JNC TY9400 2002-023

STUDY ON PB/BI CORROSION OF STRUCTURAL AND FUEL CLADDING MATERIALS FOR NUCLEAR APPLICATIONS

Part2 : Corrosion investigation in stagnant liquid Pd/Bi at 500, 550, 600 and 650℃ after 5000 h of exposure

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

Part 2: Corrosion investigation in stagnant liquid Pb/Bi at 500, 550, 600 and 650 °C after 5000 h of exposure

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

Abstract

This is the second 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 report considered the behaviour of 316FR, P122 and ODS steels during 800 and 2000 h in stagnant LBE at 500 – 650 °C. This second report describes the continuation of the tests to 5000 h. The results obtained are:

1. Still no attack on all 3 steels at 500 °C. They have protective oxide layers at the surface.
2. Starting dissolution attack on ODS and P122 but not on 316FR at 550 °C.
3. At 600 °C all 3 steels are partly and / or entirely attacked, at 650 °C all of them show severe attack on the whole surface.
4. Specimens alloyed with Al by GESA perform well at all temperatures.

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原子炉構造および燃料材料の鉛ビスマス中腐食に関する研究

第２報：500、550、600 および 650℃の停留鉛ビスマス中 5,000 時間浸漬材の腐食評価

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青砥紀身**

要　旨

本報告書は、重金属冷却炉で適用が検討されている構造材料および炉心材料と、冷却材との適合性評価に関する第２報である。

第一報では、高速炉構造用 316（316FR）、12Cr 鋼（P122）および ODS マルテンサイト鋼について 500℃~650℃の停留鉛ビスマス協商合金（LBE）中における 800h および 2,000h 腐食試験結果について報告した。第２報では、これら材料の 5,000h 浸漬試験結果について報告する。

得られた結果は以下のとおり。

1. 500℃では、3 鋼種ともにまだ腐食が観察されない。これら材料表面には保護性を有する酸化層が形成されている。
2. 550℃では ODS および 12Cr 鋼で液体金属腐食が生じていた。316FR はこのような腐食は観察されない。
3. 600℃では、3 鋼種ともに部分的もしくは全面的に腐食を受けており、650℃では全面的に激しい腐食が観察された。
4. Al による表面改質材は全ての温度域で耐食性が確認された。

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1 Introduction

This is the second 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 first part of the "Study on Pb/Bi Corrosion of structural and fuel cladding materials for nuclear applications" describes corrosion investigation of steels after 800 and 2000 hours of exposure to stagnant liquid Pb/Bi at temperatures of 500 to 650 °C in the COSTA device[1]. The concentration of oxygen in Pb/Bi was controlled at 10^{-6} wt%. This 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 first report are:

(1) The steels 316FR, P122 and ODS form protective layers on the surface at 500 and 550 °C that prevent dissolution attack of the liquid Pb/Bi eutectic (LBE) melt.

(2) Above 600 °C the oxidation behaviour of the original materials changes, the oxide scales get very thin. There are attacks of LBE on singular spots at the surface of all of the three materials. The phenomena are observed after 800 h exposure for 316FR and ODS, and after 2000 h for P122.

(3) After alloying Al into the surface by GESA materials show good corrosion resistance without any attack at all temperatures up to 2000 h of exposure. Although, a few structural defects are observed on the surface, no dissolution attack occurrs. The defect spots (small cracks) are closed with a Cr-Al spinel compound and sealed by this process.

The present report describes the results obtained by continuation of the experiments up to 5000 h of exposure to the LBE melt. Table 1 given below indicates the experiments planed and carried out. The dashed region depicts materials and parameters investigated for the first report while the grey area shows those for the present second report.

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

Material (amount)	T [°C]	O_2 content 10^{-4} w[%]				O_2 content 10^{-6} w[%]				O_2 content 10^{-7} - 10^{-8} w[%]*			
		800h	2000h	5000h	10000h	800h	2000h	5000h	10000h	800h	2000h	5000h	10000h
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 Results of corrosion experiments after 5000 h of exposure to LBE

2.1 316FR steel

2.1.1 Temperature 500 °C

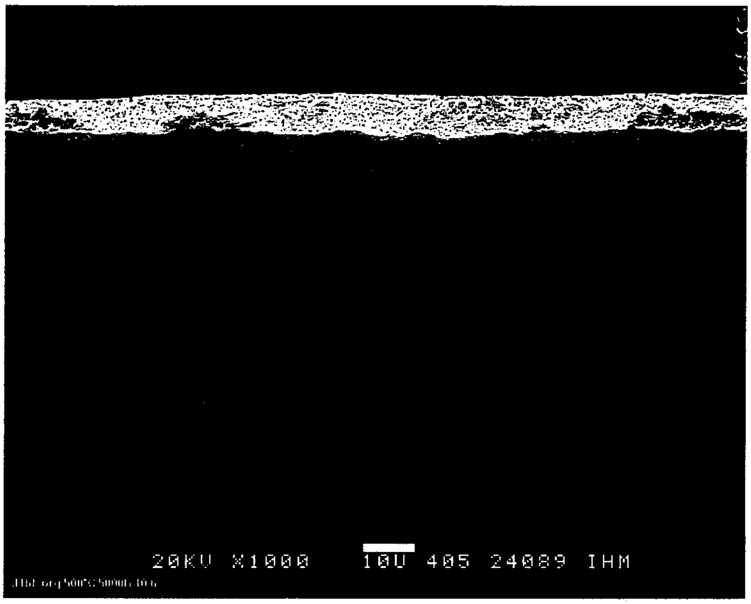


Fig. 1: Original 316FR

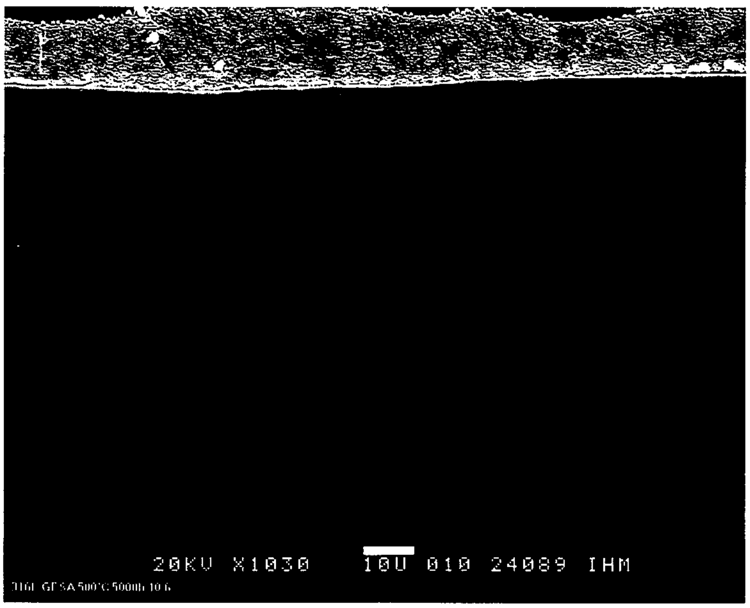


Fig. 2: 316FR surface alloyed with Al by GESA

Nothing did change in comparison to the 316FR original and GESA alloyed specimens exposed to 800 and 2000 h. The original specimen shows still partial thin oxide layers and nodes with a thick spinel and magnetite layer. The specimen with Al surface alloying is not influenced at all.

2.1.2 Temperature 550 °C

316L org 550°C 5000h 10-6 (500x) 50 μm

316L org 550°C 5000h 10-6 (1000x) 20 μm

Fig. 3: Original 316FR (different magnification)

The appearance of original 316FR is different from that of the specimens after 800 and 2000 h. There are nodes with thick layers of spinel and magnetite within large areas covered by a thin oxide layer both are still protective and prevent dissolution attack. The behavior is similar to that at 500 °C but with thicker oxide nodes (up to 15 µm in depth). Opposed to that is the appearance of the surface at 550 °C and 800, resp. 2000 h. It has a continuous oxide layer (magnetite and spinel) of up to 15 µm thickness. From the short time experiments one should expect a continuous oxide layer also after 5000 h.

The reason for the different oxidation behavior of the 800+2000 h in comparison to the 5000 h experiments could be that in the former ones an accidental intake of air occurred during first loading. Thus, if the oxygen concentration for the 800+2000 h experiment was higher during the first hours (0,1 – 1 cm^3 of air is enough), the growth of the oxide layer could be influenced. Since equilibration by the flowing cover gas needs only few hours the required conditions prevail already after this short time. In any case for both conditions, the continuous magnetite / spinel layer and the nodal one, no dissolution attack is to be expected so far.

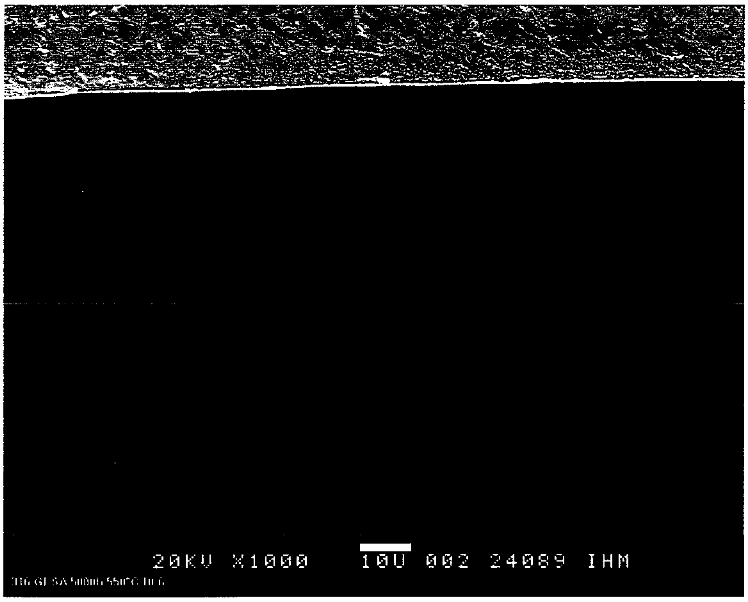
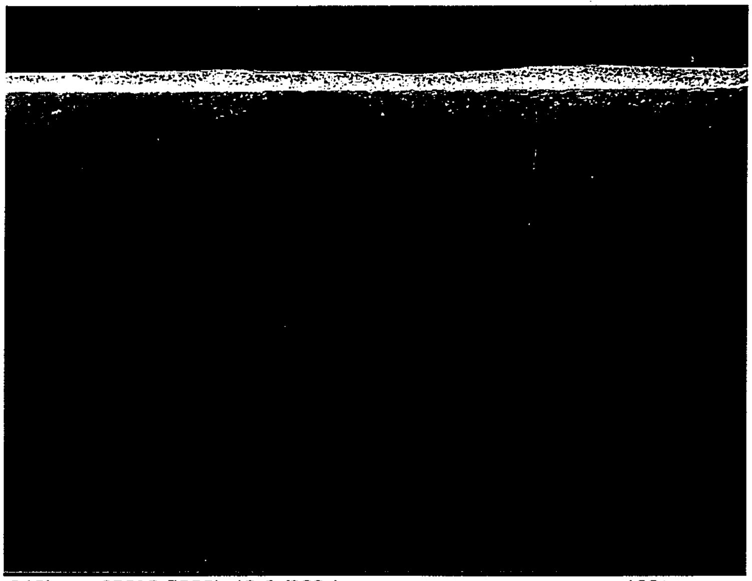


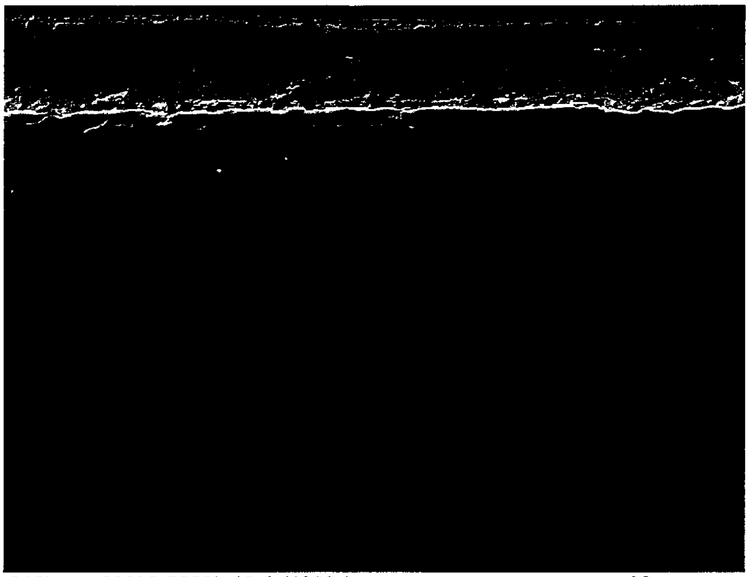
Fig. 4: 316FR surface alloyed with Al by GESA

There is no difference between the 800+2000 h and 5000 h GESA alloyed specimen. No attack can be observed.

2.1.3 Temperature 600 °C



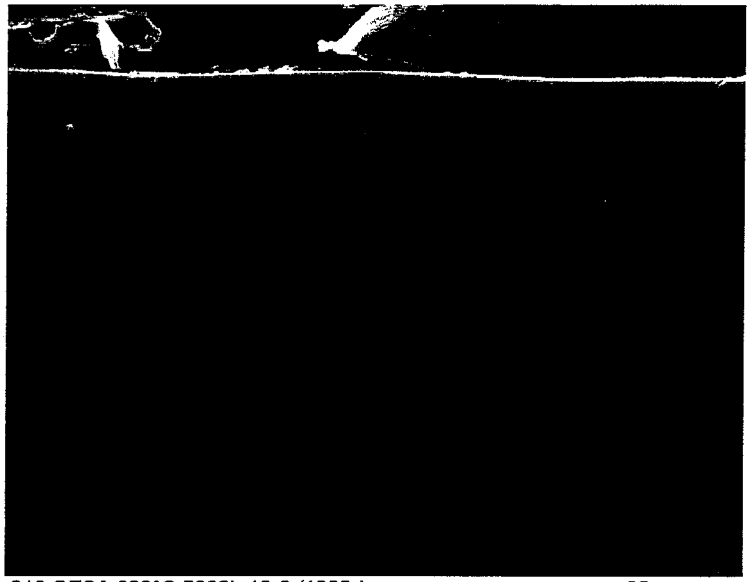
316L org 600°C 5000h 10-6 (200x) ⊢ 100 µm ⊣



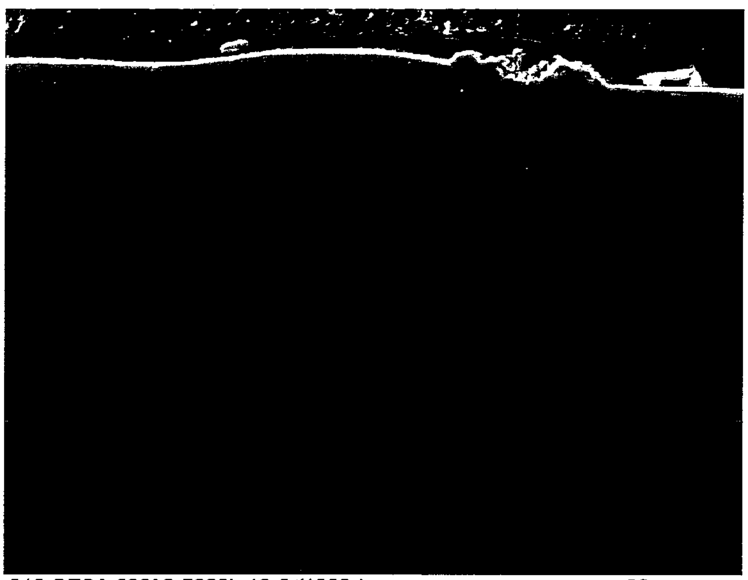
316L org 600°C 5000h 10-6 (1000x) ⊢ 20 µm ⊣

Fig. 5: Original 316FR

In contrary to 800+2000 h a great part of the surface of the original 316FR specimen is attacked. Dissolution attack on Ni leads to ferritization and infiltration of PbBi into the steel like observed after 2000 h already. There is no progress in depth. The surface is covered by a thin spinel layer which is known to grow on ferritc steels at 600 °C. This layer seems to prevent further penetration of LBE.



316 GESA 600°C 5000h 10-6 (1000x) 20 µm

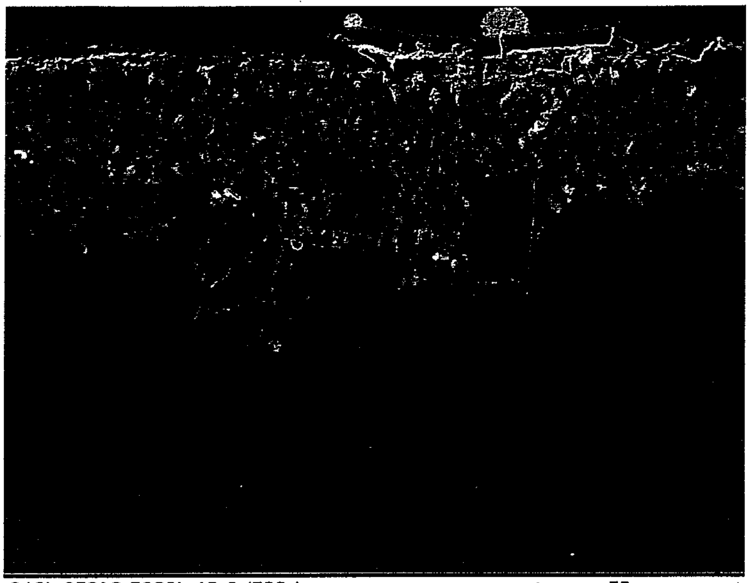


316 GESA 600°C 5000h 10-6 (1000x) 20 µm

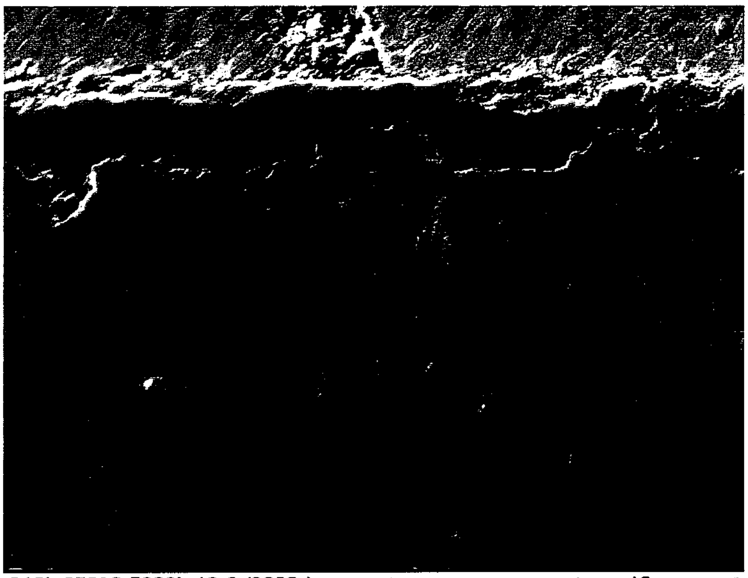
Fig. 6: 316FR surface alloyed with Al by GESA

There is again no attack to be observed at all on the GESA alloyed specimen. As an exception we see in the lower part of Fig. 6 formation of a spinel area of 20 µm extension at a place in which the Al concentration dropped to below 8 wt% by a failure in the alloying process, possibly by locally spalling off of the Al foil. The magnetite scale was ablated, but no dissolution attack occurred.

2.1.4 Temperature 650 °C



316L 650°C 5000h 10-6 (500x) 50 µm



316L 650°C 5000h 10-6 (2000x) 10 µm

Fig. 7: Original 316FR

The appearance of the original 316FR is the same as that of the 2000 h specimen. The spinel layer has about the same thickness and spalls off. The dissolution attack proceeds to a depth of 60 µm. Bright areas indicate PbBi at the grain boundaries.

2.2 *ODS steel*

2.2.1 Temperature 500 °C

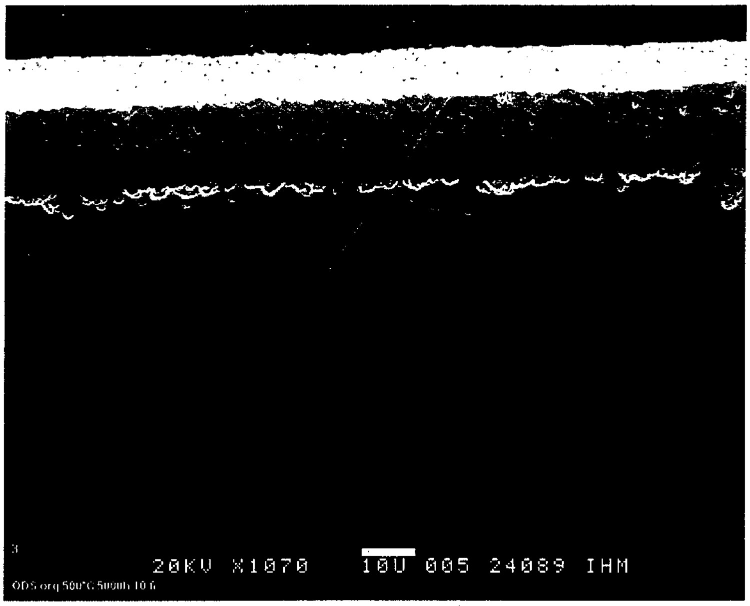


Fig. 8: Original ODS

On original ODS steel there is still a thick protective oxide layer, typical for martensites, of the same appearance as observed after 2000 h. The thickness is grown to about 20 µm. A pore belt appears below the oxide layer caused by migration of iron into the magnetite layer. This pores start to develop already after 2000 h.

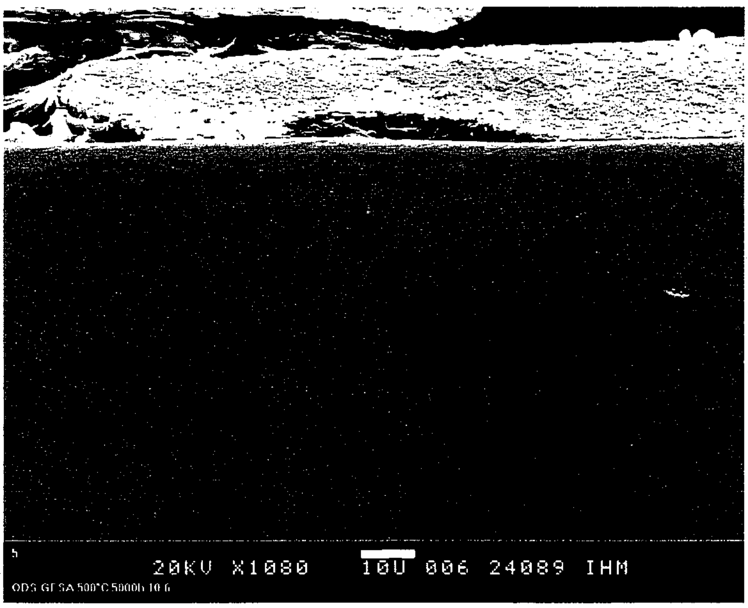
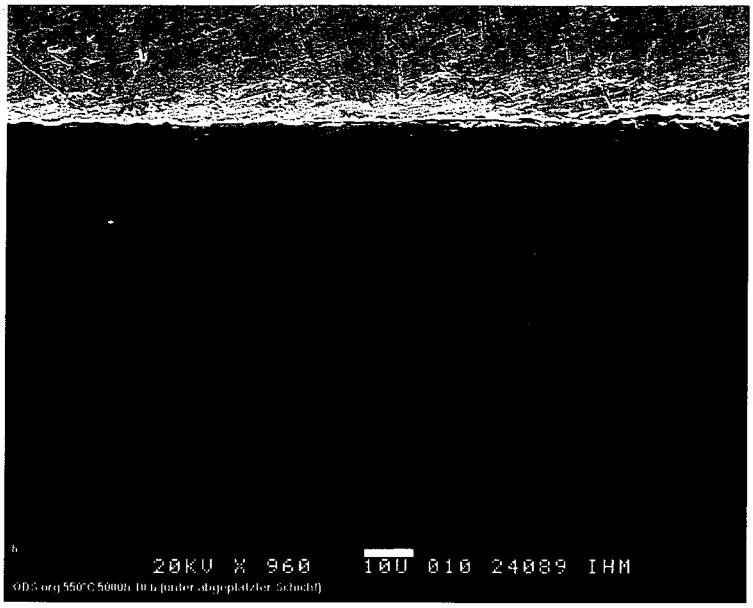


Fig. 9: ODS surface alloyed with Al by GESA

The GESA alloyed specimen shows no attack.

2.2.2 Temperature 550 °C



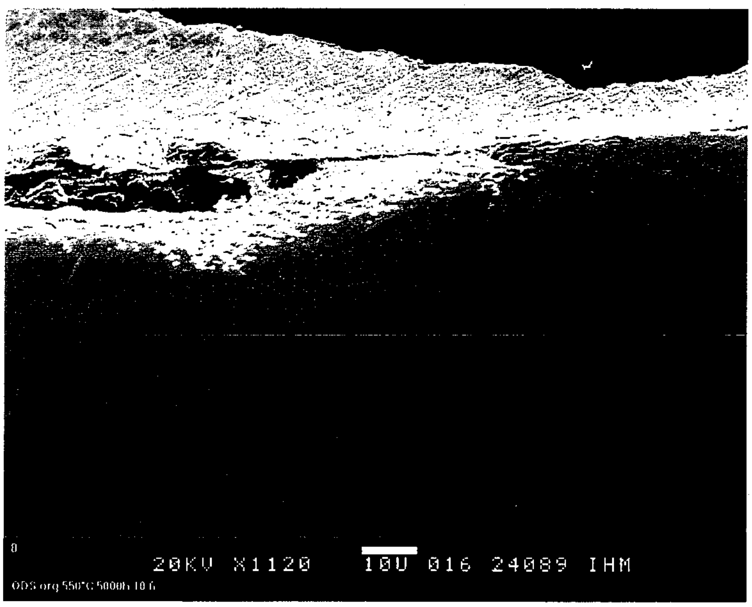


Fig. 10: ODS original

The whole magnetite and spinel layer is spalled off from the surface of original ODS. This process started already at 800 and 2000 h by a gap appearing between spinel and steel. In despite of this there occurs no general dissolution attack but a partial severe attack on some spots (up to 20 µm depth) with probably insufficient oxide scale formation.

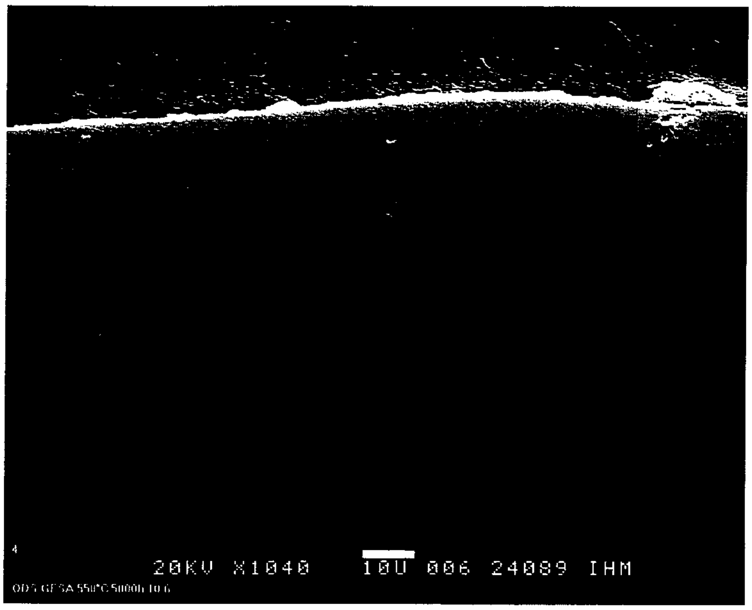


Fig. 11: ODS surface alloyed with Al by GESA

The GESA alloyed surface shows no dissolution attack but formation of some small oxide nodes of about 20 µm in diameter without dissolution attack because of a failure in the alloying process.

2.2.3 Temperature 600 °C

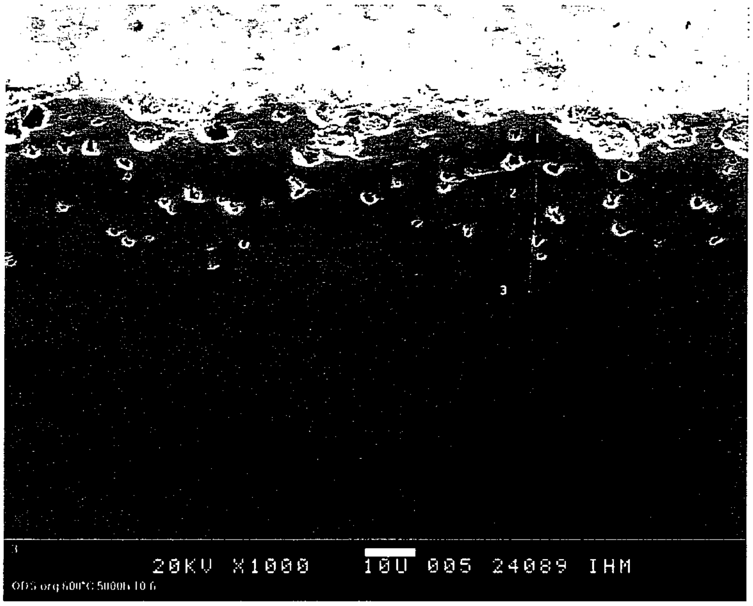


Fig. 12: Original ODS

A pore zone of up to 30 µm appears below the whole surface of original ODS on which no oxide layers nor oxide nodes are visible. Penetration of PbBi occurred to a depth of about 10 µm. The pores seem to be the places at which Cr – compounds like CrS or Cr – carbides were precipitated with C and S on their migration path to the surface (chemical potential gradient). Those precipitations appear already in some areas of the 2000 h specimen. Because of breaking out of the particles a lower Cr – concentration is observed in this region.

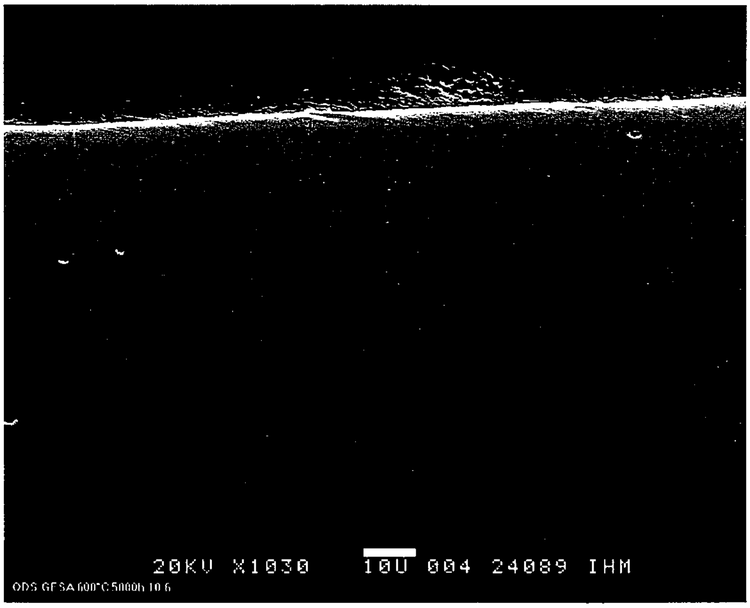
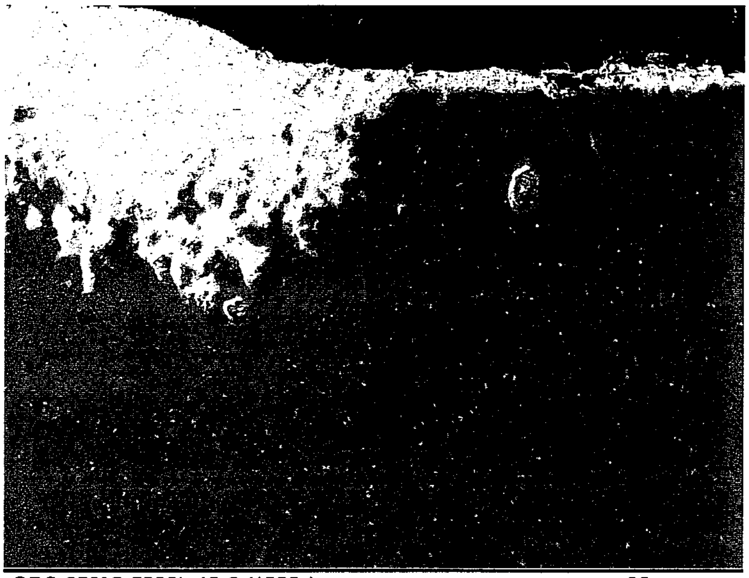


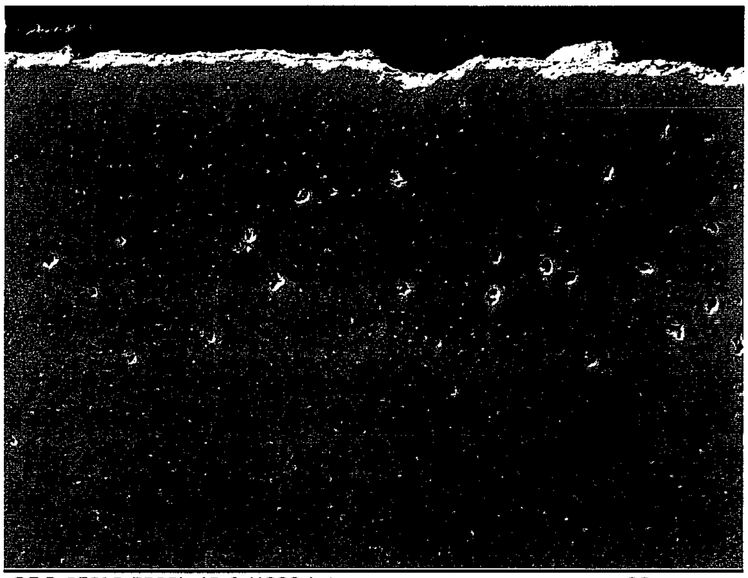
Fig. 13: ODS surface alloyed with Al by GESA

No dissolution attack can be observed on GESA alloyed specimen. Some oxide nodes appear at positions with low Al concentrations like those in specimens after 2000 h and after 5000 h at 550 °C.

2.2.4 Temperature 650 °C



ODS 650°C 5000h 10-6 (1000x) 20 µm



ODS 650°C 5000h 10-6 (1000x) 20 µm

Fig. 14: Original ODS

The original ODS steel shows the same corrosion phenomena as observed at 600 °C. But the thin protective oxide layer reported after 2000 h disappeared completely. Homogenous dissolution took place. Partial attack proceeded to a depth of 60 µm with PbBi infiltration.

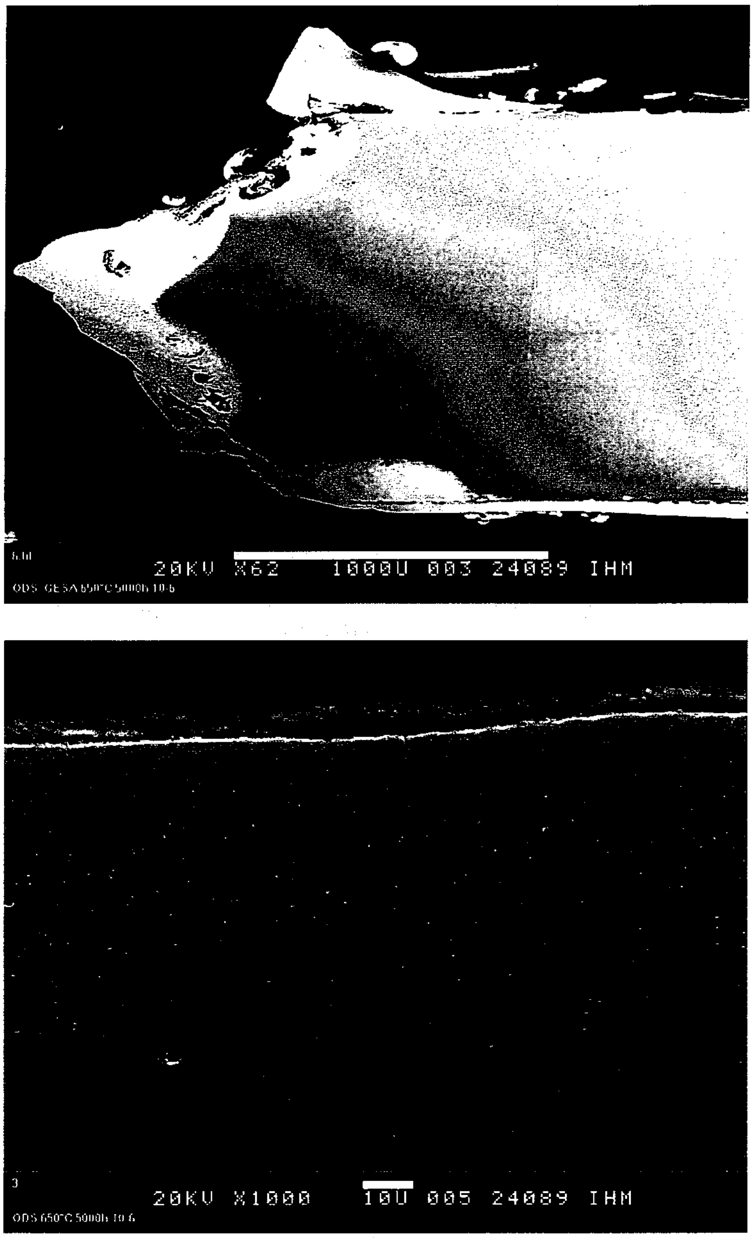


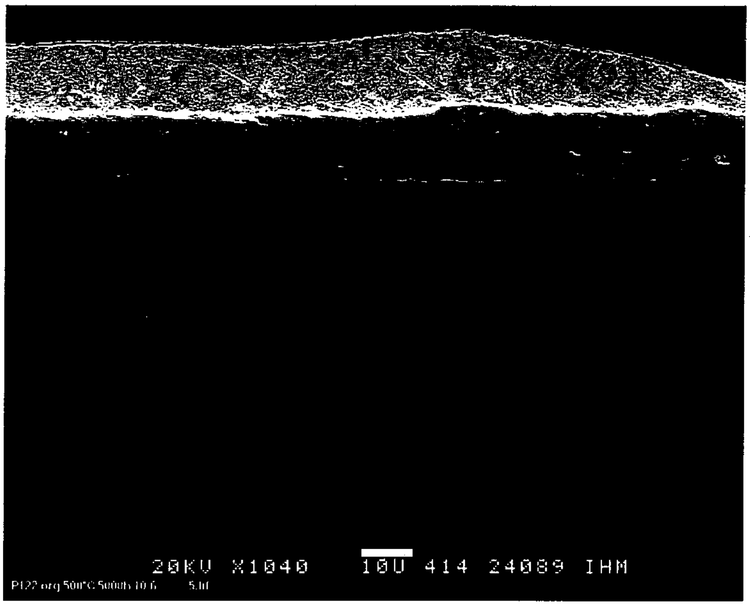
Fig. 15: ODS surface alloyed with Al by GESA

The regular surface of GESA alloyed ODS steel did not interact with the LBE. The irregular behavior on the one edge of the specimen is due to pure Al of the molten Al-foil that was not alloyed into the steel. It is known that such pure Al layers[2] do not have a protective effect because of the high solubility of pure Al in LBE.

[2] G. Müller, G. Schumacher, F. Zimmermann, Journal of Nuclear Materials, 278 (2000) 85

2.3 P122 steel

2.3.1 Temperature 500 °C



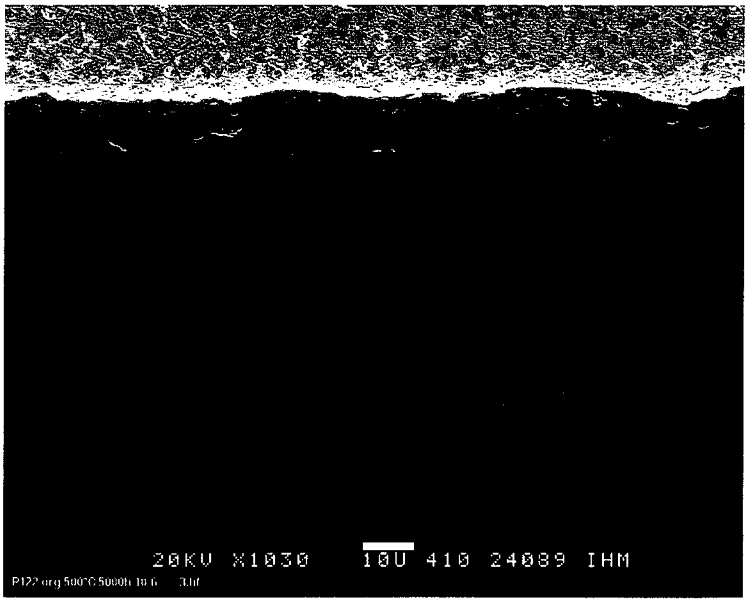


Fig. 16: Original P122

There is no change in original P122 steel as compared to the specimen after 2000 h of exposure. At some places the thickness of the oxide scale scatters and increases to 20 μm maximally.

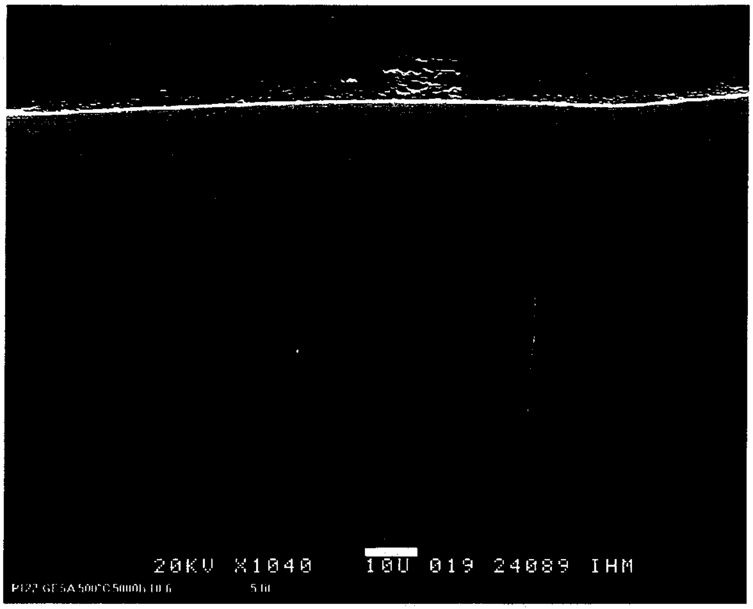


Fig. 17: P122 surface alloyed with Al by GESA

There is no attack and no change on the GESA alloyed P122 specimen.

2.3.2 Temperature 550 °C

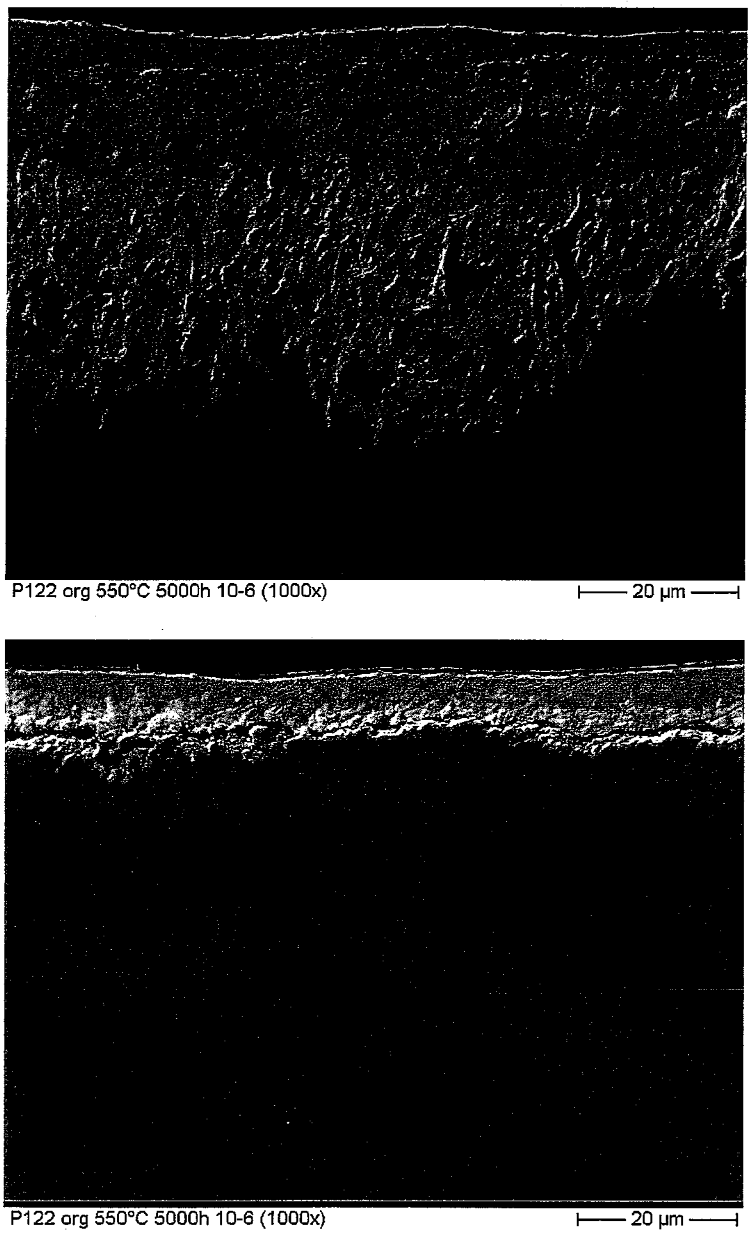


Fig. 18: Original P122

The protective oxide scale observed after 2000 h of exposure completely disappeared on original P122 steel. Overall dissolution attack occurs with frequently deep penetration of LBE up to 40 – 50 µm in depth.

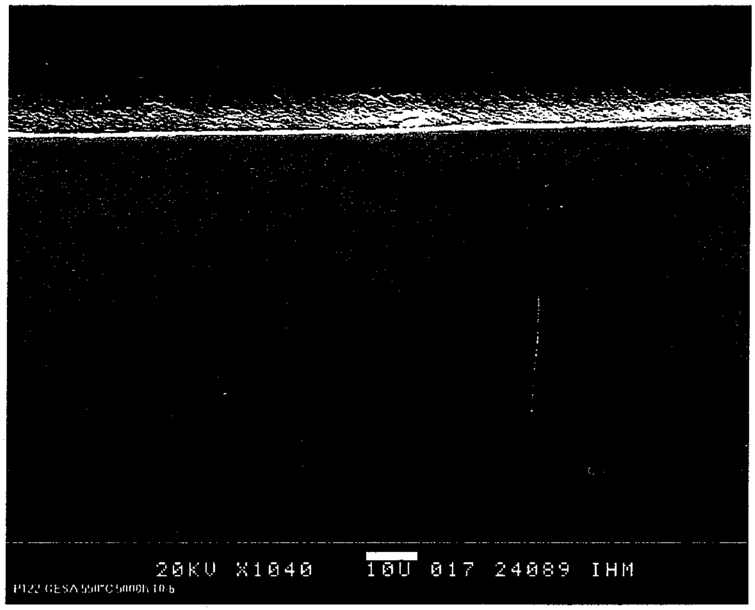


Fig. 19: P122 surface alloyed with Al by GESA

No attack occurred. There are few oxide nodes of about 15 µm width on places with less Al concentration.

2.3.3 Temperature 600 °C

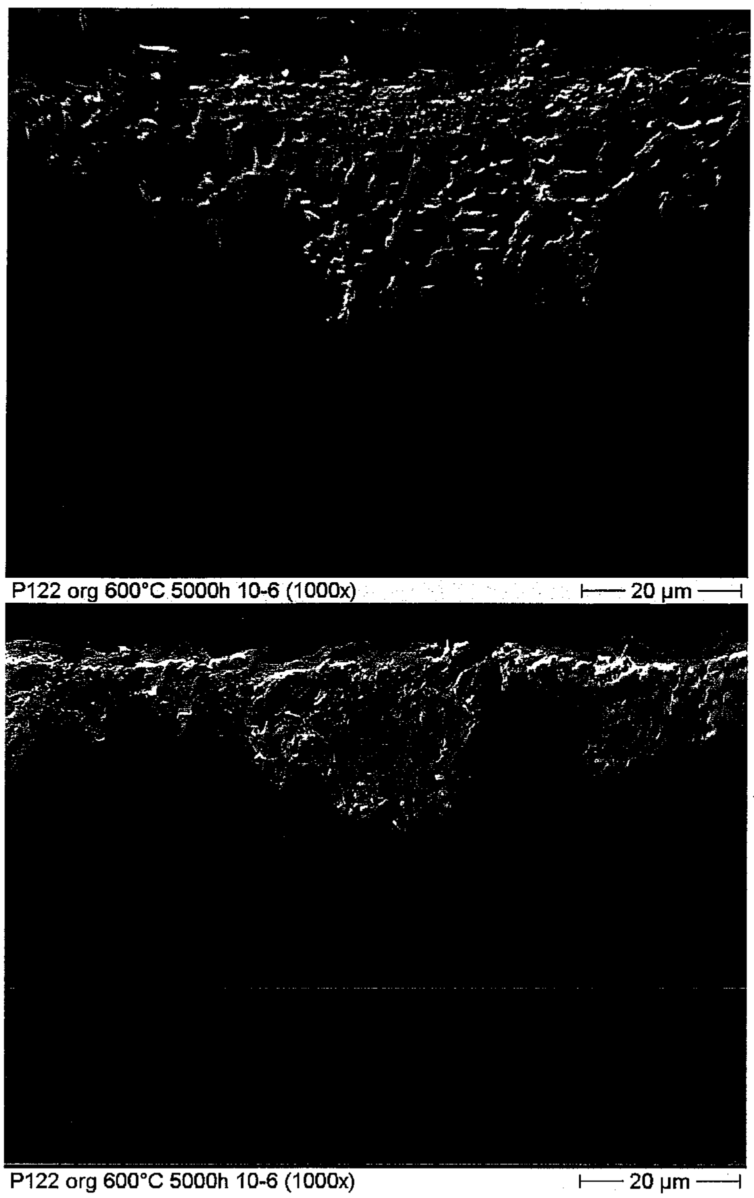


Fig. 20: Original P122

Not much changes as compared to 550 °C. There is just more frequent partial penetration of LBE.

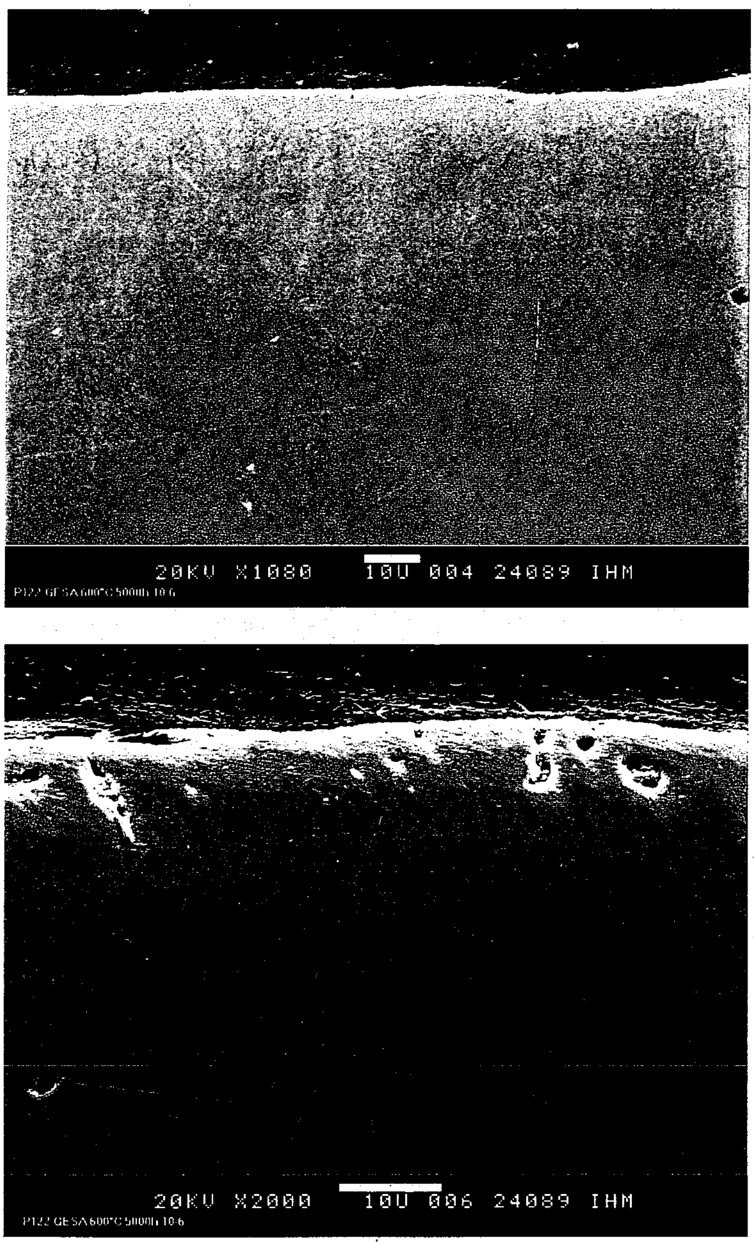
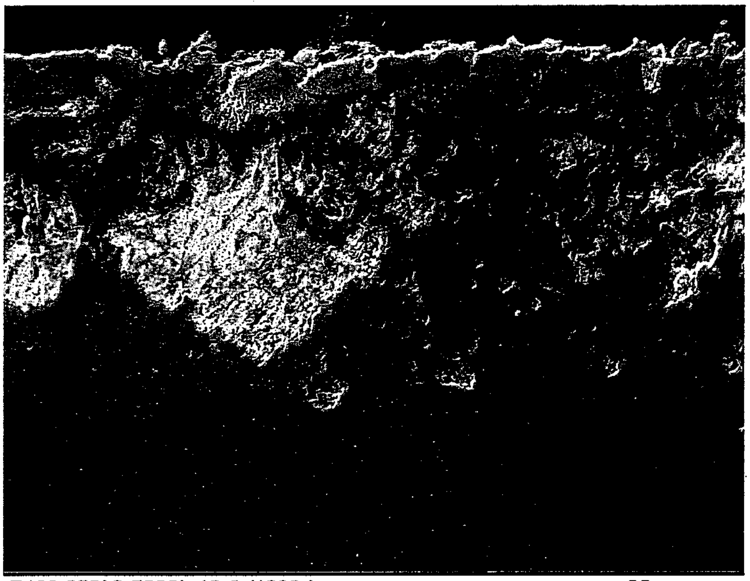


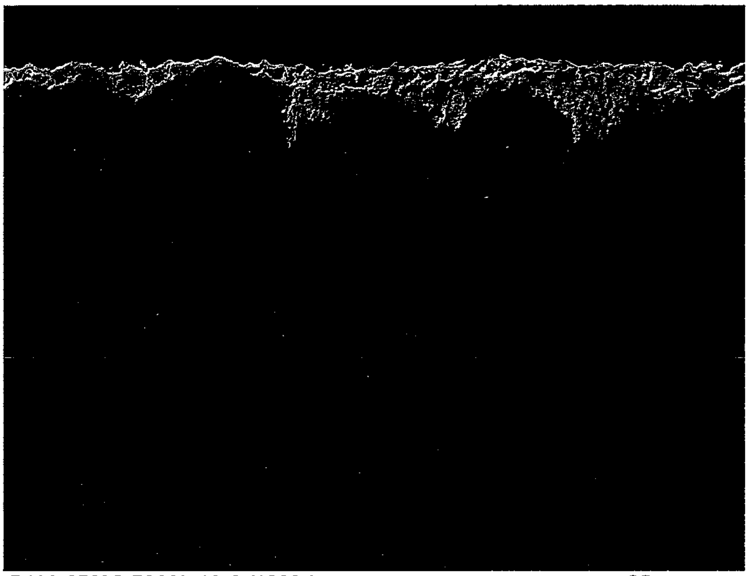
Fig. 21: P122 surface alloyed with Al by GESA

There is no attack on GESA alloyed P122. Few regions with pores below the surface appear. They are not observed after 2000 h of exposure. Therefore, this is a singular phenomenon. The pores seem to come from short small surface cracks that appeared during quenching of the melt. This regions had initially a high Al-concentration that causes brittleness and thus cracks. Small dark phase regions are Al enriched. They appear on the lower interface of the alloyed layer.

2.3.4 Temperature 650 °C



P122 650°C 5000h 10-6 (1000x) 20 µm



P122 650°C 5000h 10-6 (1000x) 20 µm

Fig. 22: Original P122

Corrosion phenomena similarly to those at 600 °C but further enhanced with a maximum penetration depth of 50 µm. Few areas have a thin protective oxide scale. Dark lines represent grain boundary oxidation and constitute mainly of Cr – oxide.

3 X-ray diffractometry of samples after 5000 h exposure to LBE

3.1 316FR

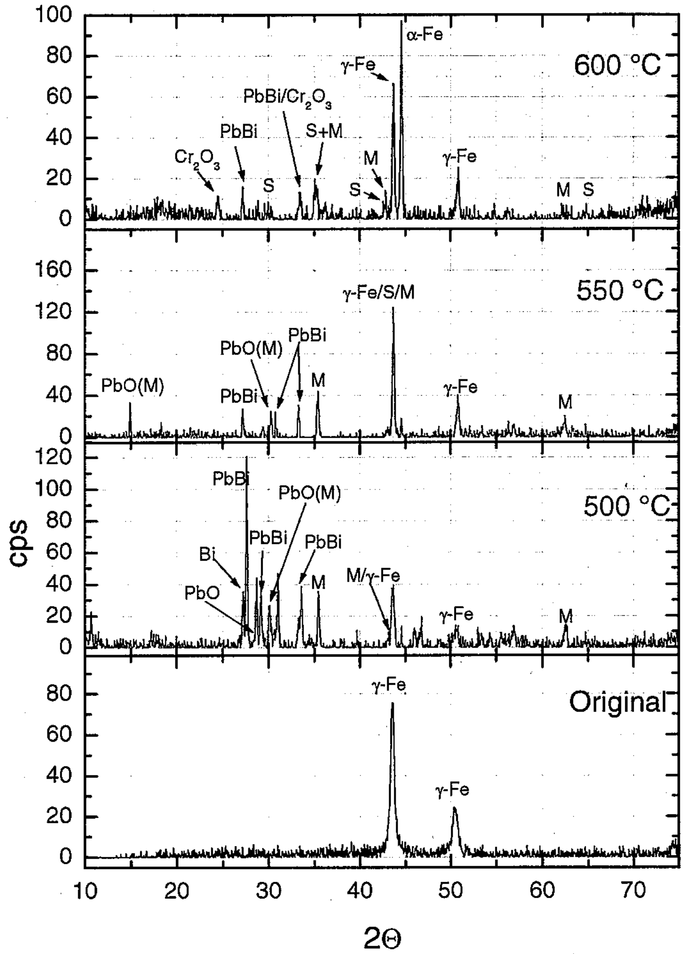


Fig. 23: XRD patterns of 316FR

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 pattern appears 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.

3.2 ODS

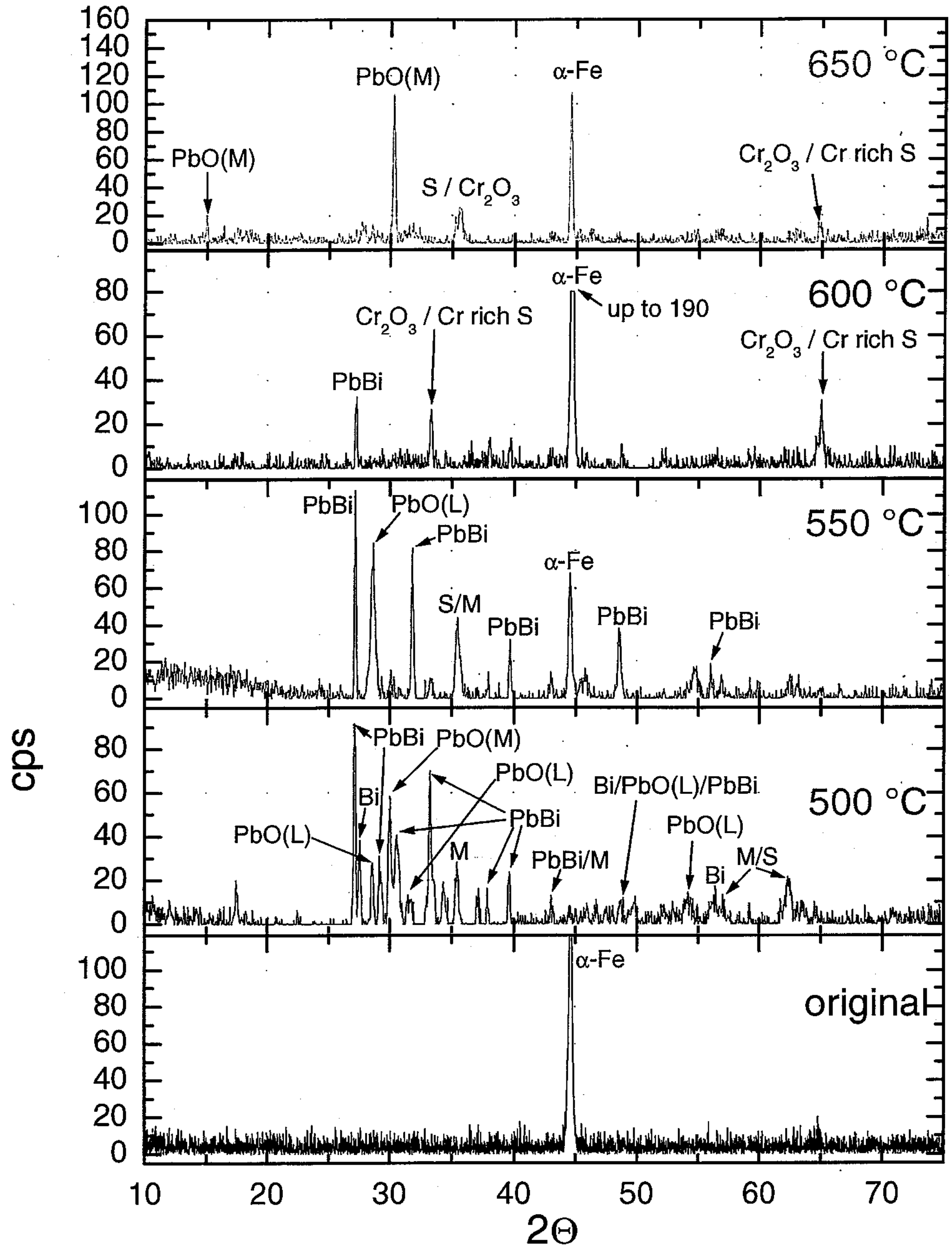


Fig. 24: XRD patterns of ODS

500 °C: Large magnetite and spinel peaks and disappeared α-Fe peaks like after 2000 h indicate a good 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.

3.3 P 122

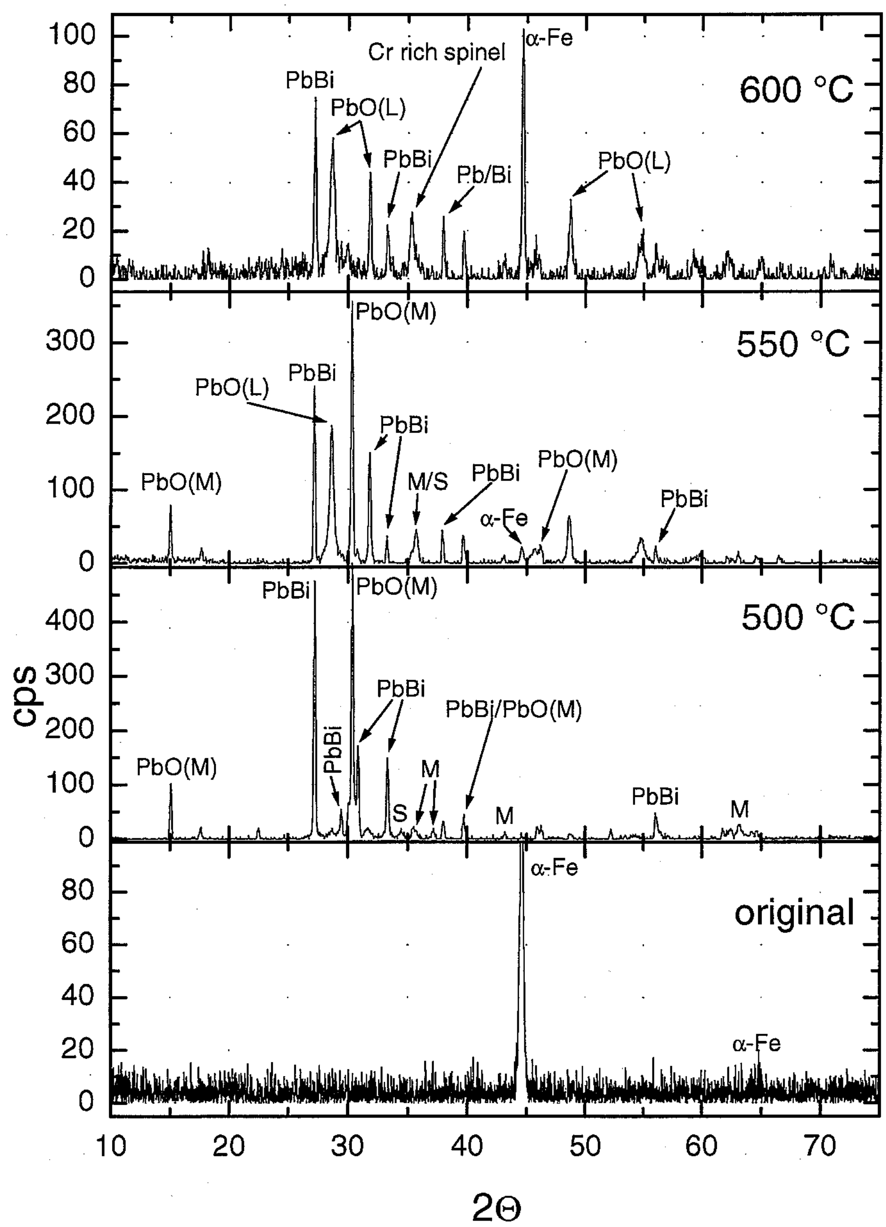


Fig. 25: XRD patterns of ODS

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 but a small Fe-peak appears indicating some break out of the oxide scale.

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

4 Summary after 5000 hours

- At 500 °C all steels still show satisfying behavior.
- At 550°C ODS and P122 lost their oxide layer completely. On 316FR, besides the thin spinel layer observed at 2000 h, there are node like magnetite-spinel scales with no dissolution attack. On ODS only partly dissolution attack occurred at some spots, on P122, however, there is overall dissolution attack with frequently deep penetration of LBE.
- At 600 °C a great part of 316FR 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.