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Long-term corrosion of austenitic steels in flowing LBE at 400 °C and 10^{-7} mass% dissolved oxygen in comparison with 450 and 550 °C

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HIGHLIGHTS

- Long-term corrosion tests of austenitic steels are performed in flowing LBE with 10^{-7} mass% O at 400–550 °C.
- Steels show slight oxidation and solution-based attack.
- Solution-based attack proceeds via selective and non-selective leaching of steel constituents.
- Incubation period for solution-based attack decreases with increasing temperature.
- Corrosion rates are ~6–26, ~120–220 and ~500–3000 μm/year at 400, 450 and 550 °C, respectively.

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ABSTRACT

Long-term corrosion tests for up to ~13,194 h on 1.4970 (15-15 Ti), 316L and 1.4571 austenitic steels were carried out at 400 °C in flowing LBE (2 m/s) with 10^{-7} mass% dissolved oxygen. The steels show general slight oxidation (Cr-based oxide film) along with local, pit-type solution-based corrosion attack. The incubation time for pit-type attack is ~4500 h. After ~13,194 h, the maximum pit depth observed was ~14, 23 and 57 μm for 1.4970, 316L and 1.4571, respectively, that corresponds to local corrosion rates of ~6, 10 and 26 μm/year. At 450 °C and 550 °C, the corrosion rates are ranged in between ~120–220 μm/year and ~500–3000 μm/year, respectively. Corrosion appearances and mechanisms are discussed.

1. Introduction

Application of heavy liquid metal (HLM) as a process medium (neutron breeder and heat transfer) in novel nuclear reactors requires solution of the compatibility issues with solid metallic materials, especially steels [1,2]. Currently, austenitic steels are considered as one of the most promising candidate structural materials for HLM reactors. First of all, this is so because of the number of available data pertaining to mechanical properties of austenitic steels and their performance under irradiation, based on the existing experiences with their operation under reactor conditions. Recently, a new batch of 15-15 Ti cladding tubes were produced for the multi-purpose hybrid research reactor for high-tech applications (MYRRHA) that is going to be built in Belgium [3].

HLM, i.e., Pb, Pb–Bi (LBE) and Pb–Li eutectics, tend to leach out steel constituents like Ni, Cr and Fe due to their significant solubility and continuous mass-transfer caused by temperature difference along liquid-metal system [1,2]. Solution-based attack (SBA), on the macroscopic scale, consists of solution reaction at the solid metal/liquid metal interface followed by transport of dissolved atoms in the boundary layer and final transfer to the bulk of the liquid metal [2,4]. Then, SBA results in the formation of corrosion zones with composition and properties different from the unaffected material. When solid metal consists of elements with different solubility limit in the liquid metal, a selective leaching of higher-soluble elements may take place. In the case of austenitic steels, especially selective leaching of Ni and Cr occurs resulting in spongy ferrite penetrated by HLM [1,2]. The concentrations of Ni and Cr change abruptly across the steel/depleted zone interface. It is indirect evidence that the depleted zone is formed as a result of selective transfer away from the boundary layer into liquid-metal bulk rather

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than selective solution transport across the steel/liquid metal interface. At the same time, low soluble iron re-deposits on steel substrate if saturation of the liquid metal is approached at the steel surface [5,6].

Oxidation, i.e., transport of steel constituents into scale due to surface reaction with oxygen dissolved in HLM, is another important phenomenon taking place in solid metal/liquid metal system. It is believed, that the protection of the steel surface by means of a continuous oxide layer separating the solid from the liquid metal might mitigate or at least delay SBA [7–9]. It is provided by the *in-situ* addition of oxygen from a gas or solid phase into HLM, so as to form or stabilize oxides of major steel constituents (Fe, Cr, Si) [8,10]. However, also oxidation is a mode of corrosion. Accordingly, oxidation also should be minimized in order to ensure an acceptable life-time for components contacting HLM. An optimum concentration of oxygen in HLM should avoid also oxidation of Pb(Bi) and at the same time provide moderate oxidation of steels. It is believed that oxygen concentration range between 10^{-7} and 10^{-6} mass% could satisfy those requirements since in the HLM with $\leq 10^{-8}$ mass% O, the SBA clearly prevails [1,7,8,11–15]. Steels in HLM oxidize usually with formation of bi-layer magnetite (Fe_3O_4)/spinel ($Fe[Fe_xCr_{1-x}]_2O_4$) scale, spinel and thin Cr-based oxide film. Both, bi-layer scale and spinel represent accelerated oxidation (AO) while Cr-based oxide – protective scaling (PS).

In oxygen-saturated LBE (~10^{-3} mass% O), a relatively fast growing bi-layer scale is formed (AO) [16].

At 10^{-6} mass% dissolved oxygen, the austenitic steels mostly show AO accompanied by spinel formation [5,17,18]. With time, after local failure of scale, a local SBA via selective leaching occurs. Additionally, a non-selective SBA was rarely observed.

Recent results obtained at 450 and 550 °C in flowing LBE (2 m/sec) with 10^{-7} mass% O showed that austenitic steels undergo SBA (selective and non-selective leaching of material) since *in-situ* formed Cr-based oxide film is not a sufficient protective barrier [19]. The incubation time decreases from ~500–4000 h to <200 h with increasing temperature from 450 to 550 °C.

In this work, the results of long-term corrosion tests for up to ~13,194 h on austenitic steels at 400 °C in flowing (2 m/sec) LBE with 10^{-7} mass% dissolved oxygen are discussed and compared with those obtained at 450 and 550 °C under the other similar conditions of test [19].

2. Experimental

The austenitic steels investigated in this work are 1.4970 (15-15 Ti), 316L and 1.4571. Besides composition, there were detected substantial differences in structure of steels in as-received state. Increased hardness (~250 HV_{30}) and presence of deformation twins indicated about stressed state of 1.4970 and 1.4571. The latter has fine-grained structure (G 9.5). In contrast, 316L is in solution-annealed state. A detailed discussion on differences in composition and structure of these steels as well as samples preparation and description of CORRIDA loop operated at the Karlsruhe Institute of Technology (KIT) are presented elsewhere [18,19].

The samples have been joined to each other by means of internal and external threaded connections. The assemblies were placed in the test sections of the loop. The corrosion tests were carried out at 400(+6) °C for 1007, 2015, 4746 and 13,194 h (Fig. 1). The temperature minimum in the cold leg was 290 °C. The LBE flow velocity was maintained during the test at 2(±0.2) m/s. The target oxygen concentration is ~10^{-7} mass%. It was calculated from a Pt/air sensor output using [9].

$$\log Co(mass\%) = -3.2837 + 6949.8/T(K) - 10.080 \times E(V)/T(K) \quad (1)$$

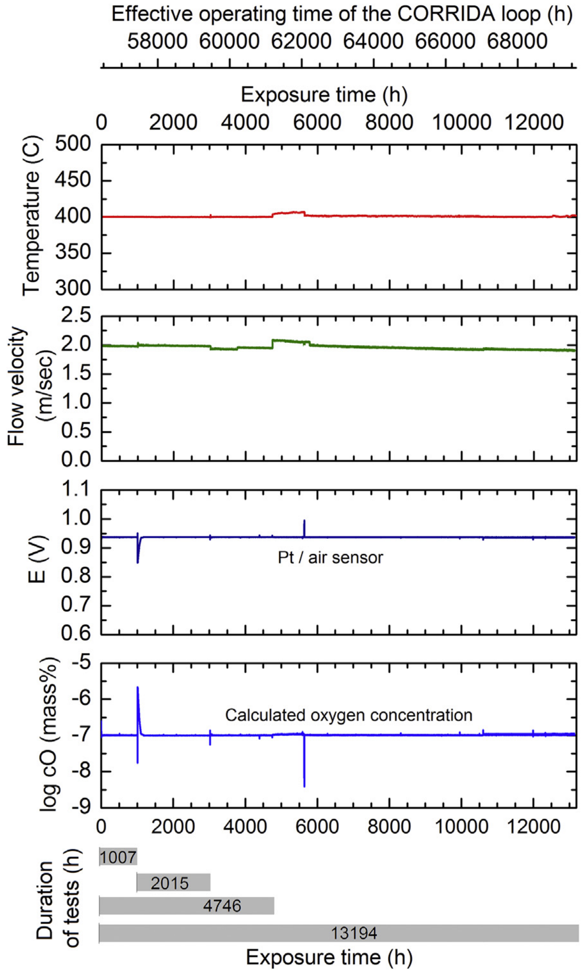

Fig. 1. Time dependence of test parameters: temperature; flow velocity; Pt/air sensor output; oxygen concentration in LBE; duration of test.

The concentration of oxygen in LBE was fairly constant during the experiment, 10^{-7} mass% on average. A short-term excursion for ~170 h to higher oxygen concentration in the LBE with a maximum of 4×10^{-6} mass% O was observed after 1008 h, immediately after removal of the first set of samples (Fig. 1).

After each test of certain duration, the portion of samples was disconnected from the assembly and then from each other. The samples with remnants of solidified LBE were segmented and transverse and longitudinal metallographic cross-sections were prepared. In order to determine the corrosion loss, initial diameter of samples had been measured, before the test, in steps of 2 mm along the length of samples, with an accuracy of 0.5 ÷ 1 μm using a laser micrometer. The diameter of samples was re-measured after the test in the light optical microscope (LOM) at 2000-fold magnification [20,21]. The systematic procedure consists of twelve measurements of diameter on the transverse circular cross-section, rotating the specimen by 15° in-between measurements. Metal recession was determined as half the difference of the initial and unaffected by corrosion diameter after the test. Percentage of surface suffered from the one or another corrosion mode was determined quantitatively by means of evaluating corrosion appearances on opposing sites on the circumference for each measurement. The longitudinal cross-sections were checked with respect to corrosion phenomena not observed in the circular cross-sections. The maximum of corrosion attack was assessed by extra