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Corrosion behavior of Fe–14Cr–2W and Fe–9Cr–2W ODS steels in stagnant liquid Pb with different oxygen concentration at 550 and 650°C

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ABSTRACT

Corrosion behavior of ferritic (Fe–14Cr–2W + Y_2O_3) and ferritic–martensitic (Fe–9Cr–2W + Y_2O_3) oxide dispersion strengthened (ODS) steels in the static isothermal liquid Pb was investigated at 550 and 650 °C depending on the oxygen concentration C_O in the melt for duration up to 1000 h. It was determined that the interaction mode of steels changes from the dissolution in the pure Pb ($C_O \leqslant 10^{-14}$ wt%O) to the formation of protective oxide layers on the surface of steels in the oxygen-added Pb ($C_O \sim 10^{-6}$ wt%O) and to formation of multiphase non-protective scales in the Pb saturated by oxygen ($C_O \sim 10^{-3}$ wt%O). In general, the observed corrosion behavior of ODS steels coincides with that of traditional chromium steels. However, specific structure of ODS steels causes some variations in corrosion process. In the pure Pb ($C_O \leqslant 10^{-14}$ wt%O) the fine-grained structure promotes inter-granular corrosion attack and penetration of lead into steel matrix along grain boundaries. Increase in Cr content in the steel promotes corrosion attack. In the oxygen-added Pb ($C_O \sim 10^{-6}$ wt%O) the fine-grained structure, vice versa, ensures formation of oxide layers with higher Cr content due to fast diffusion of Cr into growing oxide along grain boundaries. The protective properties of oxide layers are improved with temperature rise (550 → 650 °C) and chromium content in steel. In the oxygen-saturated Pb ($C_O \sim 10^{-3}$ wt%O) the ODS steels undergo severe oxidation accompanied by the formation of non-protective multiphase scale which consist of mixture of different oxide phases: plumboferrite, magnetite, Fe–Cr spinel and free Pb. The oxidation kinetics intensifies drastically with temperature and decelerates with increasing chromium content in the steel. Based on the experimental data the scheme of interaction of components in the "steel - liquid Pb" system depending on temperature and oxygen content is proposed.

1. Introduction

Oxide dispersion strengthened (ODS) steels are considered as candidate structural materials for both fission and fusion reactor concepts, while lead based melts (Pb, Pb–Bi, Pb–Li) are the main functional cooling/breeding media [1–4]. An application of ODS steels allows the working temperature limit to be increased up to about 700 °C. However, the corrosion rate of steels in liquid metals increases with temperature as well. Moreover, the specific phase-structural features of ODS steels (fine-grained structure with high length of boundaries, presence of the dispersion oxides, residual porosity etc.) can affect substantially their corrosion response in comparison with traditional steels. It is well known also that oxygen impurity in the lead melts can alter the interaction mode between solid metal and liquid metal from dissolution in the pure melt to severe oxidation in the melt saturated by oxygen. In the lead melt with optimal content of oxygen ($\sim 10^{-5}$ to 10^{-7} wt%O) the dissolution of steel's components is mitigated due to formation of protective oxide layer on the steel's surface while PbO oxide does not precipitate in the cold leg of liquid-metal loop [4–6]. An application of so-called passivation technology has been widely studied for the conventional austenitic and ferritic–martensitic steels at moderate temperatures ($\leqslant$550 °C) [4–6]. At the same time the data regarding compatibility of ODS steels with lead melts are still scarce [7–14]. The limited results testify that chromium ODS steels oxidize in lead melts similar to the conventional chromium steels, i.e. with formation of double-oxide layer $Fe_3O_4/Fe(Fe_{1-x},Cr_x)_2O_4$, outer part of which can be destroyed by flowing melt. It was determined also that with decrease in oxygen content in the melt from 10^{-4} to 10^{-6} and then to 10^{-8} wt%, the concentration of chromium in the inner spinel layer increases up to 15, 30, and 41 wt%Cr respectively [8]. Development of a thick and pronounced inner oxidation zone (IOZ) consisting of Cr-rich oxide particles finely dispersed in the Cr-depleted steel matrix, was found, to be a specific feature of oxidation of ODS steels possessing by fine-grained structure in lead

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melts under fluctuating conditions of oxygen concentration in the range between 10^{-5} to 10^{-9} wt %O [14]. Summarizing scarce literature data it can be indicated that corrosion tests are performed mainly at temperatures from 500 to 650 °C and oxygen concentration ranged from 10^{-4} to 10^{-6} wt%. The conditions representing extreme modes of interaction such as the severe oxidation and intensive dissolution are practically missed as well as the effect of specific phase-structural state of ODS steels and Cr content on the prevalence of oxidation or dissolution processes is not elucidated yet. Therefore, in this work the corrosion behavior of chromium ferritic and ferritic–martensitic ODS steels was investigated at 550 and 650 °C in stagnant liquid Pb with different concentration of oxygen providing dissolution, passivation and severe oxidation of steels.

2. Experimental procedure

Samples ($\varnothing 10 \times 3$ mm) of ODS ferritic–martensitic Fe–9Cr–1.5W and ferritic Fe–14Cr–1.5W steels strengthened by Y_2O_3 oxide particles were supplied in as-HIPed state by University of Science and Technology Beijing (China). Then, the samples were polished and cleaned in acetone followed by the vacuum heat treatment at 1000 °C for 1 h for homogenization of structure and removal of residual stresses.

Corrosion tests of ODS steels were carried out in stagnant isothermal Pb with different concentration of oxygen impurity at 550 and 650 °C for up to 1000 h. Fig. 1 shows the schematic representation of interaction modes of steels facing liquid Pb with different concentration of oxygen plotted using experimental data presented in [6]. Based on the scheme, three intervals of oxygen concentration were chosen for corrosion tests: pure Pb ($C_O \ll 10^{-7}$ wt%) providing domination of dissolution of solid metals; oxygen-added Pb ($C_O \sim 10^{-6}$ wt%) providing passivation of steels and oxygen-saturated Pb ($C_O \sim 10^{-3}$ wt%) providing intensive oxidation of steels.

In order to obtain pure Pb, the samples were fixed in the Nb ampoules. Then, ampoules were filled by liquid Pb in glow box under the argon atmosphere in order to mitigate contamination of melt with oxygen impurity. Argon atmosphere in the glow box was purified with respect to oxygen by liquid Li getter heated to ~350 °C. After the solidification of Pb, the Nb ampoules were placed into protective stainless steels capsules, which were sealed by welding in the same glow box. Then, the capsules were exposed in furnace at 550 and 650 °C. It was assumed that during test, oxygen dissolved in the liquid Pb should be absorbed by the inner surface of Nb capsule. According to thermodynamic evaluation the equilibrium concentration of oxygen in the melt should be reduced to about 10^{-14} wt%. At the same time the fine-dispersed yttrium oxides, strengthening Fe–Cr matrix, should be stable in the Pb melt since free energy of formation of Y_2O_3 is more negative in comparison to liquid Pb containing $\sim 10^{-14}$ wt%O.

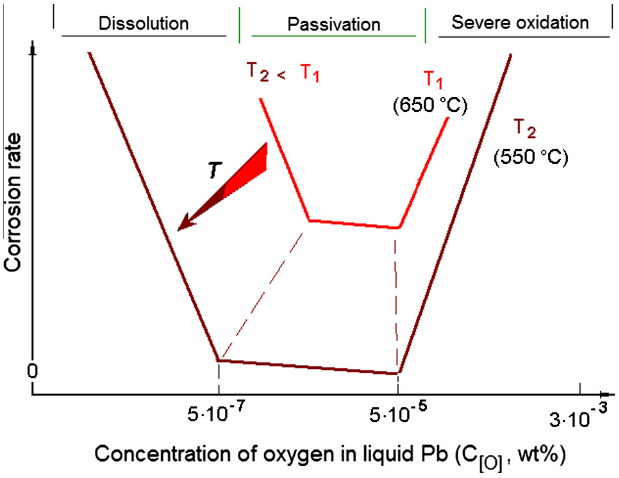

Fig. 1. Schematic representation of corrosion rate and interaction modes of steels facing liquid Pb with different concentration of oxygen depending on temperature.

The alumina crucibles were used for corrosion tests in the oxygen-added and oxygen-saturated melts. In order to provide the oxygen-saturated conditions, the liquid Pb was in a contact with dry air during the tests. The red-colored PbO oxides covered the mirror of the melt indicating that content of oxygen in Pb was nearly saturated and according to the equation $\lg C_{O[Pb]} = 3.2 - 5000/T$ [15] averaged 1.33×10^{-3} and 6.07×10^{-3} wt%O at 550 and 650 °C respectively.

In the case of the oxygen-added melt, the lead melt was in contact with controlled dynamic vacuum atmosphere ($P_{O2} \sim 2.7 \times 10^{-1}$ Pa). Based on the previous experience [9,10] the oxygen concentration in the Pb during corrosion test corresponds to about 3×10^{-6} and 10^{-5}wt %O at 550 and 650 °C.

After the tests, the surface and prepared cross-sections of the specimens were examined using the light optical (LOM) and scanning electron (SEM) microscopes, in order to determine the morphology and dimensional parameters of scales formed. Thinning of samples depending on exposure time in the oxygen-saturated Pb was measured as a half the difference between initial and post-test thicknesses of steel's matrix unaffected by corrosion. Elemental composition of scales and corrosion zones were determined by means of energy dispersive X-ray (EDX) analysis. The weight changes were determined using an electro-balance with an accuracy of 0.01 mg.

3. Results

3.1. Dissolution of ODS steels in pure Pb ($C_O \leqslant 10^{-14}$ wt%O)

After the long term contact with the pure Pb, all samples were covered by adhered solidified lead, indicating wetting of steel's surface by melt and absence of oxide film between liquid and solid metals. Therefore, the exposed samples were cleaned chemically in $CH_3COOH + H_2O_2 + C_2H_5OH$ mixture (1:1:1) at room temperature in order to remove Pb and then to determine the weight changes of samples and morphology of surface facing liquid metal medium. Samples of both steels demonstrated weight losses, which increased with temperature (Fig. 2). The weight loss of Fe–14Cr steel was always greater than that of Fe–9Cr.

After the test at 550 °C, the initially shine and smooth surface of samples become mat and relief indicating corrosion attack. It was

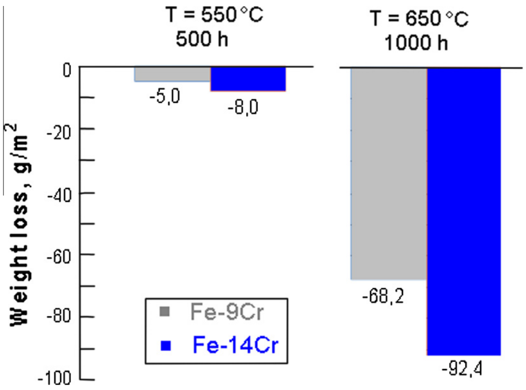

Fig. 2. Weight loss of Fe–9Cr and Fe–14Cr ODS steels after exposure to pure Pb ($\leqslant 10^{-14}$ wt%O) at 550 and 650 °C.