

Effect of Oxygen Concentration in Static Pb-Bi Eutectic on Corrosion Mode of Aluminum-Alloyed Austenitic Steels at 550 °C for 1000 h

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Abstract. Corrosion behavior of Fe-18Ni-12Cr-2.30Al and Fe-18Ni-12Cr-2.90Al-Nb-C austenitic steels was investigated in static Pb-Bi eutectic at 550 °C for 1000 h depending on the concentration of dissolved oxygen in the liquid metal. In the concentration range from 10^{-12} to 10^{-8} mass % O, both steels underwent corrosion via dissolution resulted in the formation of spongy ferrite layer depleted in Ni and Cr and penetrated by Pb and Bi. In Pb-Bi with 10^{-6} mass % O, Fe-18Ni-12Cr-2.90Al-Nb-C steel oxidizes with formation of very thin ($\leq 1 \mu\text{m}$) Cr/Al oxide film while Fe-18Ni-12Cr-2.30Al steel shows mixed corrosion behavior represented by more intensive oxidation and dissolution. The features of corrosion response are discussed depending on the composition of steels and concentration of dissolved oxygen in the Pb-Bi eutectic.

1. Introduction

Developing of Alumina-Forming Austenitic (AFA) stainless steels with improved creep resistance (strengthening with Laves phases and carbides) and oxidation resistance (formation of Al_2O_3) at high temperatures in gaseous media attracts presently a significant attention [1]. Applicability of AFA steels in Heavy Liquid Metals (HLM) such as Pb and Pb-Bi eutectic arouses interest as-well and requires experimental investigations which are very scarce up to day and briefly summarized hereafter [2–4].

Ejenstam and Szakálos performed corrosion test on Fe-14Cr-14Ni-2.5Al-1.6Mn-2.5Mo-0.9Nb steel at 550 °C in static Pb containing $\sim 10^{-7}$ mass% of dissolved oxygen [2]. It was reported that a very thin ($< 100 \text{ nm}$) protective Al-rich oxide film forms on the surface after one year of exposure, characterizing the alloy as a potential candidate for use in HLM-cooled reactors.

In the case of high-Ni alloys the Fe-(20-29)Ni-(15.2-16.5)Cr-(2.3-4.3)Al composition is proposed, based on the results of tests performed at 550 °C and 600 °C in stagnant Pb with 10^{-6} mass%O for 1000 h [4]. The formed protective oxide film was composed of Cr_2O_3 and Al_2O_3 - Cr_2O_3 solid solution.

At markedly higher concentration of oxygen (5×10^{-4} mass%) in static Pb-Bi eutectic at 520 °C for 1850 h, the Fe-14Cr-25Ni-3.5Al-2Mn-2Mo-2.5Nb alloy shows intensive oxidation via formation of bi-layer magnetite-based scale which is also observed on the austenitic steels not alloyed by Al during oxidation in the HLM [5] that indicates about no significant gain in oxidation resistance with Al-alloying in comparison with austenitic steels without Al.

The brief overview of the works on Al-alloyed austenitic steels in HLM indicates that most of the tests were performed at oxygen concentrations higher than that one required for the stability of magnetite [6]. Alumina are much more stable in comparison with magnetite and thermodynamically might be formed at substantially lower oxidation potential of liquid metal than required for the formation of Fe-based oxides. The main aim of this work, therefore, is to investigate the possibility of *in-situ* formation of Al-based oxide film on the surface of Al-alloyed austenitic steels at a constant temperature 550 °C in static Pb-Bi eutectic depending on the oxygen concentration in the liquid metal.

2. Materials, Apparatus and Conditions of Corrosion Tests

Cylindrical specimens ($\text{Ø}8 \times 10$ mm) made of Fe-18Ni-12Cr-2.3Al and Fe-18Ni-12Cr-2.9Al-Nb-C austenitic steels were used for corrosion test.

Figure 1 shows scheme of apparatus for static tests of material in HLM up to 700 °C. It consists of stainless steel capsule ended with a lid housing ports for: gas inlet and outlet; thermocouples residing in alumina tubes; an electrode (molybdenum wire) that closes the electric circuit; specimen holder (molybdenum rod); and two electrochemical oxygen sensors with Pt/air reference electrode for active monitoring and control of oxygen concentration in the HLM [6]. Alumina crucible is filled with 2 kg of Pb-Bi eutectic. The capsule is placed in the vertical furnace (Fig. 1). Working gases (Ar, Ar-5vol% H_2 , and synthetic air) are supplied over the surface of liquid metal by the Oxygen Control System (OCS) developed at Karlsruhe Institute of Technology (KIT) in order to provide the required oxygen concentration in the liquid metal.

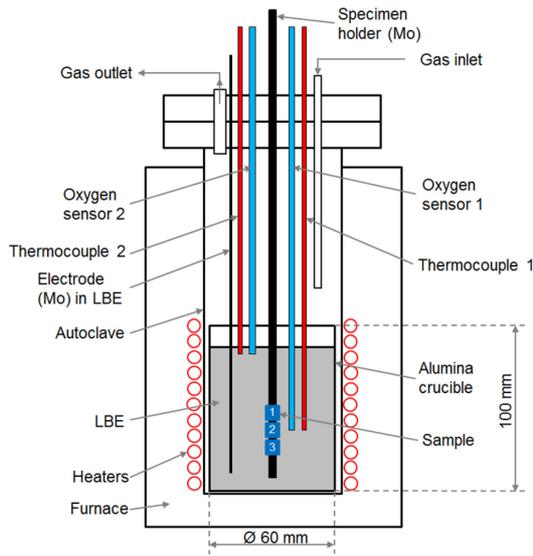


Fig. 1. Scheme of apparatus for corrosion tests.

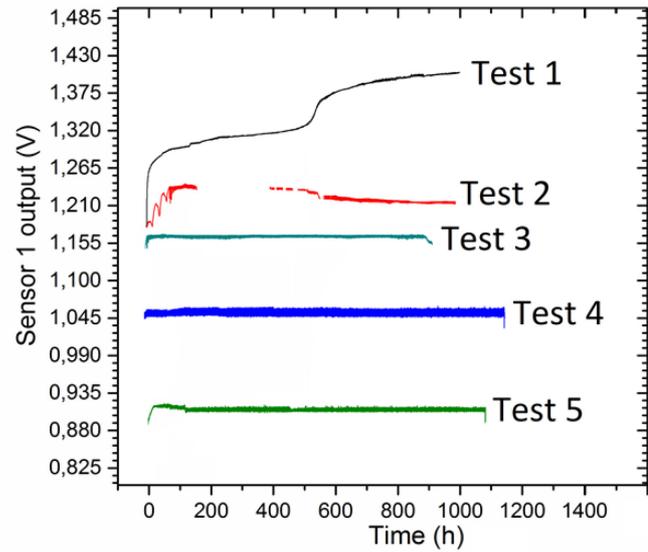


Fig. 2. Output of oxygen sensor depending on time and corrosion test.

Before the test, the liquid metal was preconditioned with respect to the target oxygen concentration. When the output of sensor 1 (S1), which is placed at the level of samples, reaches the stable target value, holder with samples is inserted into the liquid metal through the tube port (Fig. 1). The ratio of liquid metal volume (cm^3) to the surface area of samples (cm^2) is 25 cm. Five corrosion tests were carried at constant temperature 550 °C in Pb-Bi eutectic for ~1000 h depending on the oxygen concentration in the liquid metal. The same bath of Pb-Bi was used for each next test. Figure 2 shows evolution of sensor 1 output with time recorded for tests 1-5. Sensor output was recalculated into the concentration of oxygen in the Pb-Bi using following equation [6]:

$$\log(C_o) = -3.2837 + \frac{6949.8}{T} - 10080 \frac{U - U_{th}}{T} \quad (1)$$

where: C_o – concentration of oxygen in Pb-Bi (mass%); U – sensor output (V); U_{th} – thermoelectric voltage resulting from different electric leads (V) and T – temperature (K).

According to the calculations, the concentration of oxygen (mass%) in the Pb-Bi eutectic during the tests is: test No 1 – 10^{-12} - 5×10^{-11} ; test No 2 – 10^{-10} ; test No 3 – 10^{-9} ; test No 4 – 10^{-8} ; test No 5 – 10^{-6} .

Based on the thermodynamic considerations, tests might be divided into three main groups: tests No 1-3 performed at oxygen concentrations $C_{O[\text{Pb-Bi}]}$ < than thermodynamic stability of magnetite (Fe_3O_4); test No 4 at $C_{O[\text{Pb-Bi}]} \approx \text{Fe}_3\text{O}_4$; and test No 5 performed at $C_{O[\text{Pb-Bi}]} > \text{Fe}_3\text{O}_4$ [6]. The minimum concentration of oxygen in the Pb-Bi reached in apparatus during the test No 1 was $\sim 10^{-12}$ mass%O, that is still high enough to oxidize the Cr, Si and Al and also to form mixed oxides like FeCr_2O_4 and FeAl_2O_4 [6].

After the tests, the samples with remnants of solidified Pb-Bi were segmented and cross-sections were prepared. A metallographic method, was applied in order to determine the corrosion loss by means of comparing the initial diameter of the samples with post-test diameter of sample not affected by corrosion. The detailed procedure is described elsewhere [7]. Light optical microscopy (LOM) and scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDX) were used for the examination of morphologies and composition of corrosion zones. Auger electron spectroscopy was applied for determination of composition of thin oxide films using a PHI 680 Xi Auger nanoprobe. Contamination of Pb-Bi by steel constituents was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Results and Discussion

After the tests 1-4, performed at concentration of oxygen in the Pb-Bi varying between $\sim 10^{-12}$ and 10^{-8} mass%O ($\text{Al}_2\text{O}_3 < C_{\text{O}[\text{Pb-Bi}]} = \text{Fe}_3\text{O}_4$) the both steels underwent marked corrosion attack resulted in formation of continuous near-surface layer of irregular thickness (Fig. 3).

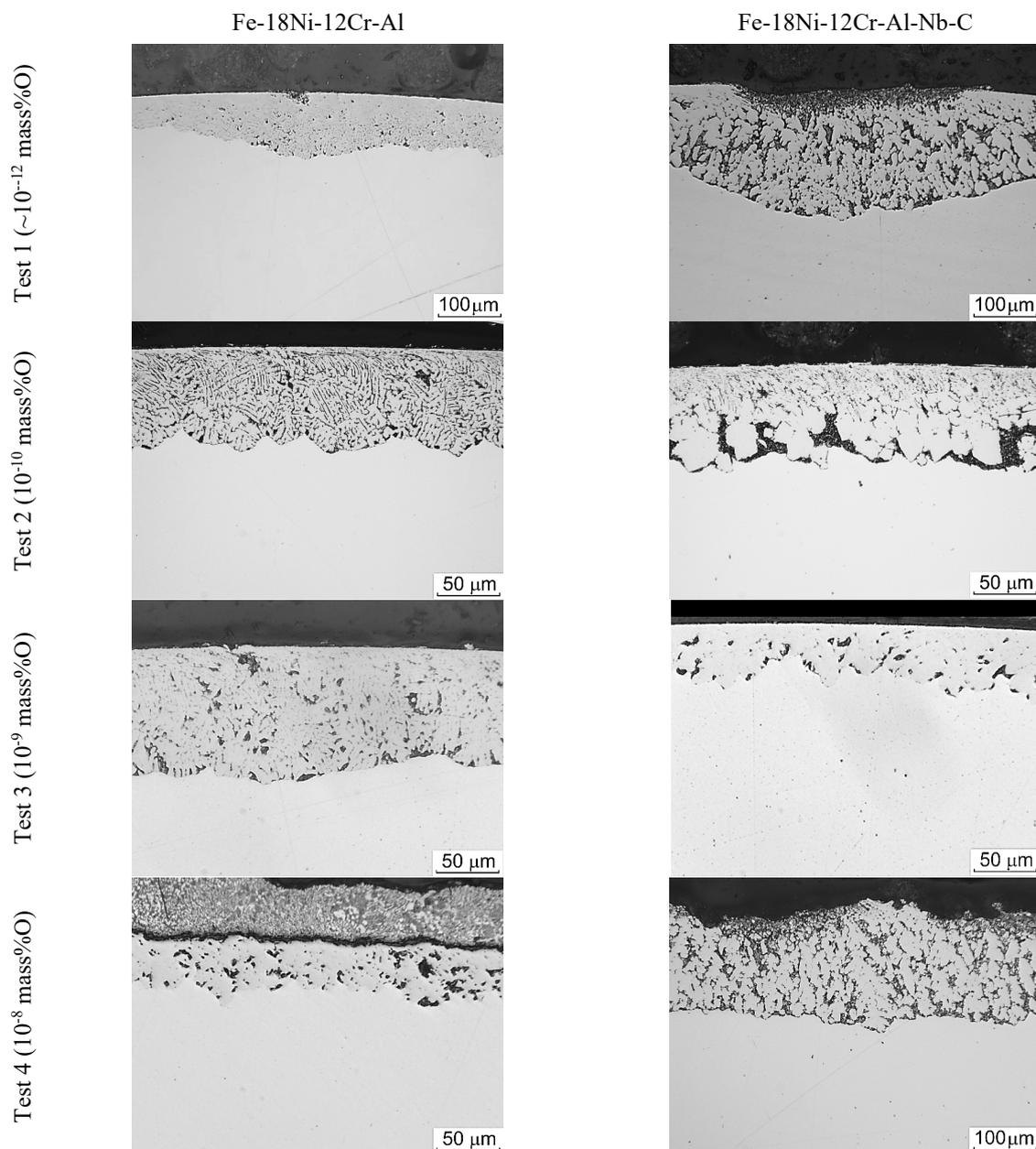


Fig. 3. Light optical microscopy of corrosion zones formed on the surface of austenitic steels after tests 1-4 at 550 °C in static Pb-Bi eutectic for 1000 h depending on the concentration of oxygen in the liquid metal.

Corrosion zones formed on the surface of both steels are represented by the spongy ferrite structure markedly depleted in Cr and Ni, in comparison with non-corroded steel composition, and penetrated by Pb and Bi (Fig. 4). Concentrations of Ni and Cr decrease abruptly when crossing the interface between not-corroded steel matrix and ferrite zone (Fig. 4).

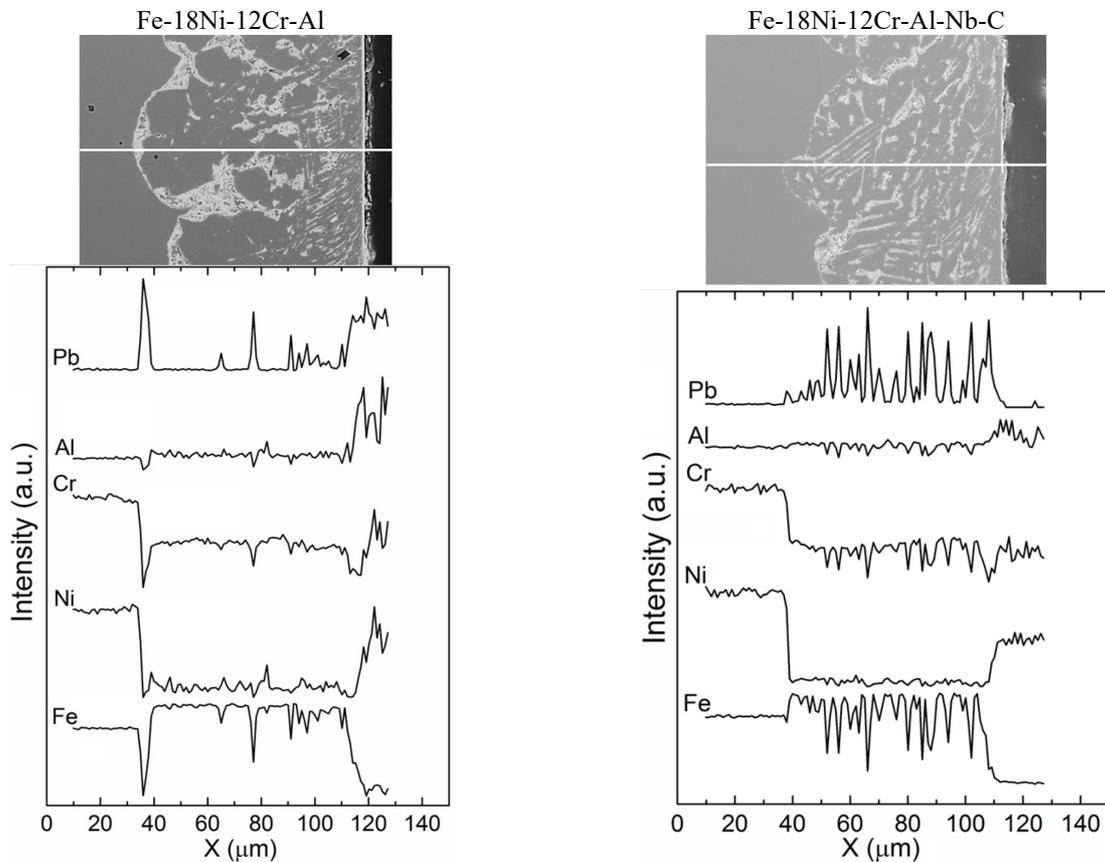


Fig. 4. Typical morphology (SEM) and elemental profile (EDX) along the corrosion zones formed on the surface of austenitic steels after tests *No* 1-4 performed at 550 °C in static Pb-Bi eutectic with concentration of dissolved oxygen from $\sim 10^{-12}$ to 10^{-8} mass%O for 1000 h.

Results obtained during tests *No* 1-4, clearly show that if the concentration of oxygen in the Pb-Bi is less or even equal to that one necessary to provide the formation of magnetite, the alloying elements like Al and Cr alone cannot guarantee the *in-situ* passivation of steel surface even if they have higher affinity to oxygen than Fe. One should also remember that Al and Cr are highly soluble in HLM. Oxides of Al and Cr, most probably, form, however not on the surface of steel but directly in the liquid metal.

Figure 5 shows the general corrosion response of steels after corrosion test *No* 5 performed in the Pb-Bi with 10^{-6} mass% dissolved oxygen that is higher than necessary to provide the stability of magnetite at 550 °C (10^{-8} mass%). In spite of the almost identical composition with respect to the main components, steels showed completely different corrosion response (Fig. 5). Fe-18Ni-12Cr-Al steel showed mixed corrosion behavior represented by formation of Fe-Cr-based oxide scale of about 10 μm in thickness, beneath which the ferrite layer, depleted in Ni and Cr and percolated by Pb and Bi, forms (Fig. 5 a). In contrast, more complex alloyed steel Fe-18Ni-12Cr-Al-Nb-C showed no measurable corrosion attack (Fig. 5 b) and visually sample looks slightly oxidized. Auger analyses of surface reveals formation of outer Cr-based oxide film and intermediate Al-based oxide film, indicating synergetic effect of Cr and Al in the formation of protective oxide layer (Fig. 6).

Chemical analysis of Pb-Bi samples after tests *No* 1 and *No* 5 shows that concentration of Ni increases in Pb-Bi (Table 1) that is in a good agreement with dissolution attack observed on samples (Fig. 3). In contrast to Ni, concentrations of Fe, Cr and Al decrease with increasing oxidation potential of Pb-Bi indicating that initially dissolved elements react with oxygen solved in the liquid metal.

Agglomerates of Fe-based oxides floated on the surface of Pb-Bi after the test *No 5* performed at $C_{O[Pb-Bi]} > Fe_3O_4$, while Cr-based oxides floated on the surface of Pb-Bi after the tests *No 1-4* performed at $C_{O[Pb-Bi]} \leq Fe_3O_4$, that indicate about good correspondence of experimental conditions, with respect to oxygen concentration in the Pb-Bi, and thermodynamic evaluations [6].

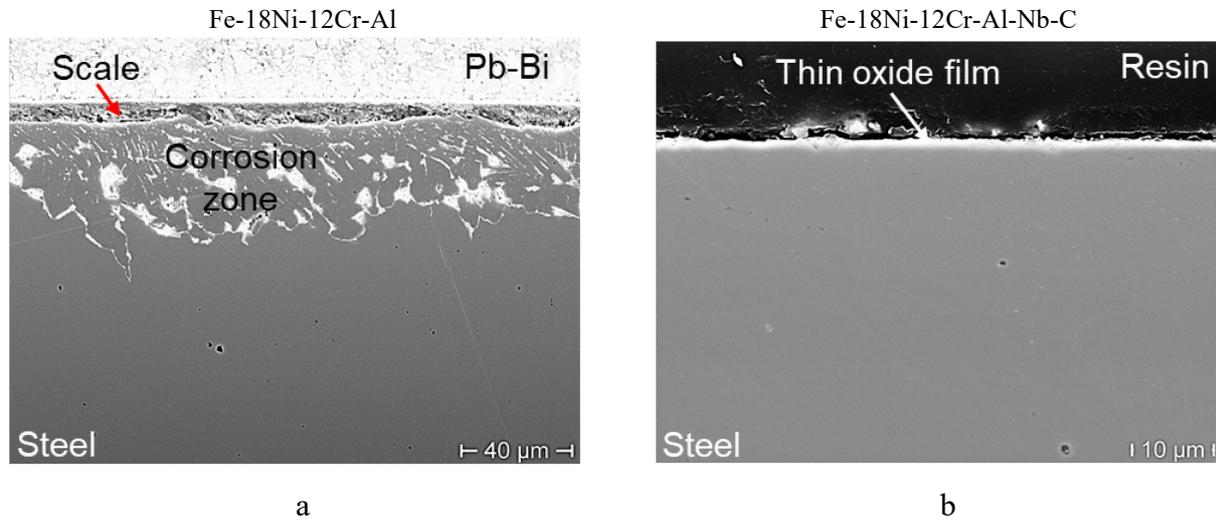


Fig. 5. General corrosion response (SEM) of aluminium-alloyed austenitic steels after test (*No 5*) performed at 550 °C in static Pb-Bi eutectic containing 10^{-6} mass% dissolved oxygen for 1000 h.

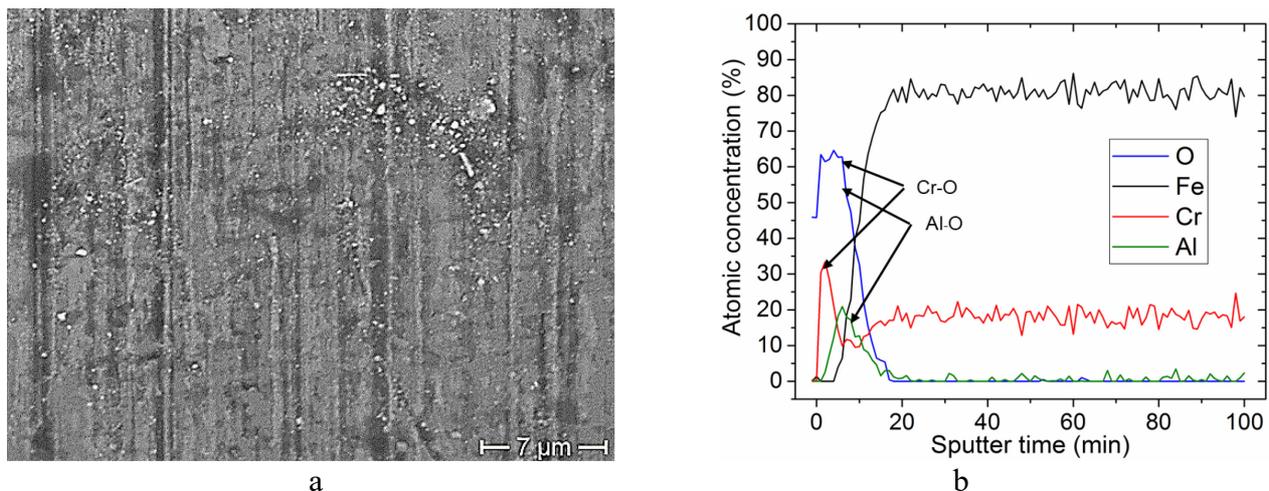


Fig. 6. Surface morphology and corresponding Auger sputter depth profile from the surface of sample of Fe-18Ni-12Cr-Al-Nb-C steel after the test *No 5* at 550 °C in static Pb-Bi eutectic with 10^{-6} mass% dissolved oxygen for 1000 h.

Table 1. Post-test chemical analyses of Pb-Bi.

Element (mass%)	Test <i>No 1</i> ($\sim 10^{-12}$ mass%O)	Test <i>No 5</i> (10^{-6} mass%O)
Al	< 0.00005	< 0.00001
Cr	0.00019 (± 0.00002)	< 0.00001
Fe	0.00023 (± 0.00007)	< 0.00001
Ni	0.00230 (± 0.00004)	0.00432 (± 0.00001)

Figure 7 summarizes the data on corrosion loss measured as a change in diameter of samples after corrosion tests depending on the oxygen concentration in the Pb-Bi. Changes in the corrosion loss of both steels with increase in concentration of oxygen are not so straight-proportional as it was expected based on the earlier findings [8]. For example, for Fe-18Ni-12Cr-Al steel, average corrosion losses caused by the dissolution decrease gradually from 134 to 30 μm with increase in oxygen

concentration in the melt from 10^{-12} to 10^{-9} mass% (Fig. 7). Then, with increase in oxygen content to 10^{-8} mass%, the corrosion loss even increases to 68 μm . The further increase in concentration to 10^{-6} mass% changed corrosion mode from pure dissolution to oxidation plus dissolution resulting in corrosion loss averaging 33 μm , that is similar quantitatively to those obtained in Pb-Bi with 10^{-9} mass%O (Fig. 7).

In the case of Fe-18Ni-12Cr-Al-Nb-C steel corrosion losses, on the contrary, increase with increasing oxygen concentration in the Pb-Bi from 10^{-12} to 10^{-9} mass% (Fig. 7). Further increase of oxygen concentration to 10^{-8} mass% decreases the corrosion loss. Corrosion mode changes from the dissolution to oxidation only at 10^{-6} mass%O, minimizing corrosion losses of steel.

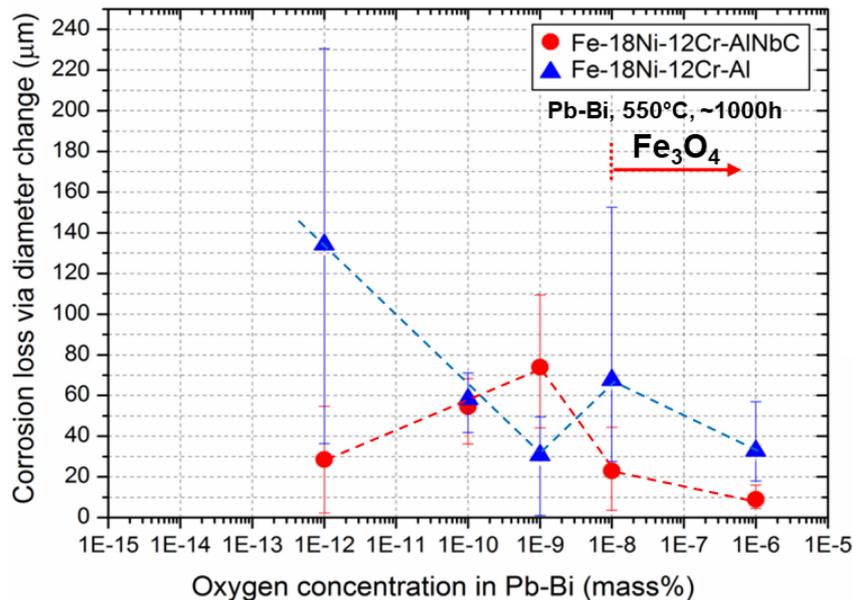


Fig. 7. Average corrosion loss with min and max deviations of austenitic steels after tests at 550 °C in static Pb-Bi eutectic for 1000 h depending on the concentration of oxygen in the liquid metal. Corrosion via dissolution - both steels in Pb-Bi with $\sim 10^{-12}$ to 10^{-8} mass%O. Oxidation plus dissolution - Fe-18Ni-12Cr-2.3Al steel in Pb-Bi with 10^{-6} mass%O. Oxidation - Fe-18Ni-12Cr-2.9Al-Nb-C steel in Pb-Bi with 10^{-6} mass%O.

4. Summary

The effect of oxygen concentration in static Pb-Bi eutectic on the corrosion behavior of Al-alloyed austenitic steels Fe-18Ni-12Cr-2.3Al and Fe-18Ni-12Cr-2.9Al-Nb-C is investigated at 550 °C for 1000 h:

- When oxygen concentration in the Pb-Bi is controlled at $\sim 10^{-12}$, 10^{-10} , 10^{-9} and 10^{-8} mass %, both steels underwent solution-based attack resulted in the formation of corrosion layer composed of ferrite severely depleted in Ni and Cr and penetrated by Pb and Bi.
- In Pb-Bi with 10^{-6} mass % O:
 - Fe-18Ni-12Cr-2.30Al steel underwent simultaneous oxidation (Fe-Cr-O spinel) and dissolution (ferrite layer) corrosion attacks averaging material loss of about 33 μm for 1000 h;
 - In contrast, Fe-18Ni-12Cr-2.90Al-Nb-C steel shows general slight oxidation resulted in the formation of very thin Cr/Al-oxide film;
 - The more complex alloying of Fe-18Ni-12Cr-2.9Al-Nb-C steel, it seems, favors the formation of more protective oxide film and should be studied in detail additionally.
- The oxidation potential of the Pb-Bi, similar to the conventional austenitic steels not-alloyed with Al, should be higher than required for the thermodynamic stability of magnetite (Fe_3O_4) in order to promote oxidation and mitigate dissolution attack.

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