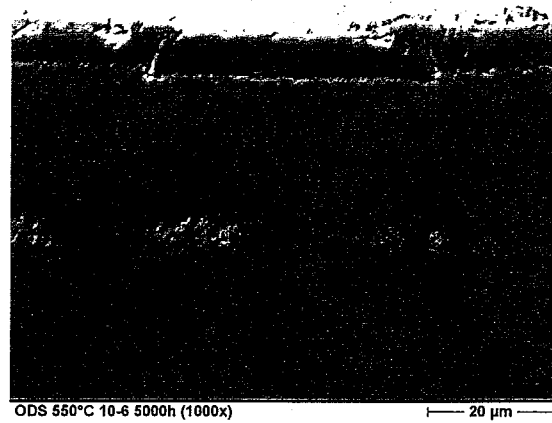


Fig. 16: Oxide scale on ODS steel after 5000 h exposure at 550 °C.

After 10000 h the oxide scale observed after 5000 h grows to a total thickness of about 100 μm. No dissolution attack can be observed on the steel, Fig. 17.

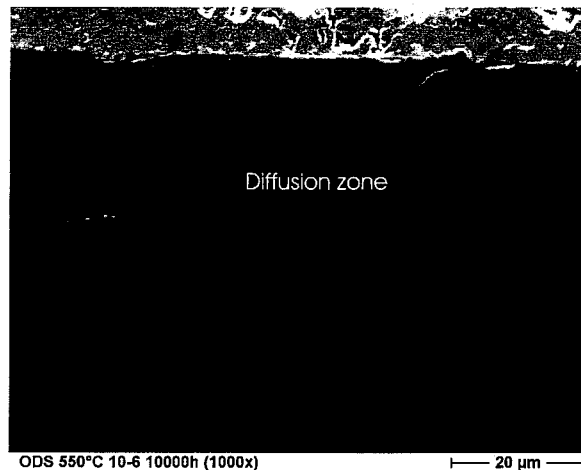


Fig. 17: Oxide scale on ODS steel after 10000 h of exposure at 550 °C, note the extended diffusion zone.

Again the growth of the three distinguished zones differs during the exposure time. Neglecting the spalling off of the oxide scale between 2000 h and 5000 h growth of the magnetite layer with a constant rate to a thickness of about 30 μm within 10000 h of exposure can be assumed. The spinel layer grows during the first 2000 h to a thickness of about 11 μm with a constant rate. In the following 3000 hours its thickness is reduced slightly which hints to a partial break off together with the magnetite layer. From 5000 to 10000 h the spinel layers grows to a thickness of 16 μm. The

diffusion zone grows in the first 800 h to a thickness of about 9 μm and finally up to about 50μm, Fig. 18.

Fig. 18 shows the parabolic oxide layer growth like described for the 500 °C specimen in Fig. 14. The parabolic constant of ODS at 550 °C is 0.44 μm²/h. Thus we can describe the oxide layer thickness as a function of time of ODS at 550 °C by:

$$d = 0.938 \cdot \sqrt{t} \quad [\mu\text{m}] \quad (2)$$

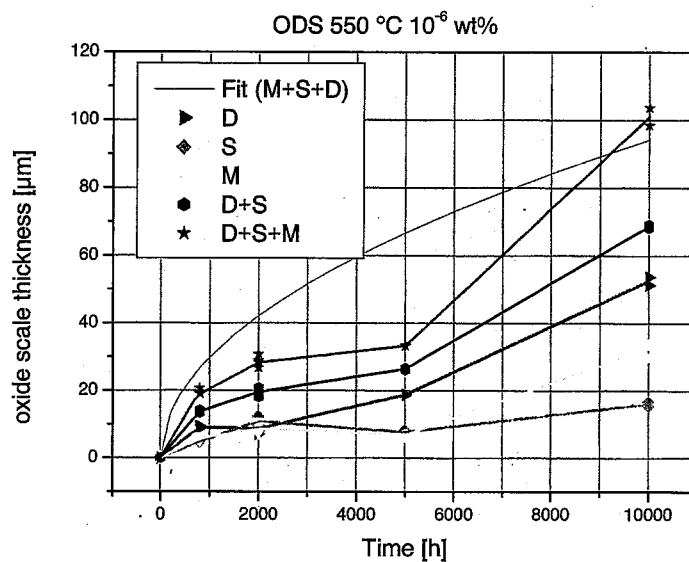


Fig. 18: Oxide scale thickness as function of exposure time for ODS at 550 °C

The GESA alloyed ODS specimens exposed to LBE for 800 and 2000 h have no dissolution attack but partly a thick magnetite and spinel layer which is caused by a too low Al-concentration. This indicates, something went wrong with the GESA alloying process.



Fig. 19: Oxide scale at the surface of the ODS steel specimen after 2000 h of exposure at 550 °C. Note the lower magnification.

The specimens after 5000 and 10000 h of exposure develop large magnetite and spinel layers also. The reason for this behaviour is again the aluminium concentration in the bulk which is far below 8 wt%. Large pores below the oxide scale indicate positions from which iron migrated into the magnetite layer. This oxidation behaviour is similar to that of normal martensites, however, without spallation.

2.2.3 Temperature 600 °C

The specimens after 800 and 2000 h of exposure have only a thin spinel layer which is penetrated by LBE locally at some spots where the oxide scale fails. Fig. 20 shows such a spot on the 800 h specimen.

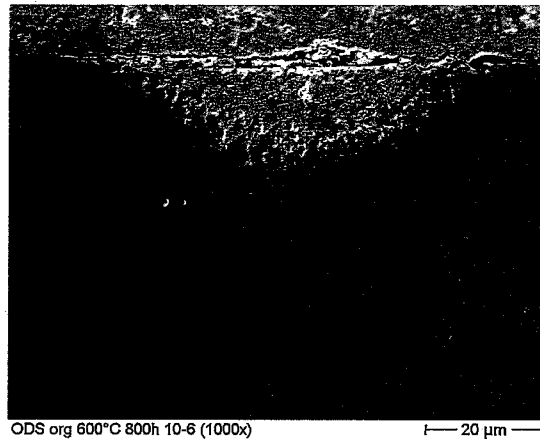


Fig. 20: Local attack on ODS steel at the position of a failure in the oxide scale after 800 h of exposure at 600 °C.

After 5000 and 10000 h of exposure the total surface of the specimens is attacked by dissolution to a depth of partially 60 μm and 85 μm, respectively. No nodes nor scales of oxide can be observed. A broad band (30 – 50 μm) of small pores appears below the attacked surface as shown in Fig. 21 of the 10000 h specimen cross section. The dissolution zone appears to be up to 30 μm deep but may be even deeper because the position of the original surface can not be identified. Around the pores there is a strong depletion in Cr.



Fig. 21: Dissolution attack and pore formation on ODS steel after 10000 h of exposure at 600 °C.

At the ODS steel specimens surface alloyed with Al by GESA there is no sign of dissolution attack after all exposure times. Only at very few spots some oxide nodes appear on the 5000 h specimen, which indicate an Al concentration below 8 wt% at those places. The behaviour of the 10000 h specimen is not considered because the melt alloying process for this specimen did not result in a relevant quality.

2.2.4 Temperature 650 °C

After exposure times of 800 and 2000 h the same phenomenon is observed like in the 600° C specimen. A thin spinel layer protects the surface just interrupted at a few spots by dissolution attack. At those places always an assembly of small pores appears which indicates lost particles of chromium carbides or sulphides, Fig. 22.

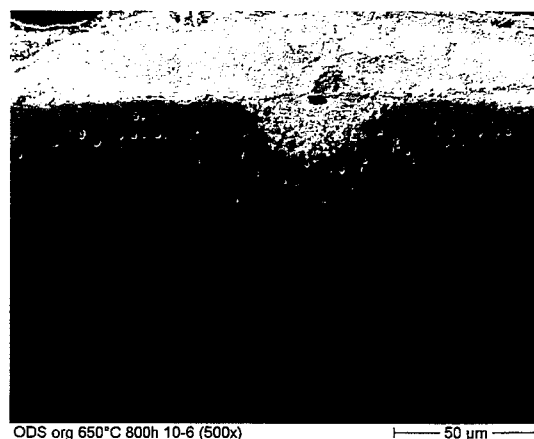


Fig. 22: Point of surface attack on ODS steel specimen after 800 h of exposure at 650 °C.

On the 5000 h specimen, the protective spinel layer disappeared completely like it is the case at 600° C. After 10000 h of exposure again the whole surface is attacked and a pore band of about 100 μm appears like shown in Fig. 23.

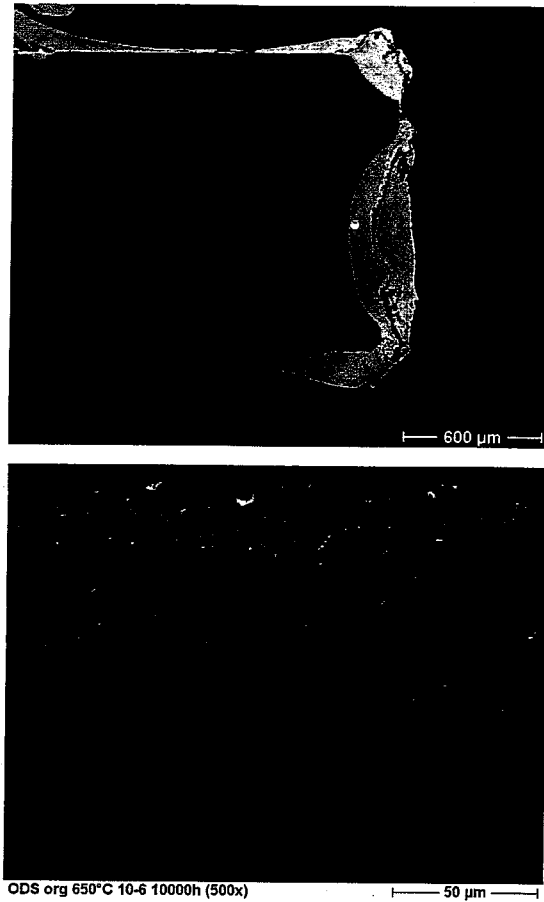


Fig. 23: Dissolution attack on the whole surface of ODS steel accompanied by a band of small pores after 10000 h of exposure at 650 °C. Low magnification above, high below.

There is no LBE attack visible at the ODS steel specimen surface alloyed by GESA after all of the exposure times. The only difference between the specimens is the appearance of some local spinel oxide scales of up to 5 μm thickness on the 10000 h specimen, Fig. 24.

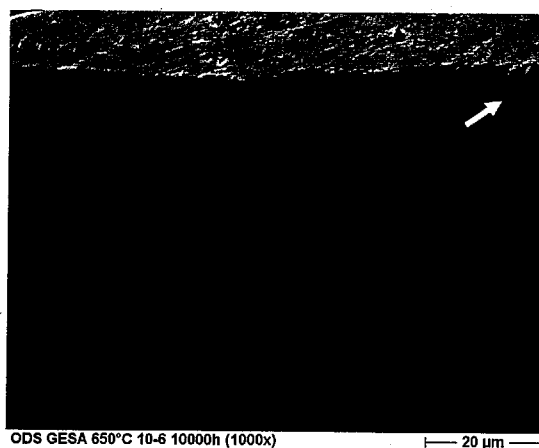


Fig. 24: GESA alloyed ODS steel specimen after 10000 h of exposure at 650 °C showing a place covered by a small spinel scale (arrow).

2.3 P122 steel

2.3.1 Temperature 500 °C

There is no dissolution attack on P122 steel during 10000 h of exposure to LBE. A thick magnetite and spinel layer scale protects the steel. The oxide scale is steadily growing from 8 μm after 800 h to 60 – 70 μm after 10000 h. After 800 h of exposure a small zone, enriched in Cr with 2 wt% Cu appears, represented by a small dark band in Fig. 25. While the oxide layers have a good density up to 5000 h, a zone with high porosity exists between magnetite and spinel layer on the 10000 h specimen, Fig. 26.

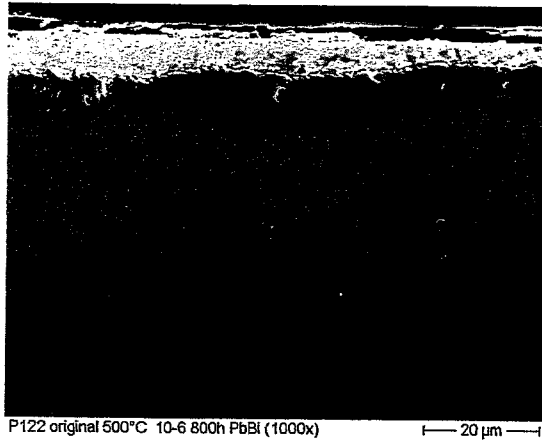


Fig. 25: Dense magnetite and spinel layer on the surface of P122 steel after 800 h of exposure at 500 °C. Small dark band is a zone enriched in Cr, 2 wt% Cu.



Fig. 26: Massive oxide scale formation on P122 steel after 10000 h of exposure at 500 °C. High porosity zone between magnetite and spinel layer.

Each of the three layers grow in the first 2000 h slightly to a thickness of 2 μm for the diffusion zone to about 5 μm in case of spinel and magnetite layer. Between 2000 and 5000 h only little growth of the spinel layer occurs. The magnetite layer stays

constant and the diffusion zone thickness drops slightly. Adding the thickness of spinel and diffusion zone together the sum stays constant. For the last 5000 h all three layers grow again with a smaller growth rate than at the beginning.

The parabolic growth constant of the entire oxide scale, was determined from Fig. 27 to be $0.18 \mu\text{m}^2/\text{h}$, which gives an overall oxide layer thickness as a function of time

$$d = 0.6 \cdot \sqrt{t} \text{ } [\mu\text{m}] \tag{3}$$

This oxidation rate is lightly higher compared to that of the ODS steel at the same temperature. The scale thickness obtained after 5000 h is lowered by spallation of the magnetite layer.

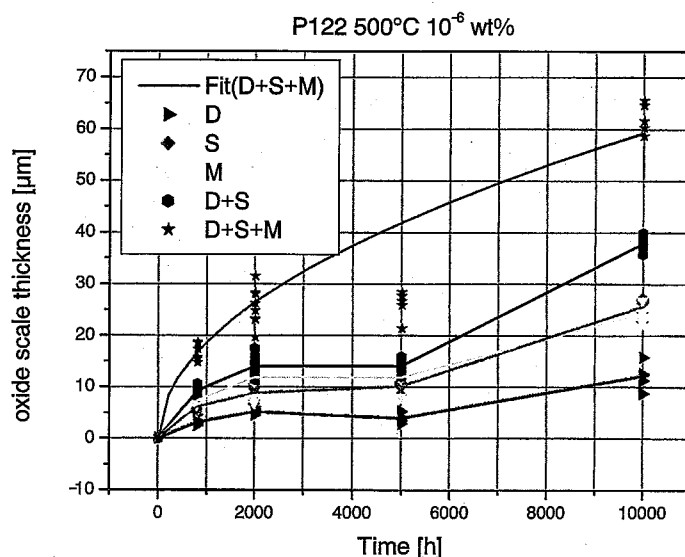


Fig. 27: Oxide scale thickness as function of exposure time for P122 at 500 °C

The GESA alloyed P122 steel surface was not attacked after all the exposure times. Fig. 28 shows the specimen after 10000 h of exposure.

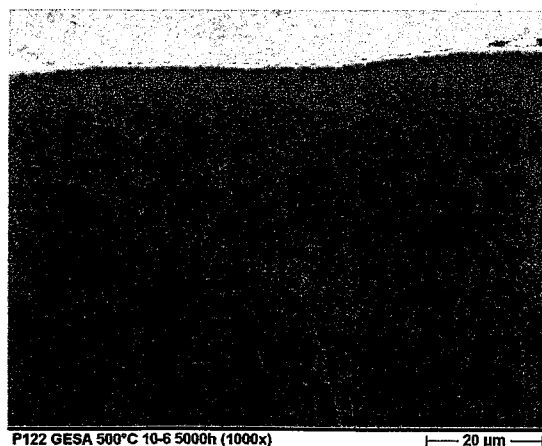


Fig. 28: P122 surface alloyed by GESA after exposure of 10000 h at 500 °C.

2.3.2 Temperature 550 °C

The P122 steel specimen after 800 h of exposure to LBE has a magnetite and spinel layer of about the same thickness as the one exposed to 500° C. However, the magnetite layer is partly broken out, Fig. 29. It also looks like the whole oxide layers starts to spall off.

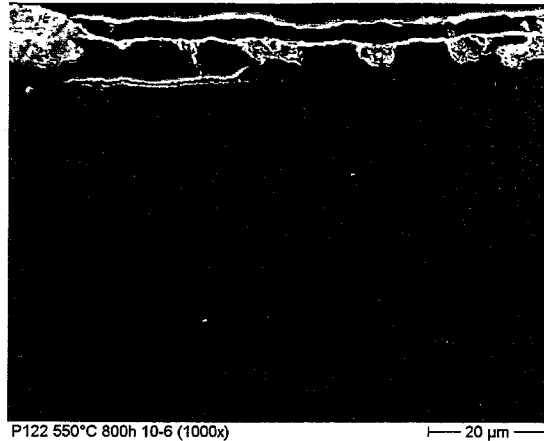


Fig. 29: Partly broken magnetite layer and scale detachment on the P122 steel surface after 800 h of exposure at 550 °C.

The protective oxide scale grows again and protects the steel for the 5000 h period, Fig. 30. As opposed to the oxide scale after 2000 h no magnetite layer can be observed. Most probably this missing magnetite scale spalls off again.



Fig. 30: Oxide scale grown again on P122 steel specimen after 5000 h of exposure at 550 °C.

After 10000 h of exposure the three layers of the multilayered oxide scale are clearly to be distinguished. The magnetite layer is very open structured with LBE penetration, Fig. 31. As in case of the ODS at the same temperature the diffusion zone grows strongly within the 5000 and 10000 h exposure period.

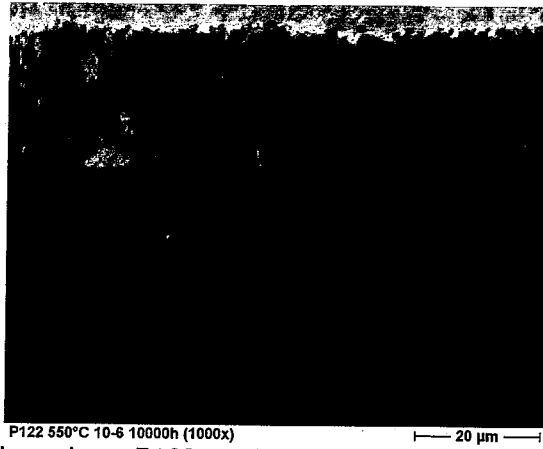


Fig. 31: Oxide scale on P122 steel after 10000 h of exposure at 550 °C.

No attack occurred on the GESA alloyed specimen at all exposure times. Fig. 32 shows the steel after 10000 h of exposure.

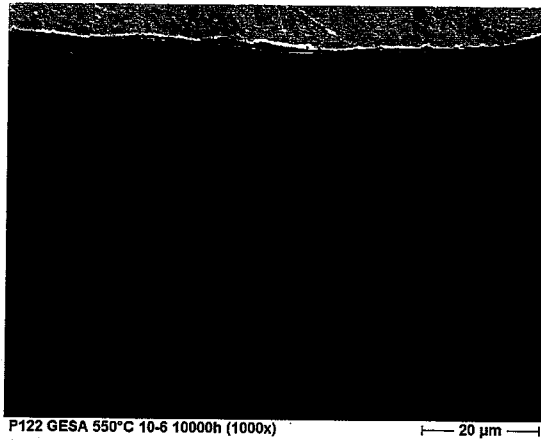


Fig. 32: P122 steel surface alloyed by GESA after 10000 h of exposure at 550 °C.

2.3.3 Temperature 600 °C

As opposed to lower temperatures no magnetite layer could be observed after 800 h at 600° C on the P122 steel specimen, Fig. 33. Furthermore, the spinel layer is much richer in Cr with a Cr/Fe ratio of 1. After 2000 h the dissolution attack starts at few spots, Fig. 34. Below these spots S and C containing precipitations appear. 20 µm deep penetration of Pb/Bi is observed. Most parts of the sample are still protected by the spinel layer.

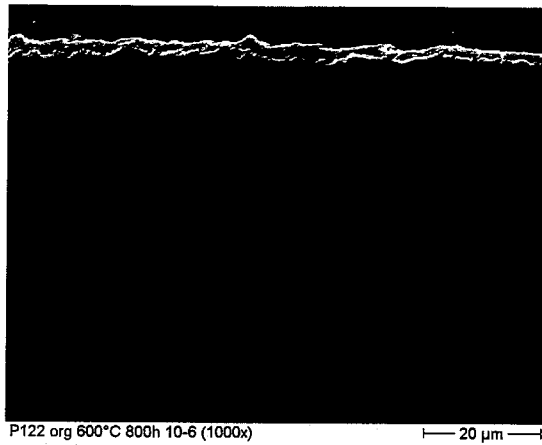


Fig. 33: Spinel scale without magnetite on the surface of P122 steel after 800 h of exposure at 600 °C.

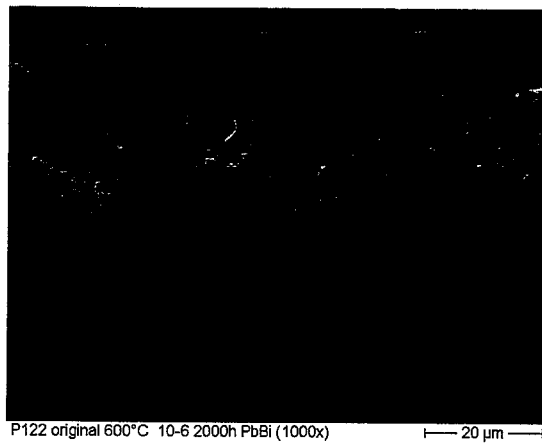


Fig. 34: Partly deep dissolution attack on P122 steel after 2000 h of exposure at 600 °C.

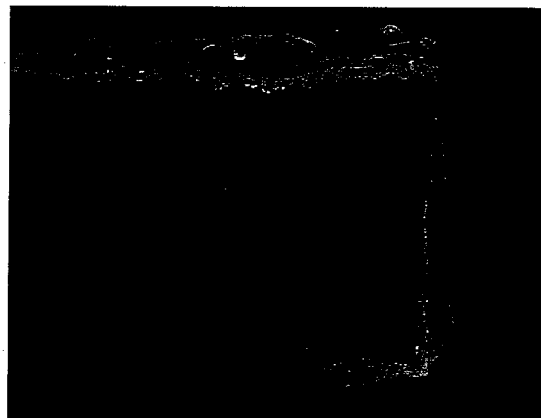
Not many changes happened in the 5000 h specimen compared to the one at 550° C. There is just more frequent partial penetration and the reaction zones along the grain boundaries are broadened like shown in Fig. 35.



P122 org 600°C 5000h 10-6 (1000x) 20 μm

Fig. 35: Broadened reaction zones along grain boundaries in P122 steel after 5000 h of exposure at 600 °C.

Complete massive surface attack occurs up to 10000 h of exposure. The original surface can not be identified anymore. The depth of attack is estimated to be up to 200 μm. Fig. 36 gives an impression of the deterioration of the specimen.



P122 600°C 10-6 10000h (40x) 600 μm



P122 600°C 10-6 10000h (200x) 100 μm

Fig. 36: Deterioration of P122 steel by dissolution attack after 10000 h of exposure at 600 °C. Low magnification above, high below.

There is no attack on GESA alloyed P122 steel also at 600 °C. On the specimen exposed for 5000 h a few micro cracks can be identified that are filled with Cr-Al oxides

and sealed by this way. They arise in regions of too high Al concentrations which also have a high brittleness, Fig. 37. Some places with oxide nodes appear on the surface of the 10000 h specimen.



Fig. 37: Unattacked surface of the GESA alloyed P122 steel containing a filled micro crack after 5000 h of exposure at 600 °C.

2.3.4 Temperature 650 °C

After 800 h most of the surface is covered by a thin protective spinel layer. There are, however, some spinel nests into which Pb/Bi penetrates and dissolves Cr. They are, therefore, depleted in Cr. This may be expected to lead to dissolution of steel components later on. After 2000 h the spinel nests grow by a factor 2. Pb/Bi penetrates into these nests to a depth of 12 μm, Fig. 38.

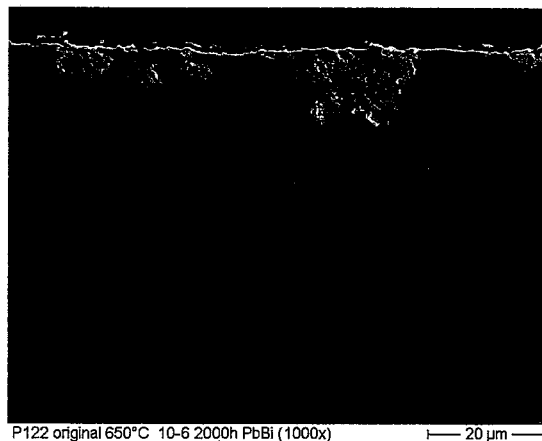


Fig. 38: Local dissolution attack after 2000 h of exposure at places which contain spinel nests after 800 h of exposure at 650 °C.

Dissolution attack occurred partially by penetration of the spinel layer after 5000 h which reached a depth of up to 40 μm, Fig. 39.

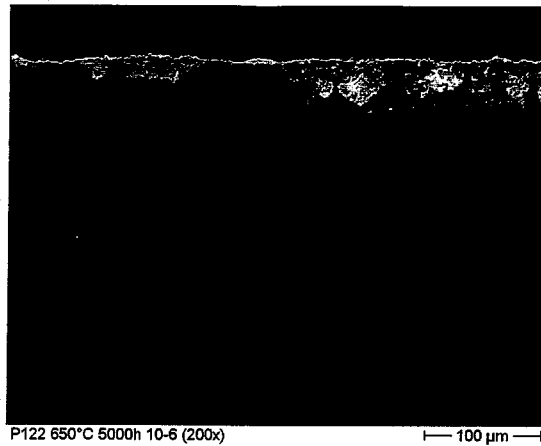


Fig. 39: Strong dissolution attack on P122 steel after 5000 h of exposure at 650 °C. Note the lower magnification!

After 10000 h of exposure a large scale surface destruction occurred, Fig. 40.

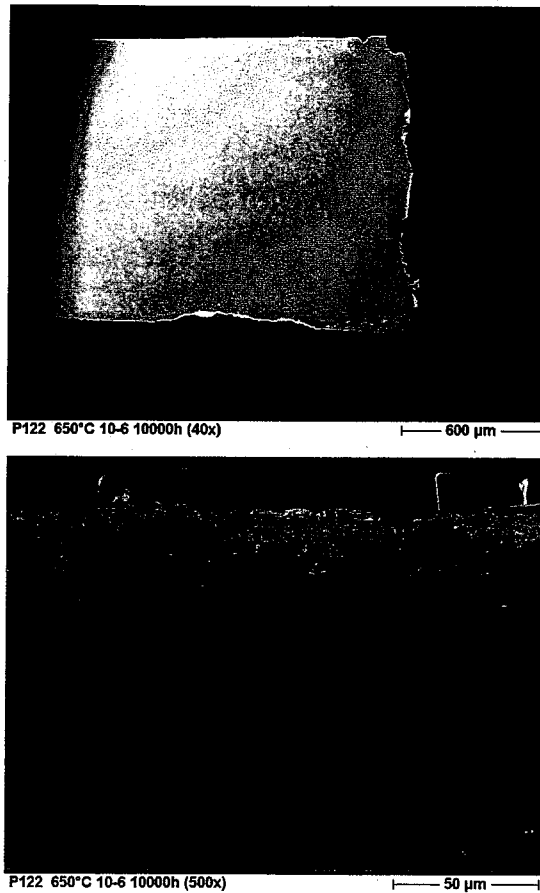


Fig. 40: Strong dissolution attack on P122 steel after 10000 h at 650 °C. Low magnification above, high below.

No GESA alloyed P122 steel specimen was exposed to LBE at 650° C.

3 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.

3.1 316 FR steel

3.1.1 Exposure 800 h

XRD patterns for the 316 FR steel in original state and after exposure to LBE at 500, 550 and 600 °C for 800 h are shown in Fig. 41. At 500 °C no oxide peaks are detected with the exception of PbO. There is some LBE remaining on the surface after the cleaning process. Small part of it is oxidized. The γ -Fe peaks of steel are still present of the same magnitude as in starting material.

At 550 °C the steel peaks disappear entirely. Dominating peaks are those of magnetite (M) and spinel (S), $(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$. Again peaks of remaining LBE, PbO appear. Note, that is specimen was shortly exposed to air during an accidental air intake in the furnace (2.1.2).

At 600 °C behaviour changes again. The γ -Fe peaks of steel are present. Only small amount of magnetite appears and again small LBE impurities.

The absence of oxide peaks at 500 and 600 °C indicates that there is a very thin protective oxide scale at the surface which protected the steel from dissolution attack.

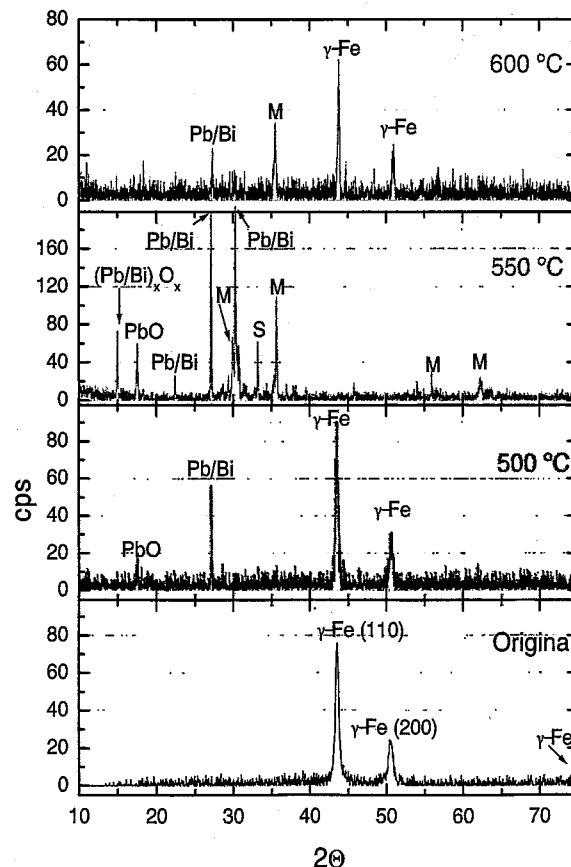


Fig. 41: XRD patterns of 316 FR steel after 800 h

3.1.2 Exposure 2000 h

The XRD patterns after 2000 h are shown in Fig. 42. At this time the γ -Fe peaks disappear already at 500 °C. Only magnetite is detectable on the surface and some impurities of LBE and its oxides.

At 550 °C again only magnetite is visible besides small indications of spinel and some LBE impurities.

At 600 °C spinel is visible together with γ -Fe and minor magnetite peaks and LBE and its oxides.

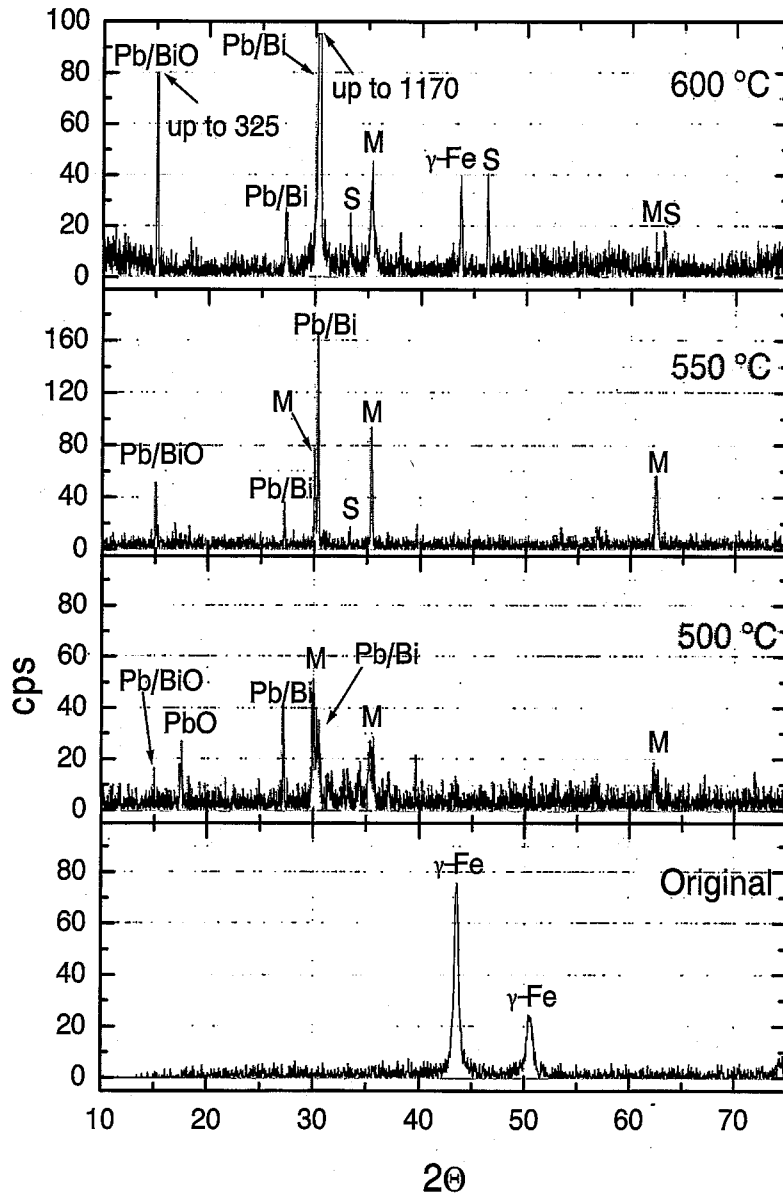


Fig. 42: XRD patterns of 316 FR steel after 2000 h

3.1.3 Exposure 5000 h

- 500 °C: γ -Fe peaks appear again like after 800 h. The magnetite peaks have about the same intensity like after 2000 h. A large part of the surface may be covered by PbBi.
- 550 °C: γ -Fe patterns appear which is not present after 2000 h indicating that in the 5000 h – specimen no continuous magnetite layer exists, but a partly thin spinel layer.
- 600 °C: α -Fe and γ -Fe peaks dominate, indicating disappearance of the oxide scale. The α appeared not after 2000 h. Dissolution of Ni from the surface layer is indicated by the α -Fe peak. Small Cr_2O_3 peaks indicate surface covering and / or grain boundary precipitation of Cr_2O_3 .

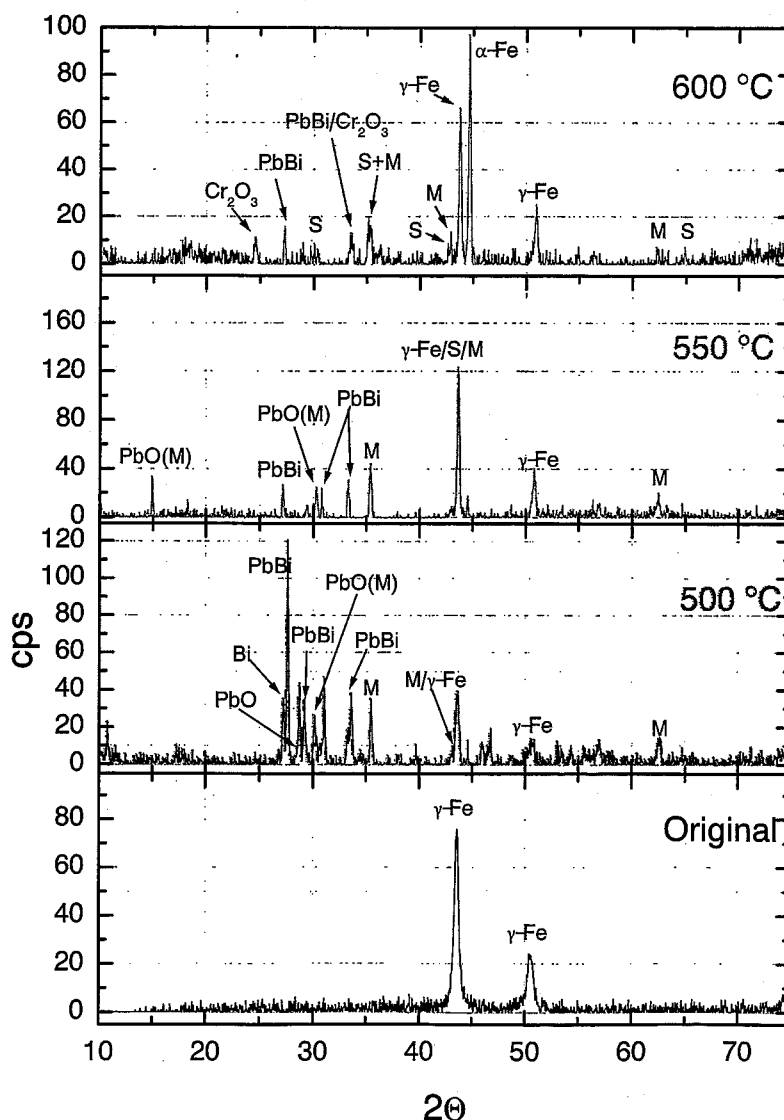


Fig. 43: XRD patterns of 316 FR steel after 5000 h

3.1.4 Exposure 10000 h

There are no changes to be observed in comparison of the 5000 and 10000 h specimens. Only the different height of the main magnetite peak indicates a larger coverage of magnetite after 10000 h. At 600 °C the XRD patterns after 5000 and 10000 h are practically identical.

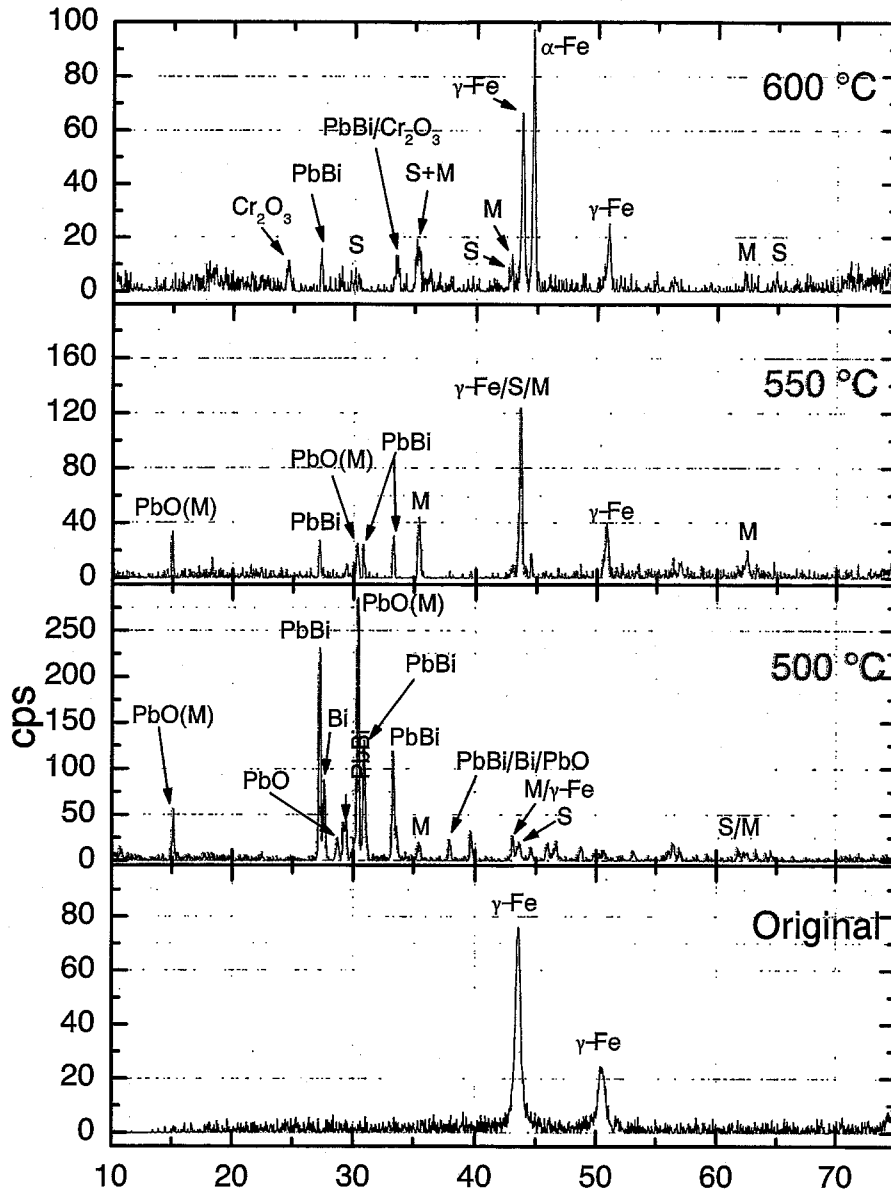


Fig. 44: XRD patterns of 316 FR steel after 10000 h

3.2 ODS steel

3.2.1 Exposure 800 h

On ODS steel already at 500 °C, Fig. 45, the metal peaks disappear completely. The peaks of magnetite are dominating.

At 550 °C the spinel peak dominates the smaller magnetite peaks, because of magnetite break off.

At 600 and 650 °C the α -Fe peaks appear again and only small peaks of spinel and magnetite are visible.

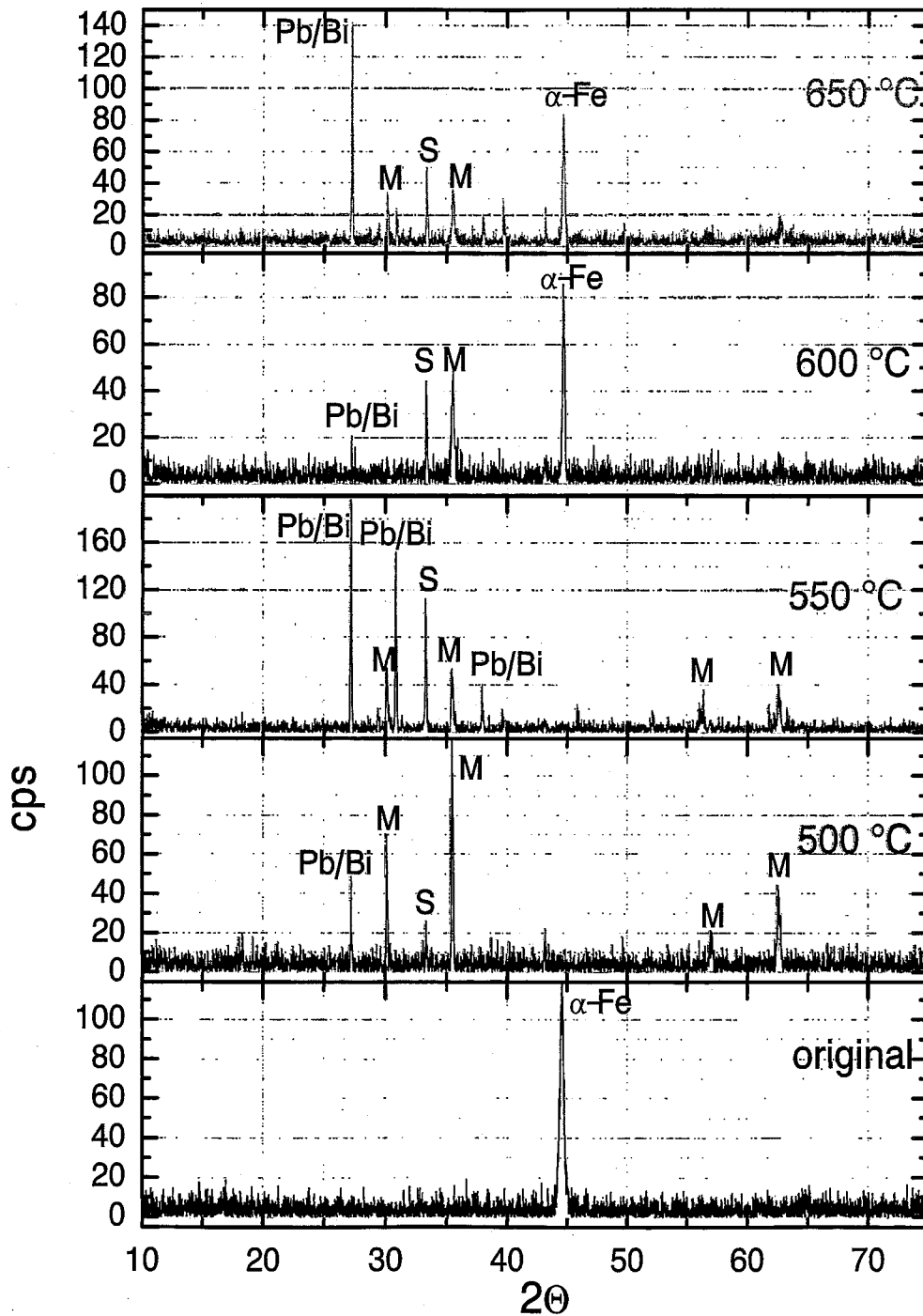


Fig. 45: XRD pattern of ODS after 800 h

3.2.2 Exposure 2000 h

After 2000 h spinel peaks disappear at 600 and 650 °C as compared to 800 h.

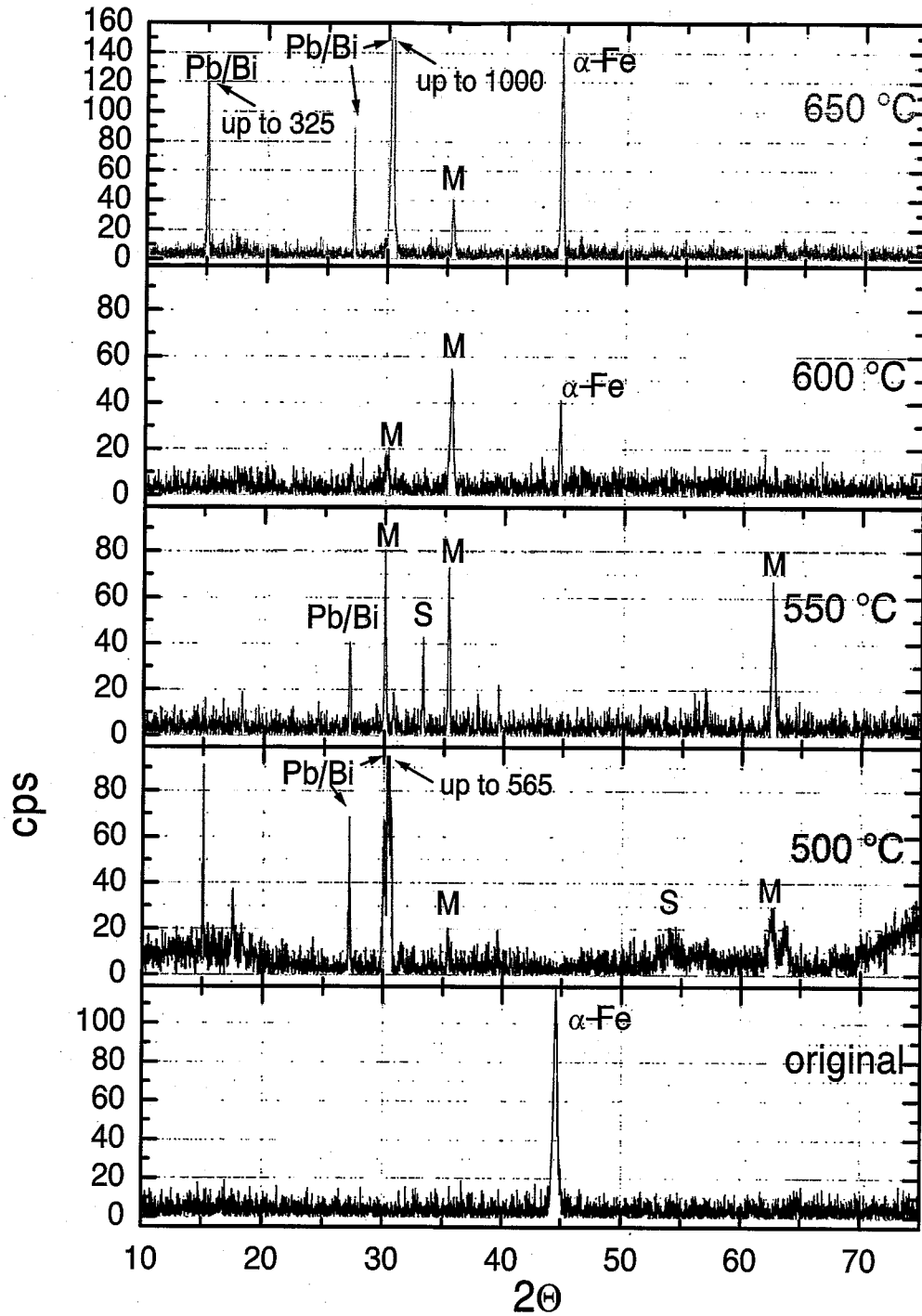


Fig. 46: XRD pattern of ODS after 2000 h

3.2.3 Exposure 5000 h

500 °C: Large magnetite and spinel peaks and disappeared α -Fe peaks like after 2000 h indicate a large coverage by a thick oxide layer.

550 °C: Appearance of the α -Fe peak and, therefore, some break out of the oxide layer.

600 °C: A large α -Fe and small oxide peaks show complete destruction of the surface oxide layer. This process is now more pronounced than after 2000 h.

650 °C: Like 600 °C.

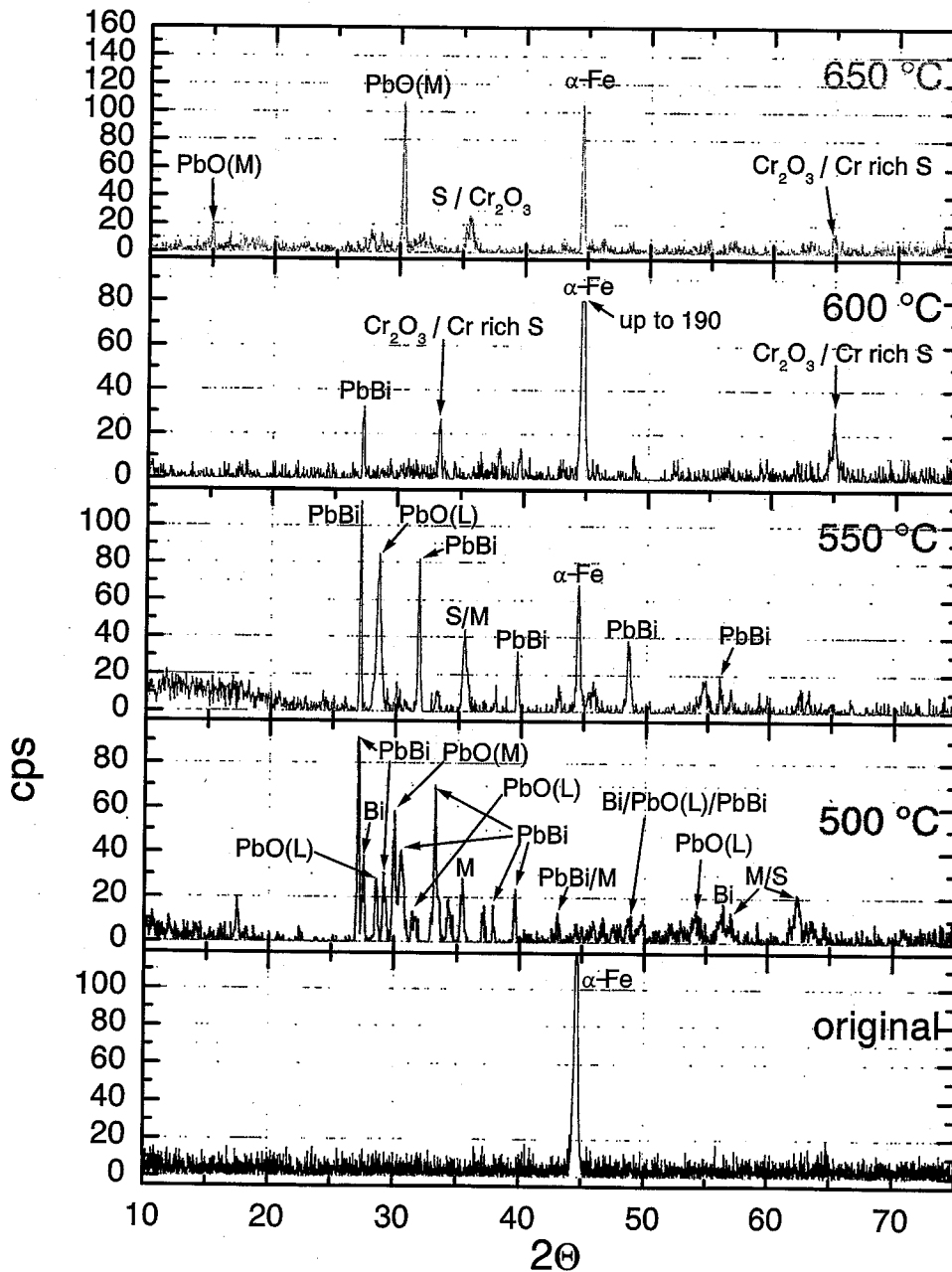
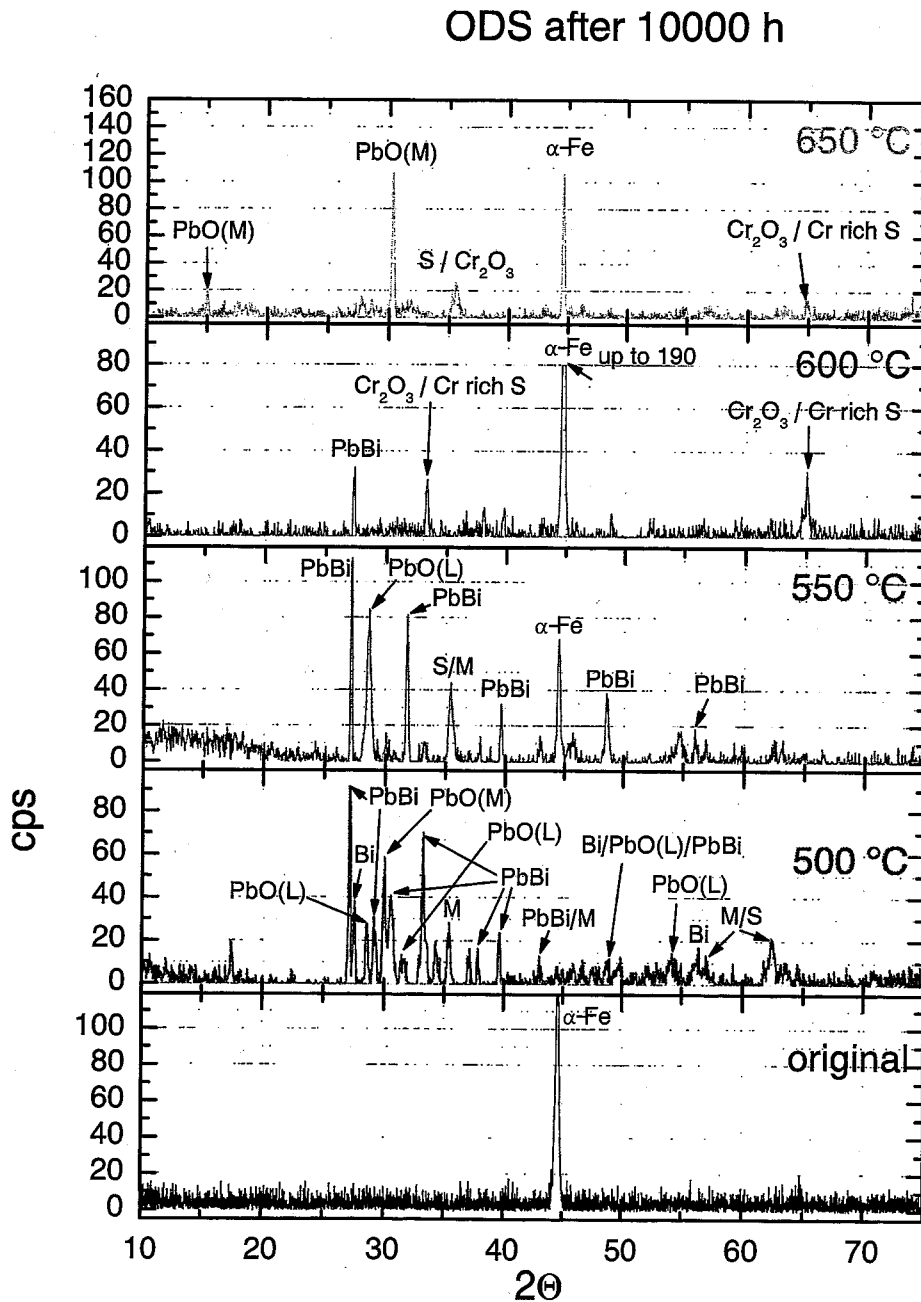


Fig. 47: XRD patterns of ODS after 5000 h

3.2.4 Exposure 10000 h

After 10000 h of exposure the spinel peaks disappeared at all temperatures. The dominant PbBi peaks result from insufficient cleaning of the specimen surface prior to the XRD examination. Beside these peaks at 500 °C the magnetite peaks are dominating like in the patterns obtaining after the shorter exposure times. The α -Fe peaks at 550 °C hint at a break away of the magnetite layer during the cleaning procedure. At 600 °C and above no magnetite can be observed and the dominant α -Fe hints at a not closed spinel layer.



7

Fig. 48: XRD patterns of ODS after 10000 h

3.3 P122 steel

3.3.1 Exposure 800 h

At the lower temperatures, 500 and 550 °C, the metal peaks disappeared, Fig. 49, and only spinel and magnetite peaks are present. At 600 °C the oxide peaks are diminished and α -Fe peaks dominate.

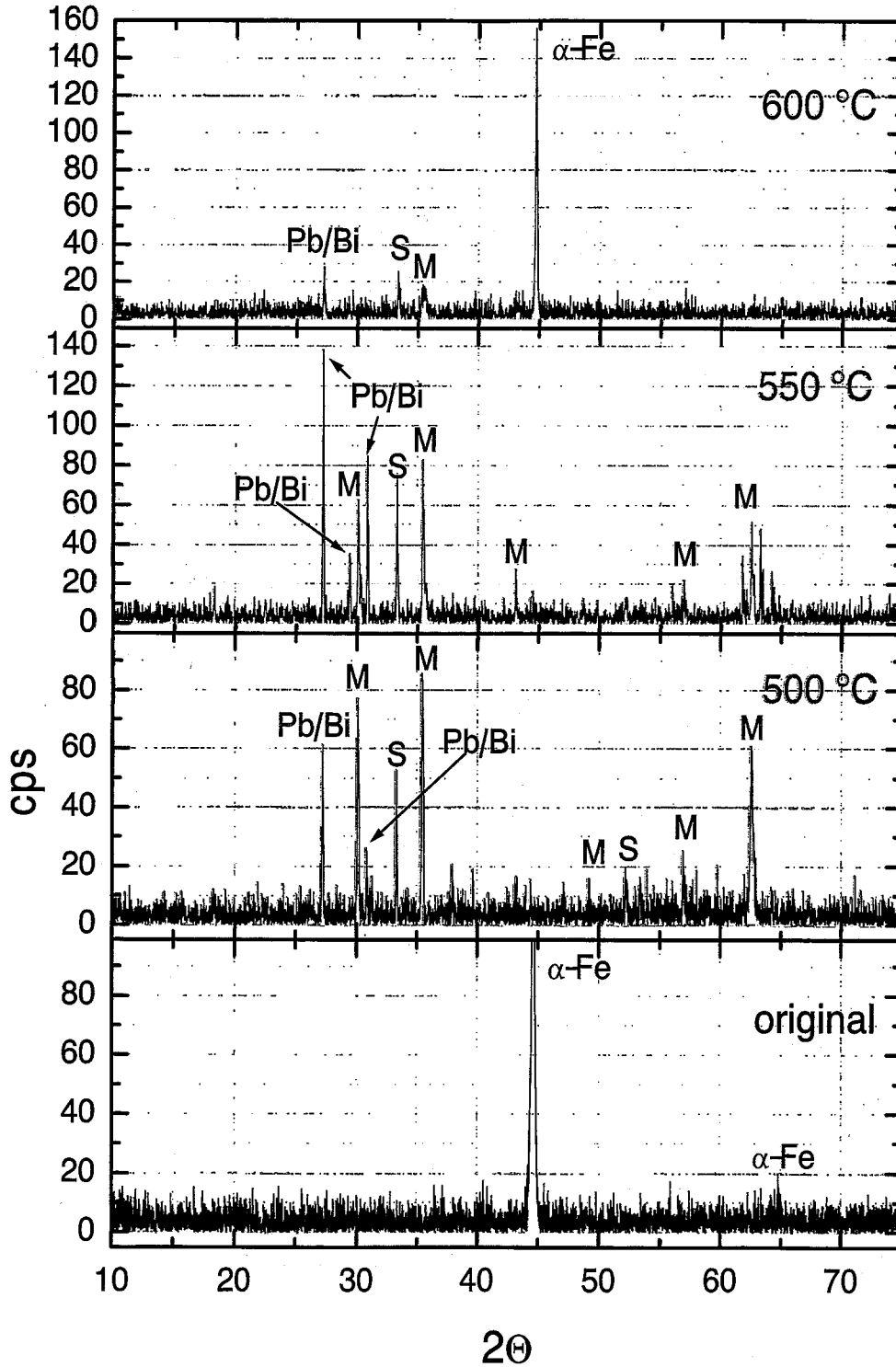


Fig. 49: XRD pattern of P122 after 800 h

3.3.2 Exposure 2000 h

After 2000 h, Fig. 50, the oxide layer of magnetite appears to be thick with diminishing spinel part. At 600 °C small magnetite peaks are visible without spinel. The α -Fe peak is only marginal. This, however, does not agree with the observations obtained from the cross sections.

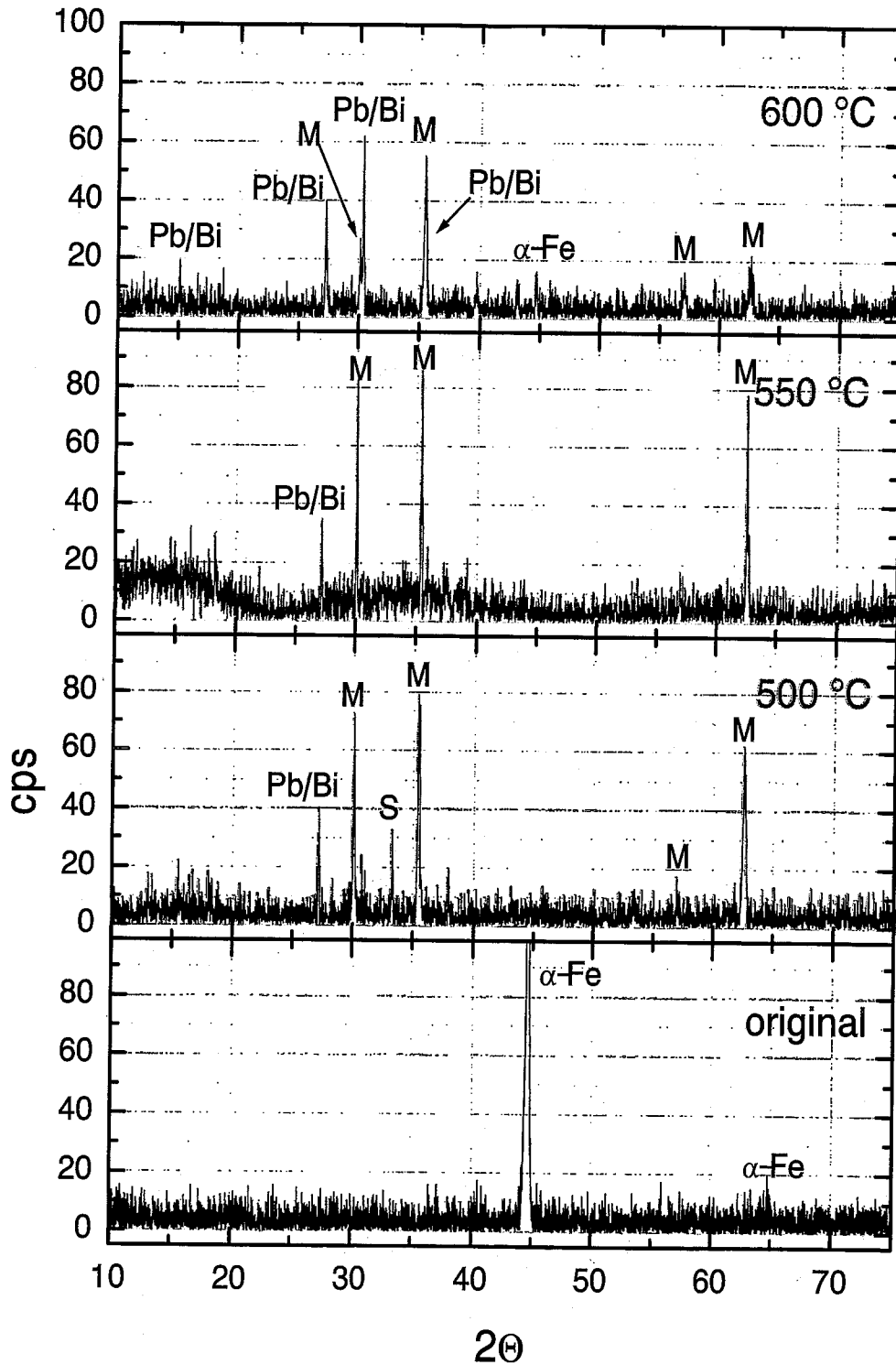


Fig. 50: XRD pattern of P122 after 2000 h

3.3.3 Exposure 5000 h

500 °C: A large amount of PbBi sticks to the surface oxide layer probably in pores.

Spalling off of the layer is not detectable like after 2000 h.

550 °C: Same like at 500 °C.

600 °C: Complete destruction of the thin oxide layer existing after 2000 h, indicated by a large α -Fe and a small spinel peak.

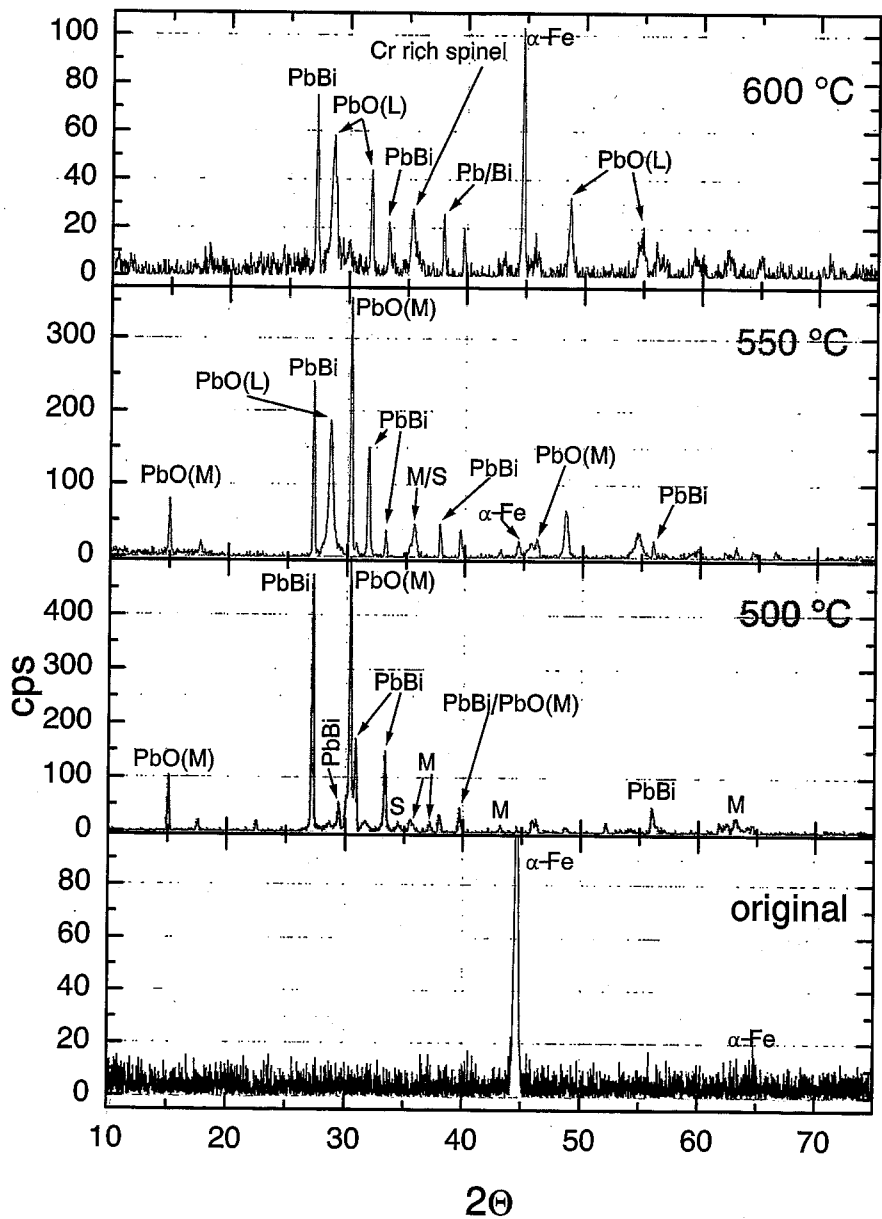


Fig. 51: XRD patterns of P122 after 5000 h

3.3.4 Exposure 10000 h

Dominating magnetite peaks without any spinel and Fe peaks indicate a magnetite scale with large coverage. The oxide scale disappears at 600 °C and α -Fe becomes the dominating peak.

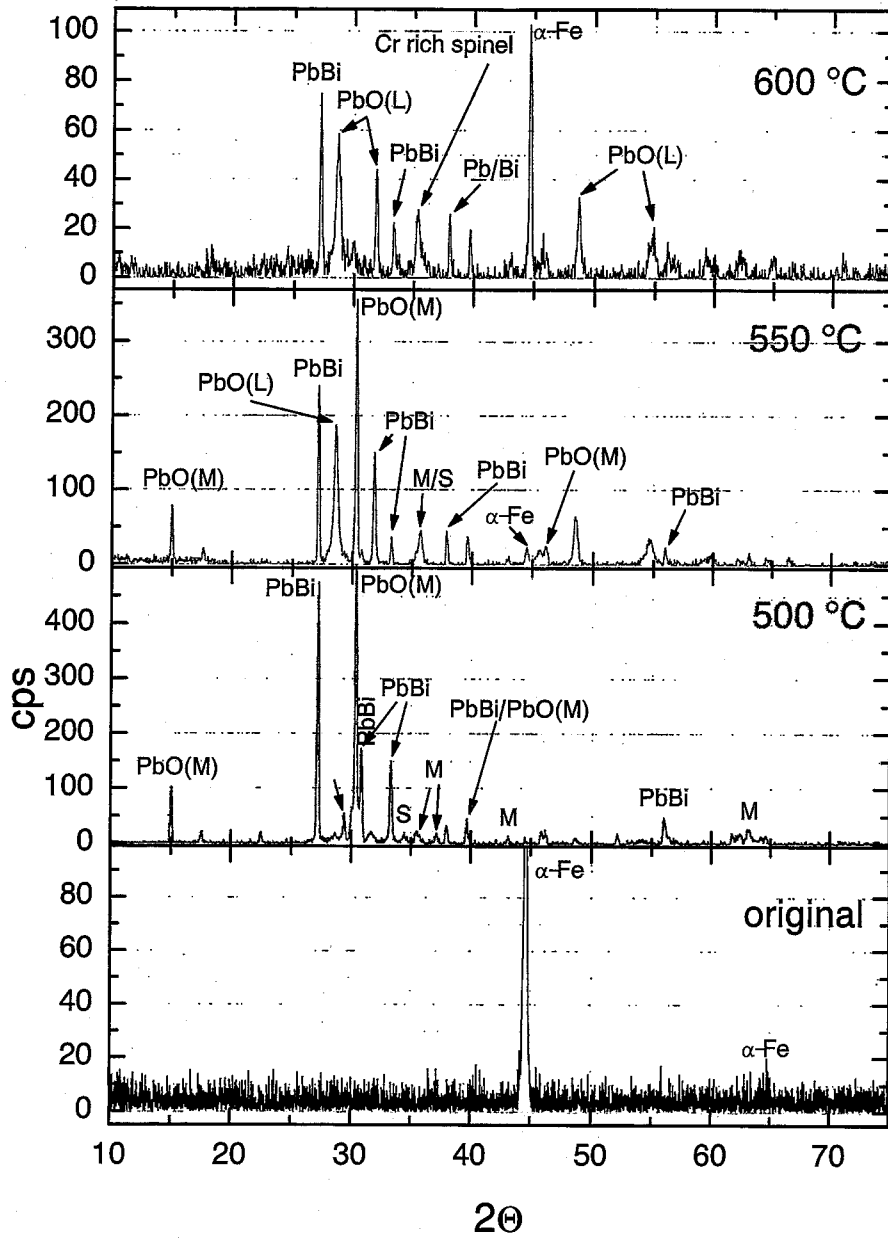


Fig. 52: XRD patterns of P122 after 10000 h

4 Steels in the gas atmosphere of the COSTA facilities after 800 h

Specimens are exposed to Ar – H₂/H₂O atmosphere prevailing in the experiments with 10⁻⁶ wt% of oxygen in LBE. Because of the oxide scale thickness of up to 70 μm, which grows already after 800 h of exposure, no experiments at longer exposure times are conducted.

4.1 316 FR steel

No oxide scales are visible in the cross sections at 500, 550 and 600 °C. They must be very thin. Fig. 53 shows the cross section through the 500 °C specimen.



Fig. 53: 316 FR after 800 h oxidation in furnace atmosphere at 500 °C

At 650 °C after 800 h in the furnace atmosphere thick magnetite and spinel layers appear.



Fig. 54: 316 FR after 800 h oxidation in furnace atmosphere at 650 °C

The x-ray pattern show up to 600 °C γ-Fe peaks. At 650 °C magnetite and spinel peaks appear and a small γ-Fe peak.

4.2 ODS steel

On ODS steel after 800 h the oxide scale grows with temperature from 500 to 600 °C. However, the scale is porous and subjected to spallation. Therefore, especially at 650 °C it is not visible on the cross section, but some oxide nodes appear.

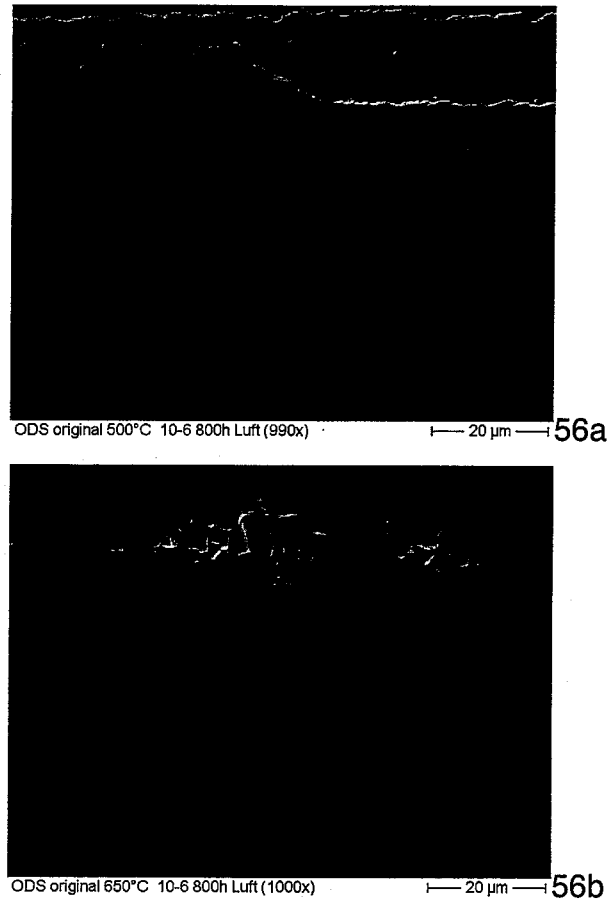


Fig. 56: ODS steel after 800 h oxidation in furnace atmosphere at 500(a) and 650 °C (b)

At 500 and 550 °C no metal peaks are visible any more on the x-ray patterns but only magnetite and spinel peaks. The fact that large spinel peaks appear besides magnetite indicates that large parts of the magnetite top layer is spalled off. The presence of α -Fe peaks at 600 and 650 °C shows that also a large part of spinel is spalled off at these temperatures.

4.3 P122 steel

On P122 steel after 800 h the oxide scale grows continuously with temperature from 20 up to 60 μm . The magnetite layer gets very porous at high temperatures. Partially spallation is observed of the magnetite layer.

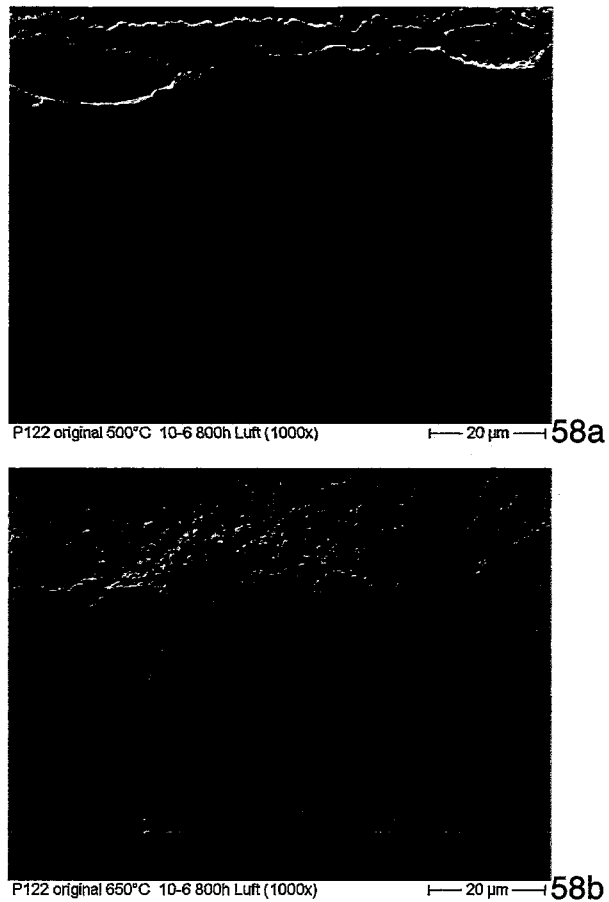


Fig. 58: P122 steel after 800 h oxidation in furnace atmosphere at 500(a) and 650 °C (b)

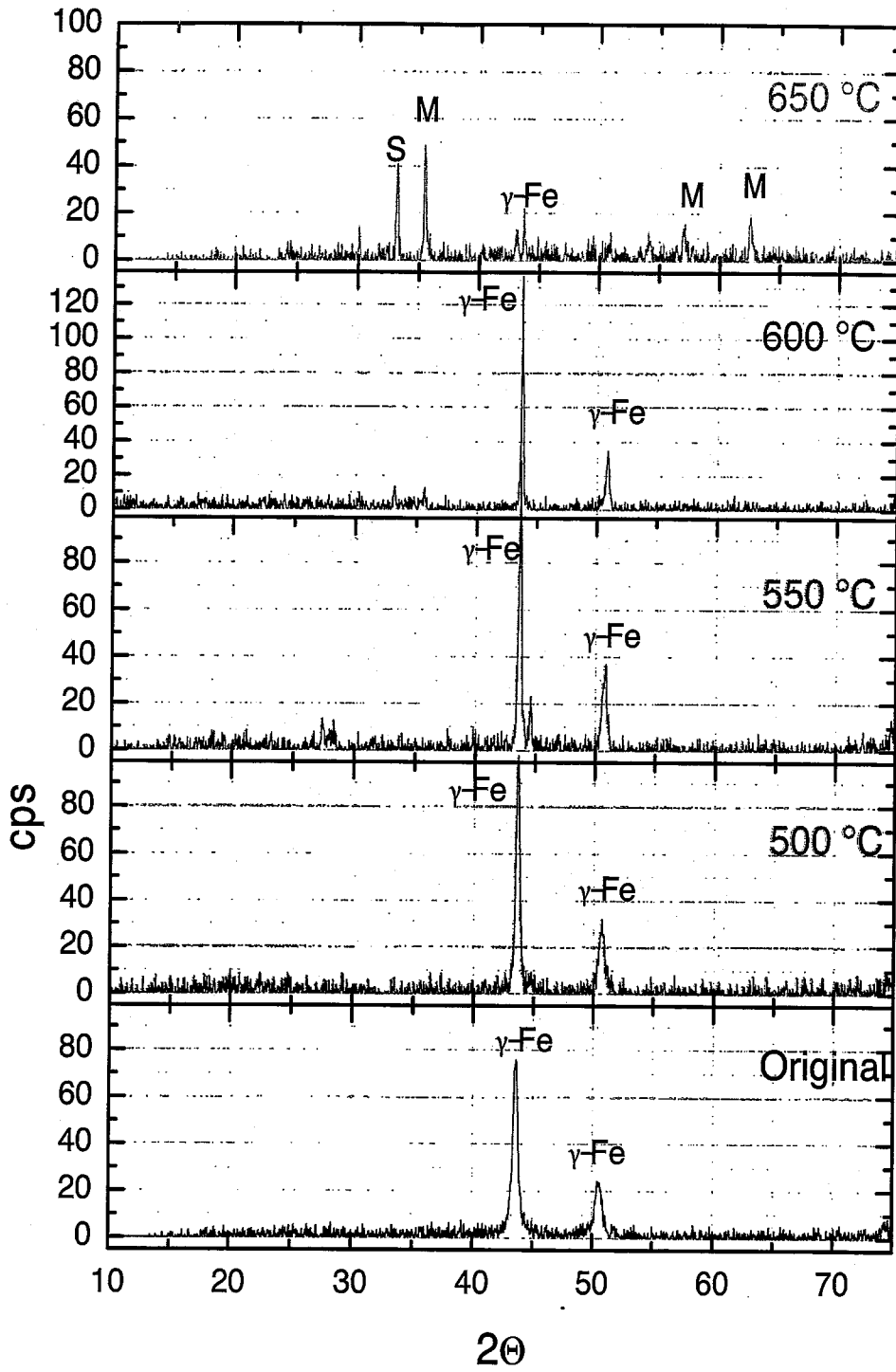


Fig. 55: XRD pattern of 316 FR exposed 800 h to furnace atmosphere

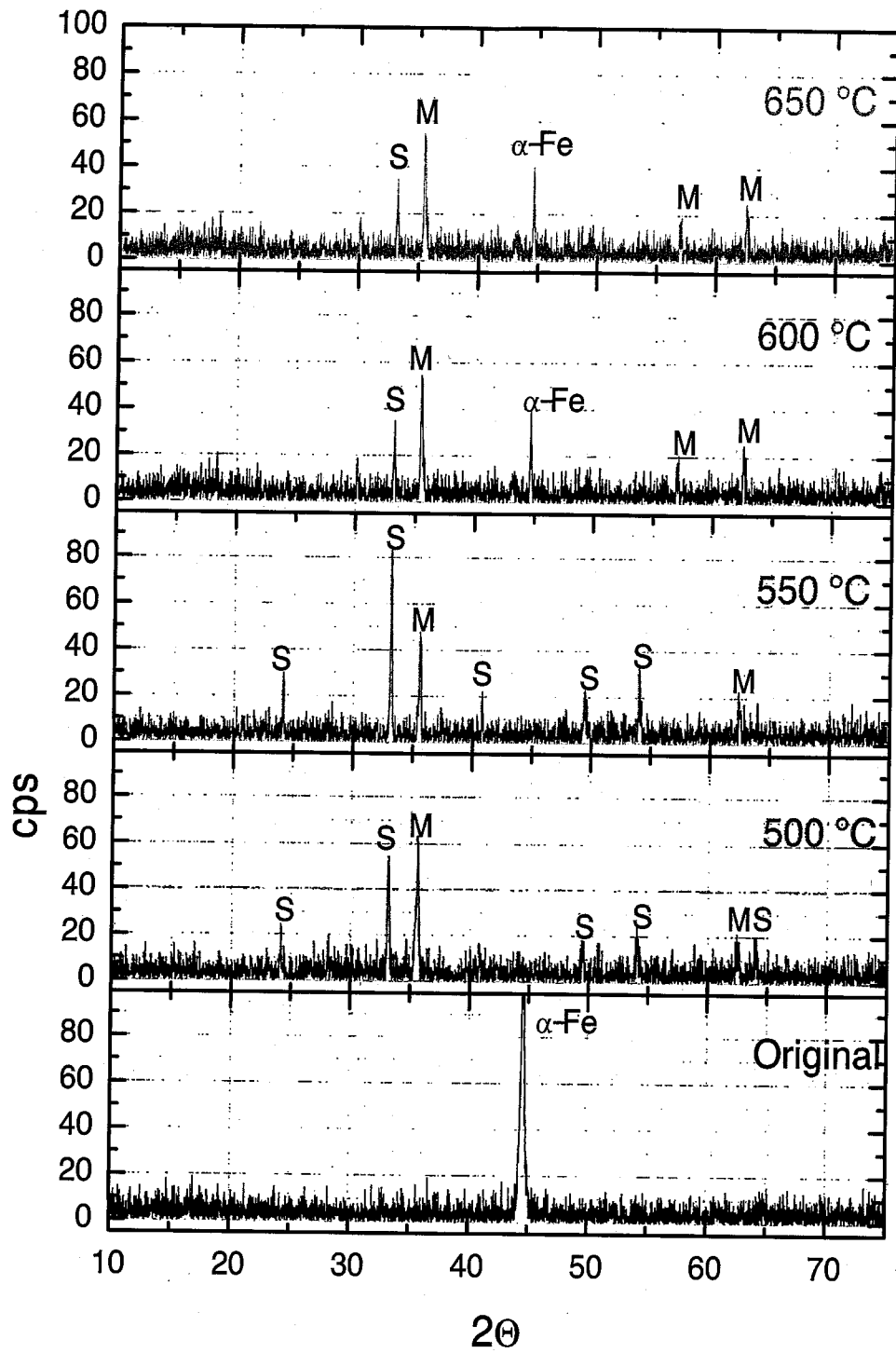


Fig. 57: XRD pattern of ODS steel exposed 800 h to furnace atmosphere

Only oxide patterns are observed on P122 X-ray pattern after exposure to LBE at 500 – 600 °C. The spinel peaks indicate partial spallation of the magnetite scale.

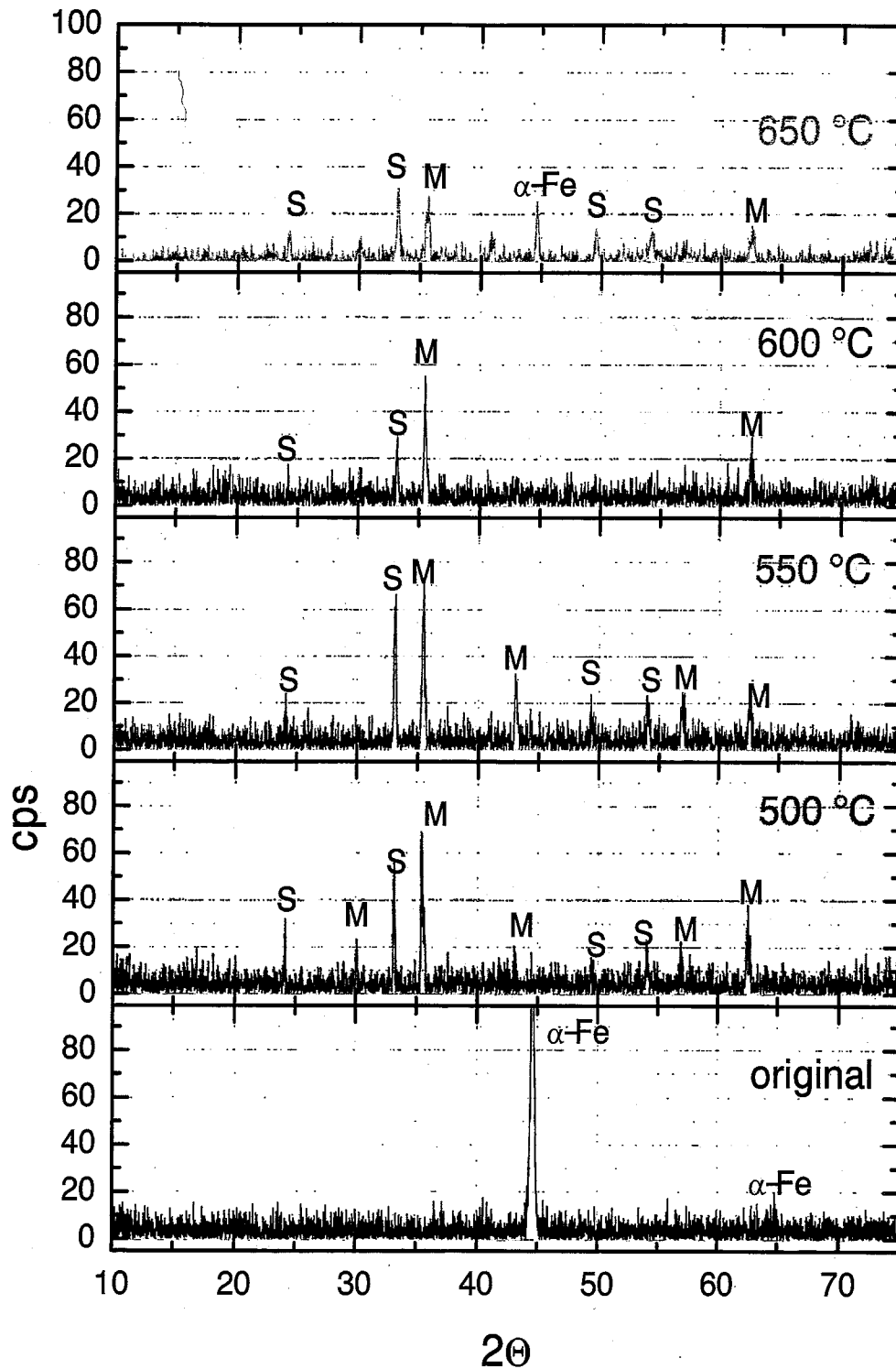


Fig. 59: XRD pattern of P122 steel exposed 800 h to furnace atmosphere

5 Summary

5.1 Experiments of 800 h duration

- At 500 °C all 3 steels show satisfying protection behaviour.
- At 550 °C the steels have still a protective oxide layer.
- At 600 °C the oxidation behaviour changes, the oxide scales are very thin. There is attack of LBE at singular spots at the surface of AISI 316 L and ODS steel. On 316 L Ni is dissolved and LBE penetrates. ODS shows attack at spots that contain sulphur impurities. P122 is not attacked.
- At 650 °C the ODS steel shows some spots at which sulphur impurities lead to a weakening of the very thin protective spinel layer (sulphur reduces locally the amount of Cr in the bulk by forming chromiumsulfide precipitations, so at this places there is not enough Cr to form the protective oxide layer!). P122 also shows in most surface parts a satisfying protective behaviour, which is disturbed only at a few spots. Severe attack is observed at 316 L steel up to 30 µm depth also only at some spots.
- GESA alloyed surfaces performed well without attack at all 3 steel surfaces at all temperatures. There are only few structural defects, which can be avoided by proper selection of the treatment parameters. Nevertheless although at those defect spots (small cracks) no dissolution attack was observed or has to be expected so far. This small cracks were filled with Cr-Al spinel which hinders Pb/Bi to penetrate.
- Oxidation behaviour in COSTA atmosphere is the same as the one in liquid Pb/Bi containing 10^{-6} wt% oxygen up to temperatures of 550 °C. Only, the oxidation rate is enhanced. Above 550 °C the oxidation behaviour differs from that in the liquid metal. Magnetite layers are still present and of much higher thickness which is not the case in LBE.

5.2 Experiments of 2000 h duration

- At 500 °C all 3 steels still show satisfying protection behaviour. The oxide layers are thicker than after 800 h.
- At 550 °C the steels have still a protective oxide layer.

- At 600 °C the attack continues on singular spots like observed after 800 °C on ODS and 316 L steel. Attack at singular spots starts at P122 steel.
- At 650 °C the attack of LBE at single spots continues and reaches for instance on 316 L steel a depth of 50 µm.
- The GESA alloyed specimens do not show any attack at all temperatures.

5.3 Experiments of 5000 h duration

- At 500 °C all steels still show satisfying behavior.
- At 550°C ODS and P122 the spalled off oxide layer grows again and protects the steel. On 316 FR, besides the thin spinel layer observed at 2000 h, there are node like magnetite-spinel scales with no dissolution attack. However LBE penetrates the oxide nodes and precipitates at the border of the metallic phase.
- At 600 °C a great part of 316 FR is still protected by a thin oxide layer only partly attacked by LBE. ODS and P122 show completely, partly deep, surface attack.
- At 650 °C all of the original steel specimens are completely attacked with partly deep LBE penetration.
- GESA alloyed steels performed well at all temperatures. Some exceptional deviations occurred like described after 800 h but with no attack also at those irregularities.

5.4 Experiments of 10000 h duration

- At 500 °C no dissolution attack takes place on ODS and P122 steel. The maximal oxide layer thickness is 40 – 70 µm. Migration of iron causes a pore belt below the spinel layer. Some spallation starts on ODS. A partly deep dissolution attack occurs on 316 FR. LBE penetrates the spinel layer and migrates along the steel grain boundaries.
- At 550 °C no dissolution attack took place on the P122 and ODS steel. Multilayered oxide scales with a thickness of up to 100 µm cover the steel. Strong dissolution attack occurs on 316 FR of up to 200 µm.
- At 600 °C a complete massive surface attack occurs on all of the steels up to a depth of 200 µm.

- At 650 °C a large scale surface destruction takes place on all of the steels.

5.5 Steels Al-surface alloyed by GESA

After alloying Al into the surface by GESA, materials show good corrosion resistance without any attack at all temperatures up to 10000 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 10000 h.

6 Discussion

At 500 and 550°C martensitic steels ODS and P122 are protected against dissolution attack up to 10000 h by a thick double oxide layer with magnetite on the top and Cr rich spinel underneath. The magnetite layer is build up above the original steel surface by iron that migrates through the spinel layer onto the surface where it gets oxidized to Fe_3O_4 , magnetite. In a first step of the process a Cr-spinel layer is formed because of the high affinity of Cr to oxygen. With increasing time the spinel and magnetite layer grow, the first one by diffusion of oxygen inwards and the second one by diffusion of iron outwards onto the steel surface. This is the classical protection mechanism of martensitic steel in LBE with an oxygen concentration above that necessary for iron oxidation which works well at 500 and 550 °C up to the exposure times of 10000 h which is the longest exposure time applied in these experiments. The defects that occur after this time in the ODS oxide scale by starting spallation processes are neutralized by self healing. At 550°C spallation of these protective scales starts already between 2000 and 5000 h. The successive growing fresh oxide scales prevent the steels from dissolution attack and proof the self healing of these scales.

At higher temperatures up to 650 °C the martensitic steels fail by dissolution attack in a very early state of exposure. It is of interest that the oxidation mechanism changes for the martensites at 600 °C. Thick double layers do not appear any more. Very thin

spinel layers are build up in the early exposure stage which protect the steel only for a short time at this high temperatures.

The austenitic steel 316 FR shows a different mechanism of protective oxide scale formation. At 500 °C a very thin oxide scale protects the surface at least up to 5000 h of exposure. At some spots on the surface oxide nodes of about 6 µm thickness appear which, however, do not disturb the protection mechanism. But, after 10000 h wide parts of the surface show dissolution attack at 500 °C already. Some parts of the surface area are still protected, partly by a thick double oxide layer. At temperatures of 600 and 650 °C deep grain boundary attack occurs already in the early stage of exposure. The problem with the austenites is caused by the Ni component. Once LBE gets access to the grain boundaries, it proceeds with dissolution of Ni along the grain boundary very fast to a high depth.

The steels surface alloyed with Al by GESA are the only group which forms protective layers that are stable at all temperatures and exposure times considered in this work. Deviations from this principal observations happen only when failures in the alloying process occur. Those failures can be aberrations from the optimal concentration region of Al alloyed into the surface. This optimal region is between 8 and 15 wt% of Al. Below 8 wt% the concentration is too small for formation of continuous alumina layers under the prevailing conditions. Above 15 wt% micro cracks appear because brittleness of the steel increases with increasing Al content. At much higher concentrations than 15 wt% dissolution attack on the steel grows so rapidly because of the high Al activity that oxide scale formation is suppressed.

All the samples examined at FZK are always taken from the lower end of the specimens that is located in a depth of 1.5 cm below the LBE surface inside the test crucible. After a first examination at JNC it was ascertained that the corrosion behavior of the martensites varies with the distance from the LBE surface². Below an immersion depth of 1 cm dissolution attack occurs at 550 °C after 5000 h while in the upper specimen part still a protective oxide scale exists. The oxide scale broken away between 2000 and 5000 h covers the LBE surface and acts as an additional diffusion-barrier for oxygen. Therefore only the upper part of the samples located close to the surface receives the required oxygen and forms as expected thick multilayered oxide scales, while the lower part shows strong dissolution attack due to the reduced oxygen concentration. Such differences did not appear at 500 °C. In this case the lower end was also covered by a protective oxide scale, which did not spall off up to 5000 h

of exposure. Therefore no differences have to be expected between the upper and lower part of the specimen immersed into LBE. There is also no influence of the immersion depth to be observed for temperatures of 600 °C and 650 °C. This is, because the oxide layers at these temperatures are generally very thin and the diffusion rate is higher than at 500 °C. Thus, only at 550 °C and for the martensitic material the influence of the immersion depth has to be considered.

7 Conclusion

Steels surface alloyed with Al are the only ones which can be employed in LBE containing about 10^{-6} wt% oxygen at 500 – 650 °C without dissolution attack up to at least 10000 h which is the maximal exposure time applied to the specimens in these experiments. Martensites, ODS and P122 without Al – surface – alloy survive this maximal exposure time only at 500 and 550°C. Above, they fail the earlier the higher the temperature is. The same holds for the austenite 316 FR which fails, however, at 500 °C already during 5000 h.

The immersion depth of the sample in the crucible has an effect only if an oxide layer spalls off and covers the whole surface of the LBE in the crucible. This process prevents or hinders the diffusion of oxygen into the crucible, as it is observed on martensitic steels at 550 °C after 5000 and 10000 h of exposure.

8 References

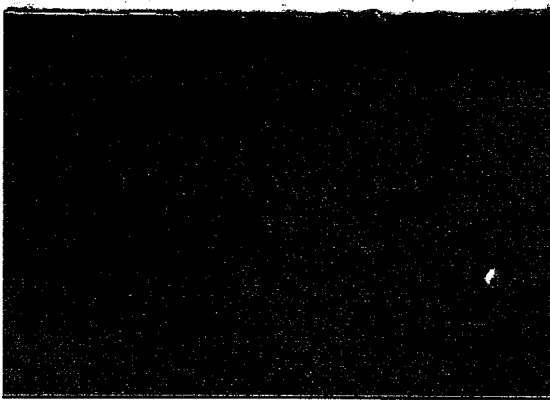
- [1] JNC report TY 9400 2002-016, Study on Pb/Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications, Part1, June 2002, Japan
- [2] JNC report TY 9400 2002-023, Study on Pb/Bi Corrosion of Structural and Fuel Cladding Materials for Nuclear Applications, Part2, December 2002, Japan

9 Annex 1

Why does the corrosion behaviour of martensitic steels exposed for 5000 and 10000 h at 550 °C in LBE containing 10^{-6} wt% oxygen differs depending on the vertical sample position in the crucible, i.e. from the distance of the investigated part to the LBE surface?

Observation of different behaviour at 550 °C:

SEM – pictures of the samples showing different corrosion behaviour depending on the distance to LBE surface are shown below. Close to the surface oxide scales grow again after previous breaking away – pictures on left side. Near the bottom, pictures on the right side, showing the parts of the samples with strong dissolution attack.



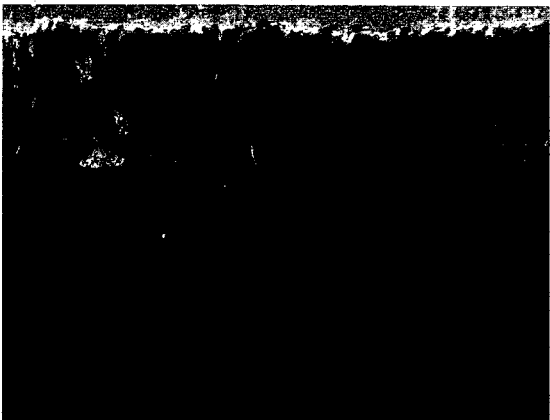
P122 550°C 10-6 5000h (1000x)

Oxide scale on P122 steel after 5000 h of exposure – near LBE surface - top of crucible



P122 org 550°C 5000h 10-6 (1000x)

Dissolution attack on P122 steel after 5000 h of exposure – near bottom of crucible



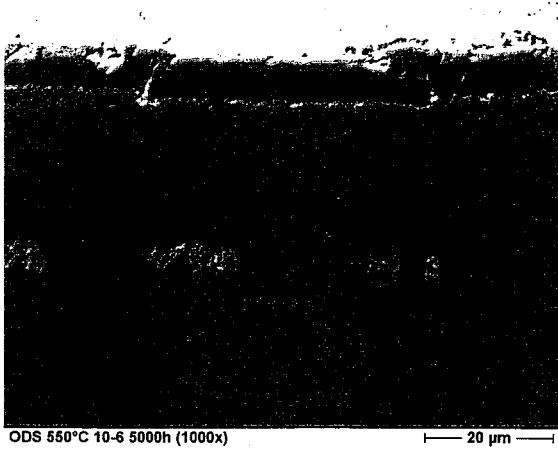
P122 550°C 10-6 10000h (1000x)

Oxide scale on P122 steel after 10000 h of exposure – near LBE surface - top of crucible

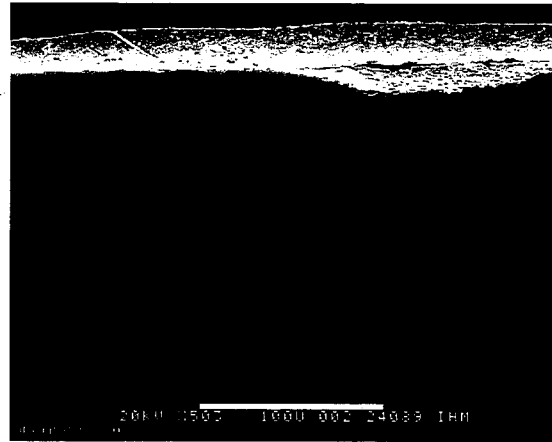


P122 550°C 10-6 10000h (1000x)

Dissolution attack on P122 steel after 10000 h of exposure – near bottom of crucible



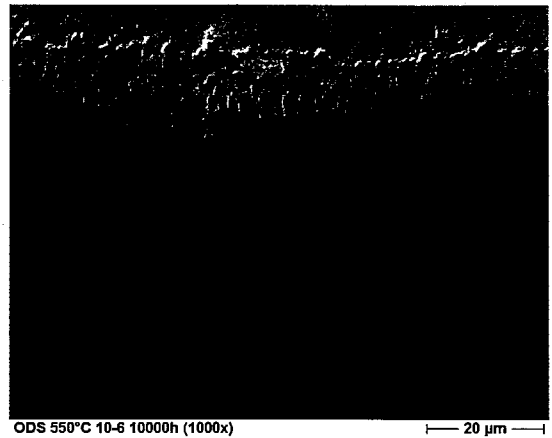
Oxide scale on ODS steel after 5000 h of exposure – near LBE surface – top of crucible



Dissolution attack on ODS steel after 5000 h of exposure – near bottom of crucible



Oxide scale on ODS steel after 10000 h of exposure – near LBE surface – top of crucible



Dissolution attack on ODS steel after 10000 h of exposure – near bottom of crucible

Fig 1: Comparison of corrosion behaviour of ODS and P122 martensitic steel depending on distance to LBE surface

Most probable explanation:

As observed frequently fast growing oxide scales on martensitic steels have the tendency to spall off in between 3000 and 5000 h. This oxide scale will swim up and cover the surface of the LBE, see Fig 2.

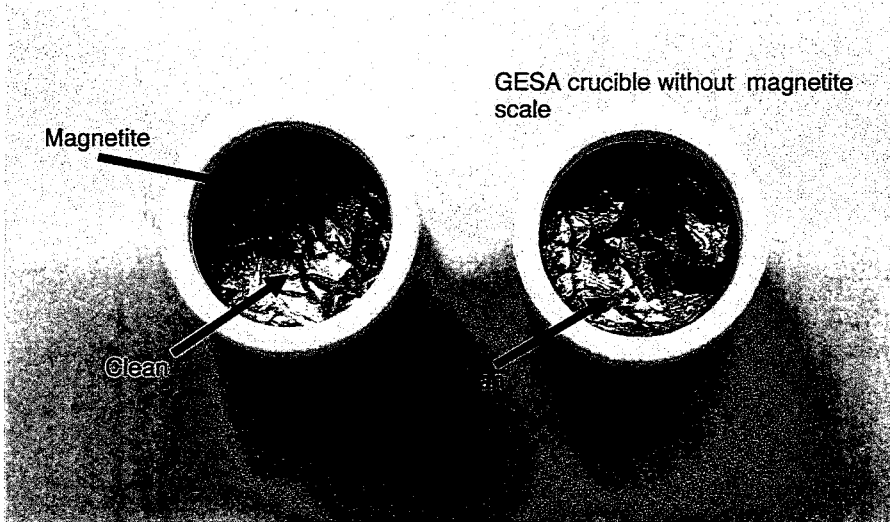


Fig. 2: Alumina crucible with and without oxide scale covering the LBE surface

In our experiments the surface of the samples exposed in LBE is larger than the free surface of the LBE. If the entire oxide scale spalls off, it is possible that it covers the whole LBE surface. Comparing now the oxygen diffusion coefficient in LBE and magnetite an orders of magnitude higher diffusion rate in LBE is expected compared to magnetite. Consequently the oxygen concentration below such a covering layer has to be smaller than without such a layer. Especially the farer away from the surface the lower the concentration will be. Forming of oxide scales is therefore only possible close to the LBE surface.

Conclusions from these results:

The observed oxidation of the parts close to the LBE surface displays the real behaviour of steel exposed to LBE at 550 °C containing 10^{-6} wt% of oxygen. The observed dissolution attack after 5000 h for the parts close to the bottom of the crucible is strongly related to the reduced oxygen concentration in LBE at this position.

Long term exposures > 3000 h require crucibles which allow a significantly larger LBE surface than the specimen surface. In addition the LBE should be changed frequently to avoid covering layers, which may reduce oxygen diffusion. Longitudinal sectioning of samples exposed to LBE should be favoured to avoid any miss interpretation. Performing experiments in flowing LBE these problems do not occur.