Increasing Corrosion Resistance of 1.4970 and T-91 Steels Exposed to Heavy Liquid Metal with the Help of Microsecond-Pulsed Intense Electron Beam

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Abstract – Heavy liquid metals (HLM), as Pb and Pb–Bi alloys, are considered as coolants for fast nuclear reactors due to their thermal and neutronic properties. The improvement of the corrosion resistance of the 1.4970 and T-91 steels, exposed to Pb- and Pb–Bi-eutectic melt, was obtained by steel surface modification/alloying with aluminium (Al) using Microsecond-pulsed Intense Electron Beams (MIEB-Al). The procedure consists in two steps: (i) pre-coating the surface steel with Al or an Al-containing alloy layer and (ii) melting the coating layer and the surface layer of the steel using intense pulsed electron beam. By applying this procedure, the corrosion resistance of the T-91 and 1.4970 steels, exposed to Pb- and Pb–Bi-eutectic melts, with different oxygen concentrations and at different temperatures, was drastically improved. The reason for this improvement is the formation of an alumina layer on the steel surface (< 1 μm) acting as anti-corrosion barrier.

1. Introduction

The reference structural materials, selected for the nuclear systems using HLMs, are ferritic-martensitic (F/M) steels and austenitic steels. The corrosion behaviour of these steels exposed to Pb- or Pb–Bi-eutectic (LBE) melt is affected by several parameters, such as the oxygen activity in the liquid metal and the temperature. With appropriate oxygen activity in the HLM, dissolution of steel elements in the liquid metal can be minimized or suppressed through the formation of a protective oxide scale on the steel surface [1, 2]. As far as the temperature effect is concerned, it was shown that austenitic steels suffer from severe corrosion attack in Pb or LBE melt at temperatures above 500 °C, while F/M steels form thick oxide scales, which could compromise the efficiency of the heat transfer. Therefore both steel systems are restricted to application at temperatures below 500 °C [2].

In order to improve the corrosion resistance of the steels exposed to HLM above 500 °C, one possibility is to change the oxidation behaviour of the steels exposed to oxygen-containing HLM. In previous works it was shown that this can be achieved by alloying the steel surface with Al, using a procedure called GESA process (Gepulste ElektronStrahl Anlagen – pulsed electron beam installations) [3, 4]. The goal of this procedure is to form an alumina layer as a result of the interaction of Al with the oxygen dissolved in HLM. It is well known that the formation of an alumina scale on steel surfaces increases substantially the resistance of steels against dissolution attacks in HLM [5].

The procedure consists in two steps: (i) coating the steel surface with Al or Al-containing alloy and (ii) melting both the coating and the steel surface by irradiation with microsecond-pulsed intense electron beam (MIEB). Such treatment leads to the mixing of the steel elements with coating elements, finally leading to a modified Al-containing layer on the steel surface. The thickness of Al-containing layer (tens of microns) is around the penetration depth of electrons into the steel. Therefore mechanical properties of the bulk steel are not changed by surface modification/alloying using the MIEB-Al procedure.

Two steels, namely, “T91” and “1.4970”, are candidates for the construction of the core components of advanced nuclear systems. The aim of this work is to improve the corrosion behaviour of these steels, when exposed to HLM, by surface alloying with Al using MIEB process. The influence of the MIEB process parameters on the corrosion behaviour of the surface-modified steels is also discussed.

2. Experimental

The modification/alloying of steel surfaces, using the MIEB-Al procedure is intended to be used for improving the corrosion resistance of fuel elements cladings for nuclear systems using HLM as coolants. The experimental work was carried out on tubular samples: diameter of 8.5 mm, wall thickness of 0.5 mm and length varying in the range 20–150 mm. Flat samples were also used for optimization of the MIEB-Al procedure.

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As a first step of the process, homogeneous Al coatings, with the thickness in the range of 5 to 20 μm, were deposited on flat and cylindrical specimens using vacuum arc deposition.

The MIEB process, which allows the melting of large surface area to a depth from few to several tens of micrometers, was used for mixing the coating with the steel matrix. The irradiation of the coated samples with microsecond-pulsed intense electron beam was performed using the GESA-1 facility, described in [6]. The main characteristics of the facility are: accelerating voltage 100–150 keV, beam energy density 20–50 J/cm² and pulse duration 20–35 μs. The beam has cylindrical shape with diameter of 5–6 cm. For e-beam parameters lying in these ranges, the calculated thickness of the modified layer lies in the range of 10–25 μm.

The flat specimens were irradiated directly, while the tubes were irradiated through a diaphragm with a sample rotation of 30° after each pulse.

The corrosion and creep-to-rupture tests were performed at IPPE-CRISM “Prometey”. Specimens were tested in lead and LBE under a wide range of conditions: temperatures from 400 to 700°C, flow velocities from stagnant up to 3 m/s, oxygen concentration from 10⁻⁷ wt.% up to saturation level, isothermal and non-isothermal.

The evaluation of the specimen was performed using Light Microscopy (LM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX).

3. Results

The Al concentration, the thickness and homogeneity of the superficial modified layer depend on the MIEB process parameters, such as energy density and number of pulses, as well as on the steel composition, surface preparation and coating thickness.

Figure 1, a shows that the MIEB with the energy density in the range 20–50 J/cm² provides a modified layer with the thickness from 10 to 25 μm, for an initial 10 μm Al-coating thickness. It should be mentioned that the melting depths depend on the coating thickness. The melting depths were calculated using the ORION code, which takes into consideration the heat conduction [7].

Ongoing experiments have shown a variation of the Al-concentration profiles perpendicular to the surface, depending on the number of MIEB pulses and the initial thickness of the Al coating. The analysis shows that Al penetrates into the steel within the molten surface layer. Fig. 1, b depicts the Al-concentration profiles, after the exposure of samples (covered with 10 μm thick Al-layer) to MIEB with 45 J/cm² and pulses number between one and four. After three pulses the profile of Al-concentration is almost constant around 20 μm.

The amount of the Al, which can be introduced in the superficial layer, is a function of the coating thickness and the energy input. In previous works it was shown that an energy input in the range 30–50 J/cm² allows for up to 30% of the original Al amount to be alloyed [3]. The optimal thickness for Al-coating was defined being between 5 and 10 μm for an energy input of 45 J/cm².

Based on our experimental work and calculations, the optimal MIEB-Al procedure consists in the following:

- preparing the steel specimen surfaces before Al-coating deposition by:
  - electropolishing of the austenitic steels and mechanical polishing of the ferritic-martensitic steels;
  - ultrasonic cleaning and ion beam etching;
  - Al deposition using vacuum arc process (thickness: 5–10 μm);
  - thermal treatment of coated steel specimens (200°C, 2 h, argon);
  - application of MIEB process: melting the Al-coated steel surfaces using intense pulsed electron beam (GESA-1 facility) with accelerating voltage 120 kV; energy density 40–45 J/cm²; pulse duration 30 μs; number of pulses: 2–3.

For nuclear application, a homogeneous Al distribution of defined concentration has to be guaranteed for an entire modified surface, especially in case of cladding tubes. The main goal of the experimental evaluation was to verify that MIEB-Al procedure, applied to different steel grades, which are envisaged for advanced nuclear systems, can provide protection in different HLMs.

Steel specimens, in original polished state and after surface alloying of Al by electron beam melting, were exposed to liquid lead and LBE under different normal and abnormal conditions related to nuclear applications:

- oxygen concentration: 10⁻³, 10⁻⁴, and 10⁻⁸ wt.%;
exposure time: hundreds to more than fifteen thousand hours;
- temperature range: 450–650 °C;
- stagnant and flow conditions;
- different coatings: Al, Al–Fe, Al–Cr–Fe.

The experiments performed at three different temperatures showed that the oxidation of specimens made out of T-91 with no Al-coating is intensive even at low temperature. The thickness of the spinel-type oxide scale varies from approx. 15 µm, for exposure at 476 °C, to 20 µm at 490 °C and 25 µm at 550 °C (Fig. 2). An internal oxidation zone (IOZ) was observed after exposure at 490 and 550 °C.

Fig. 2. LM of cross section of T91 steel specimens after exposure to LBE (2500 h, 550 °C, 1–4 $\cdot 10^{-6}$ wt.% oxygen content) showing thick spinel oxide scale and IOZ

Up to now, the maximum exposure time to LBE at 550 °C was 16547 h. After this period the non-alloyed T-91 specimens have shown a duplex oxide scale (spinel with magnetite on top) with the thickness ranged from 30 to 300 µm.

A completely different aspect was observed in the cross section of the surface-alloyed T-91 specimens after 16547 h exposure to 550 °C (Fig. 3): a very thin oxide scale (< 1 µm) on top of the surface. This layer protects the steel from LBE attack and from oxygen diffusion into the coating and bulk material. The diffusion of Fe through the surface, to form a magnetite layer on top, is also prevented by the thin alumina scale. In order to form protective alumina scale, the minimum Al concentration in the modified layer should be higher than 3 wt.%. The upper limit of Al content is approx. 10 wt.% and is determined by the occurrence of cracks in the modified layer during MIEB treatment.

Generally, the corrosion tests have confirmed that the MIEB-Al procedure leads to an improved corrosion resistance of the steels exposed to HLMs, by changing the type of the oxide formed on the surfaces. However, the occurrence of area covered by spinel-type oxide requires further optimization of the procedure.

Currently, three directions for the optimization of the MIEB-Al procedure are under evaluation: (i) multi-stage modification, (ii) usage of composite pre-coatings and (iii) irradiation of tubular samples by radially converging electron beam.

In the multi-stage modification the MIEB-Al procedure is repeated several times. Two-stage modification showed a significant improvement of the modified layer homogeneity. It should be noted that tests performed under creep conditions with thermal cycling, showed that the two-stage modification of the T91 steel promotes an appreciable increase of the creep resistance (Fig. 4).

Fig. 4. Comparison of creep-to-rupture experiments of original and two-stage modified T91 steel in Pb–Bi flow (2 m/s) at 550 °C with and without thermal cycling ($10^{-6}$ wt.% oxygen in LBE)

As already mentioned, the protective effect of the GESA modification of steels in oxygen-containing HLM is based on the formation of a thin alumina film on top of the modified layer. The addition of Cr in binary Fe–Al alloys has been shown to reduce the level of the Al content needed to form a protective Al$_2$O$_3$ layer (third element effect) [8]. Therefore, in particular, the quality of the protective layer on the austenitic steel containing high amount of chromium is better than the quality of the protective layer on the F/M steels. Based on experimental data, the Fe$_{100-x-y}$Cr$_x$Al$_y$ alloy system ($x = 10–20$ wt.%; $y = 6–20$ wt.%) was chosen for coating the steel surfaces. After the deposition of alloys, the GESA process was used to melt and bond the coating on the steel surface.

Corrosion tests of steel samples, coated with FeCrAl-alloys with different compositions, are performed in HLM in a wide range of parameters values. As an example, Fig. 5 shows two specimens made out of the T91 steel, initially coated with Fe$_{78}$Cr$_{14}$Al$_8$ alloy (thickness: 10 µm) and subsequently MIEB-treated (energy density 45 J/cm$^2$, pulse duration 30 µs; number of pul-
Modification of Material Properties

Fig. 5. Surface coated with Fe$_{78}$Cr$_{14}$Al$_8$ alloy and subsequently GESA-treated tubes made out of T91 steel showing a shiny aspect after 5000 h exposure to LBE (10$^{-6}$ wt.% oxygen) flowing with 1–1.2 m/s at 600 °C. As one can see there is no dissolution attack and no area with magnetite or spinel on the whole samples surface. The evaluation of the nature and the thickness of the protective layer is underway, but one can conclude that the application of the Fe–Cr–Al pre-coating is rather promising.

As already mentioned, the irradiation of the cylindrical samples was done with MIEB through a diaphragm with a sample rotation after each pulse. It is obvious that this procedure is not optimal since the chemical composition and, implicitly, the properties of the modified layer in overlapping zones can differ from that in the main part of the layer. In order to solve this issue, it would be better to irradiate the samples by radially converging pulsed electron beam. A new facility called GESA IV, able to generate radially converging pulsed electron beam, was designed and manufactured [9]. Currently, the irradiation procedure, using this facility, is under development.

4. Conclusions

The improvement of the corrosion resistance of the 1.4970 and T-91 steels, exposed to Pb and Pb–Bi–eutectic melts, was obtained by steel surface modification/alloying with Al using Microsecond-pulsed Intense Electron Beams. The procedure consists in two steps: (i) pre-coating the surface steel with Al or an Al-containing alloy layer and (ii) melting the coating layer and the surface layer of the steel using intense pulsed electron beam. In order to obtain a homogeneous and crack-free Al-alloyed layer on the steel surface, the following experimental conditions were required: Al pre-coating thickness range 5–10 µm, electron kinetic energy 120 keV, pulse duration 30 µs, energy density 40–45 J/cm$^2$, number of pulses 2–3.

By applying this procedure, the corrosion resistance of the T91 and 1.4970 steels, exposed to Pb and LBE melts with different oxygen concentrations and different temperatures, was drastically improved. The reason for this improvement is the formation of an alumina layer (< 1 µm) on the steel surface, acting as anti-corrosion barrier.

Further development of the MIEB-Al technology should be directed to developing the procedure of pre-coating deposition on full-length fuel claddings and the procedure of irradiation by radially converging MIEB.

References