

# **Pulsed E-beams to improve corrosion barriers for lead alloy cooled reactors: overview and dedicated mechanical tests**



## **Creep resistance of Al-surface alloyed T91 steel exposed to heavy liquid metals**

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Introduction – why do we need corrosion barriers

Corrosion barrier concept

Mechanical tests - Creep to Rupture  
Influence of liquid lead alloy  
Behavior of corrosion barrier

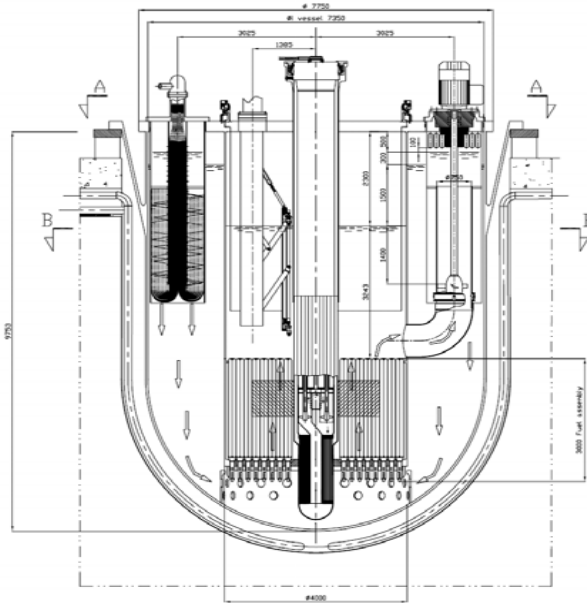
Summary

# Actual and planned nuclear facilities cooled with liquid lead alloys

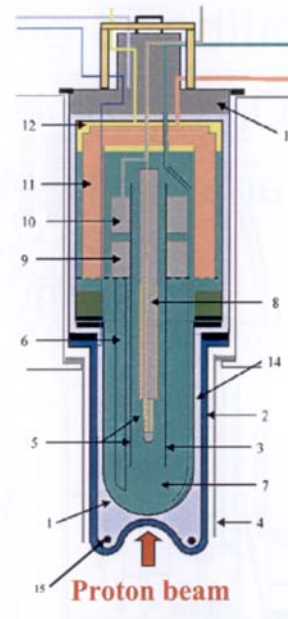
Subcritical systems for  
transmutation

Neutron source -  
spallation

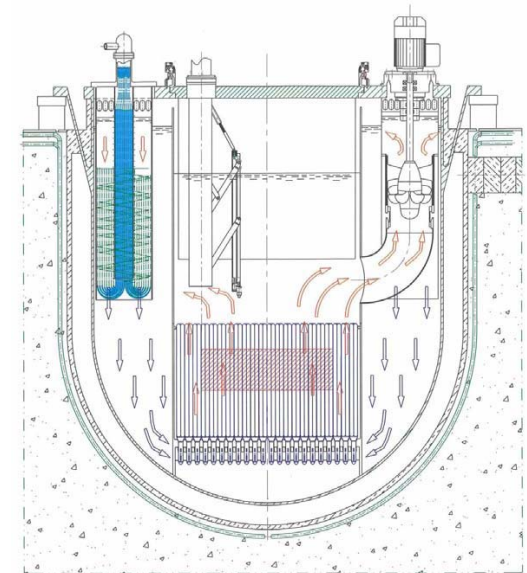
Future GEN IV  
reactors



EFIT, XT-ADS, **MYRRHA**  
Coolant + target: Pb, PbBi



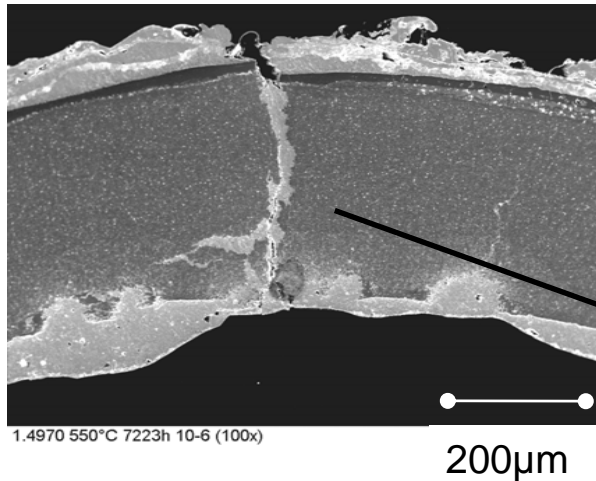
MEGAPIE  
Coolant + Target: Pb, PbBi



LEADER - Pb,  
**SVBR-100** – PbBi

# Material compatibility of steels with lead alloys

austenitic steel / 1.4970  
550° C ~7000h's



Dissolution of alloying elements  
(solubility :  $\text{Ni} \gg \text{Cr} > \text{Fe}$ ).

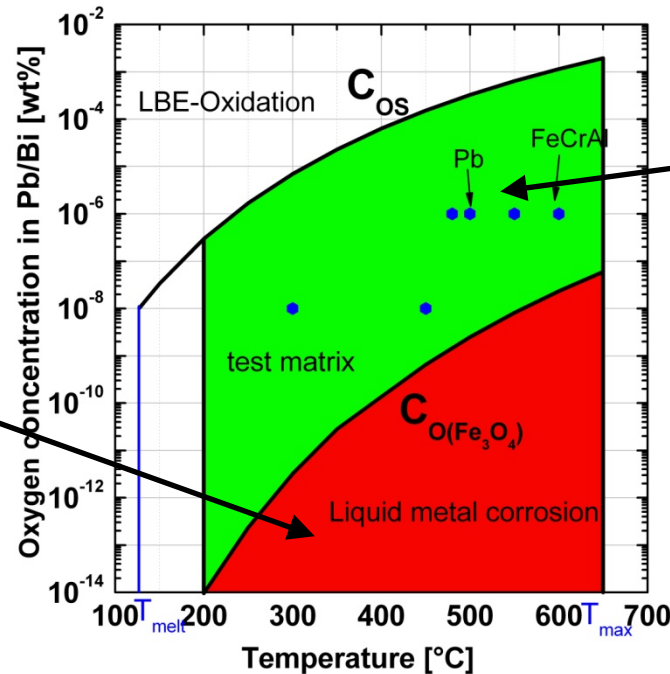
Dissolution rate up to 1 µm/h

Two main effects of corrosion:

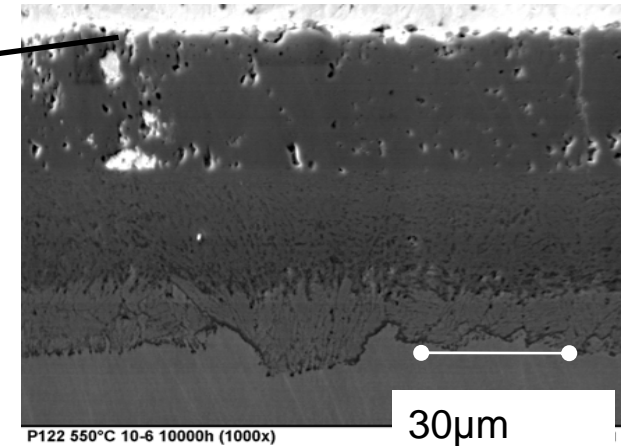
**structural integrity** – material loss of metal – dissolution attack, oxidation (Spinel + IOZ)

**heat removal** - : oxidation (magnetite + spinel)

> 500°C additional corrosion barriers are needed

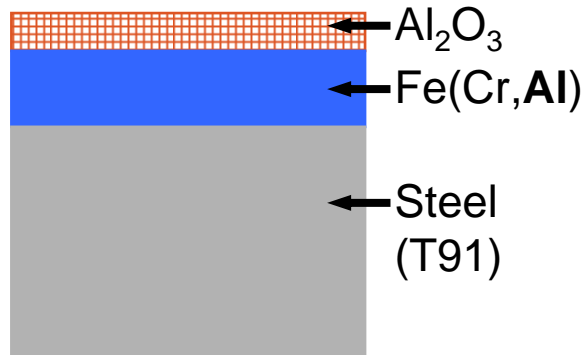


f/m Stahl / T91  
550 ° C ~10000h's



- strong oxide scale growth  
frequent spallation inter alia  
growth stresses  
- reduced heat removal

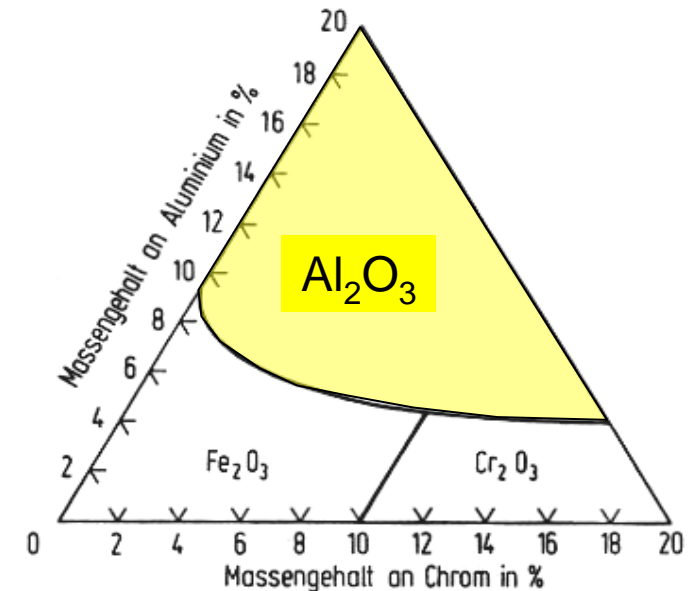
# Corrosion barrier concept against dissolution and strong oxidation: thin, protective, slow growing oxide scales



## Requirements

- Corrosion resistant in HLM up to ca. 650 °C
- Self healing of mechanically damaged layers
- No negative influence on mechanical properties
- Irradiation stability under relevant fluxes
- The coating / alloying process *must be of industrial relevance*

## Oxide map FeCrAl – Oxide at 1000°C



## Thermal conductivity of $\text{Al}_2\text{O}_3$

(400°C) = 8 – 12 W/mK

(500°C) = 14 W/mK

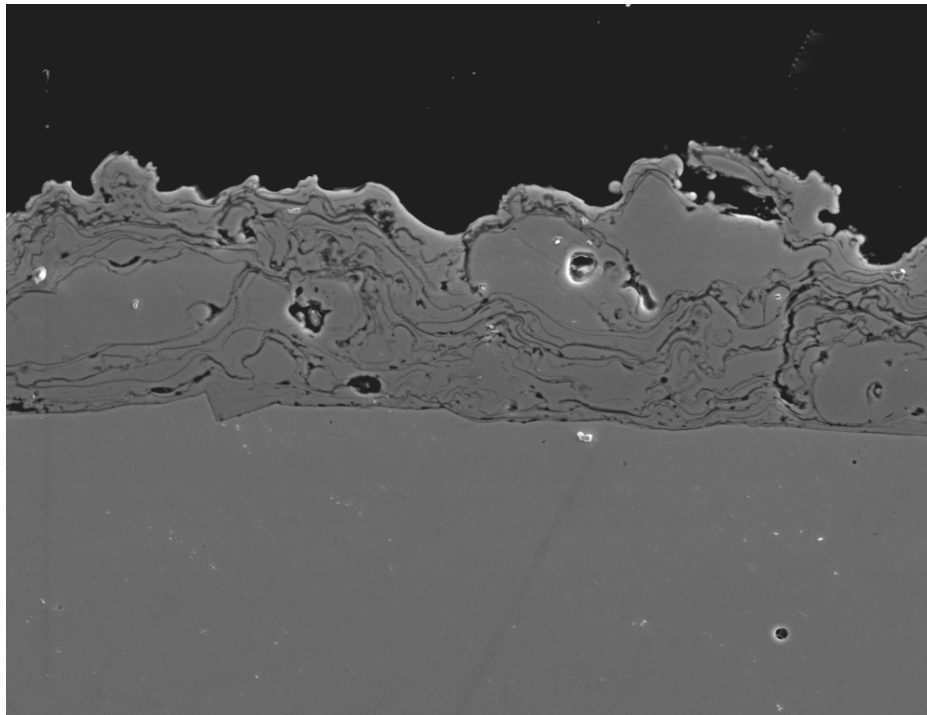
# LPPS sprayed FeCrAlY coating on T91 steel

*Al content of powder eg. around. 11 wt% Al – particle size ~ 30 $\mu$ m -*

*Al content still under investigation*

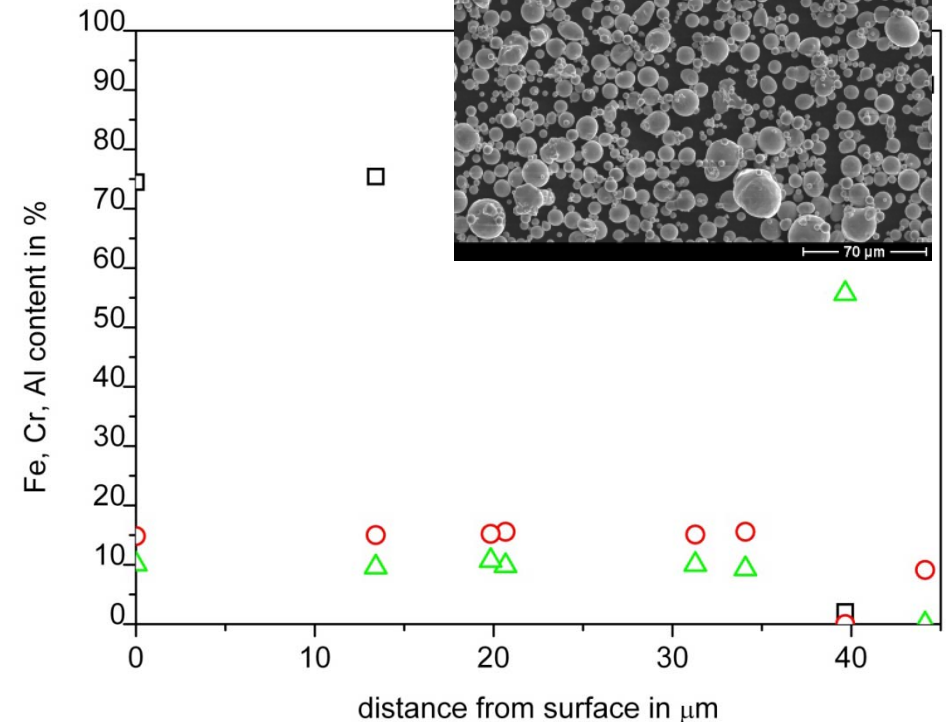
*specific LPPS process that allows spraying of 20 to 30 $\mu$ m thick scales*

*Substrate temperature during spraying < 600°C*



T91 FeCrAlY 10S0028 (1000x)

30  $\mu$ m



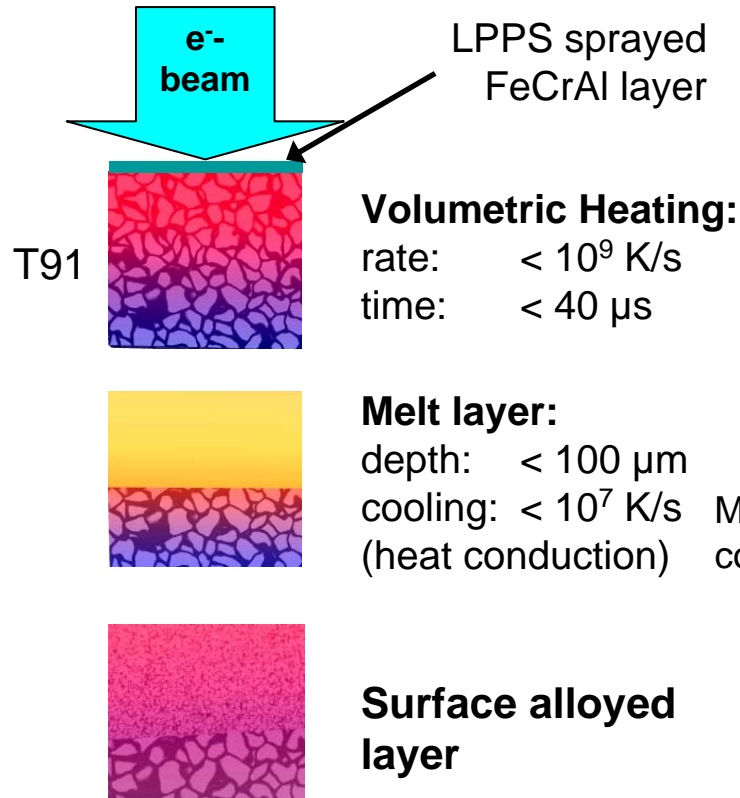
*Layer is porous, rough with significant variation in thickness, bonding to substrate only mechanical*

*→ GESA – Re-Melting of deposited layer by pulsed electron beams – T91 has to stay < 650 °C*

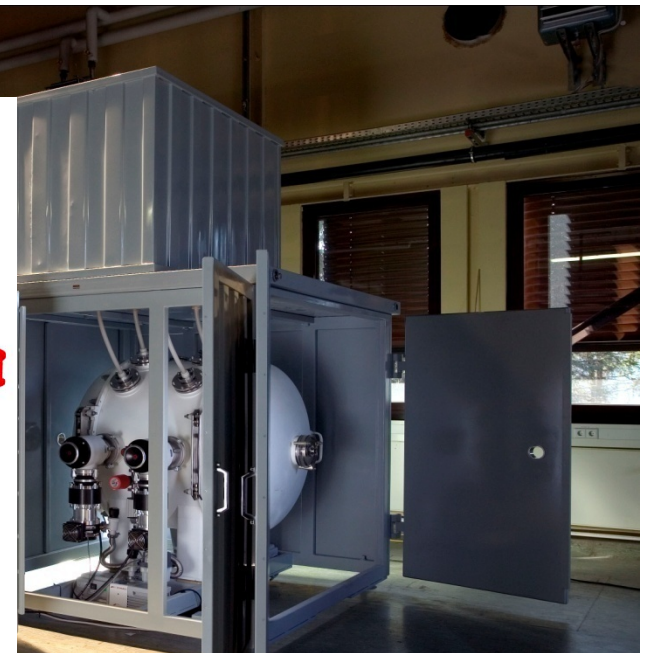
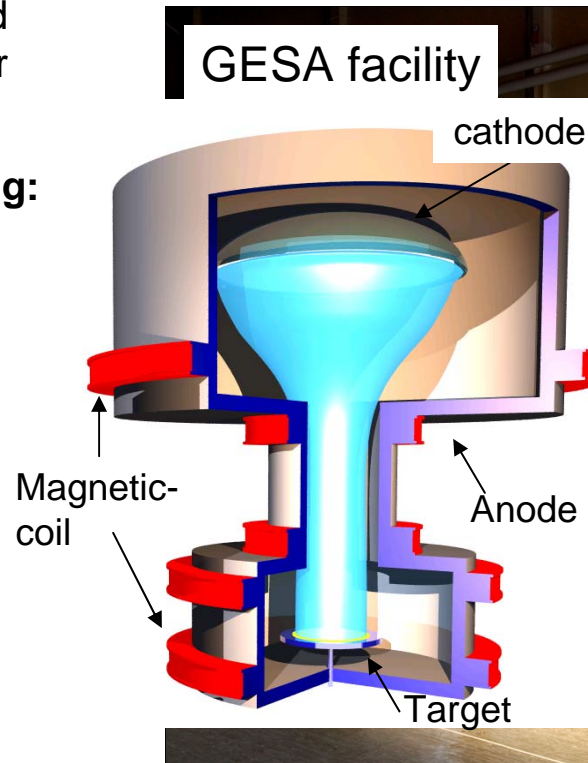


# Surface modification using Pulsed Electron Beams (GESA)

(Process development in cooperation with NIEFA, St. Petersburg)



**Substrate temperature remains relatively low – no micro-structural changes in T91 observed**



## Electron beam Parameter:

Electron Energy: 125 keV

Power density :  $\sim 2$  MW/cm<sup>2</sup>

Pulse duration

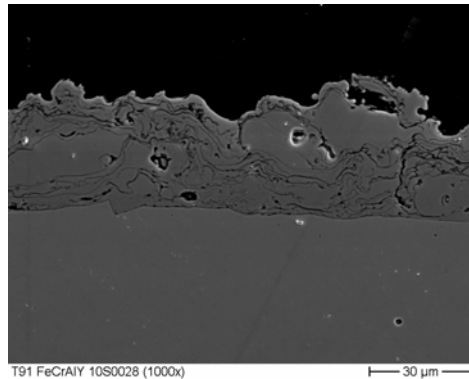
controllable:  $< 40$   $\mu$ s

Beam diameter:  $\sim 4$ cm GESA I

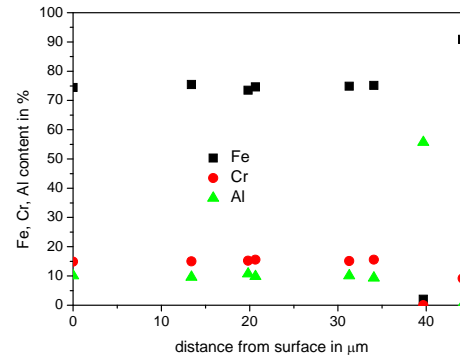
Treatable length  $\sim 30$  cm GESA IV

# T91 + FeCrAlY layer before and after surface modification

*As sprayed*

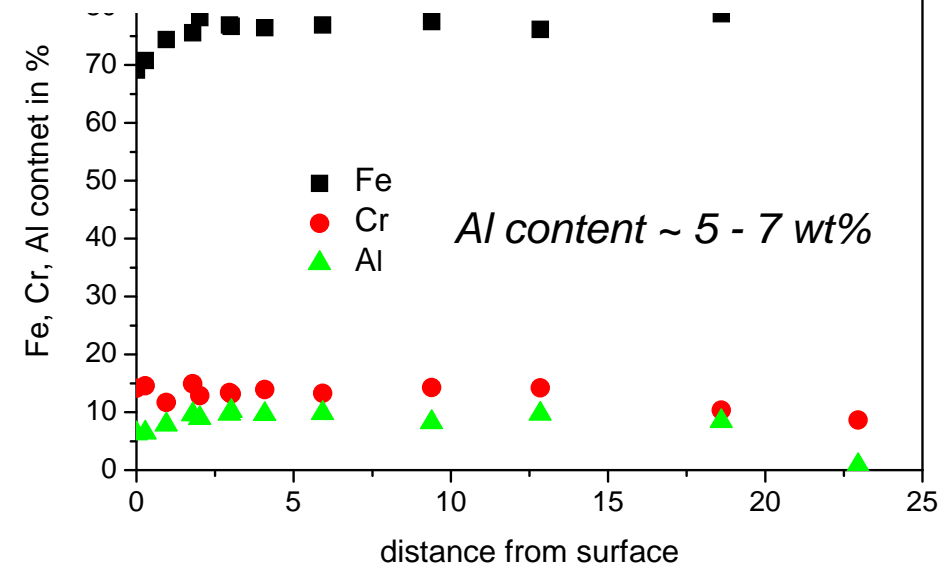
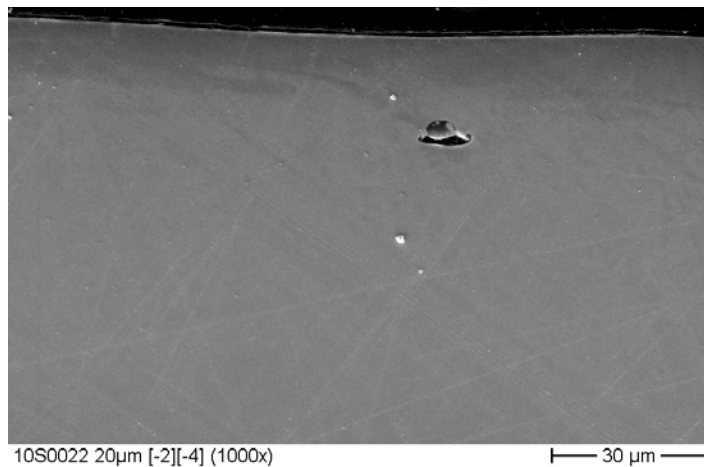


*Al content ~ 10 wt%*



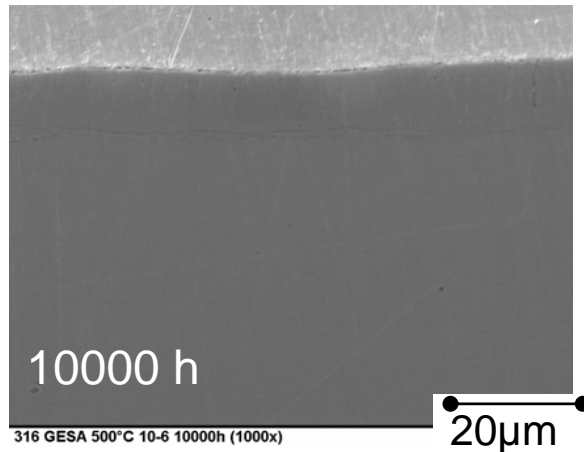
*Surface smoothed, pores are removed, layer densified, metallic bonding to substrate → surface alloyed material*

*After GESA treatment*

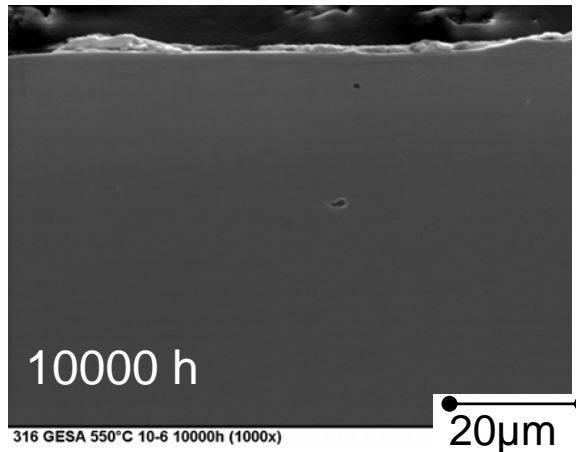


# Influence of temperature – “perfect” Al surface alloyed steel at optimal oxygen concentration $10^{-6}$ wt%

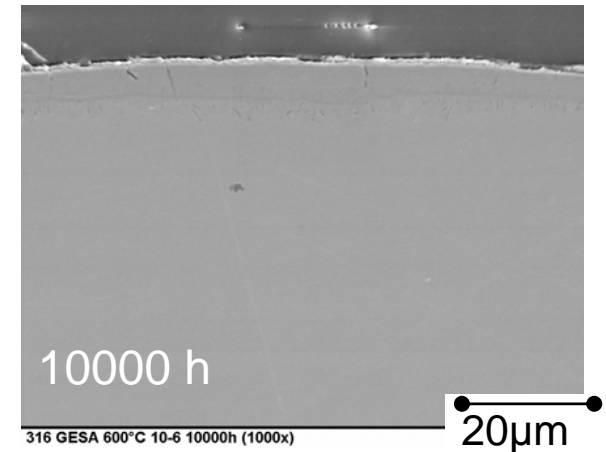
500° C



550 ° C



600° C



*GESA treated FeCrAlY*



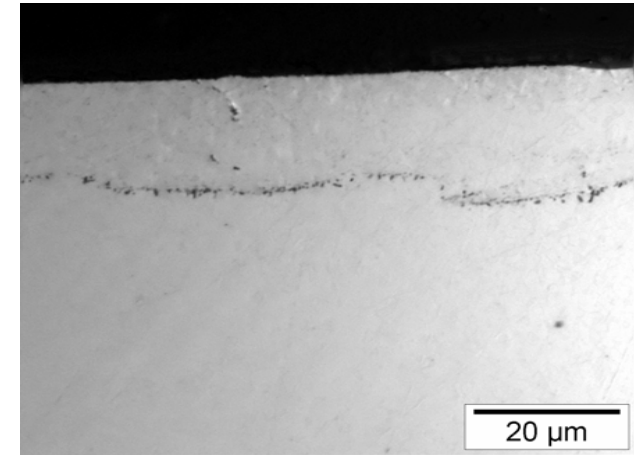
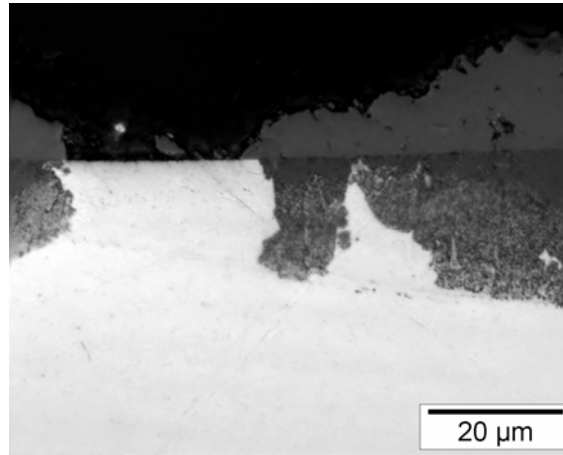
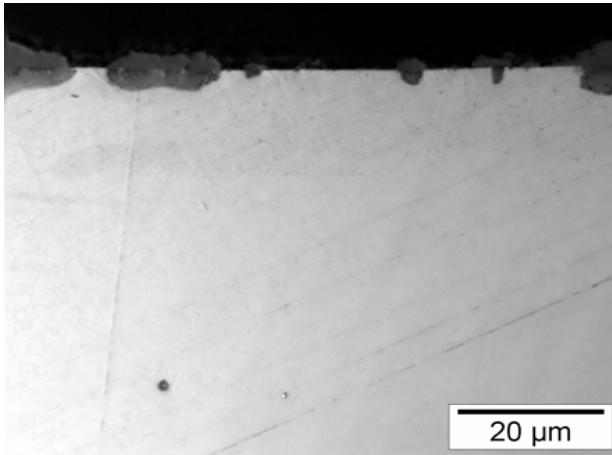
**5000 h at 600 ° C in flowing LBE ( $10^{-6}$  wt%)**

Up to 600°C and 10000 h no corrosion attack and no visible oxidation.

Thin alumina scales protect the surface alloyed steel.



Exposed to PbBi having  $10^{-6}$  wt% oxygen 2000h at  $10^{-6}$  wt  
Oxide scale formation at different temperatures ( $\text{Al}_{\text{powder}}$  7wt%)



480 ° C

600 ° C

Large areas showed unexpected oxidation especially at 480 and 550°C

Al content (~4 wt%) before and after exposure

➔ Optimisation of coating and post treatment process to increase Al content

550 ° C

*Al content required for selective Al-oxide formation –preliminary results*

*At 476°C Al > ~6.2 wt%*

*At 490°C Al > ~5.6 wt%*

*At 550°C Al > ~5.2 wt%*

# Creep to rupture of T91 in PbBi and air

## *T91 with and without GESA modified FeCrAl layer*

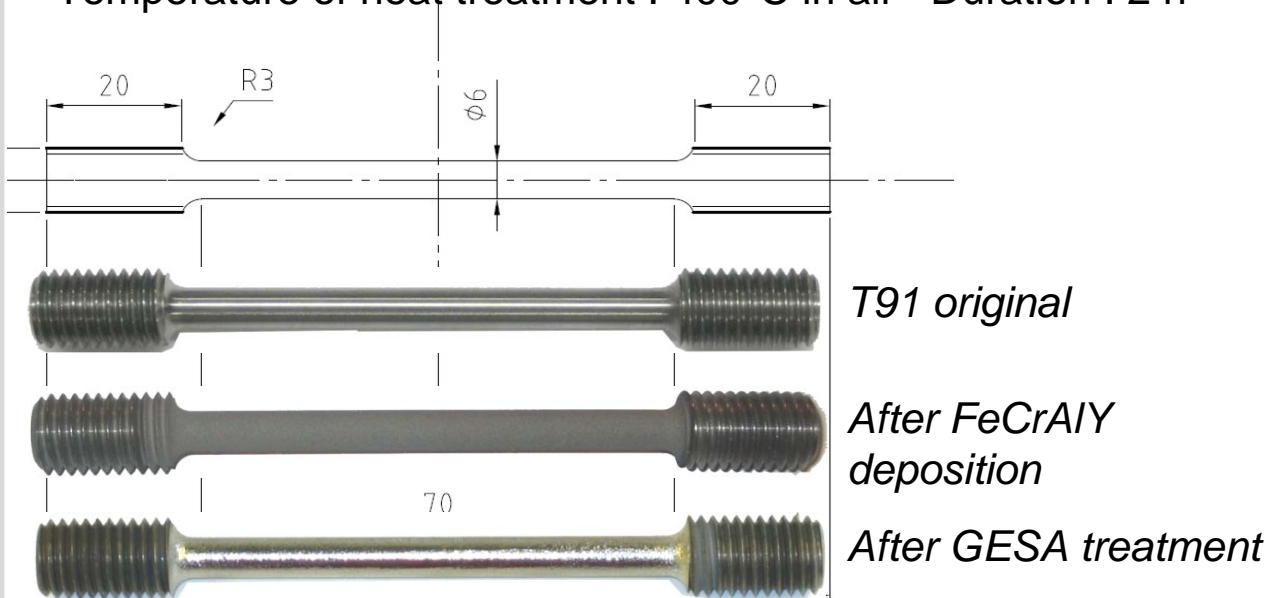
Specimens: cylindrical test-length 70 mm – diameter 6 mm

Material:

T91 : normalized [1050° C (30 min)] – air quenched followed by tempering [770° C (1h)]

GESA surface modified specimens are heat treated to release possible residual stresses

Temperature of heat treatment : 400°C in air– Duration : 2 h



*Test environment:*

*Air at 550 and 600°C*

*LBE at 500, 550°C and 600°C*

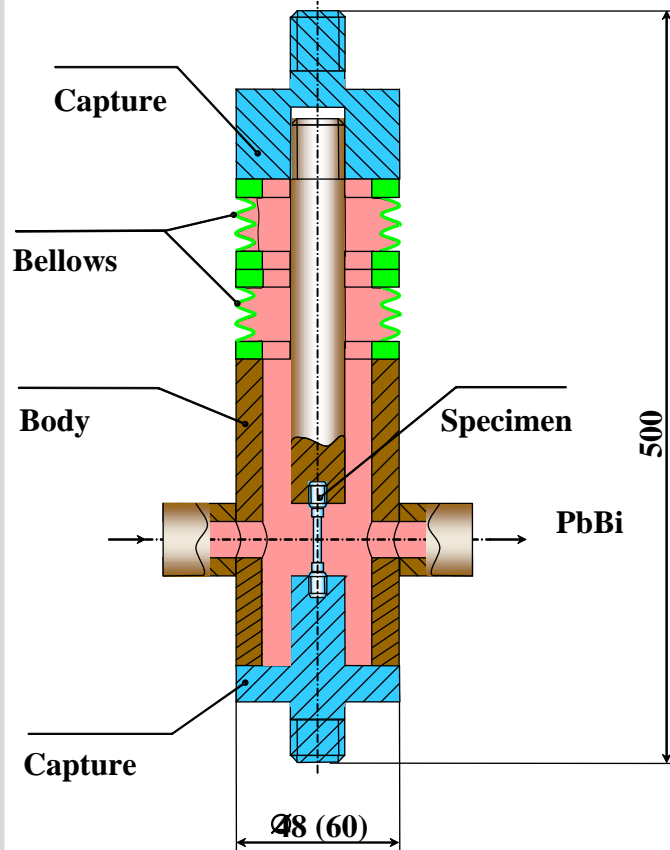
*LBE contains 10<sup>-6</sup>wt% oxygen*

*Stress levels:*

*in air: 140 to 220 MPa*

*in LBE: 60 to 220 MPa*

# Test – setup of creep rupture experiments examined at Prometey St. Petersburg (gratitude A. D. Kasthanov, V. G. Markov)



*PbBi:*  
 $10^{-6}$  wt% oxygen

*Flow velocity :*  
0.5 m/s



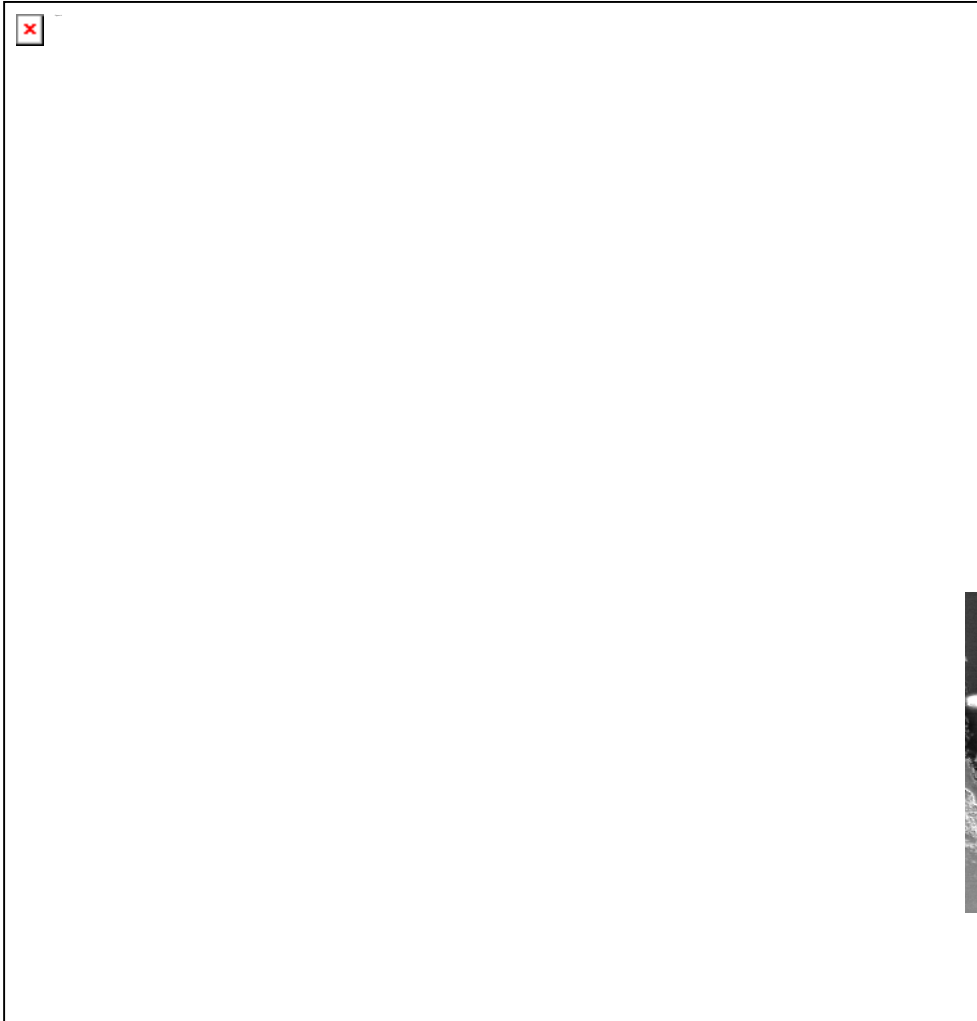
*Specimens 100h in test section prior to stress initiation*

*Measurement of strain outside at capture*

*Using calibration curve from air experiments strain at specimen is calculated*

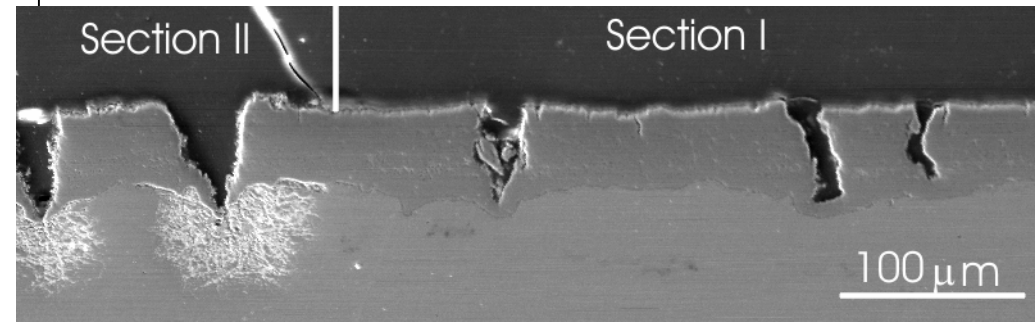
# Influence of PbBi on time to rupture of T91 orig at 550°C

Journal of Nuclear Materials 394 (2009) 102–108



Significant reduction in time to rupture of T91 due to contact with PbBi

Oxide scale cracks → PbBi penetrates and reduces the surface energy –  
Rebinder effect – stress corrosion cracking



# Comparison of secondary creep rates of T91 in air and PbBi at 550 °C

Stress [MPa]	Ratio of 2 <sup>nd</sup> creep rates, LBE/air
140	27
160	35
180	44
200	53

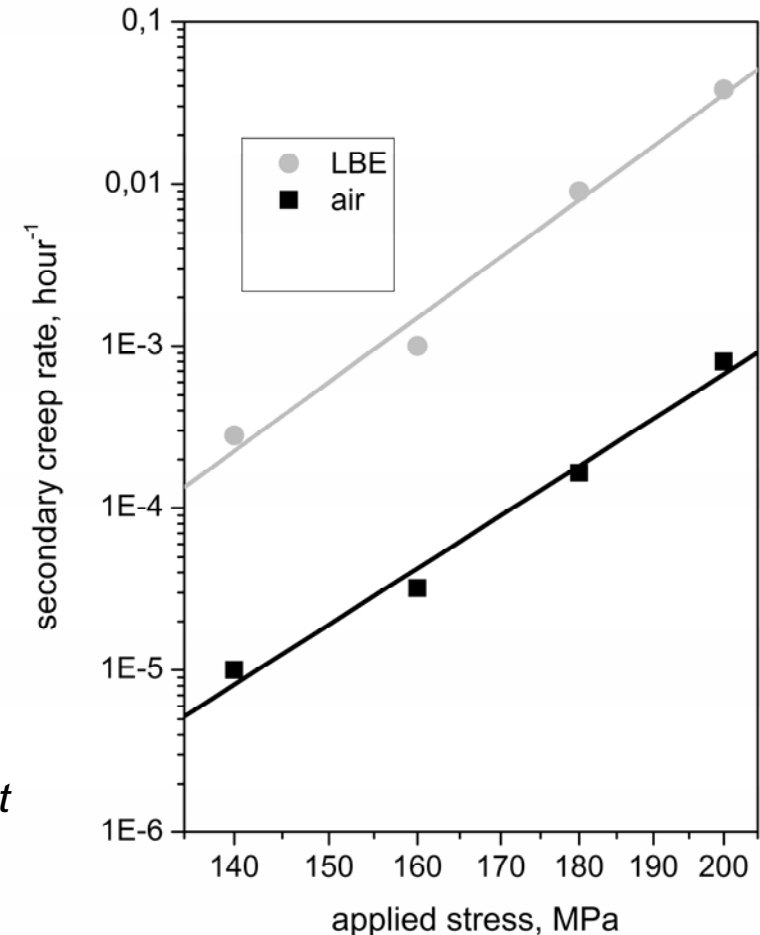


**Influence of PbBi**

*Creep rate in PbBi up to 50 times higher than in air*

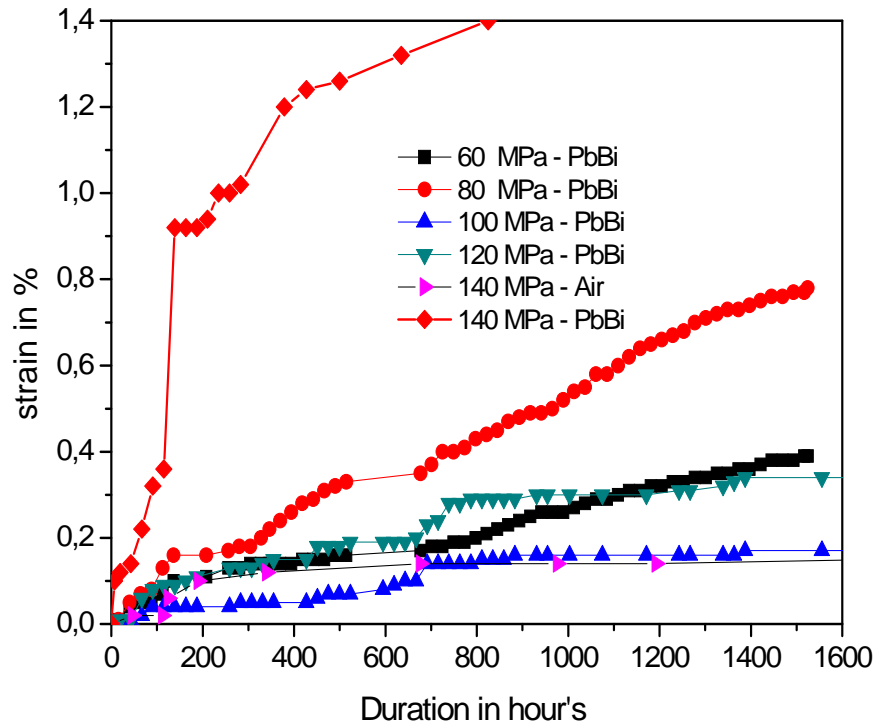
*Ratio of creep rate in PbBi and air is stress dependant*

*At low stresses – no cracking of oxide scale ?? – no direct contact with PbBi – no influence on creep strength - threshold stress ??*



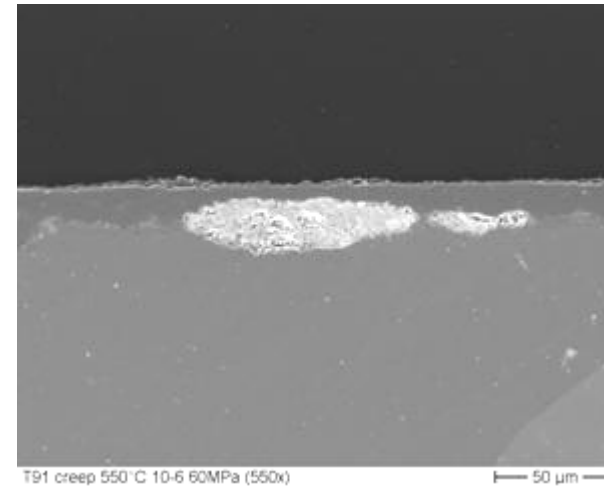


# Creep tests at low stresses at 550°C – Threshold stress ??



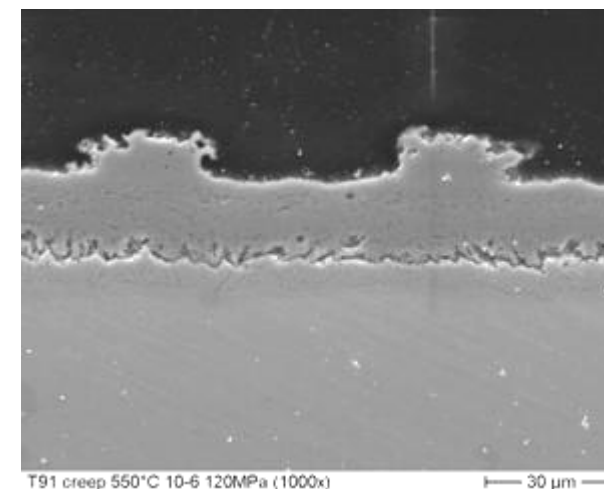
**60 to 120 MPa no change - as long as oxide scale intact no influence → cracks at 60 and 80 MPa → reduction in strength**

**Any deterioration of the oxide scale results in reduced creep strength**



60Mpa

*Cracks  
PbBi can  
penetrate*



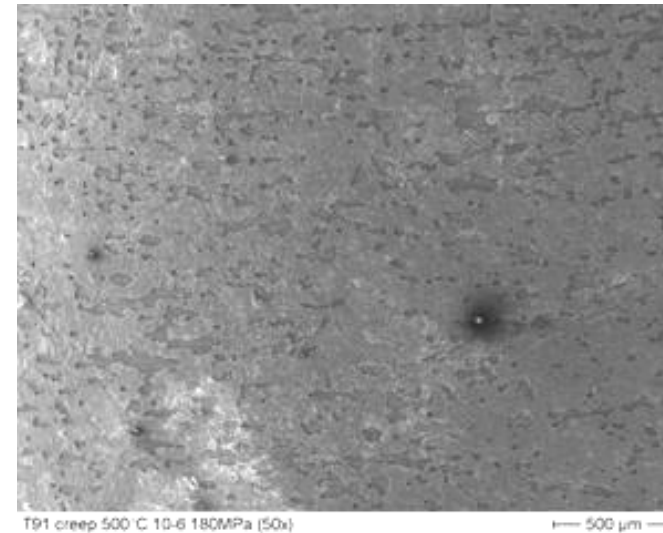
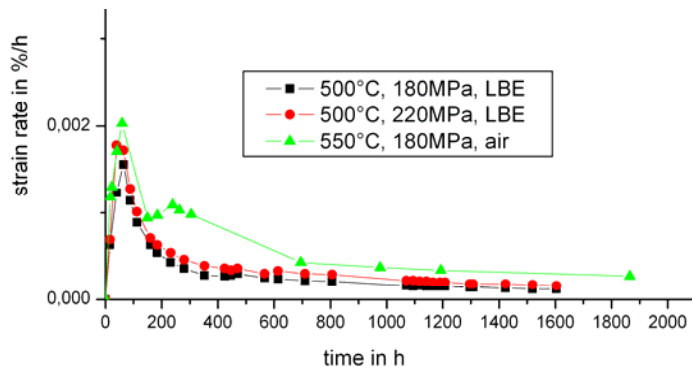
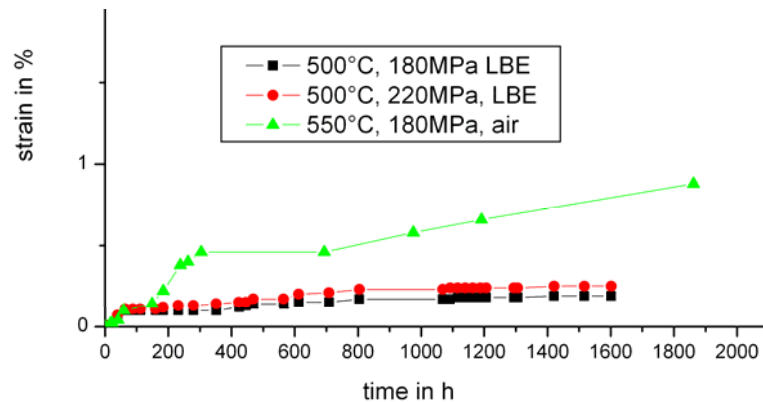
120 MPa

*No cracks  
No PbBi  
No influence*

# Creep tests at lower Temperature of 500°C – reduced diffusion and sliding reduced strain

*Reduction of temperature to 500°C lead to significant differences*

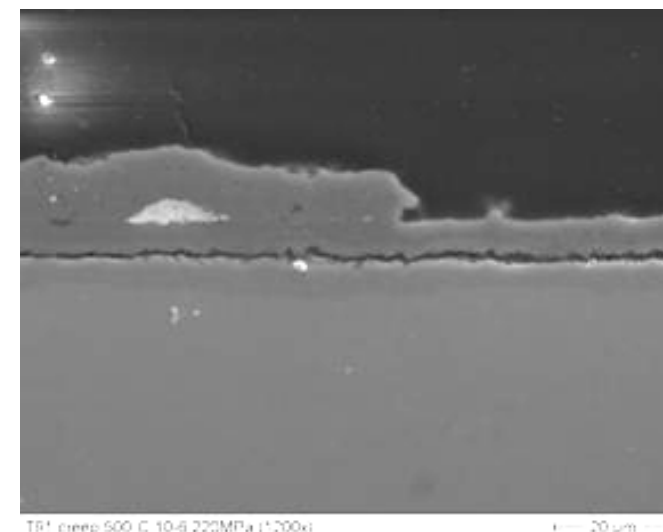
*→ Reduced strain → no cracks in oxide scale → neglect able influence of PbBi*



180 MPa

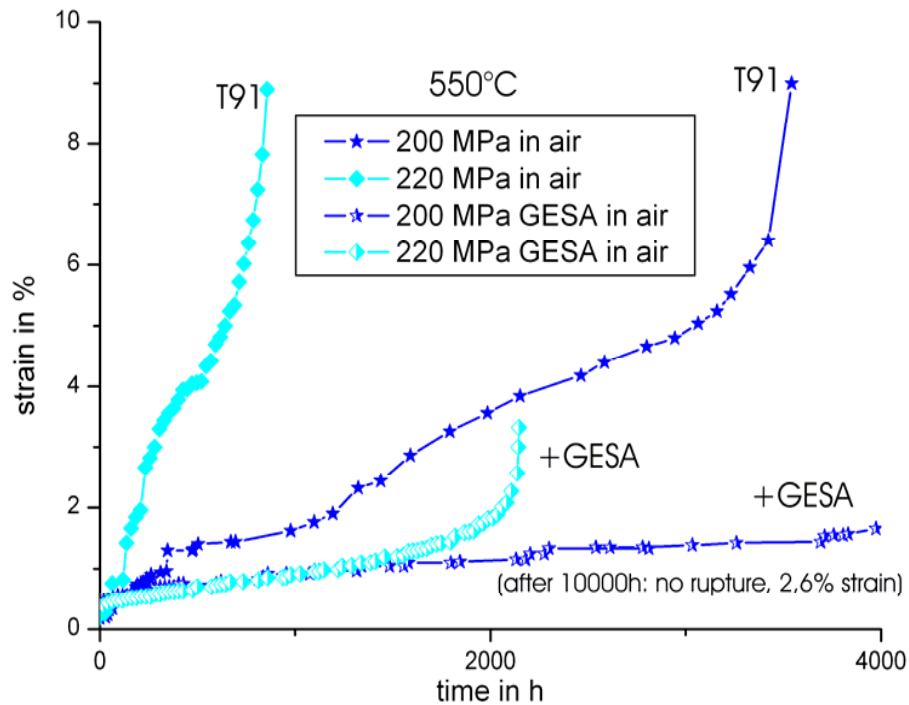
Slow strain  
<0.4%

No cracks in  
oxide scale

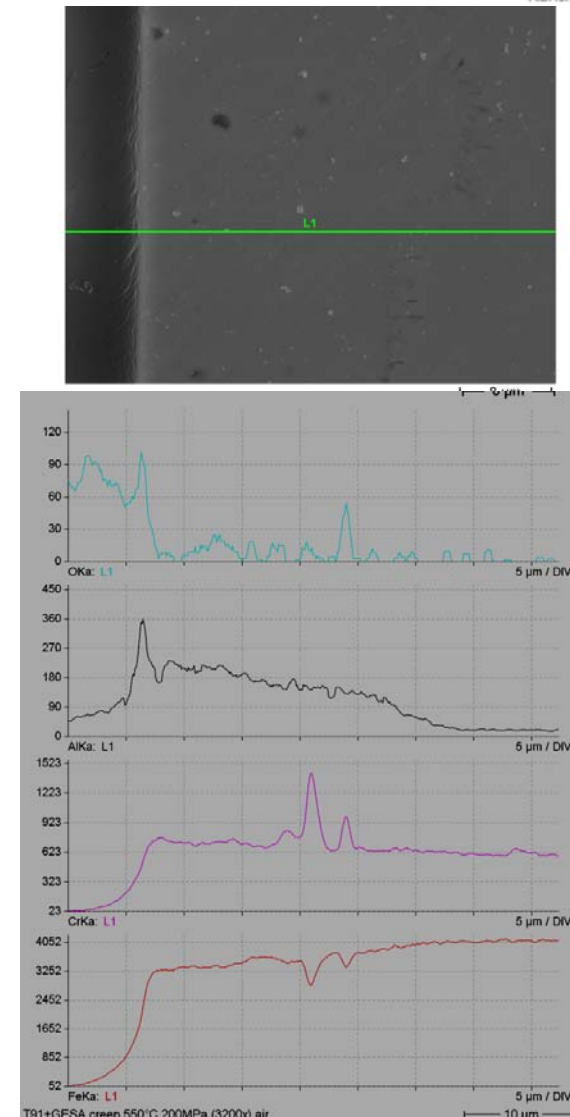


220 MPa

# Creep to rupture test of T91 orig. and GESA surface modified T91 in air at 550°C

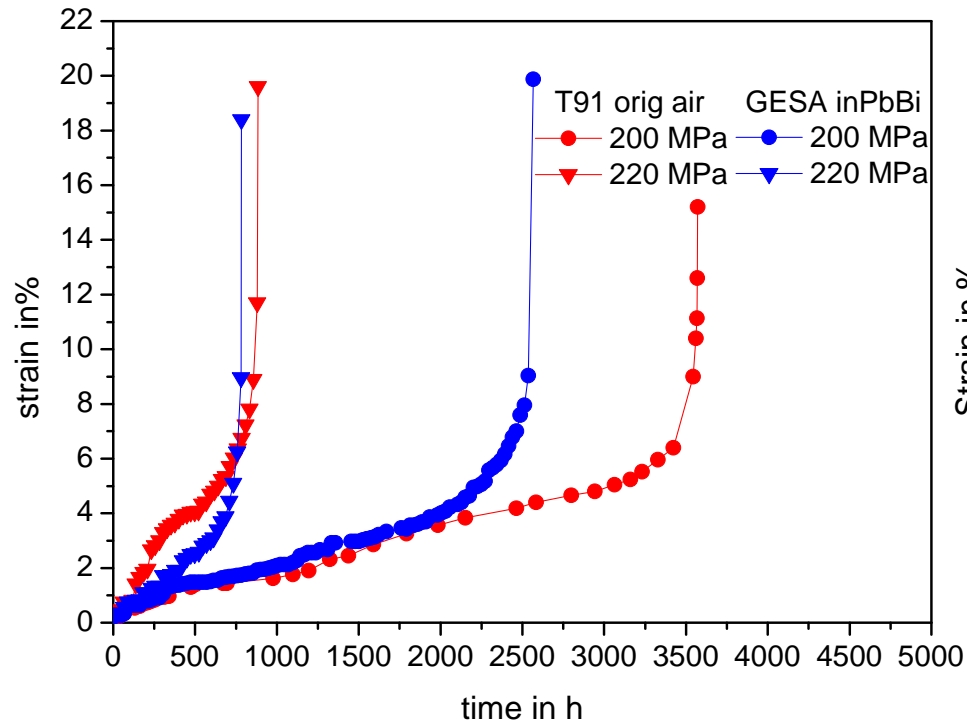


*Significant longer rupture times of GESA modified T91*  
*Surface alloyed layer improves creep strength*  
*Thin  $Al_2O_3$  scale formed at surface*

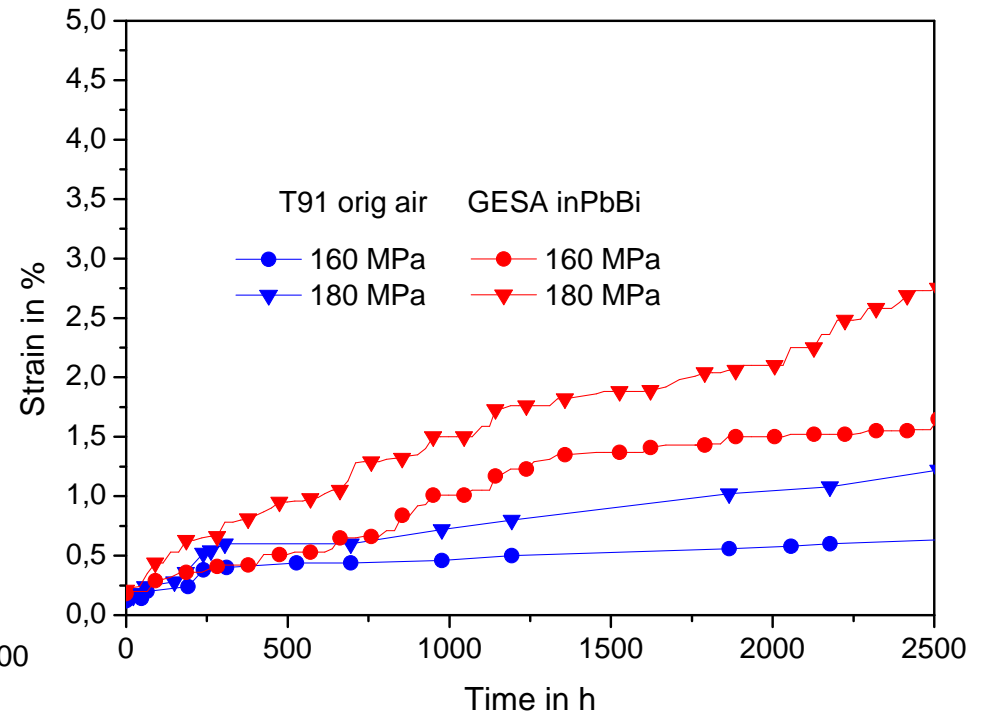


# Comparison of creep of GESA surface modified T91 in PbBi and T91 orig. in air at 550°C

Stress: 200 and 220 MPa

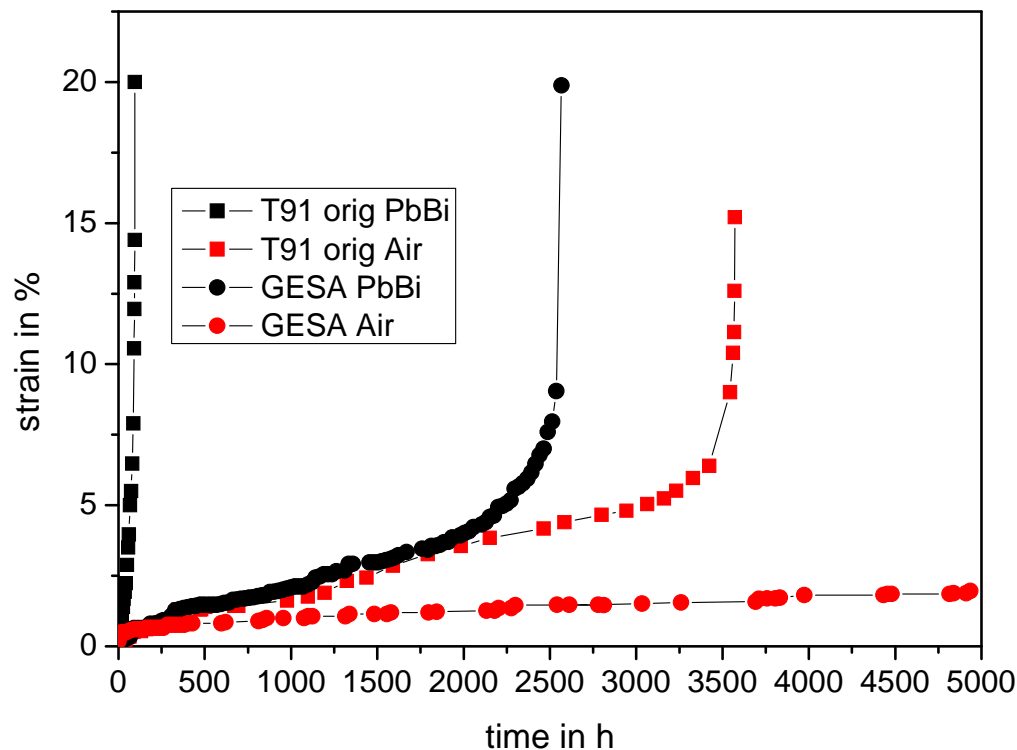


Stress 160 and 180 MPa



***T91 with GESA modified FeCrAl layer also shows an influence of LBE. However, this deterioration is significantly reduced compared to the T91 original. At 200MPa still a reduction in time to rupture from 3500 auf 2500h is observed. At a strain of about 3.5% influence of PbBi becomes visible.***

# Comparison of creep to rupture (200 MPa) of GESA surface modified T91 and T91 orig. in air and PbBi at 550°C

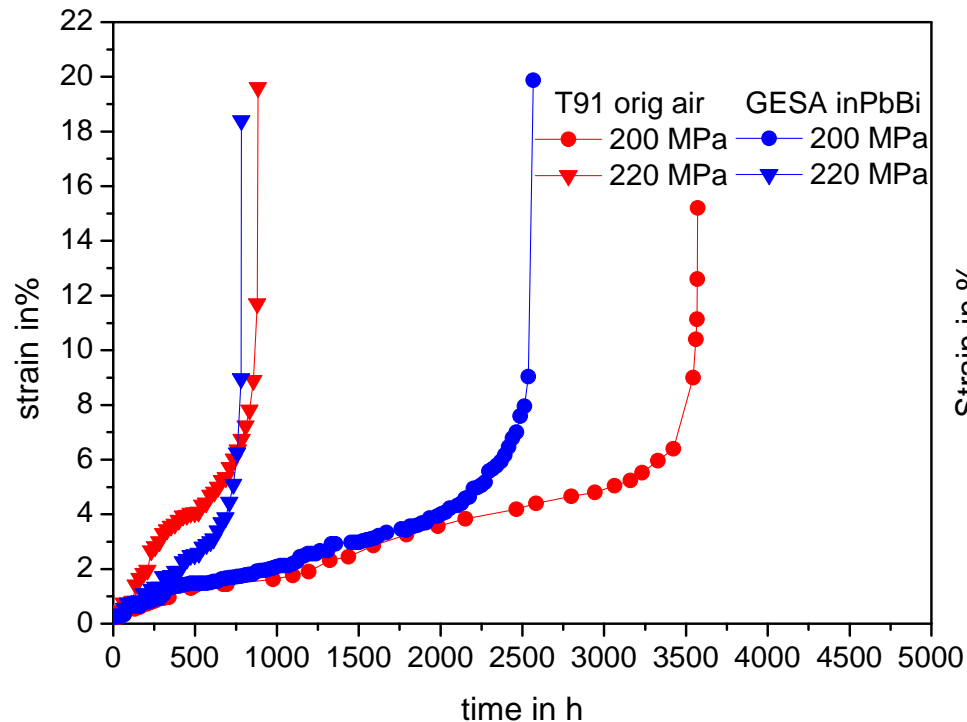


*Negative influence of LBE on creep strength of T91 is strongly reduced by the surface alloyed layer*

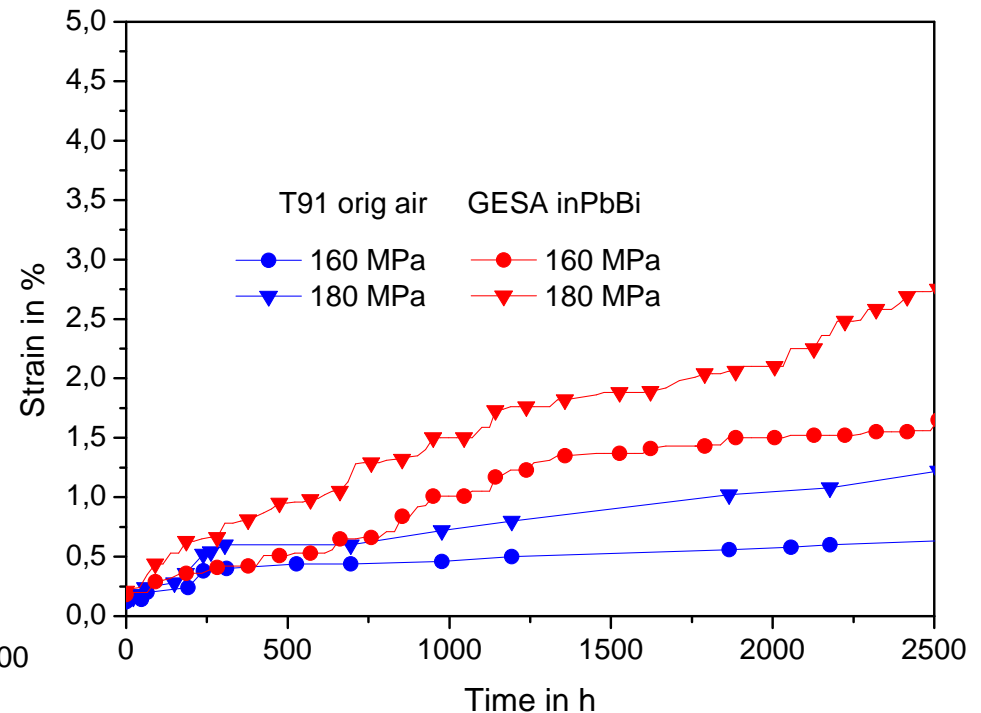


# Comparison of creep of GESA surface modified T91 in PbBi and T91 orig. in air at 550°C

Stress: 200 and 220 MPa



Stress 160 and 180 MPa

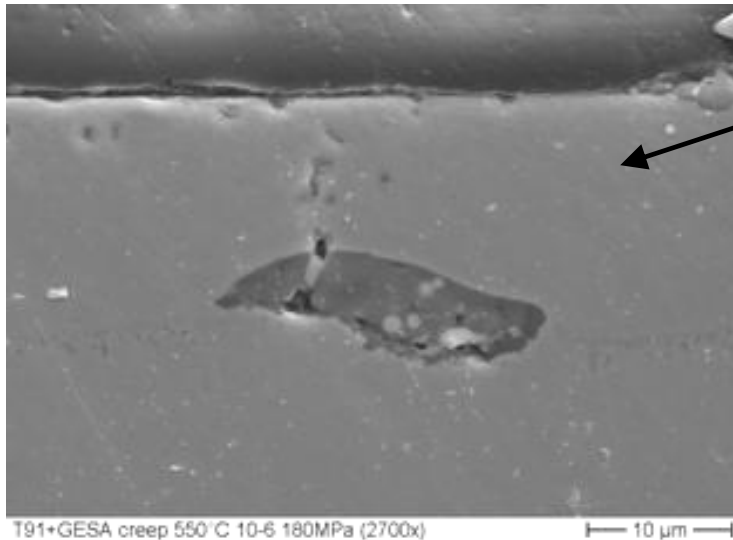


***T91 with GESA modified FeCrAl layer also shows an influence of LBE. However, this deterioration is significantly reduced compared to the T91 original. At 200MPa still a reduction in time to rupture from 3500 auf 2500h is observed. At a strain of about 3.5% influence of PbBi becomes visible.***

# GESA Specimens after creep to rupture experiments in PbBi 180 and 220 MPa 550°C

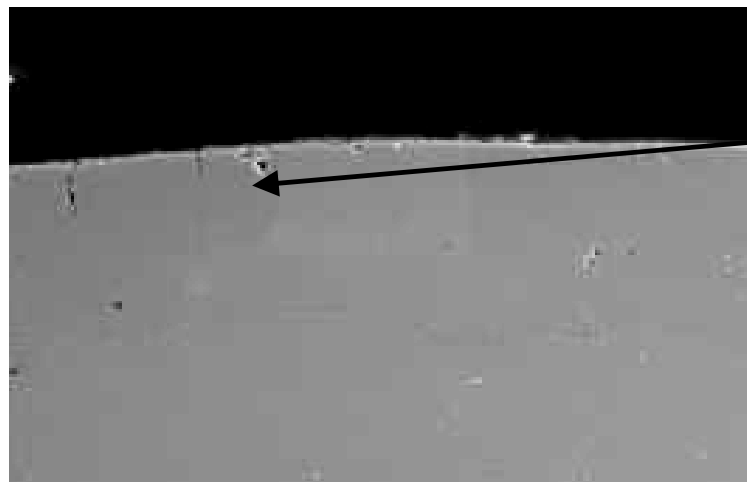
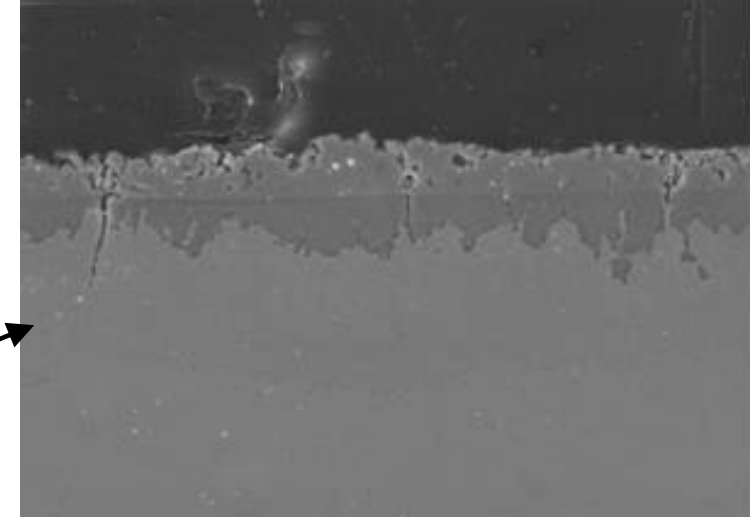
*Al-content sufficiently high → Alumina*

*Al-content < 4wt% → Spinel und Magnetite*



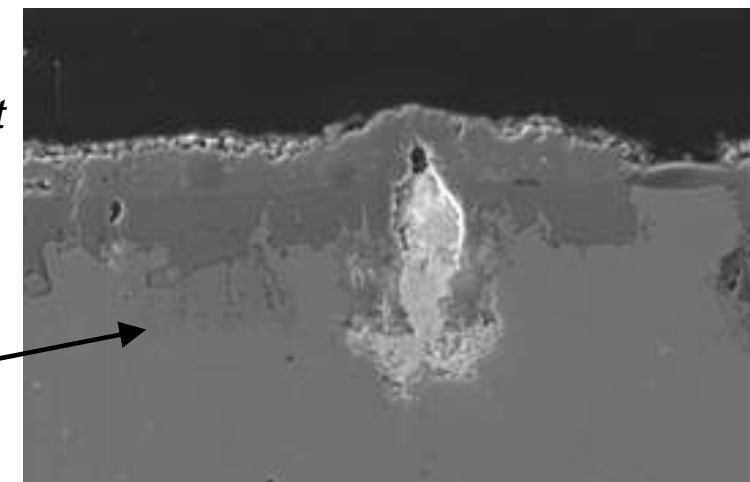
*180 MPa 2.2% strain  
→ only minor cracks*

*Cracks in magnetite  
and spinel  
Up to now no PbBi  
penetrated*



*At the border to the  
necking region cracks but  
no PbBi*

*Cracks in magnetite und  
spinel  
PbBi penetrated*



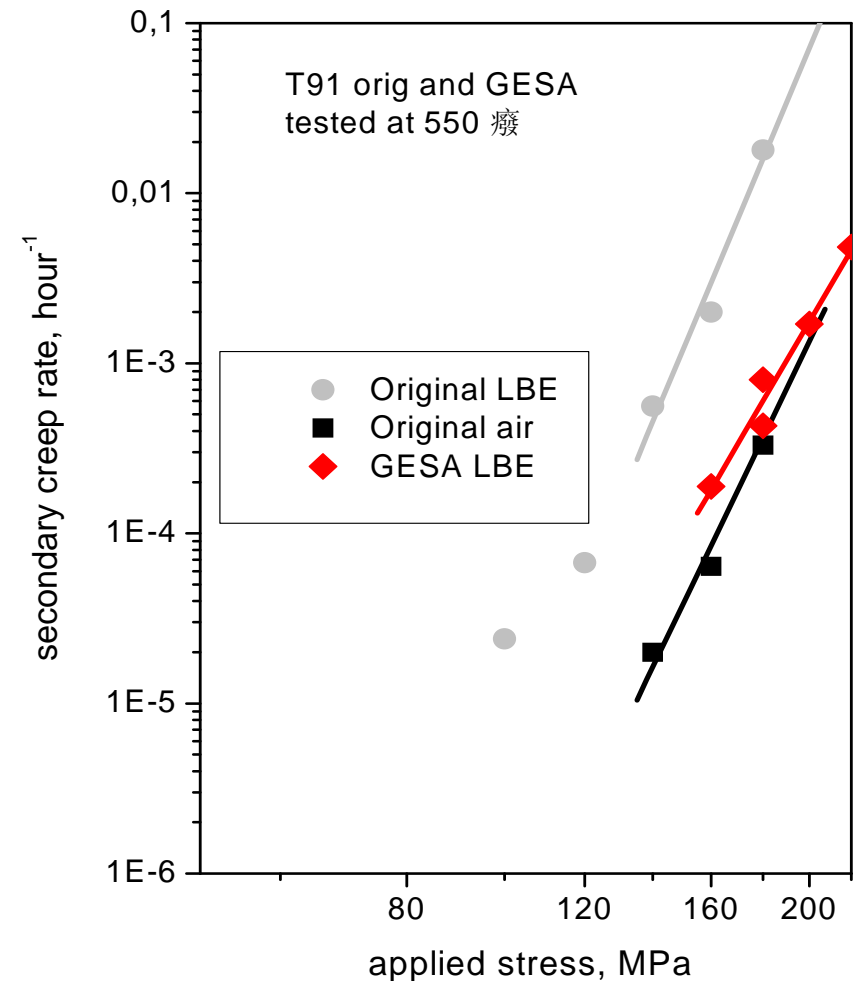
# Comparing 2<sup>nd</sup> creep rate of T91 original at 550 °C in air and PbBi and T91 GESA in PbBi

## ***T91 GESA:***

- ***2<sup>nd</sup> creep rate in PbBi similar that of T91 original in air***

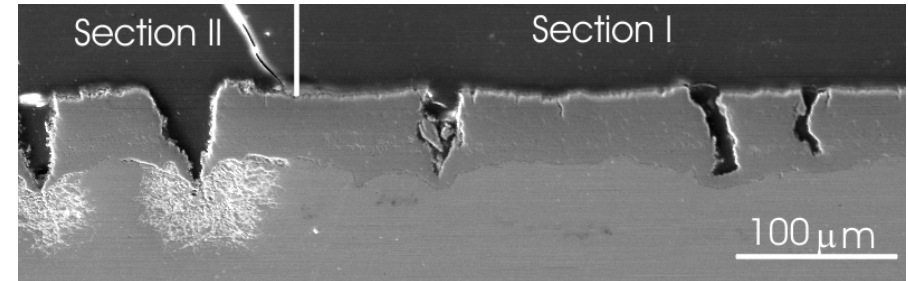
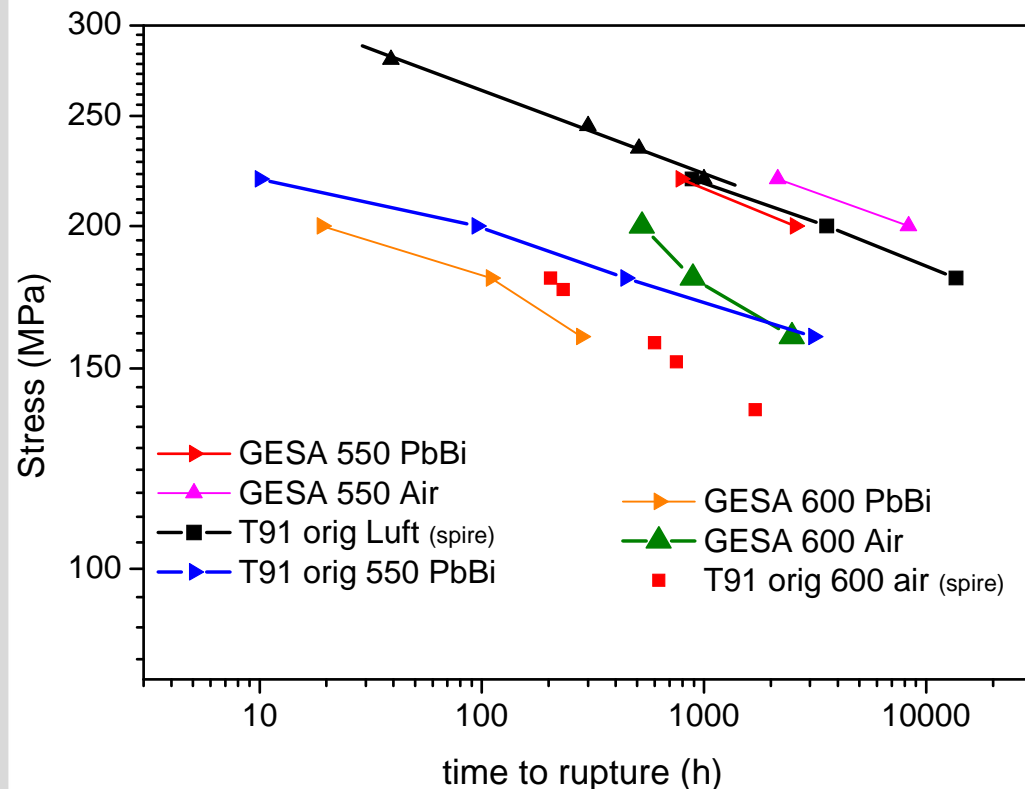
***GESA modified FeCrAlY reduces the negative influence of PbBi at 550°C***

***Specimens not entirely protected by thin alumina scale → with optimized specimens an even better result to be expected***

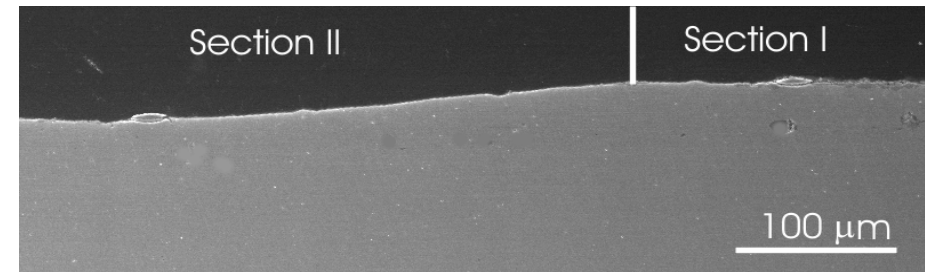


# Creep to rupture of T91 with and without GESA in PbBi and air at 550°C

Stress over time to rupture of T91 original and T91 GESA



Oxide scale cracks → PbBi penetrates the crack → PbBi reduces surface energy of steel → dissolve steel elements and penetrates the grain boundaries → crack propagation



GESA modified FeCrAlY layer reduces the negative influence of PbBi  
No cracking of oxide scale → no influence of PbBi

# Summary

**Concept of strong oxide formers improves significantly the compatibility between steel and PbBi**

**Al content has to be high enough to ensure the formation of slow growing thin and stable scales**

**Process optimization towards Al-content, homogeneity and reproducibility is ongoing**

**Negative influence of PbBi on creep strength of T91 f/m steel tested at high stress at 550°C**

**At 550°C low stress and at 500 °C significant reduced influence – Oxide scale stays intact – no cracks – no direct contact**

**Surface alloyed layers improve significantly the creep behaviour in liquid PbBi**

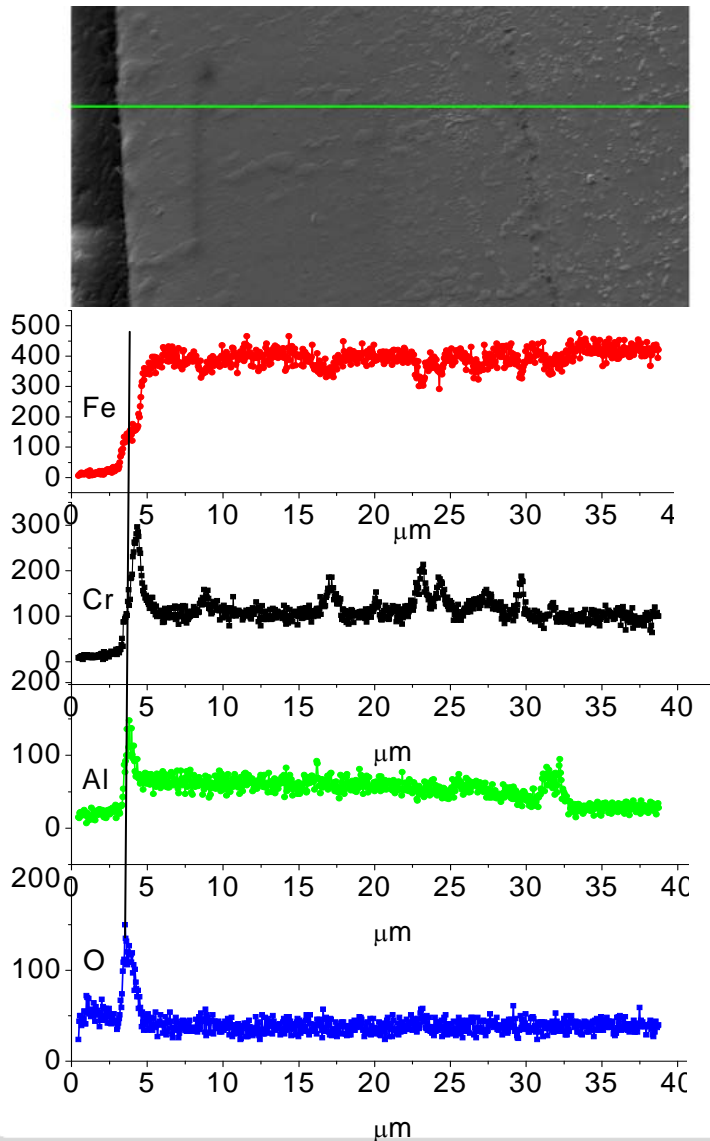
**At 550°C very similar to T91 orig. in air**

## **Acknowledgement:**

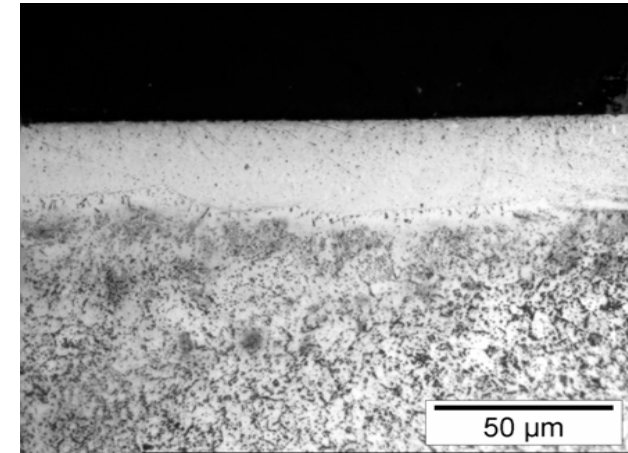
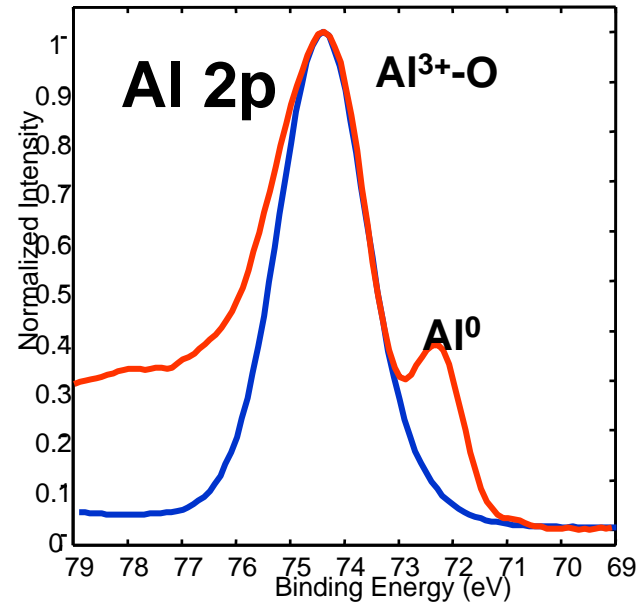
V.G. Markov, A.D. Kashtanov Central Research Institute of Structural Materials – “Prometey”, 49 Shpalernaja, St. Petersburg, 191015, Russia



# T91 surface modified specimens after 2000h of exposure 600 °C



XPS Measurement



Outer scale of Al oxide followed by chromium

Al precipitations at boundary layer ( $\text{Fe}_3\text{Al}$ )

No diffusion of Al into the bulk

Thin stable oxide layer protects the T91 cladding