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The impact of the composition of structural steels on their corrosion stability in liquid Pb–Bi at 500 and 400 °C with different oxygen concentrations

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Abstract

In recent years, heavy liquid metals have found exercise as possible coolants and targets in the conversion of radioactive elements in accelerator driven systems (ADS). Liquid lead–bismuth eutectic alloy is one of candidates for this using tanks to its suitable nuclear and physical properties. Performed examination was aimed at research of compatibility choice materials for parts of ADS with liquid Pb–Bi eutectic alloy, influence of composition choice materials on their corrosion resistance, influence of temperature and oxygen content. We performed corrosion tests of 1000 h each on approximately 20 types of structural steels (austenitic, ferritic and martensitic) in convection loops with flowing Pb–Bi at 500 and 400 °C and using different oxygen concentrations. The impact of Fe, Cr, Ni, Mn, Si, Al and Mo content on the corrosion stability of these steels was measured without and after preliminary passivation through creating thin spinel or oxide layers on their surface.

1. Introduction

Technology heavy liquid metals have been studying in connection with exercise of heavy liquid metal (Pb–Bi eutectic alloy or Pb) as coolants and targets in ADS system. As a result, material research efforts are becoming increasingly intensive.

Heavy liquid metals have acceptable melting points and high boiling points while at the same time being inert to water and air. Corrosion of structural materials is caused by chemical and physical process and is dependent on many influencing factors. There currently exist two methods for reducing this corrosive effect – oxidation and inhibition technology.

Corrosion in liquid lead alloys is caused by high solubility of the main alloying elements in structural materials. Refractory metals, such as Mo and W, have the lowest solubility; the solubility of other elements rises in the following order: Fe, Cr, Mn and Ni. Chromium–nickel and chromium–manganese steels without protective films are consequently subject to corrosion to a high extend. Medium-alloy chromium steels with approximately 12% of Cr as well as Cr–Mo and Cr–Mo–Si steels have a relatively higher corrosion resistance. Steels with 9–12% of Cr and 1.5–2.0% of Si are subjected to very little corrosion in their passivated state. Silicon increases corrosion resistance in the Pb–Bi eutectic by creating a protective layer with SiO_2. This

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attribute has been demonstrated even for Cr–Ni austenitic steels [1,2].

2. Experimental

2.1. Convectional loop in NRI

The convection loop in the NRI (Fig. 1) was designed based on extensive experience with the use of convection loops in monitoring the corrosion of structural materials in heavy liquid metal [3]. The loop was manufactured from stainless chromium–nickel steel (18Cr–10Ni–Ti) with its surface passivated for 50 h at 400–450 °C by steam containing 5% of H_2 before being put into service.

The loop comprises of high- and low-temperature legs and heating and cooling legs. Oxygen content is controlled by expansion tank in liquid Pb–Bi. Expansion tank is also capable of holding a large amount of corrosion products; consequently the loop may operate for long periods while adhering to the required parameters. The oxidation mixture was made in generator. Gaseous mixture Ar + H_2 was leaded in generator (Fig. 1).

2.2. Materials

We monitored over 20 types of materials of various compositions, ranging from pure Fe and Ni to pure Mo as well as various chromium–nickel steels (type AISI 304, 316 and 321 and also with an increased Si content), chromium and chromium–molybdenum steels with medium and low Cr content, non-stabilized and stabilized with Ti or Nb (Table 1).

Specimens were monitored with various surface conditions: ground, passivated and original.

The specimen holders with three rows of specimens with a total length of over 200 cm are placed into the testing section. These specimens are usually flat tensile bodies approximately 0.5–1.0 mm thick and 60 mm long or 20-mm specimens used for metallographic and other analyses. Specimens intended for one of a total of four holders to be used in a second experiment at 500 °C are depicted in Fig. 2 before insertion into the loop.

2.3. Corrosion tests

The loop test parameters are given in Table 2.

Consequently, the first series of experiments were performed at 500 and 400 °C. These values are corresponding to the high-temperature and the low-temperature legs of the loop. The temperature of the expansion tank, which supplied the loop with the oxidation mixture, was 300 °C. This temperature allowed us to keep the oxygen concentration in liquid Pb–Bi between 10^{-5} and 10^{-7} wt% by varying the H_2/H_2O ratio. The oxygen concentrations for experiments were $3\text{–}4 \times 10^{-6}$ and 2×10^{-5} wt%, respectively [4–6]. In the first experiment oxidation mixture was injected above the level of the liquid metal in the expansion tank while in second experiments it was bubbled through the liquid metal. The duration of experiments was 1000 h. The liquid metal flow velocity was 1–2 cm/s in both experiments. The required temperature was kept constant throughout the

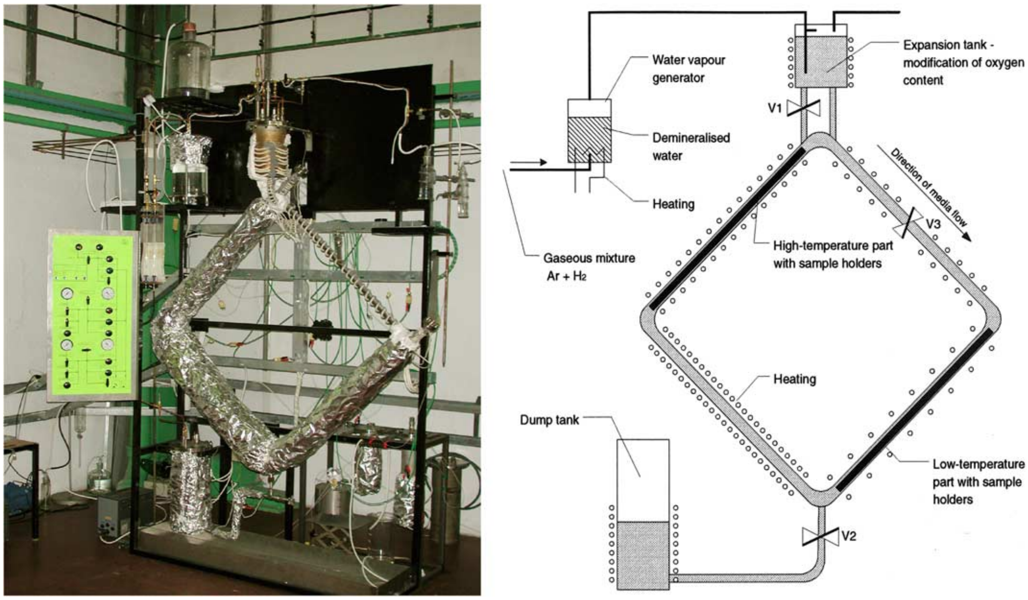

Fig. 1. Convectional loop in NRI and scheme.

Table 1
Selected materials and their composition

Composition	AISI, ČSN
08Cr18Ni10	304
06Cr16Ni10	304
03Cr18Ni11	304L
08Cr20Ni13Si2	EI211
08Cr18Ni10Ti	08Ch18N10T
06Cr18Ni10Ti	321
08Cr18Ni10Ti	321 (SG pipe)
06Cr16Ni12Mo2	316
08Cr15Ni12Mo3	316
03Cr18Ni32Ti	Incoloy 800
07Cr20Ni76Ti2	Nimonic
Ni	
Mo	
08Cr18Ni5Mn8N	17460
10Cr17	17041
11Cr9W1Mn0,4V0,2Ta0,15	Eurofer
12Cr7AlSi1	17113
12Cr5Mo	17102
07Cr5MoNiTi0,44	Exp.
07Cr2Mo4NiTi0,42	Exp.
10Cr3Mo	15412
07Cr2MoNiNb1,18	HT8X6
13Cr2MoNiNb0,92Ti0,17	Exp.
07Cr2MoNiNb0,6	Exp.
Fe armco	

corrosion tests – within a limit ± 1 °C for the testing legs with specimens and ±2–5 °C for the expansion tank.

3. Results and discussion

The results of the corrosion tests two in four experiments at 500 °C are presented in Figs. 3 and 4.

In the high-temperature part, the corrosion rate of stainless Cr–Ni steels without Mo ranged from 0 to 800–1200 μm/yr depending on whether the surface of the specimen had been passivated or ground. Specimens of AISI 316 steel with a ground surface – corroded at a rate of about 400–1500 μm/yr (Fig. 5).

The results of other Cr–Ni stainless steels clearly show that steels stabilized with Ti are subject to relatively less corrosion because the presence of Ti increases their capacity to be passivated (Fig. 6). In the experiment where the oxygen content was kept at $3–4 \times 10^{-6}$ wt% and the oxidation mix was injected above the level of Pb–Bi, their corrosion did not exceed 30–40 μm/yr.

Cr–Ni steels with 2% of Si were found to be very corrosion resistant; these steels are used to make high-temperature legs of dynamic loops in IPPE in Obninsk on which corrosion tests were performed for CEA, ENEA and FZK [7–9]. The lowest corrosion rate of all stainless chromium–nickel steels was detected regardless of the conditions and surface. The higher Si content enabled the steel to form a protective layer even during corrosion tests – to a smaller extent in the lower oxygen-content and fully in the higher oxygen-content variants of Pb–Bi (Fig. 7). Intercrystalline attack is noticeable on all specimens of this material.

Corrosion tests performed showed that materials with a higher Cr and Ni content are subject to relatively high corrosion and thus were not included in the rest of the experiments (18Cr–32Ni, 20Cr–76Ni and Ni). The last two materials completely corroded at 500 °C with the 1-mm thick Ni specimen doing the same at 400 °C.

The corrosion tests have shown that Cr–Ni–Mn austenitic steels corrode a little less than 'pure' Cr–Ni steels. After being passivated, ferritic steels with 17% of Cr were subject to practically no corrosion. However, ground specimens in both experiments corroded at 500 °C at a rate of 500–760 μm/yr – the same value as its corrosion rate in Pb–Bi deoxidized with Mg and without inhibitors [10]. We also examined specimen from the Eurofer – martensitic steel in the shape of a 16 × 1 pipe with a passivated, ground and one original surface. The passivated surface was subject to practically no corrosion while the ground surface, especially in first experiment with a lower oxygen content, corroded at a rate

Fig. 2. Specimens of selected materials before insertion into one of the four specimen holders.

Table 2
Loop test parameters

	Exp. 1	Exp. 2
Liquid medium	Pb–Bi	Pb–Bi
$T_{\text{high part}}$ (°C)	500 °C	500 °C
$T_{\text{low part}}$ (°C)	400 °C	400 °C
Duration (h)	1000	1000
Velocity (cm/s)	1–2	1–2
Oxygen (wt%)	$3–4\times10^{-6}$	2×10^{-5}
Ratio H_2/H_2O	1:2	1:10

of up to 1000 µm/yr (Fig. 8). Other Eurofer specimens with ground and original surfaces corroded at a rate of 150–200 µm/yr. The corrosion rate of ground Eurofer specimen at 400 °C in Pb–Bi with lower oxygen content was up to 40 µm/yr.

7%Cr–1%Si–Al steel specimens were subject to relatively lower corrosion, especially after being passivated. One of the specimens with a ground surface corroded at a rate of up to 700 µm/yr in Pb–Bi with a lower oxygen content. The oxidation environment thus had no protective effect, as was the case for Eurofer.

Although it did not exceed 40 µm/yr, other materials tested with 2–5% Cr1–4%Mo (Ni) – non-stabilized or stabilized with Ti or Nb and passivated – were subject to relatively higher corrosion at 500 °C in first experiment with a lower oxygen content. Specimens of steels with ground surfaces and low oxygen content usually corrode quite rapidly – from approximately 100 to 1100 µm/yr Fig. 9.

Steel specimens located in the cold leg of the loop were usually not subject to corrosion at 400 °C. Certain Cr–Ni steel specimens with ground surfaces and a higher Ni content, especially those alloyed with Mo (AISI 316) and steels with a medium Cr content and alloyed with W, Mo, or Nb, corroded at a rate of 20–60 µm/yr at 400 °C in Pb–Bi with a lower oxygen content.

4. Conclusions

The results and the conclusions drawn from the said 1000 h corrosion tests of variously alloyed steels at 500 and 400 °C in liquid Pb–Bi with an oxygen content of 2×10^{-5} and $3–4\times10^{-6}$ wt% can be summarized as follows:

- Most of tested steels exhibited almost no corrosion in the low-temperature leg at 400 °C. The positive impact of passivation was detected for almost all specimen exposed to the high-temperature leg of the loop even at 500 °C.

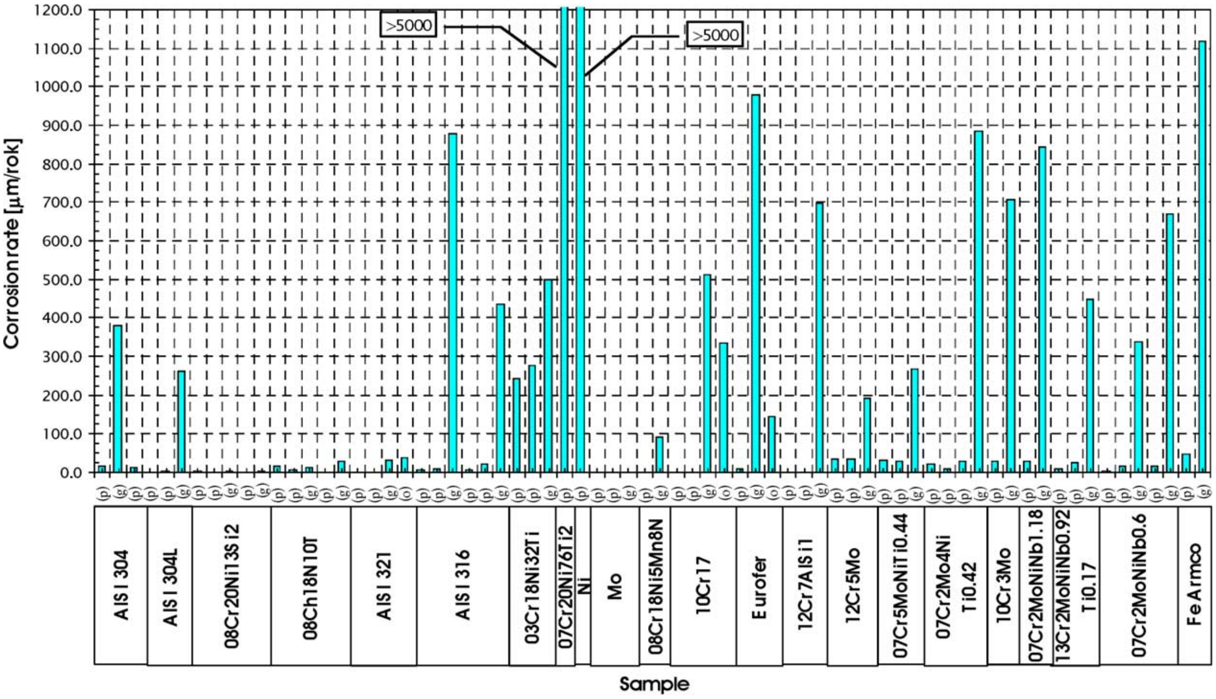

Fig. 3. Corrosion rate of various kinds of steels in liquid Pb–Bi at 500 °C with oxygen content of $3–4\times10^{-6}$ wt% after 1000 h exposure (exp.1, $H_2/H_2O = 0.5$, surface: g – ground, p – passivated, o – original).

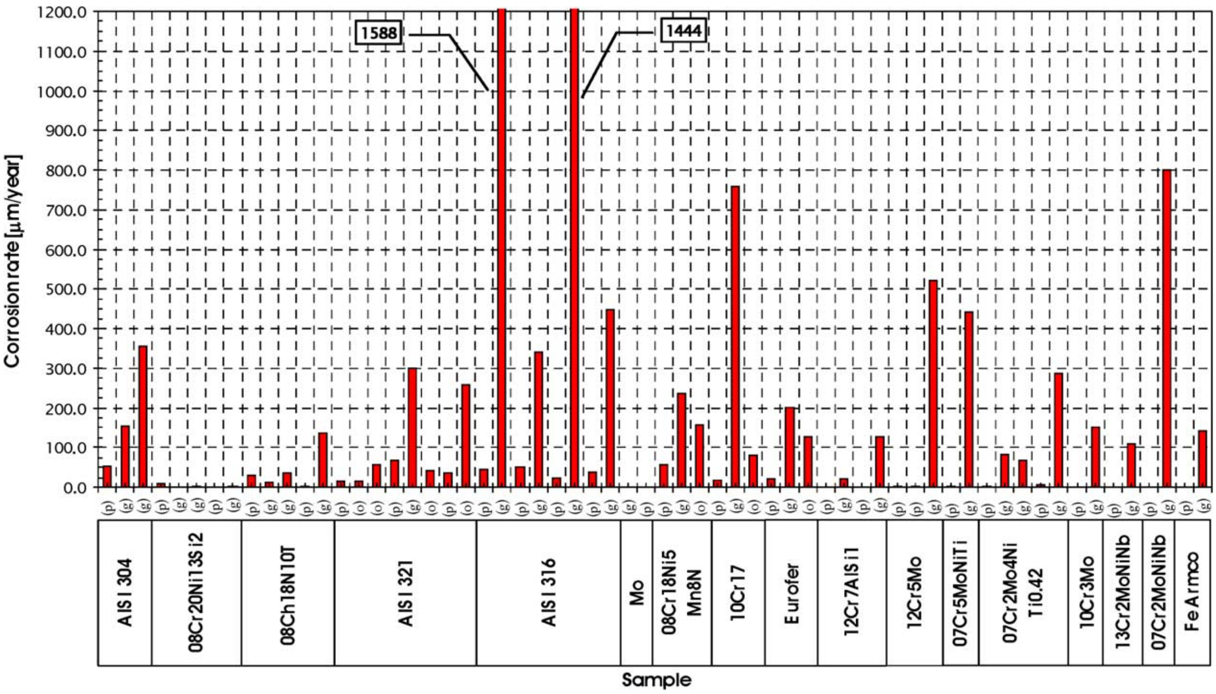

Fig. 4. Corrosion rate of various kinds of steels in liquid Pb–Bi at 500 °C with oxygen content of 2×10^{-5} wt% after 1000 h exposure (exp.2, $H_2/H_2O = 0.1$, surface: g – ground, p – passivated, o – original).

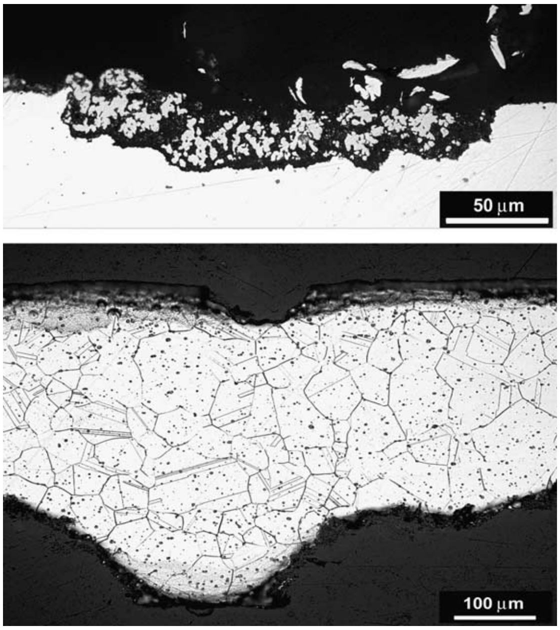

Fig. 5. Microphotography of a cross-section of an AISI 316 with a ground surface exposed for 1000 h to flowing Pb–Bi at 500 °C with 3–4 × 10^{-6} wt% O_2.

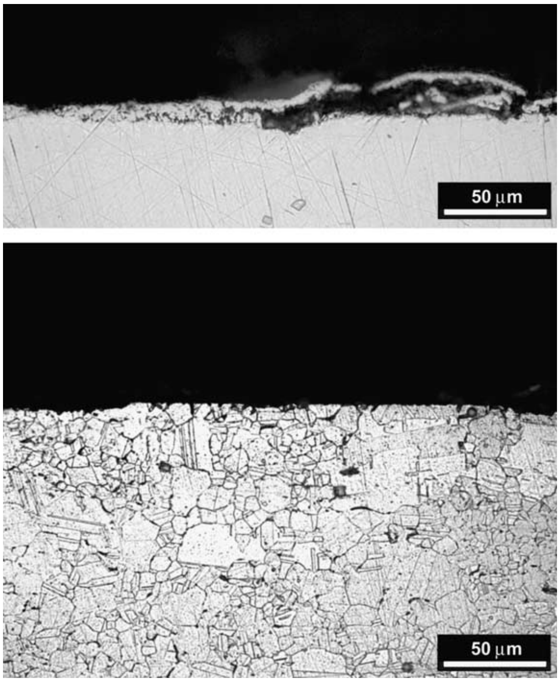

Fig. 6. Microphotography of a cross-section of a 08Ch18N10T with a ground surface exposed for 1000 h to flowing Pb–Bi at 500 °C with 3–4 × 10^{-6}wt% O_2.

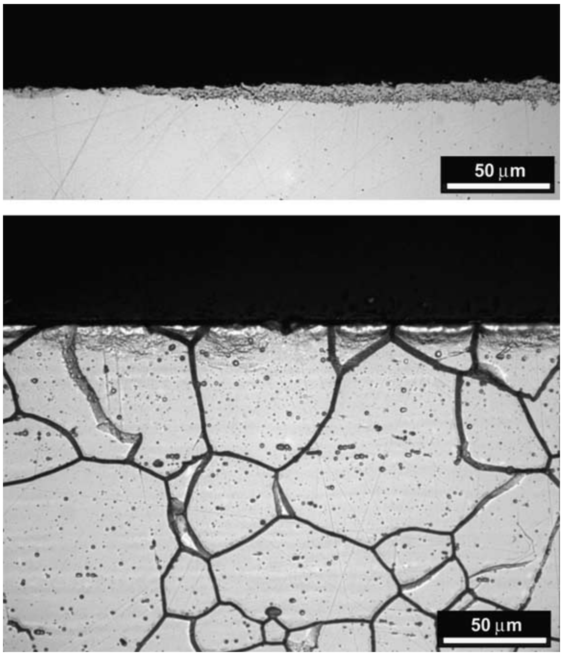

Fig. 7. Microphotography of corrosion damage to a Cr–Ni steel with 2% Si with the ground surface exposed for 1000 h to flowing Pb–Bi at 500 °C with 2×10^{-5} wt% O_2.

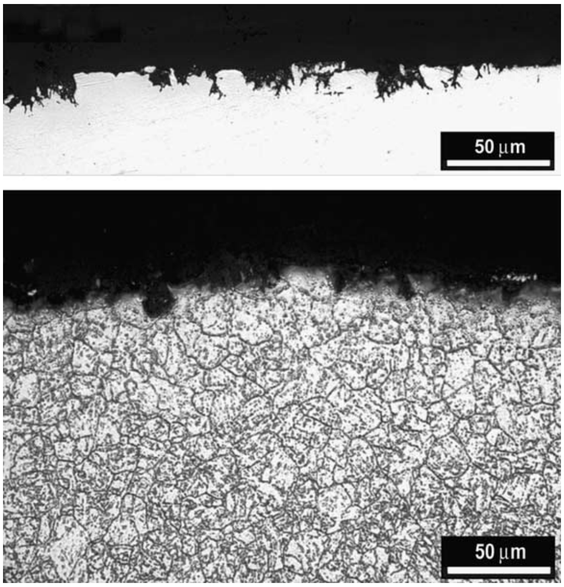

Fig. 8. Microphotography of corrosion damage to an Eurofer with ground surface exposed for 1000 h to flowing Pb–Bi at 500 °C with an oxygen content of $3\text{–}4 \times 10^{-6}$ wt%.

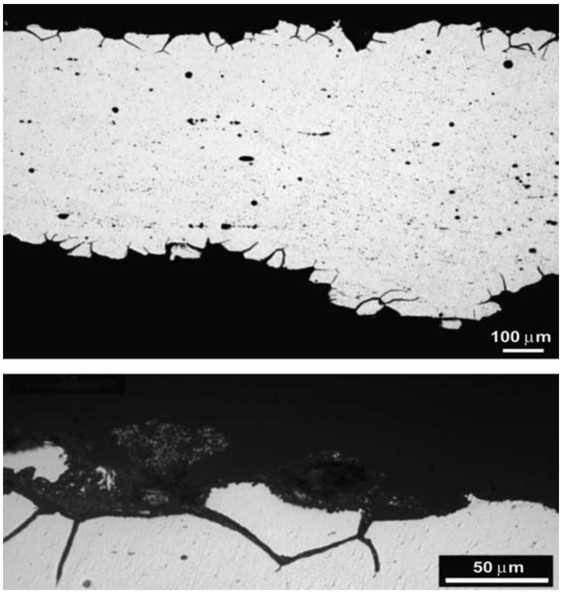

Fig. 9. Microphotography of corrosion damage to a Fe-armco with a ground surface exposed for 1000 h to flowing Pb–Bi at 500 °C with an oxygen content of $3\text{–}4 \times 10^{-6}$ wt%.

- The chromium–nickel steel with a higher Si content (EI211), both with a passivated and ground surface, was subject to almost no corrosion at 500 °C under tested conditions with an oxygen content of $3\text{–}4 \times 10^{-6}$ wt%. That means that this steel can passivate itself during the experiment running and may even possess repair-damaged areas, if any.
- Molybdenum significantly impedes the passivation of AISI 316 steel, which – especially when not passivated – corrode at a rate of 1000–2000 µm/yr.
- Stabilization of Cr–Ni steel with Ti (AISI 321 steel) has a positive impact on their corrosion resistance compared to AISI 304 steel at higher oxygen concentration.
- Pb–Bi with lower oxygen content causes higher overall corrosion for stainless Cr–Ni steels as well as medium- and low-alloy steels compared to when the oxygen content is higher in Pb–Bi.
- However, higher oxygen content give rise to a higher attack on grain boundaries in Cr–Ni and low-alloy steels.
- The optimal oxygen content for various types of steels must be ascertained experimentally.
- The corrosion experienced by various steels when influenced by oxygen in LBE is often significantly higher (2–3 times) than corrosion in Pb–Bi deoxidized with Mg [10]. Among the steels that exhibit a higher corrosion rate are Cr–Ni steels – since Ni and Cr selectively corrodes, consequently no compact protective Fe_3O_4 layer can be formed on their surfaces; Fe oxides with no capability to lower corrosion are formed instead. The corrosion of steels in Pb–Bi deoxidized with Mg after the Ni and Cr dissolution and formation of non-protective layers is driven by the physical

dissolution of Fe. The corrosion rate of stainless Cr–Ni steels is only about 30% higher than that of low- and medium-alloy ferritic steels.

- It is recommended that a new R&D project should be undertaken concerning the protection of exposed parts of structural materials cooled by heavy liquid metals using thin layers of inert materials, such as Mo, W and Re, which do not corrode in Pb–Bi – for both the oxygen control technology and for Ti/Zr inhibition processes even at high temperatures (up to 700–800 °C) [11].

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