CHARACTERISTICS OF OXIDES ON A PRE-STRESSED T91 STEEL EXPOSED TO LIQUID LEAD-BISMUTH EUTECTIC

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Abstract

Compatibility of structural materials with a coolant, in conditions relevant to power plant operation, is a field of research of primary importance to nuclear safety. The current work describes the behaviour of T91 steels, under such conditions. Three-point-bend specimens were pre-stressed up to yield strength and subsequently exposed to lead-bismuth eutectic (LBE) in static conditions for 2000 hours. The aim was to identify the susceptibility to crack initiation in the selected experimental conditions. Post-test examination by means of SEM equipped with EDX demonstrated the formation of oxide scales without any trace of crack initiation. The oxide was characterised by a two-layer structure. By FIB cutting, lamellas were produced and analysed in HRTEM. EELS technique was used for elemental evaluation of the oxides. Characteristics of the oxide and its interface with the steel were thoroughly characterised.

Keywords: Ferritic-martensitic steel, lead-bismuth eutectic, oxidation, FIB lamellas

1. INTRODUCTION

Materials interaction with Heavy Liquid Metals has been a topic of wide interest for several years [1] because of their potential use in energy-related applications, due to their optimal thermal and neutronic properties. In general, the issue of materials interaction with HLM is the focus of many studies with relation to phenomena such as mass transfer through dissolution and liquid metal embrittlement (LME).

Oxide scales are known to be able to prevent the direct contact with the liquid metal. Their stability and long term protective properties depend on the oxygen content in the environment and mainly on the composition and microstructure of the steel exposed.

This work focuses on the fundamental understanding of mechanisms of interaction of the ferritic-martensitic steel T91 in PbBi eutectic under constant load after long term exposure. The oxygen contained in the liquid metal was sufficient to grow an oxide on the steel and thus preventing dissolution and LME crack initiation. The oxide developed on the steel was characterized by TEM with the use of lamella prepared by a FIB lift-out technique.

2. EXPERIMENTAL

MATERIAL.The ferritic-martensitic steel T91 (Grade 91 Class 2/S50460) of nominal composition (wt. %) Fe-8.9Cr-0.9Mo-0.4Mn-0.2Si-0.2V was produced by Industeel, Arcelor Mittal group [1]. The material was normalized at 1150°C for 15 min with the subsequent water cooling to the room temperature and finally annealed at 770°C for 45 min, slow cooling in the air. The typical microstructure formed by this heat treatment consists of laths of martensite and original austenitic grains.

SPECIMENS. Specimens were fabricated by means of wire cutting using electrical discharged machining (EDM). The surface was ground to 600 grit finish. Flat smooth specimens of dimensions 14.9x3x1 mm^3 were designed to fit the holders. The specimens were cleaned by acetone in an ultrasonic bath, then mounted into holders and pre-loaded (**Figure 1**). Six specimens were loaded to the Yield Strength, YS. The load was applied by tightening the holder screw at room temperature, the respective elastic deflection was calculated according to the ISO7539-2: 1989.

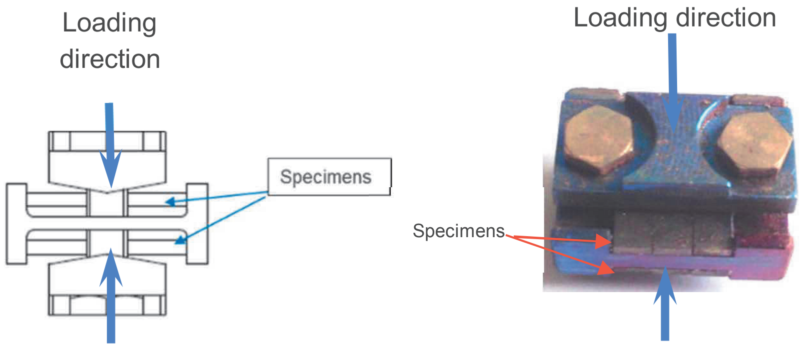

Figure 1 - Schematic and picture of specimens in the holder

EXPERIMENT Pre-loaded specimens were inserted in the PbBi at 350°C for 2000 hour exposure in a static tank. The concentration of dissolved oxygen in the liquid PbBi was changed by dosing of gases. The content was monitored by using oxygen sensors (Bi/Bi_2O_3); the measured concentration was oscillating in the range of 10^{-7}-10^{-5} wt. %.

EXAMINATION: After exposure, the specimens were observed and analysed in a dual beam FIB-SEM system LYRA3 GMU (fy TESCAN). The sample surfaces with cracks were recorded in a secondary electron mode at working voltage 20 kV and electron beam current ~1 nA. The FIB milling and polishing procedure using Ga^+ ions at working voltage 30 kV and ion beam currents ~1 nA and ~0.2 nA carried out to create a lamella. A standard FIB lift-out technique was used for the TEM lamella preparation. TEM observations of the lamellas were carried out in the JEOL JEM 2200FS Field Emission Transmission Electron Microscope operated at an accelerating voltage of 200 kV. The composition of different features was analysed by electron diffraction, EDS and confirmed by EELS technique.

3. RESULTS

After 2000h exposure to PbBi eutectic at 350°C, the T91 developed an oxide up to 1.5μm with a two-layer structure (**Figure 2**) which prevented the direct contact with the liquid metal. The oxide prevented both dissolution and crack initiation. The applied experimental conditions were not sufficient to crack the oxide layer. Observation of the surface of the specimens did not evidenced any cracking (only localized macro-defects due to specimens handling). Moreover, observation and elemental analyses of their cross-section by a qualitative EDS line scan highlighted the enrichment of the internal oxidation zone in Cr and the outer layer in Fe. The external part also contained embedded Pb clusters. No cracking was observed in the cross-sections.

a) SEM cross section
b) EDS line scan position on the no stress zone

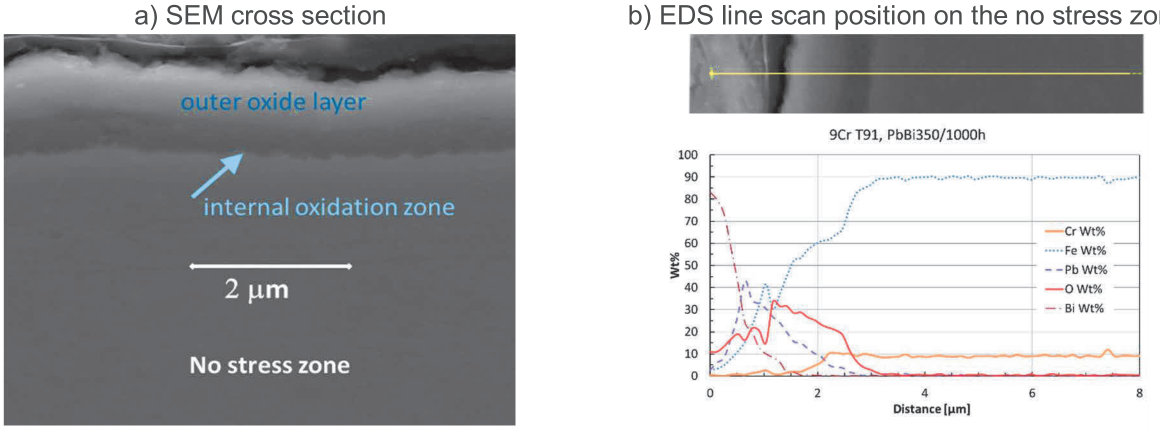

Figure 2 - SEM image of T91. Cross-section with a qualitative EDS line scan.

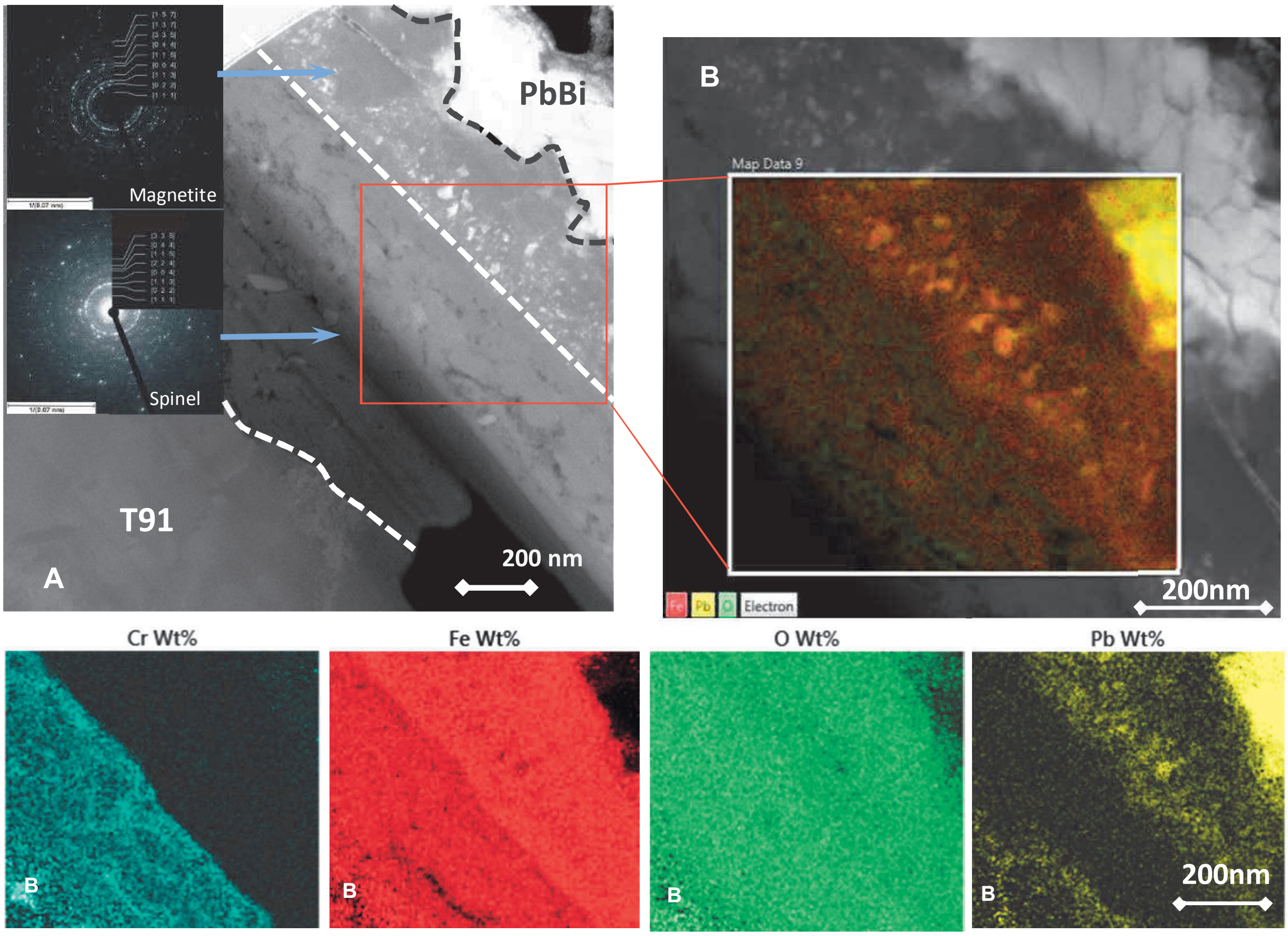

Figure 3 - A) STEM image of T91 lamella with highlighted oxide layers (white dotted lines) and diffraction patterns; B) STEM-EDS qualitative elemental maps showing the distribution of Cr, Fe, O and Pb in the selected area

For a deeper understanding of the formed oxide and its structure and composition, FIB in situ lift-out technique was used to produce lamellas for the TEM examination. In order to reduce contingent artefacts and obtain fine surface on FIB cross-section plane, the surfaces for FIB sectioning were protected by a thin platinum layer and, in addition, the last FIB milling steps were carried out with the lowest possible ion beam current.

In the lamella there were areas that were about 100nm thick (or thinner), which was confirmed by TEM. These areas were used for the TEM analyses.

The TEM examination of the lamella (**Figure 3**) confirmed a general microstructure of the ferritic martensitic steel T91 matrix and the two-layer oxide. **Figure 3** highlights, with the use of Scanning Transmission Electron Microscopy (STEM), the layers with dotted white lines. The inner oxidation zone was characterized by elements Fe-Cr-O with a typical spinel structure, $FeCr_2O_4$ (**Figure 3A,** bottom diffraction pattern). The outer layer, with a typical diffraction pattern of magnetite, Fe_3O_4, (**Figure 3A,** upper diffraction pattern) contained Pb particles. EDS mapping (**Figure 3B**) was used to visually highlight the presence of the main alloying elements, combined with oxygen and the presence of pure Pb in the outer magnetite. The red square in **Figure 3A** highlights the position of the map, confirming that this is mostly the oxide (O enrichment in all the EDS scanned area), with a clear distinction for the outer layer that contains only Fe. Element which is slightly depleted in the spinel area, where Cr is abundant.

4. DISCUSSION

Cracks were not observed in any of the specimens. The absence of cracking in these conditions is possibly due to lack of wetting and the fact that only small plastic strain corresponding to YS was applied. It is a known assumption that oxides prevent dissolution of steels in the liquid metal and also form a barrier preventing wetting, which is being considered as one of pre-conditions for the LME initiation. Moreover, another characteristics of the LME is its occurrence in the regime of higher plastic deformation, which was out of the scope of this study and was not applied.

Oxidation of the steel T91 in contact with oxygen containing PbBi was extensively studied [2-5]. It was stated that the outwards diffusion of Fe to form Fe_3O_4, leaves an accumulation of vacancies in the Fe-Cr alloy. The fast growth also accounts for the formation of pores and the presence of small amount of Pb embedded in the outer oxide. As a consequence, the spinel layer growth is established by oxygen transported across the defects in the outer magnetite layer. The Fe-Cr spinel growth rate was found to be linked to the magnetite growth rate [3] and consequently also limited by the iron diffusion in the oxide scales lattices [4]. Therefore, the limiting mechanism is the iron diffusion that allows the creation of available space for the Fe-Cr spinel growth [3]. According to these assumptions, the Fe-Cr spinel layer thickness depends on the capability of magnetite formation, which is also affected by the microstructure of the surface layer. In fact, an inward oxidation may take place due to fast oxygen diffusion along the grain boundaries and defects. Due to the fact that grain boundaries can serve as high-diffusivity paths for reactive elements in polycrystalline materials, the grain size of the substrate plays an important role for the diffusion controlled oxidation behaviour of steels. The uneven metal/oxide interface indicate an internal/intergranular oxidation mechanism by which the scale grows inward. Therefore, the thickness of the internal oxidation is greatly affected by the microstructure but also by the oxygen activity in the environment, which drives the element inwards.

Embedded intrusions of pure Pb in the outer, fast growing Fe_3O_4 have the potential to create internal stresses in the fast growing Fe_3O_4 layer and with time it might favour damage. In fact, it was observed that dissolution/damage of the oxide was already ongoing (bottom of **Figure 4a**) despite the fact that the system was a static liquid. The Pb cluster may play an active role on accelerating the process. The reason why the intrusions are of pure Pb are assumed to be related to the thermodynamic state of the PbO, which is possibly present in forms of particles in the liquid metal since the beginning of the test. This oxide particles might be in contact with the clean, original surface (during filling of the static tank, the PbO would have the tendency to deposit on all the steel surfaces). The fact that the oxide particles are rich in oxygen and the outward diffusing Fe would be fast reacting with the oxygen in the environment, could create even an acceleration of the Fe_3O_4 formation.

5. CONCLUSION

Specimens of the ferritic-martensitic steel T91 pre-stressed to the yield strength were exposed to static PbBi at 350°C for 2000h.

A two-layer continuous oxide grew on the surface of the specimens. The outer layer was magnetite and the internal a Fe-Cr spinel.

No oxide failure was observed and this prevented any local wetting during the exposures up to 2000 hours. No LME crack was observed in any of the bend specimens on the surface and the corresponding cross sections.

The absence of the LME in these test conditions is most likely a consequence of (i) the absence of wetting and (ii) the absence of a local high plastic deformation.

Pb clusters in the Fe_3O_4 might be generated by particles of PbO sticking to the original surface of the steel, embedded during fast growing of the Fe_3O_4.

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