Karlsruhe Institute of Technology

24th International Conference on Nuclear Engineering (ICONE24)
June 26–30, 2016, Charlotte, North Carolina

Corrosion of 9%Cr Ferritic / Martensitic Steels at 450 and 550°C in Flowing Pb-Bi Eutectic with 10^{-7} mass% Dissolved Oxygen

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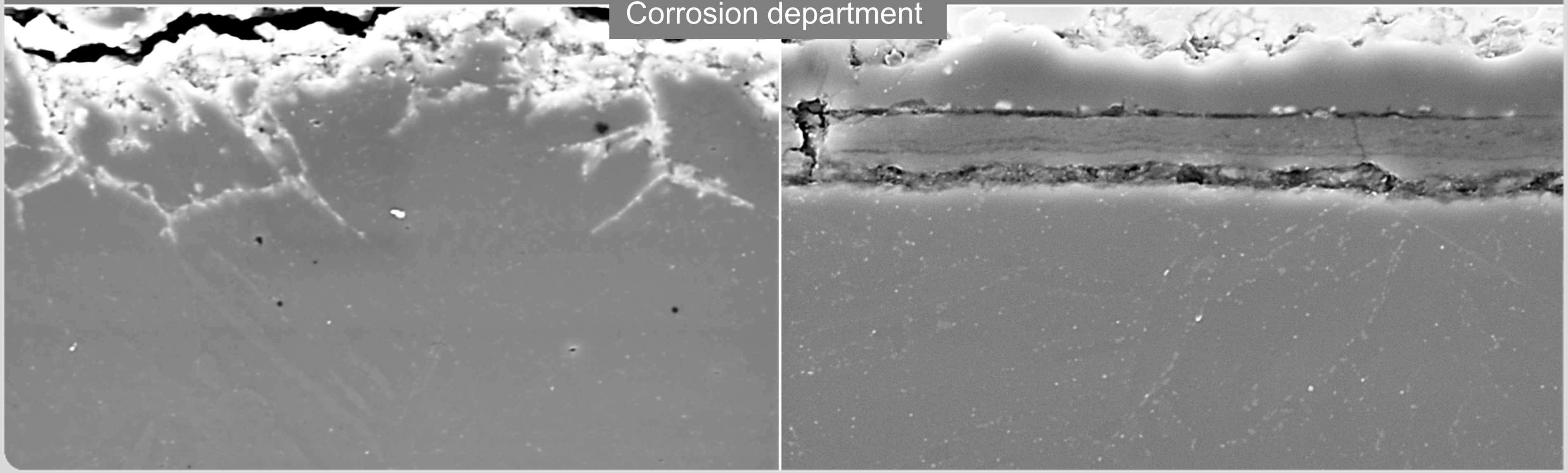
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-WPT)

Corrosion department

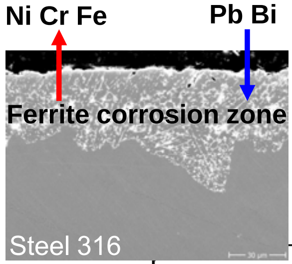


Liquid metal corrosion - background

Issue !

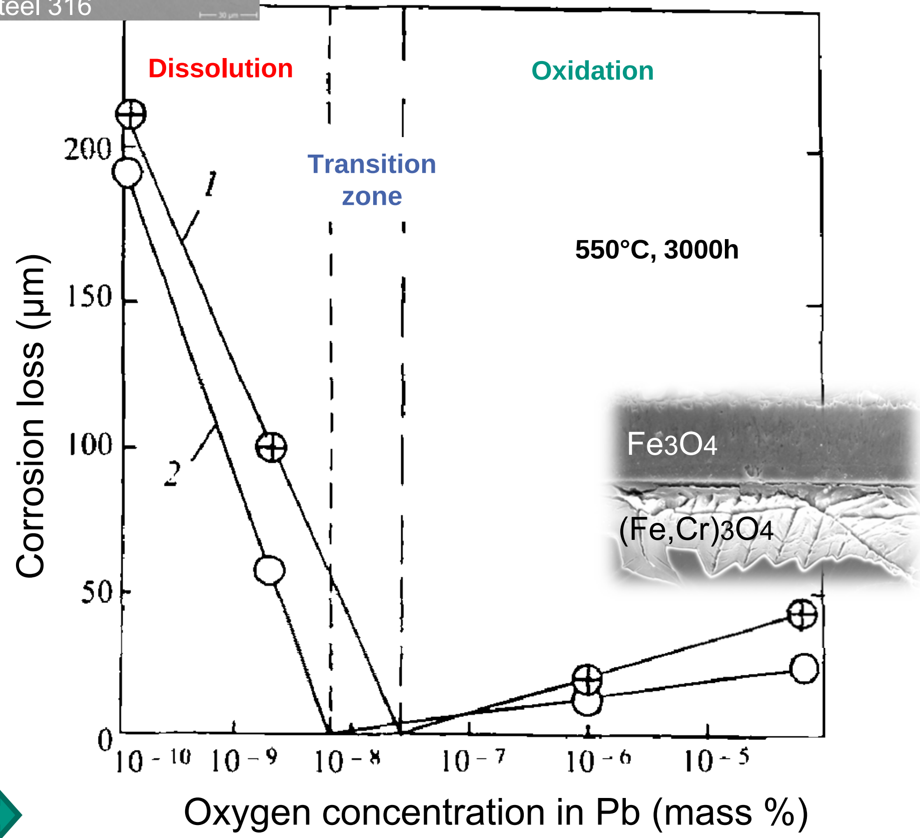
❑ Dissolution of Ni, Cr and Fe from the steel by liquid metal:

- Formation of week corrosion zone with ferrite structure on austenitic matrix
- Liquid metal penetrates into the ferrite



Earlier findings !

I.V. Gorynin et al. Met. Sci. Heat Treat. 41 (9) (1999) 384–388.



1 and 2 – austenitic steels of 316L type

Solution !?

❑ Oxidation instead of dissolution:

- Formation of continuous and protective oxide layer
- Long-term operation of scale in protective mode

Thermodynamic basis for in-situ addition of oxygen into liquid Pb-Bi

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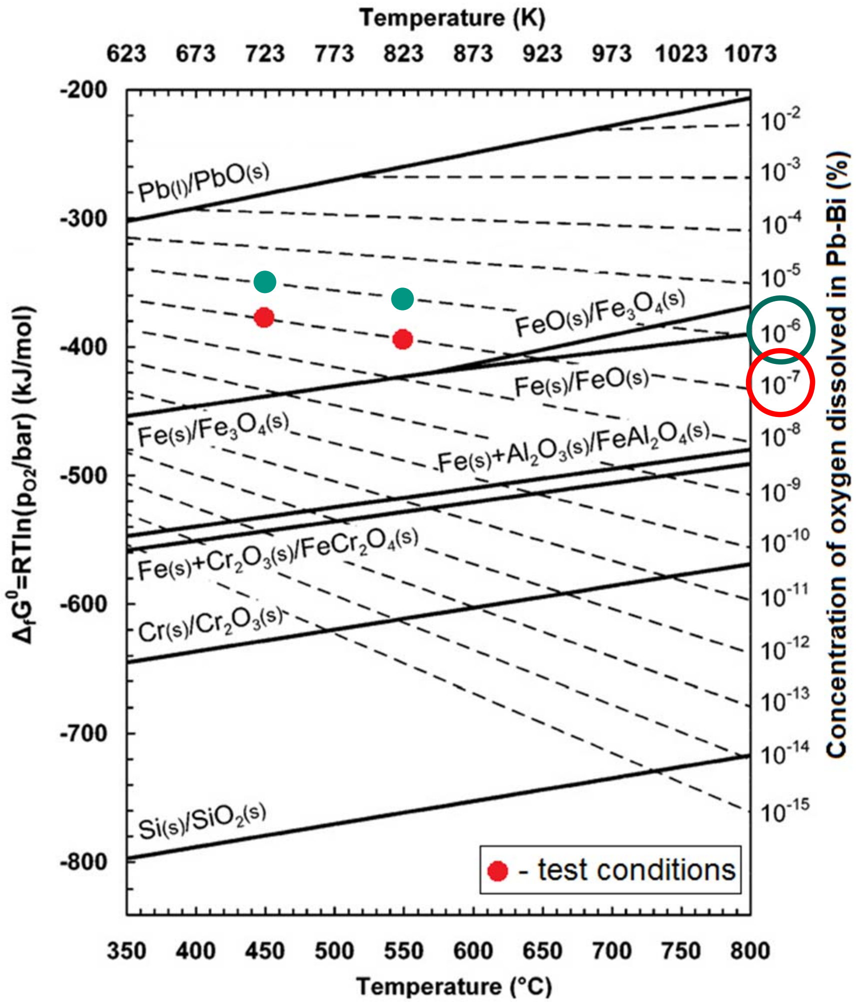


BASIS of Pb-Bi technology

- Pb-Bi dissolves and transports the oxygen;
- Components of steels (Si, Cr, Fe…) have high affinity to oxygen than Pb or Bi.

- **Main aim of the corrosion tests** is to determine the optimum temperature-oxygen concentration parameters for save and long-term operation of structural materials in contact with liquid Pb-Bi eutectic.

Previous test:

● **Co = 10^{-6} mass%, T = 450 and 550°C**

This work:

● **Co = 10^{-7} mass%, T = 450 and 550°C**

F/M steels tested in the CORRIDA loop

Concentration (in mass%) of alloying elements other than Fe

	Cr	Mo	W	V	Nb	Ta	Mn	Ni	Si	C
T91-A	9.44	0.850	<0.003	0.196	0.072	n.a.	0.588	0.100	0.272	0.075
T91-B	8.99	0.89	0.01	0.21	0.06	n.a.	0.38	0.11	0.22	0.1025
P92	8.99	0.49	1.75	0.20	0.06	-	0.43	0.12	0.26	0.11
E911*	8.50-9.50	0.90-1.10	0.90-1.10	0.18-0.25	0.06-0.10	-	0.30-0.60	0.10-0.40	0.10-0.50	0.09-0.13
EUROFER	8.82	0.0010	1.09	0.20	n.a	0.13	0.47	0.020	0.040	0.11

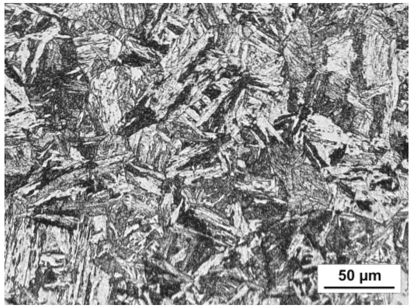
*nominal composition

⇧ Nominally 9 mass% Cr

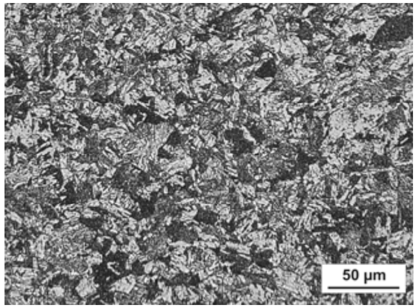
⇧ Element besides Cr that improves oxidation resistance

Martensitic microstructure of F/M steels

E911, T91-A, T91-B, P92



Grain size



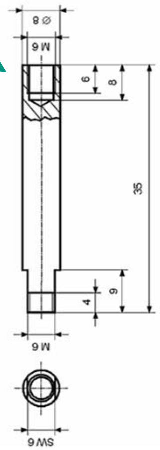
EUROFER

Samples and test facility

Sample with fine finishing by turning

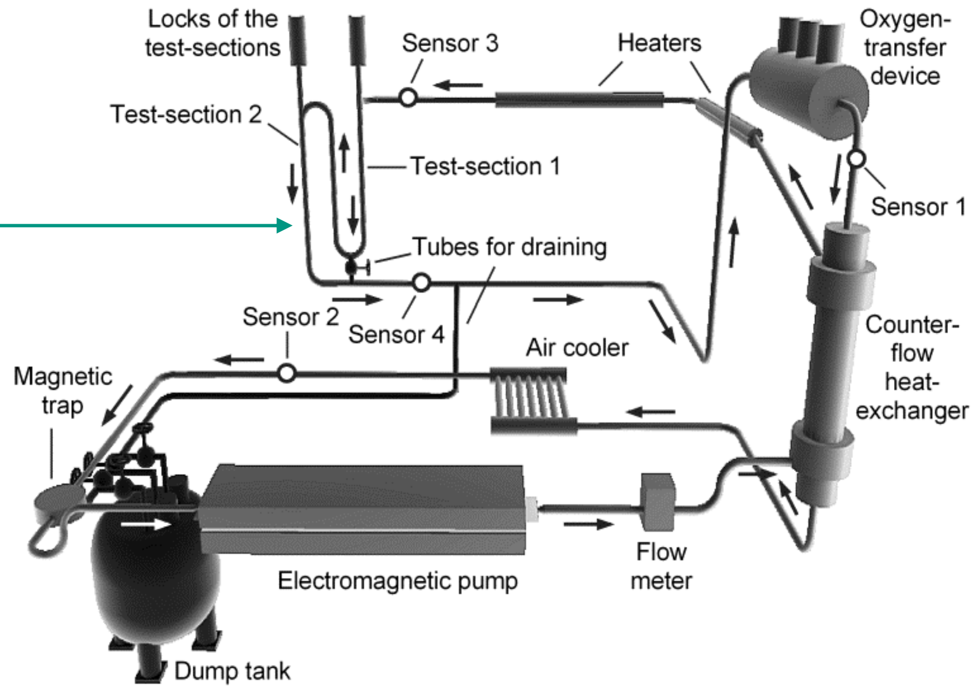
Outer and inner threaded connection

Sample drawing



Sample assembly

CORRosion **I**n **D**ynamic lead **A**lloys
CORRIDA loop



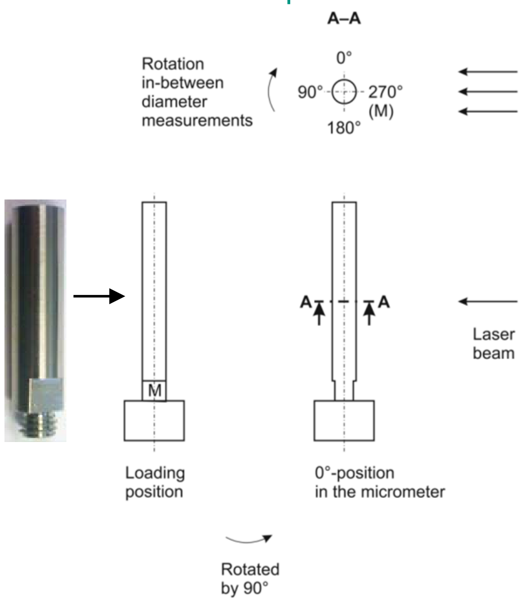
The CORRIDA facility – a forced-convection loop made of austenitic stainless steel (1.4571) designed to expose material (steel) specimens to flowing (2 m/s) Pb-Bi eutectic (~1000 kg) <u>with controlled oxygen concentration</u>.

Quantification of corrosion loss

- **Goal of quantification**
  - Material loss, average of general corrosion and maximum of local corrosion
  - Thickness of adherent (oxide) scale
  - Overall change in dimensions, including the scale
  - Amount of metals transferred to the liquid metal

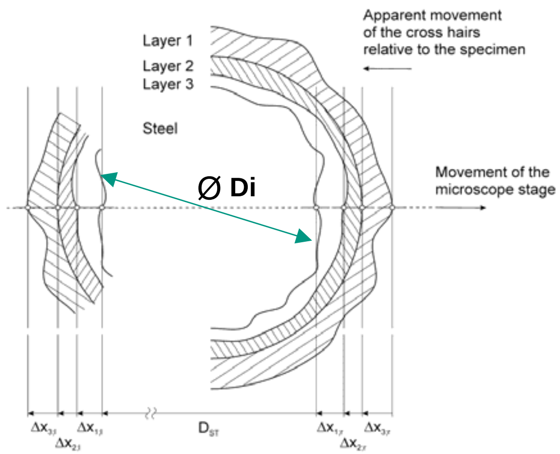
- **Metallographic method (cylindrical specimens)**

Initial parameters - Ø



- Measurement of <u>initial diameter</u> in a laser micrometer with 0.1 µm resolution
- Diameter of unaffected material (12th measurements with rotation angle 15°) and thickness of corrosion zones determined in a microscope (LOM) with 1 µm resolution
- Corrosion modes on opposing sides of the re-measured diameter are evaluated (% of surface circumference)

Post-test examination



Transverse circular cross-section

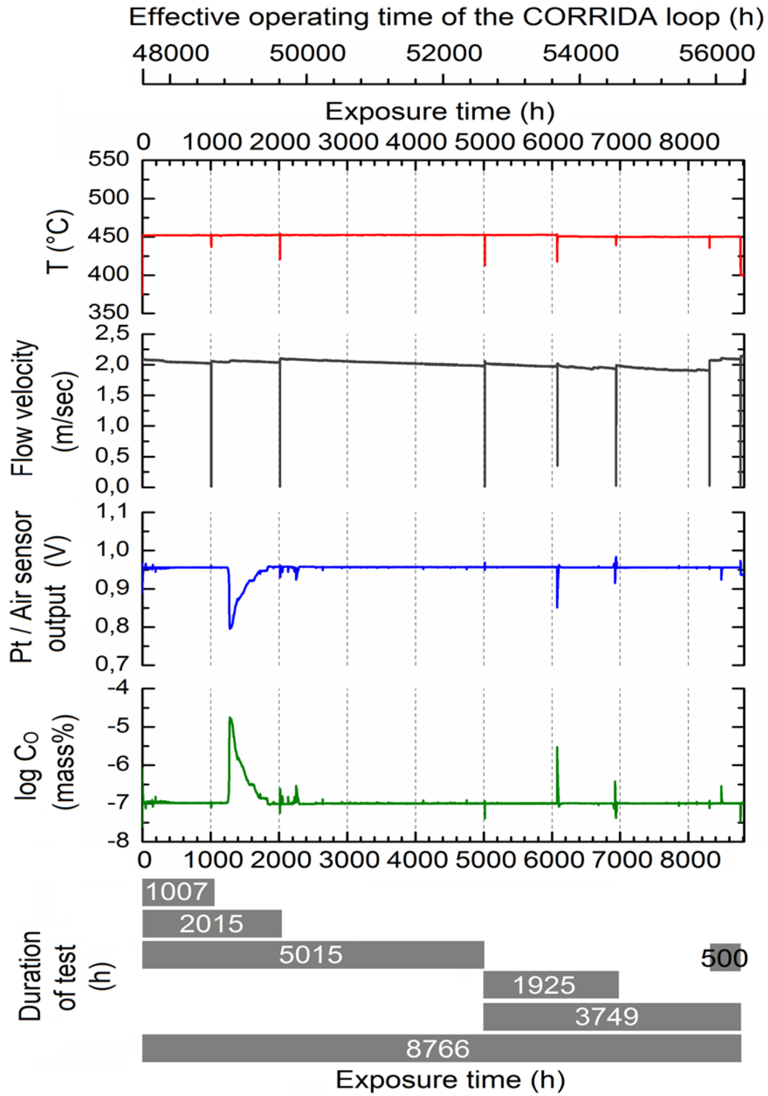
$$\Delta X_{ST} = \frac{1}{2}\left(D_0 - \left(\frac{\sum D_i}{i}\right)\right)$$

Corrosion test at 450°C in flowing Pb-Bi (2 m/s) with 10^{-7} mass% dissolved oxygen

- T = 450(+5)°C
  $T_{min} \approx$ 350°C
  $c_O = 10^{-7}$ mass%, excursion to 10^{-5} mass%
  v = 2(+/–0.2) m/s
  t = 500h

1007h
1925h
2015h
3749h
5015h
8766 h

Time



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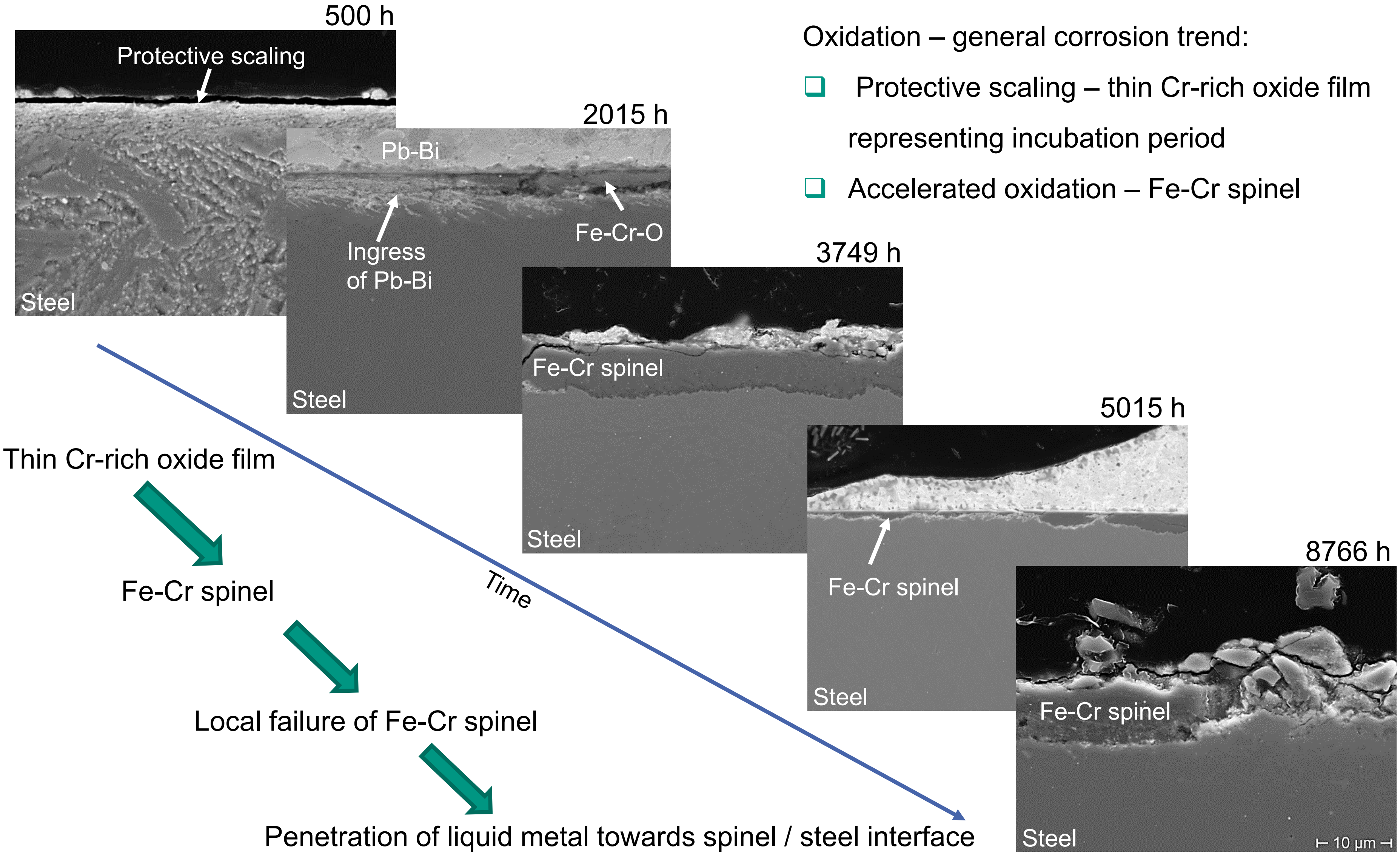
Corrosion appearances on surface of 9%Cr steels after test at 450°C in flowing Pb-Bi and 10^{-7}% dissolved oxygen

Oxidation – general corrosion trend:

- Protective scaling – thin Cr-rich oxide film representing incubation period
- Accelerated oxidation – Fe-Cr spinel



Thin Cr-rich oxide film

Fe-Cr spinel

Local failure of Fe-Cr spinel

Penetration of liquid metal towards spinel / steel interface

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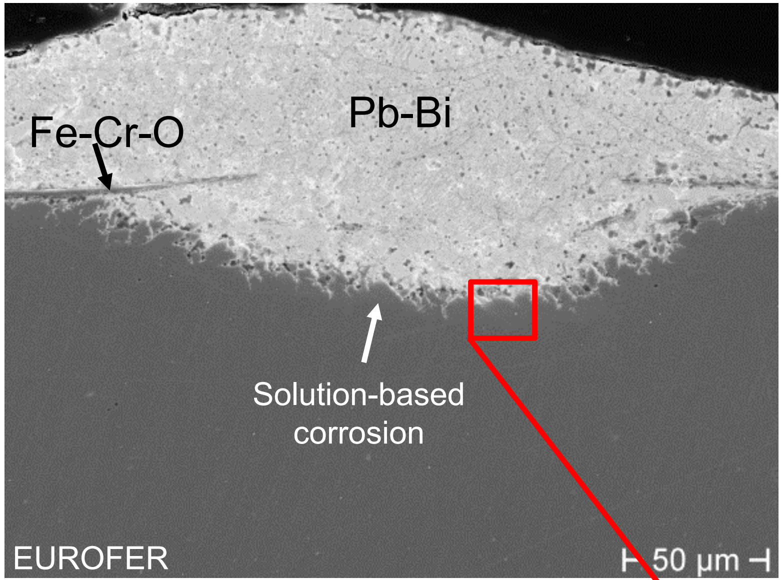
450°C, Pb-Bi with 10^{-7}% dissolved oxygen

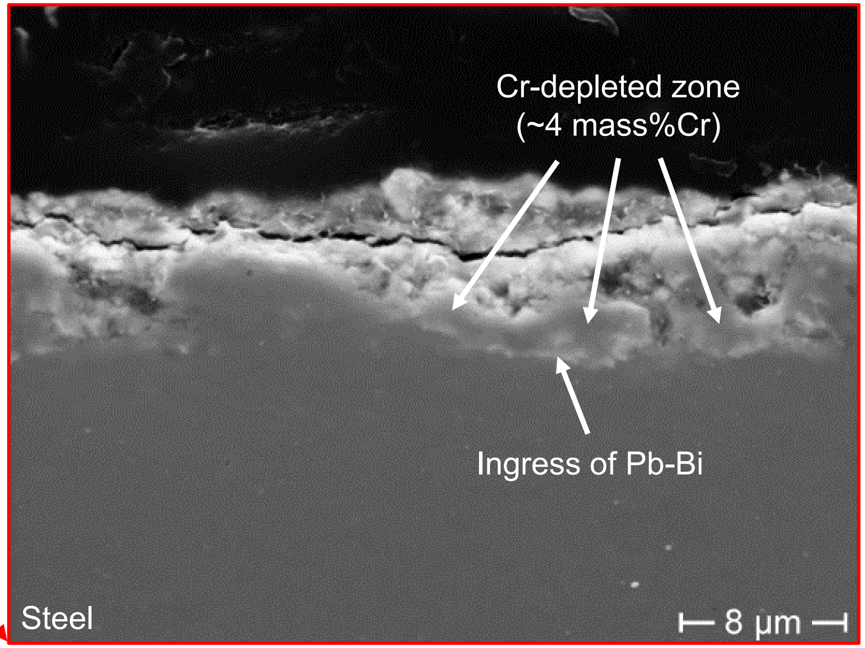
Solution-based attack – local corrosion trend

5015 h



Pit-type corrosion attack

8766 h



Detailed examination of near surface corrosion zone

Effect of increasing oxygen concentration

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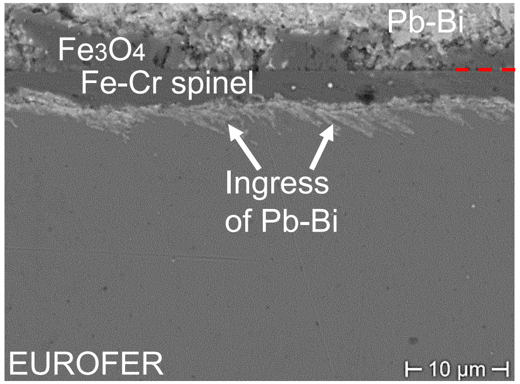
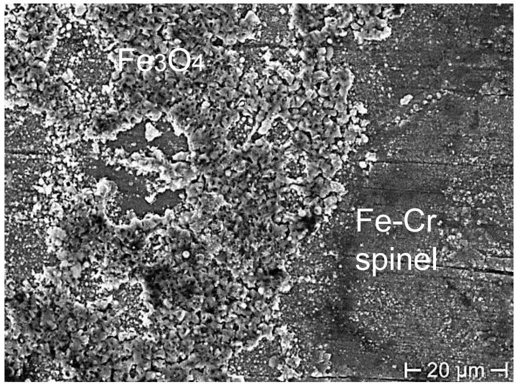
2015 h

Cross-section



X=0 – initial interface steel / Pb-Bi

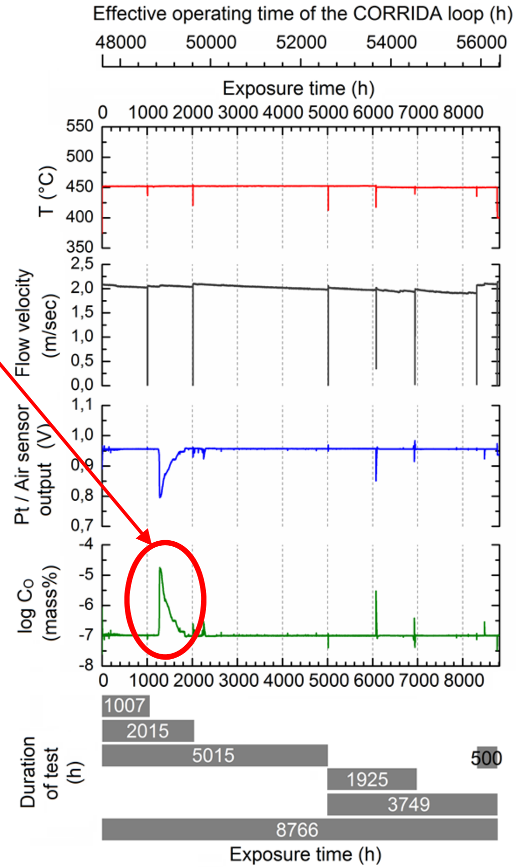
Surface



Magnetite crystals non-uniformly populate steel surface (Fe-Cr spinel surface)

- **Magnetite formation**
  - Magnetite forms as a result of temporary increase in oxygen concentration from 10^{-7} to ~10^{-5} mass%
  - Magnetite is not observed after return to target 10^{-7} mass% O

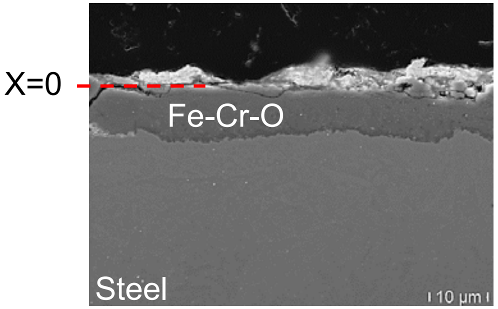
Magnetite dissolves!

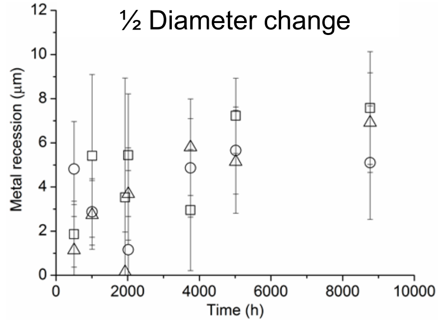


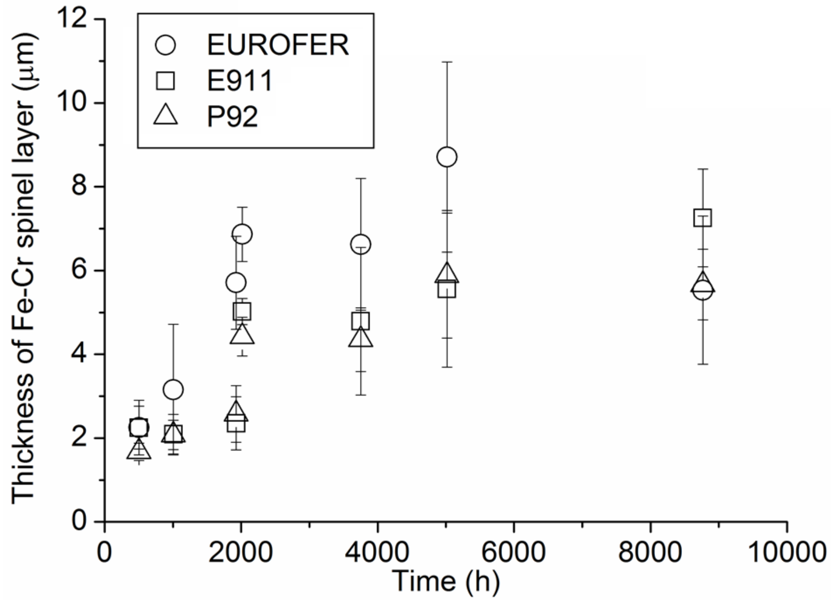
Quantification of corrosion loss on 9%Cr F/M steels after exposure to flowing Pb-Bi at 450°C, 2 m/s, 10^{-7} mass% O

Accelerated oxidation

General corrosion trend

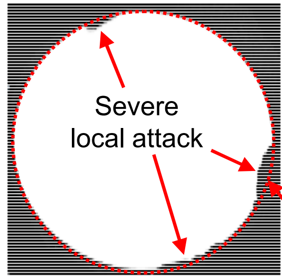




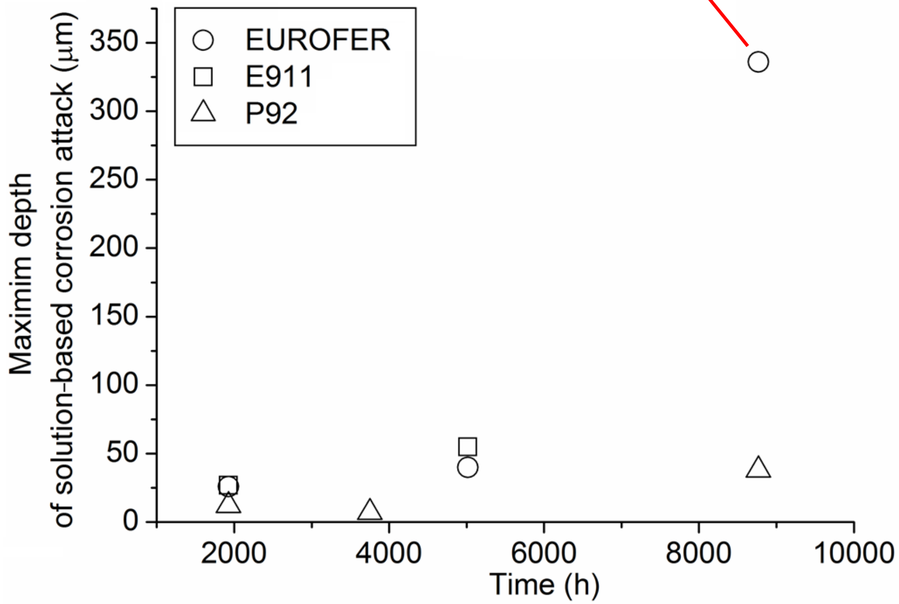


Solution-based leaching of steel constituents (Fe, Cr)

Local corrosion trend



Incubation time 500-2000h



Corrosion test at 550°C in flowing Pb-Bi (2 m/s) with and 10^{-7} mass% dissolved oxygen

- T = 550(+5)°C

  $T_{min} \approx 385$°C

  $c_O = 10^{-7}$ mass%, excursion to 10^{-4}–10^{-5} mass%

  v = 2(+/–0.2) m/s, initially 1.5–1.6 m/s

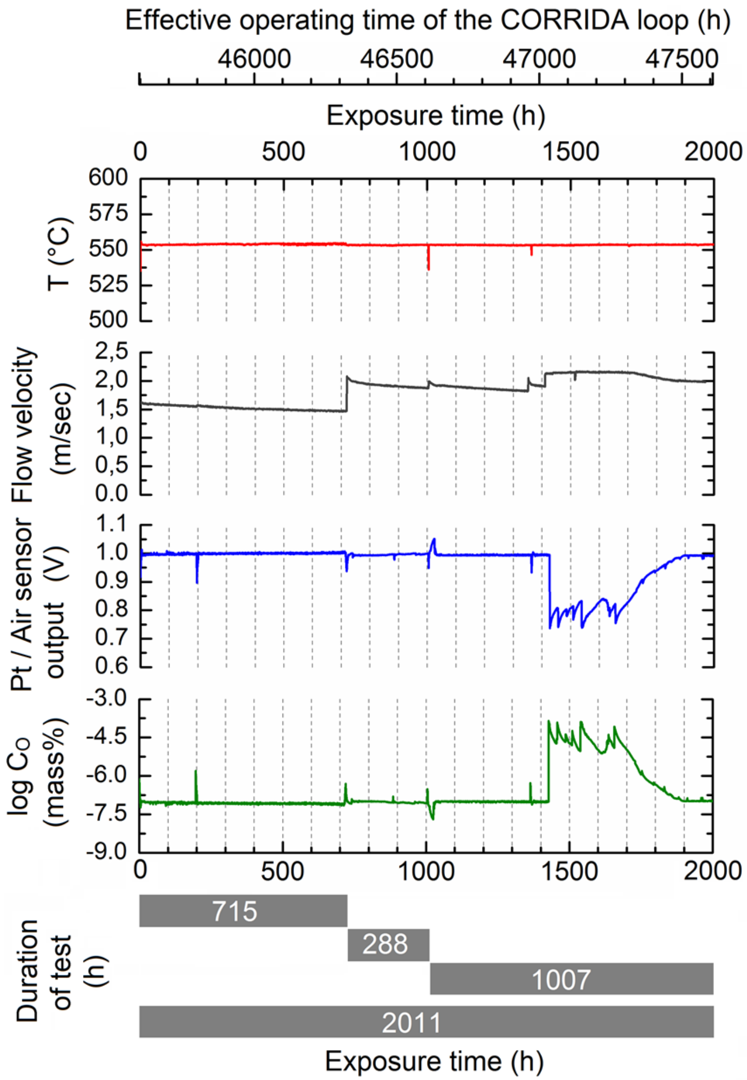
  t = 288h

  715h

  1007h

  2011 h

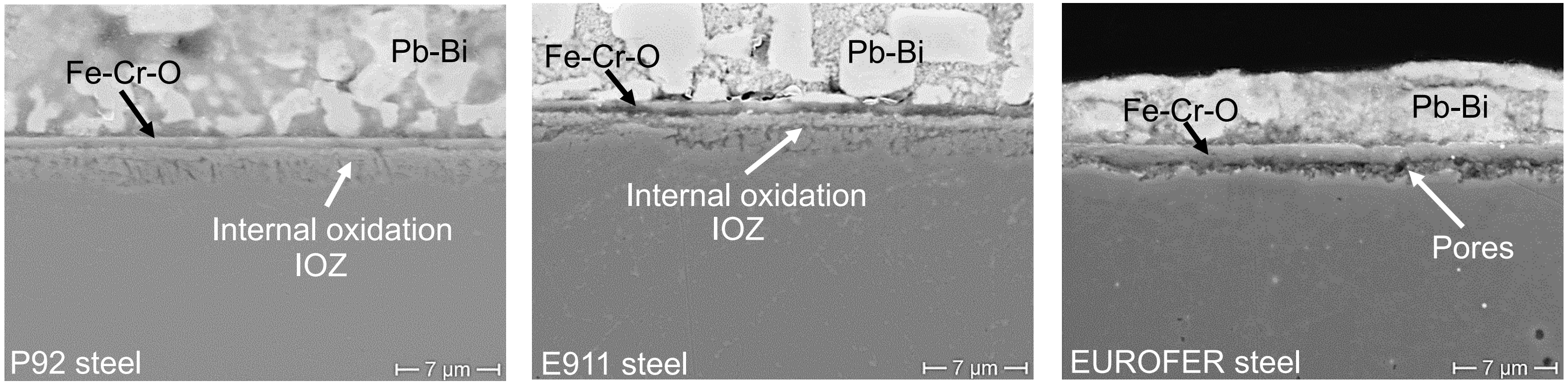
Time

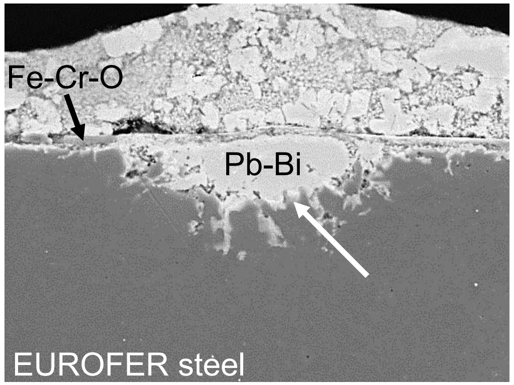


Phenomena observed on 9%Cr steels after test at 550°C in flowing Pb-Bi and 10^{-7}% dissolved oxygen

288 h

General corrosion trend





Local corrosion trend

- ❑ Oxidation (Fe-Cr spinel + IOZ) – general corrosion trend
  - IOZ – Cr-based oxides in non-oxidized Fe-matrix
- ❑ Pit-type solution-based attack – local corrosion trend

550°C, 10^{-7}% dissolved oxygen

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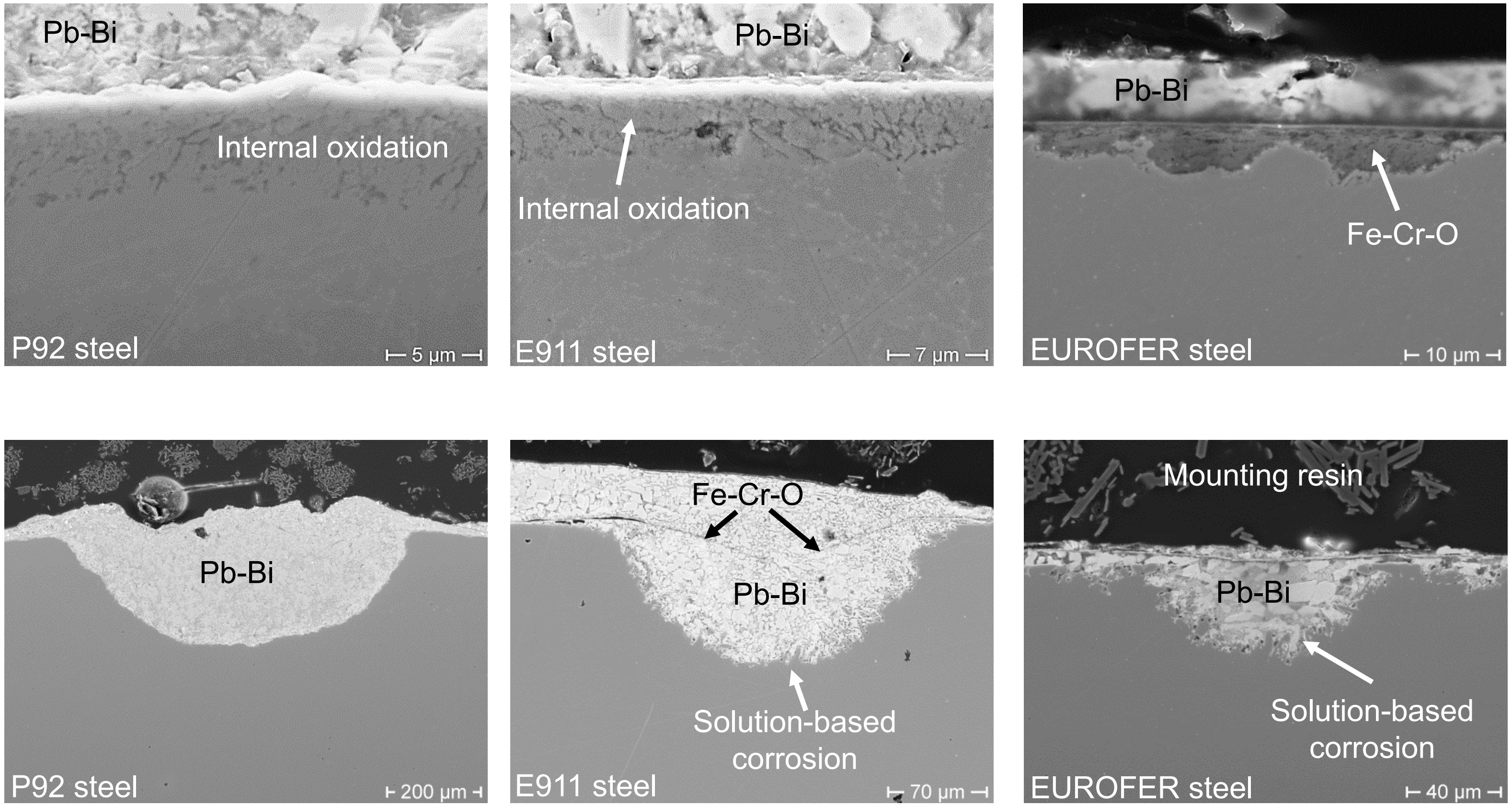
715 h

General corrosion trend

Local corrosion trend

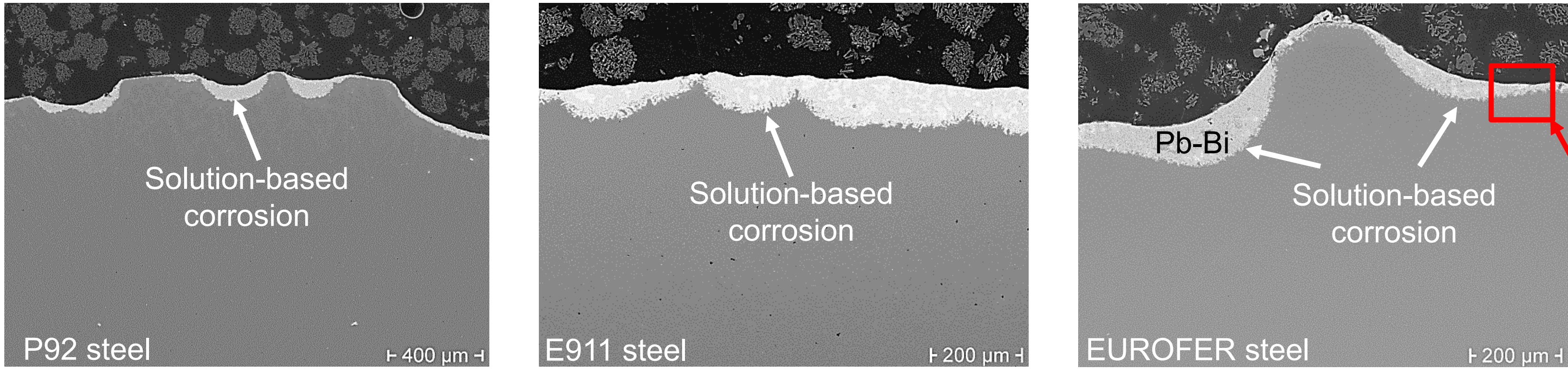


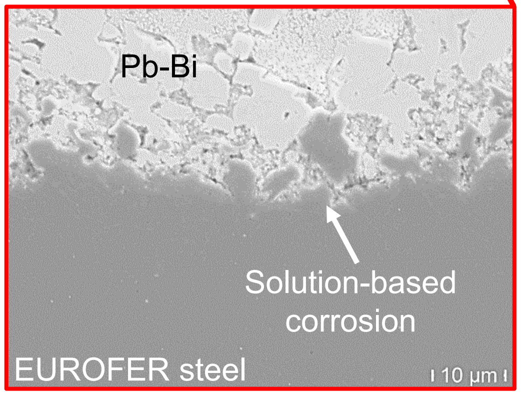
- Oxidation (Fe-Cr spinel + IOZ) – general corrosion trend
- Pit-type solution-based attack – local corrosion trend

550°C, 10^{-7}% dissolved oxygen

1007 h

General corrosion trend

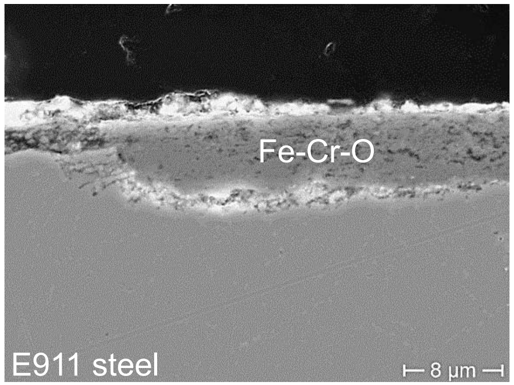




- Severe material ablation due to solution-based attack – general corrosion trend

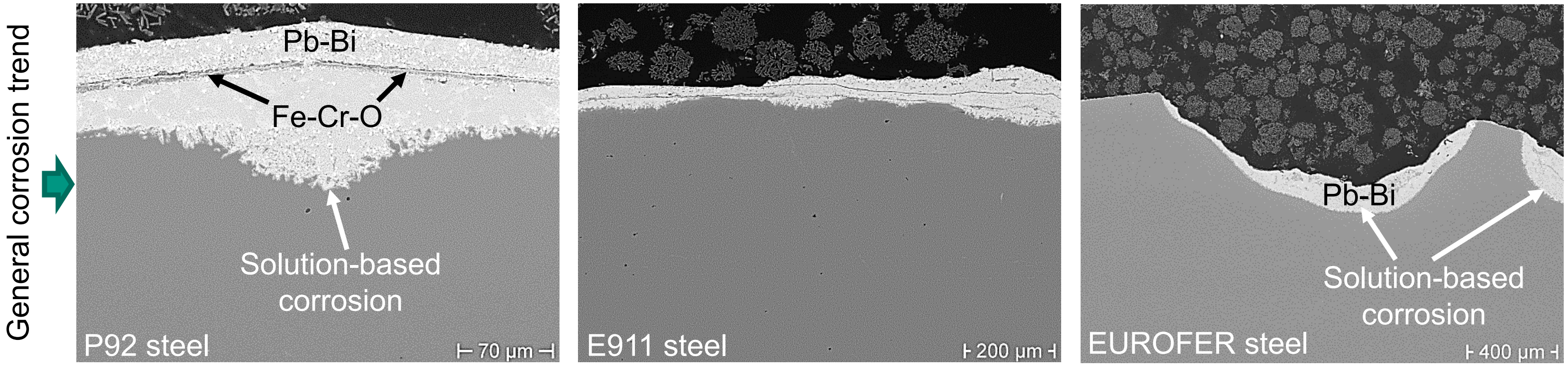
- Oxidation (Fe-Cr spinel) – local corrosion trend

Local corrosion trend



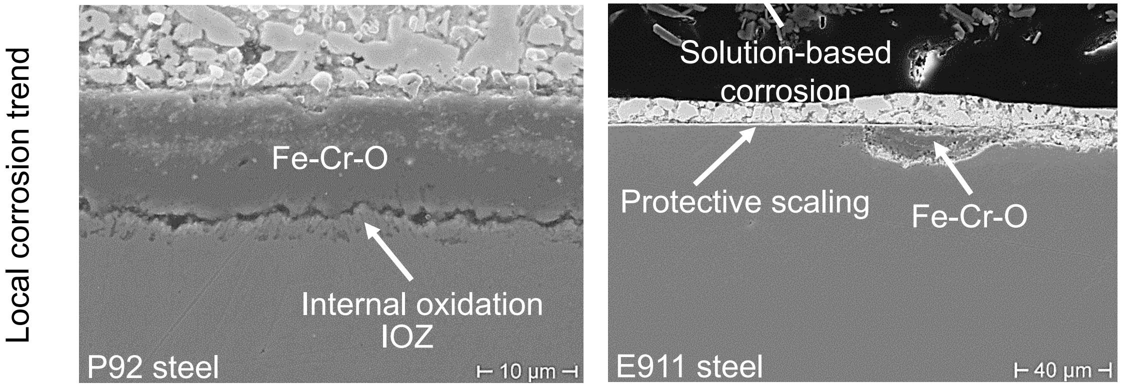
550°C, 10^{-7}% dissolved oxygen

2011 h



- Severe solution-based attack – general corrosion trend

- Oxidation – local corrosion trend:
  - Fe-Cr spinel + IOZ
  - Cr-rich film - protective scaling



Quantification of corrosion loss on steels after exposure to flowing Pb-Bi at 550°C, 2 m/s, 10^{-7} mass% O

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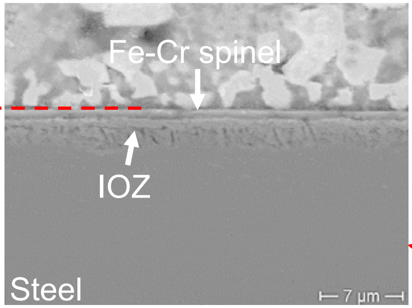
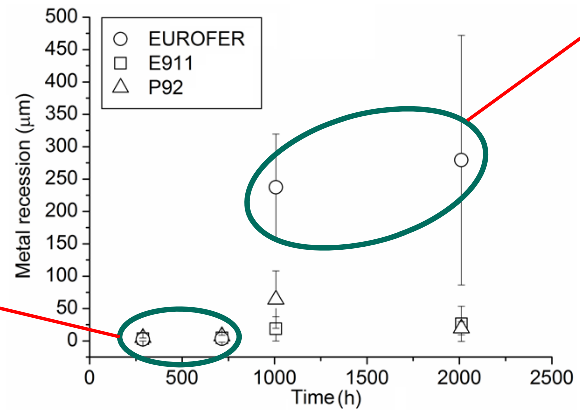
Accelerated oxidation

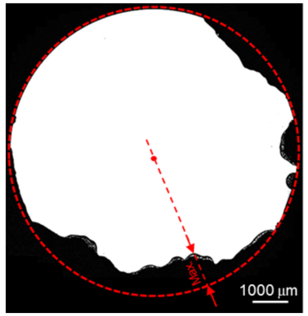
X=0



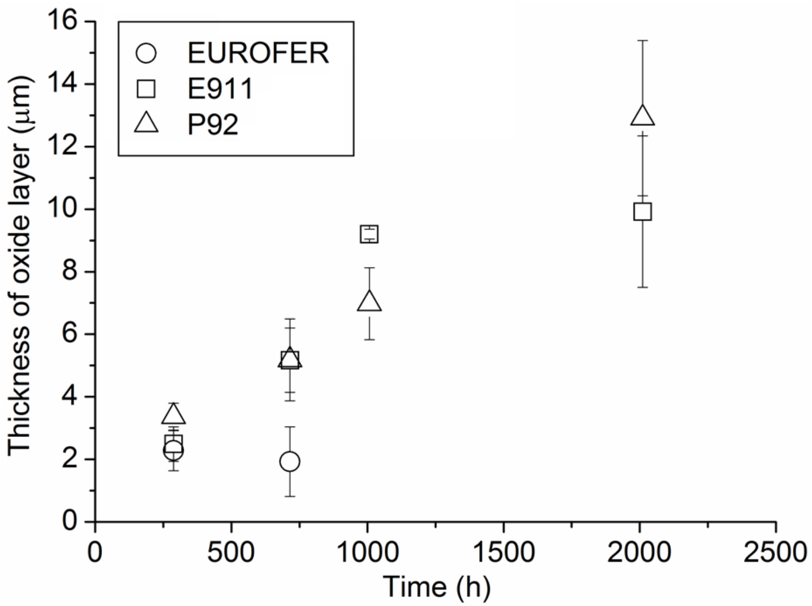
½ Diameter change



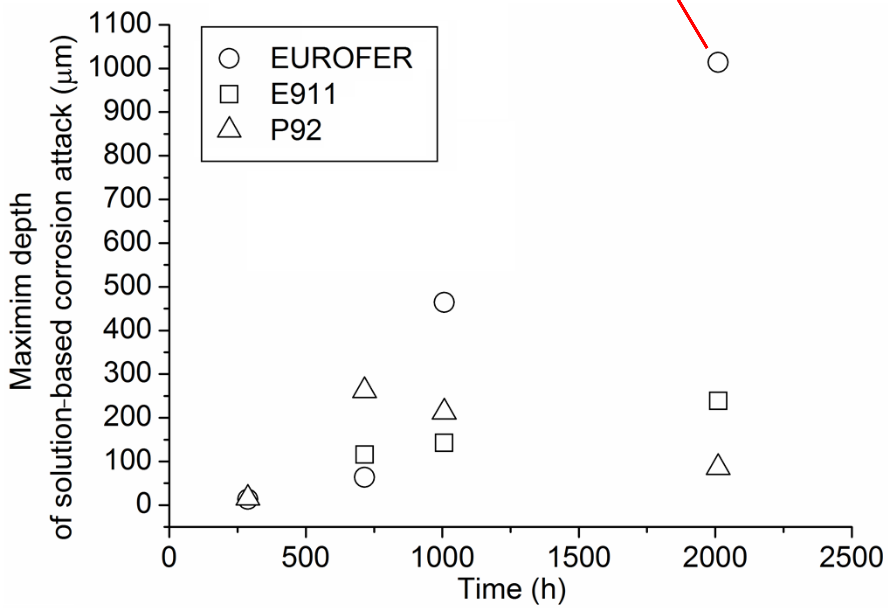
Solution-based leaching of steel constituents (Fe, Cr)



Severe general attack



Incubation time < 300 h



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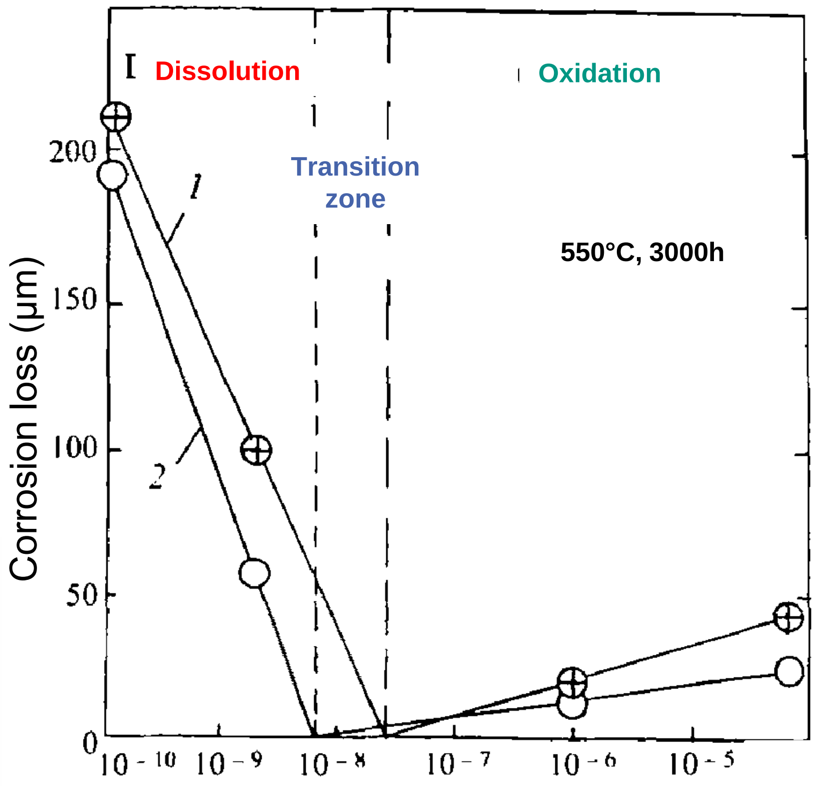
Comparison of earlier findings with last ones !

Earlier findings !

Todays findings !

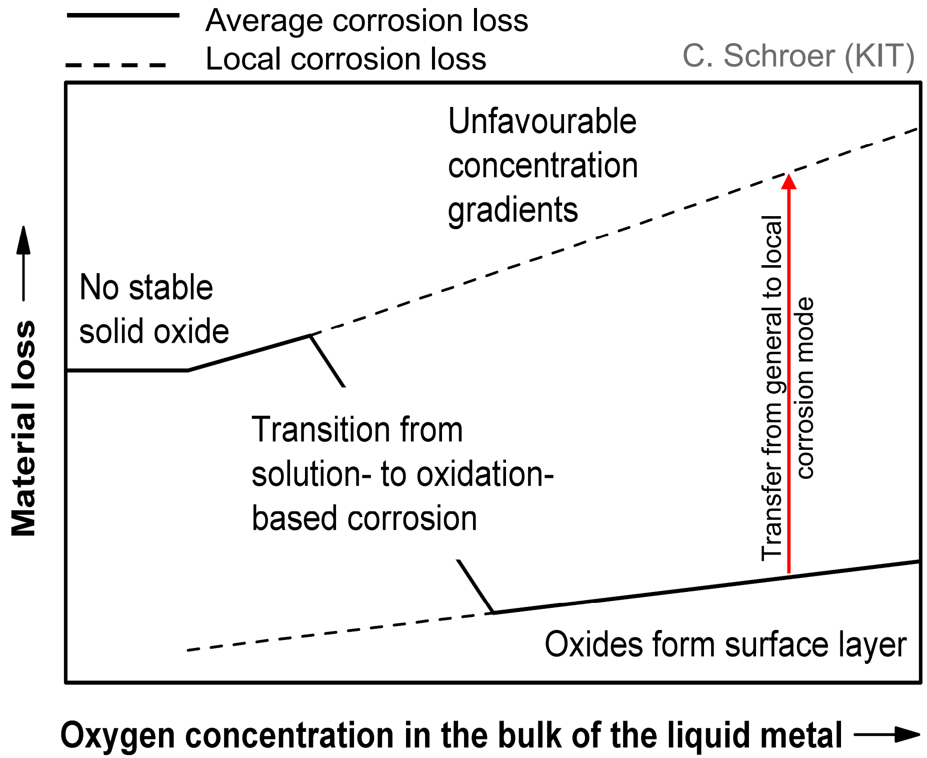
I.V. Gorynin et al. Met. Sci. Heat Treat. 41 (9) (1999) 384–388.



1 and 2 – austenitic steels of 316L type

- In general correct, but in particular too idealistic !

C. Schroer (KIT)



- In the oxide-protection regime the local failure of scale results in more severe solution-based corrosion attack instead of expected re-oxidation of steel surface!
- Task is to postpone the appearance of local attack!

Comparison of corrosion behaviour of 9%Cr steels in Pb-Bi depending on the oxygen concentration in the melt

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10^{-7} mass%O

Increase in oxygen concentration →

450°C

- Oxidation
  - Protective scaling – thin Cr-based film
  - Accelerated oxidation – thicker Fe-Cr spinel
- Local solution-based attack as a result of spinel failure
  - Incubation time 500-2000 h

550°C

- Oxidation
  - Protective scaling – thin Cr-based film
  - Accelerated oxidation – thicker Fe-Cr spinel
- General solution-based attack as a result of spinel failure and Cr-based oxide film
  - Incubation time < 300 h

10^{-6} mass%O

450°C

- Oxidation
  - Accelerated oxidation – Bi-layer scale Fe_3O_4 / $Fe(Fe,Cr)_2O_4$
- Local solution-based attack as a result of bi-layer scale failure
  - Incubation time > 8000 h

550°C

- Oxidation
  - Protective scaling – thin Cr-based film
  - Accelerated oxidation – thicker Fe-Cr spinel
- Local solution-based attack as a result of spinel failure and Cr-based oxide film
  - Incubation time 5000-15000 h

SUMMARY

- At 450 and 550°C, in flowing oxygen-containing LBE (2 m/s and 10^{-7} mass% O), **F/M steels with 9% nominal content of Cr (P92, E911, EUROFER) show following corrosion modes:**
  - Protective scaling – short term or local phenomenon (thin Cr-based oxide)
  - Accelerated oxidation – the general corrosion mode (thicker $Fe(Fe_xCr_{1-x})_2O_4$ scale) resulted in metal recession at 450°C of ~ 6 µm after one year
  - Solution-based corrosion
    - local at 450°C and ranged between 7-336 µm
    - general at 550°C and reached 13-1000 µm
- **EUROFER showed the largest corrosion loss** among the steels tested via accelerated oxidation and solution-based corrosion that might be caused by
  - less Si content, which normally improves protective properties of scales formed on P92 and E911 and prolongs incubation period
  - fine-grained structure that in combination with less protective oxide film might favor development of local solution-based corrosion attack after failure of scale
- **Comparison between 10^{-7} mass% O and 10^{-6} mass% O**:
  - Shorter incubation time for 10^{-7} mass% O
  - Slower accelerated oxidation for 10^{-7} mass% O in terms of metal recession but only at 550°C
  - Decrease in scale thickness for 10^{-7} mass% O at 450°C due to missing magnetite, but an equivalent amount of Fe is dissolved by liquid metal
  - The material loss caused by oxidation is generally lower at the lower oxygen concentration, but the risk of initiation of local solution-based corrosion attack increases;
  - 10^{-6} mass% is closer to the optimum oxygen content in LBE than 10^{-7} mass% at least for 9%Cr steels

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Thank you for attention !!!

Acknowledgements

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