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T91 cladding tubes with and without modified FeCrAlY coatings exposed in LBE at different flow, stress and temperature conditions

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Abstract

Corrosion tests of 2000 h duration are conducted on tubes consisting of the steel T91 in liquid metal loops containing eutectic lead–bismuth melt with 10^{-6} wt% oxygen in solution. The experiments include tests at temperatures of 480–600° C, at liquid metal flow velocities of 1, 2 and 3 m/s and under mechanical stress due to an internal pressure of 15 MPa. The surface of tubes exposed to 600 °C and to different flow velocities are coated with a FeCrAlY alloy to examine its suitability as a protective coating for high loaded parts like cladding tubes. The coating was remelted by an electron pulse of GESA to homogenize the coating and improve its bonding to the bulk material. In all of the tests no liquid metal attack was observed. As received steel specimens developed multilayer oxide scales of a thickness increasing with temperature and internal pressure, while coated tubes had a thin protective alumina scale. Flow velocities above 2 m/s permanently removed formed magnetite at 550 °C. No influence of the flow velocity was observed for the coated surfaces which keep their stable thin alumina scale. The internal pressure of 15 MPa caused a strain of 0.7% in the tube wall, which obviously increases iron diffusion and enhances magnetite formation.
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1. Introduction

During the last years several authors examined the suitability of austenitic and ferritic steels as a structural and cladding material in liquid, eutectic lead–bismuth (LBE) loops [1–3]. The LBE contains around 10^{-6} wt% oxygen to allow formation of a protective oxide scale on the surface. It is confirmed that austenitic steels suffer from severe corrosion attack in lead or LBE melt at temperatures above 500 °C, while martensitic steels form thick oxide scales that periodically may spall off and eventually block cooling channels. Furthermore the thick oxide scale hinders the heat transfer through the cladding wall of fuel pins. Both materials are therefore restricted to temperatures below 500 °C.

Structure parts that are exposed to temperatures above 500 °C have to be protected by a suitable surface modification. A well understood measure is surface alloying of strong oxide formers. Al has shown its potential to protect steel surfaces against corrosion and severe oxidation in contact with lead alloys, when its concentration in the surface region amounts to 5–15 wt% [2–5]. Stable thin alumina scales are formed in this case that protect the steel from dissolution attack and from internal oxidation as well as from Fe diffusion through the surface.

This paper will focus on the influence of different temperatures, LBE flow rates and mechanical stresses on the corrosion behavior of T91 steel tubes in liquid metal loops of the Institute for Power Physics and Engineering (IPPE) in Obninsk, Russia. Part of the tubes is coated with the Al containing alloy FeCrAlY because of its ability to form protective alumina scales. The behavior of the surface

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Table 1
Measured composition of T91 steel and of the coating FeCrAlY

	C	Si	Mn	Cr	Al	Y	Mo	Fe	Ni	V	Nb
T91 (wt%)	0.105	0.43	0.38	8.26			0.95	Rest	0.13	0.20	0.075
FeCrAlY coating (wt%)				15.89	5.95	0.64		Rest	<0.03		
FeCrAlY coating + GESA (wt%)				15.2	4–5	<0.5		Rest			

Table 2
Mechanical properties and thermal treatment of the T91 tube specimens

Grain size (μm)	6–9	Normalization: 1040 °C, 15 min
Ultimate tensile strength σ_{uts} (MPa)	744	
Yield strength $\sigma_{p0.2}$ (MPa)	607	Tempering: 710 °C, 40 min
Total elongation ε_t (%)	21.5–22.7	
Uniform elongation ε_u (%)	9.3–10.6	

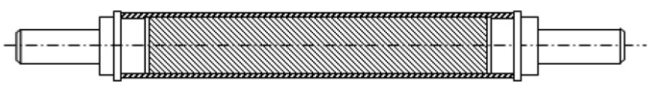

Fig. 1. Scheme of the test specimen used in tests without internal pressure.

coating, modified by GESA, is examined for the highest temperature of 600 °C and in the experiments with different LBE flow rates. Examination of the influence of mechanical stresses is conducted because swelling of the fuel by irradiation or fuel cracking will lead during operation to an increase of stresses on the cladding wall. This is simulated in experiments where an internal pressure is applied to a T91 cladding tube.

2. Materials and test specimens

The specimens tested in the loops are tubes of 8.0 × 0.5 mm of T91 steel. Part of the test tube is in as received condition (original), other tube specimens are coated at the surface with FeCrAlY. The composition of both materials represents Table 1.

For the first time cladding tube specimens with dimensions relevant for reactor loops have been produced by the IPPE, for conducting the corrosion experiments. Mechanical properties and thermal treatment are given in Table 2.

It is known that alloys containing Al in a concentration range of 4–15 wt% have a very good oxidation resistance because the alumina scale that forms in presence of oxygen is thin and stable [2]. Therefore a FeCrAlY coating of about 30 μm thickness was precipitated by Sulzer, Wohlen, Switzerland onto the surface of some of the specimens to improve the corrosion resistance against the LBE containing oxygen. This coating, however, is relatively porous and of varying thickness because the coating is not much thicker than the size of the melt drops in the low pressure plasma spray (LPPS) process applied. The GESA pulse power process [6] was employed to modify the coated surface layer, a process that allows large area surface melting of materials to a depth of several 10 μm in some 10 μs without influencing the material structure of the bulk material. By this way the coating becomes homogeneous and, moreover, the bonding of the coating to the steel surface was improved because the melting depth is slightly deeper than the thickness of the coating.

Fig. 1 shows the scheme of the test specimens which consist of the test tube plugged at the ends by connection pins that are welded into the tube. The tubes have a length of 100 mm and 49 mm for the original and coated tubes, respectively. Inside each tube there is a displacer that fits in with a 0.1 mm gap.

The scheme of the specimen used for testing with internal pressure is drawn in Fig. 2. In this case the displacer is a tube to allow easy expansion of the gas inside the tube. One end plug has an axial bore hole for the gas inlet. The tube diameter is again 8.5 × 0.5 mm and the length 150 mm.

3. Test equipment and experimental conditions

Two loops are employed in the examination of the steel specimen tubes, the loops Tsu-2M and SM-1, both in the IPPE [7]. They are non-isothermal loops driven by an

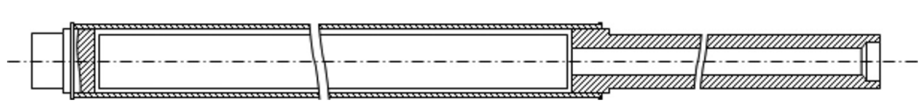

Fig. 2. Scheme of the test specimen used in tests with internal pressure.

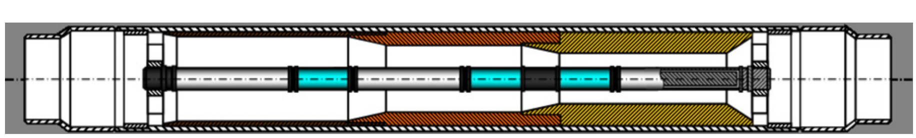

Fig. 3. Test section for exposure of tubes to LBE with different flow velocities (axial extension in a smaller scale then the radial one).

impeller pump with a capacity of 5 m^3/h at 1.5 MPa. The loop capacity is 80 l. After passing the test section the LBE is cooled to 270 °C and than heated up to the desired temperature by direct electrical heating before entering the test section. An electromagnetic flow meter is used to measure the velocity of the liquid metal flow. The oxygen concentration in both loops is set to 10^{-6} wt%. Loop Tsu-2M is used to examine the behavior of the test tubes at 480, 550 and 600 °C with a LBE flow velocity of 1–1.2 m/s. The lower temperatures are applied to the original tubes, the high temperature of 600 °C to the coated ones only. The second loop, SM-1, which works at 550 °C, is in a condition to allow exposure of tubes at liquid metal velocities of about 1, 2 and 3 m/s by employing a special test section. Another test section is used to pressurize the tubes for examination of the influence of mechanical stresses on steel corrosion and oxidation, respectively.

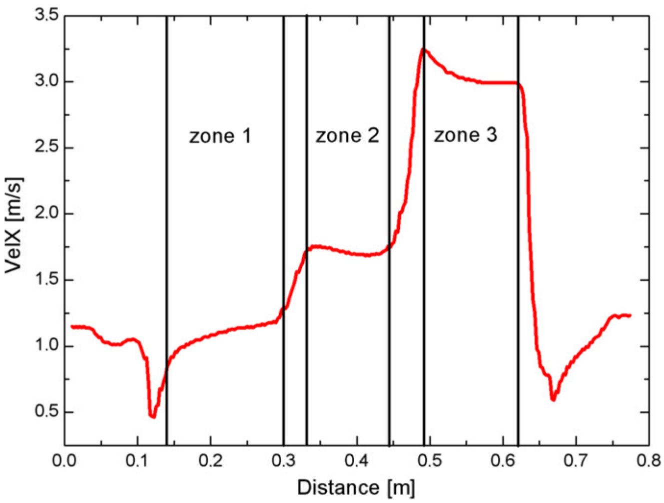

Fig. 4. Flow speed profile in the test section for different flow velocities.

The test section for different LBE velocities consists of a tube with 48 mm outer diameter that in its interior has three areas of different diameters that should force the LBE to flow with velocities of 1, 2 and 3 m/s in the corresponding areas, respectively. A scheme of the test section is depicted in Fig. 3. The tube specimens are placed in the center of the test section tube in a way that always one original and one coated specimen are in each one of the three

Fig. 5. Original (above) and surface coated (below) test tubes after 2000 h exposure to LBE flowing with 1–1.2 m/s at 550 °C; the original one shows a dark layer, the surface coated one is still shiny.

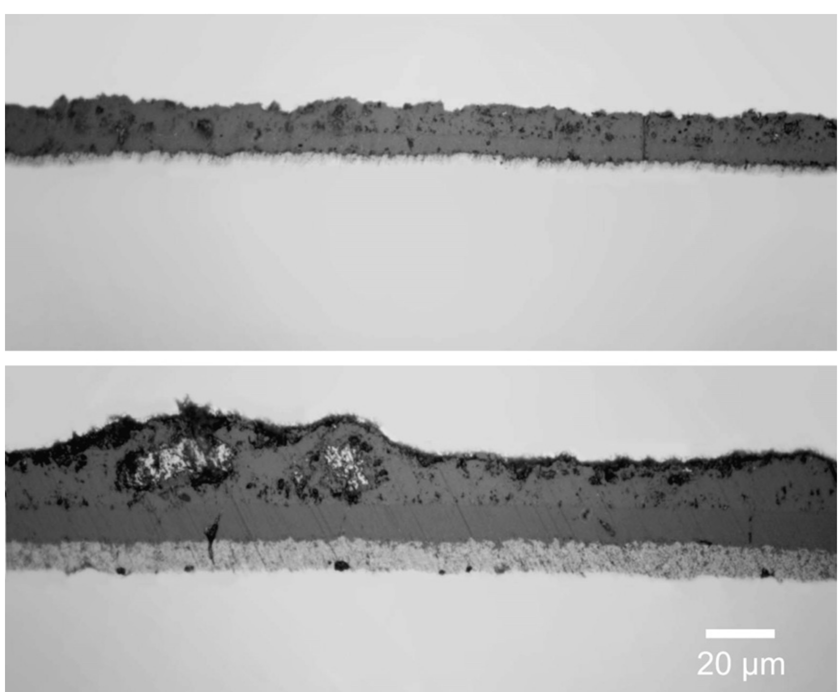

Fig. 6. LM's of cross sections of T91 steel specimens after 2000 h exposure to LBE with 480 (above) and 550 °C (below), respectively. Both specimens show the typical three layered oxide scale, magnetite–spinel layer–internal oxidation zone.

velocity areas. The geometrical sizes are not proportional, the axial extension is on a smaller scale then the radial one.

A numerical calculation with the program *fluidyn*™ – *MP, vers.5.0.2* yields the speed of the liquid LBE which has to be assumed inside the test section. The result is presented in Fig. 4. It can be seen that the desired flow velocities are close to the intended ones.

The test section for pressurized tubes contains two specimens. One of them is connected to a gas pipe for introduction of the gas from an external reservoir with 15 MPa pressure. The other is without pressure for comparison. The tangential stress σ_t in a thin walled pressurized tube is given by [8]

$$\sigma_t = Pd/2\delta, \quad (1)$$

where P is the internal pressure in MPa, d the tube internal diameter and δ the wall thickness of the tube, both in mm. This leads to a $\sigma_t = 112.5$ MPa. The diameter of the tube specimen is measured at 5 equidistant places along the tube axis before assembling the test section to allow determination of the strain rate.

4. Examination of specimens

After completion of the tests the tube specimens were removed from the working sections. Traces of LBE left on the surface are washed off with oil at 180 °C. The surface was brushed with a coarse calico drenched with ethyl alcohol. Cleaning of the surface allows to identify possible corrosion damages and to find areas of interest for metallographic studies.

Discs were cut from the tubes at selected places that were ground and polished with a Struers Tegrapol 31. Light microscopy (LM) analyses were done by using the microscopes Leitz Aristomet and Olympus BX60H. Scanning electron microscopy (SEM) was conducted with the Leitz AMR1000 and Hitatchi S800. The EDX analysis was performed with the Thomson WIN EDS that is attached to the Hitatchi S800.

5. Results

5.1. Tests at different temperatures

After 2000 h of exposure to flowing eutectic Pb–Bi melt (LBE) with 1.0–1.2 m/s at temperatures of 480 and 550 °C the tubes without surface modification exhibit an oxide scale of dark smooth appearance on the whole surface. The tube with surface modification by GESA shows a shiny metallic surface with only few dark places after exposure to 550 and 600 °C. The original and surface coated tube specimens exposed at 550 °C are shown in Fig. 5.

The metallographic analysis of the cross sections of original specimen tubes after exposure to 480 and 550 °C shown in Fig. 6 yields an oxide scale thickness of 18–25 and 25–45 μm, respectively. As expected, the oxide scale grows faster at the higher temperature. The upper magnetite scale and the spinel layer below can clearly be distinguished and also the third zone in which oxygen penetrates into the bulk material by diffusion along the grain boundaries. The oxygen diffusion zone is very weak after exposure to 480 °C but becomes prominent at higher temperatures. The figures are taken from the unetched metallography to make the diffusion zone visible. The above observed oxidation behavior is well known already

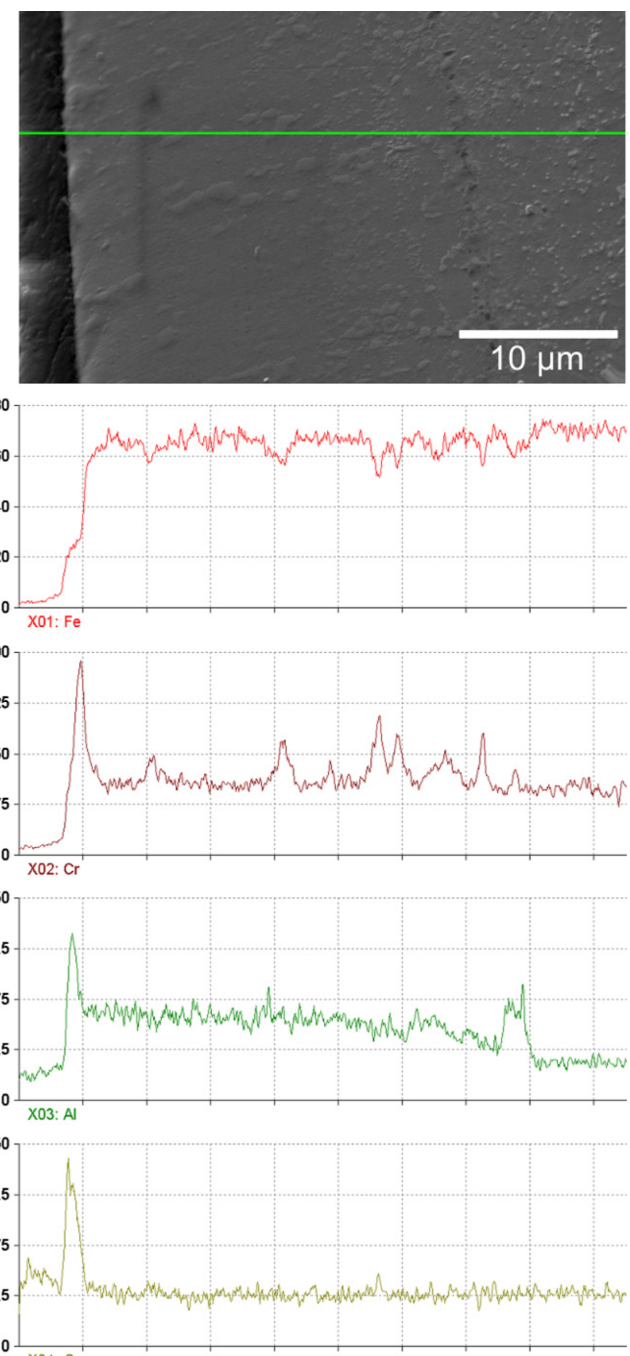

Fig. 7. SEM of the cross section of the coated T91 tube specimen after 2000 h exposure to LBE at 600 °C. Below is the EDX line scan through the surface region. A very thin Al-oxide scale was formed.

from other experiments with ferritic steels in stagnant and flowing LBE [1–5].

A completely different appearance is offered in the cross section in Fig. 7 of the coated surface region after 2000 h exposure to 600 °C. Despite the higher temperature there is only a very thin oxide scale (<1 μm) on top of the surface. It is not visible from the metallography but can be recognized in the line scan below. It becomes clear from Fig. 7 that the Al peak reaches its maximum about 0.5 μm before the Cr maximum. That means, the top oxide scale must consist mainly of alumina followed by a thin layer enriched in Cr. These layers protect the steel not only from LBE attack but also from oxygen diffusion into the coating and bulk material although the temperature is higher than that in the experiments with the original specimens which have thick oxide scales. The diffusion of Fe through the surface to form a magnetite layer on top is also prevented by the thin alumina scale.

Furthermore it becomes obvious from the line scan in Fig. 7 that the depth of surface melting reaches down to about 30 μm represented by the range containing Al. Some small Cr peaks indicate the presence of precipitations enriched in Cr. Remarkable is also the Al enrichment at the boundary between the melting zone and the steel bulk.

The extension of the region of GESA surface melting is also good visible on the etched LM presented in Fig. 8. It covers not only the coating but also some μm of the bulk material. This results in an improvement of the bonding between coating and bulk. The Al concentration in the melt region was analyzed to be between 4 and 5 wt%. The small zone of Al enrichment is good visible on the border between melt zone and bulk material. On few places of the surface there exists a multilayer oxide scale like on original tube surfaces. Analysis of the Al concentration at these places yields less then 4 wt%. This is obviously not sufficient for protective alumina scale formation.

5.2. Tests at different flow velocities

Original and coated tube specimens are exposed to LBE at different flow velocities of about 1, 2 and 3 m/s at 550 °C for 2000 h. The metallographic cross sections of the original tube specimens are depicted in Fig. 9. After all three flow velocities the specimens show a spinel and diffusion zone and only the 1 m/s specimen has a magnetite layer on top. On the 2 m/s specimen there are only some remains of the magnetite layer which is completely missing at the 3 m/s specimens that have a shiny spinel surface. This is probably due to erosion by the LBE stream at the high flow velocities. In any case there is still a stable protective oxide scale on top which consists of a dense spinel layer. The pictures of the cross sections are taken from unetched metallography to depict the oxygen diffusion zones that have about the same extension at all flow velocities.

The coated tube specimens show again a different behavior, Fig. 10. After exposure for 2000 h at 550 °C to LBE with the three different flow velocities all specimens respond in the same way by formation of a thin oxide scale that consists mainly of alumina like shown in the EDX line scan in Fig. 6. The etched structure depicts nicely the extension of the surface zone remelted by GESA which includes the FeCrAlY coating. The alumina oxide scale is too small to be visible on the metallographic pictures. There is only one small spot on top of the 3 m/s specimen which shows

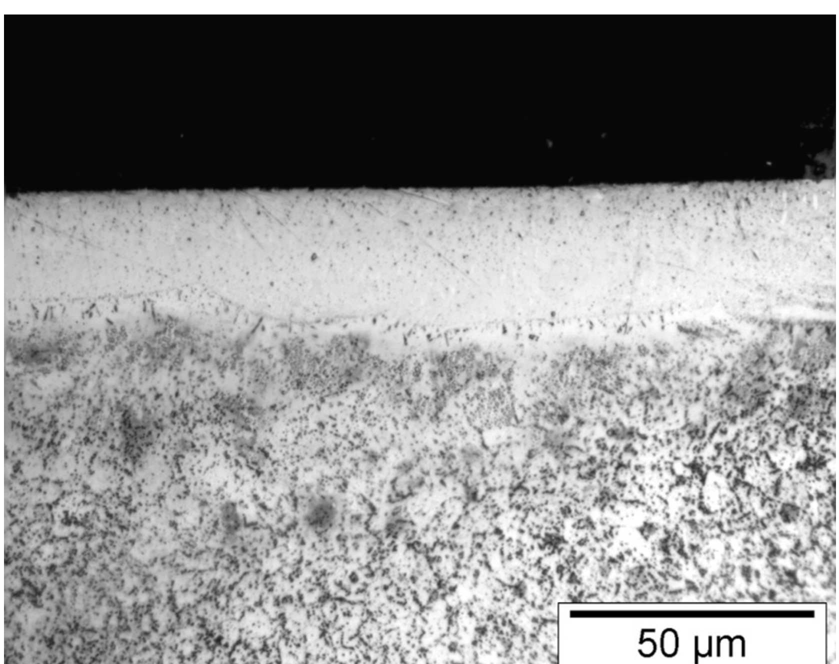

Fig. 8. LM of the etched cross section of the coated T91 tube specimen after 2000 h exposure to LBE at 600 °C. A thin protective oxide scale is formed on the specimen.

a visible oxide formation. It may be a place at which the Al concentration is below 4 wt%.

5.3. Tests with pressurized tubes

The influence of a tangential wall stress σ_t of 112.5 MPa on the formation of the oxide scale at 550 °C can be seen from Fig. 11 by comparison of the cross section through the wall of the tube without (left) and the one with pressure (right). The tube with pressure is protected as well as the tube without pressure, however, it has a thicker oxide scale. Since the oxygen diffusion zone is the same in both cases it can be assumed that the diffusion barrier for oxygen, the spinel layer, has the same effect in both cases. Indeed it is mainly the magnetite layer that is responsible for the difference in thickness, which does not influence oxygen diffusion into the bulk. The measurements of diameters before and after the exposure yield a strain of 0.7% after 2000 h of exposure.

6. Discussion of results

Since oxide scales serve as a good protection against the attack by liquid LBE, coatings like used for protection of turbine blades [9] appear to be a suitable choice. Therefore, a FeCrAlY coating is being chosen for protection of the high temperature structures. It has an average thickness of 30 μm and is remelted by the pulsed large area electron beam of GESA [10] to gain a dense coating layer and to improve the bonding between the coating and the bulk material.

The beam energy of GESA is adjusted in a way to melt the entire coating together with a few μm thin region of the bulk to create a perfect intermixing at the boundary. This

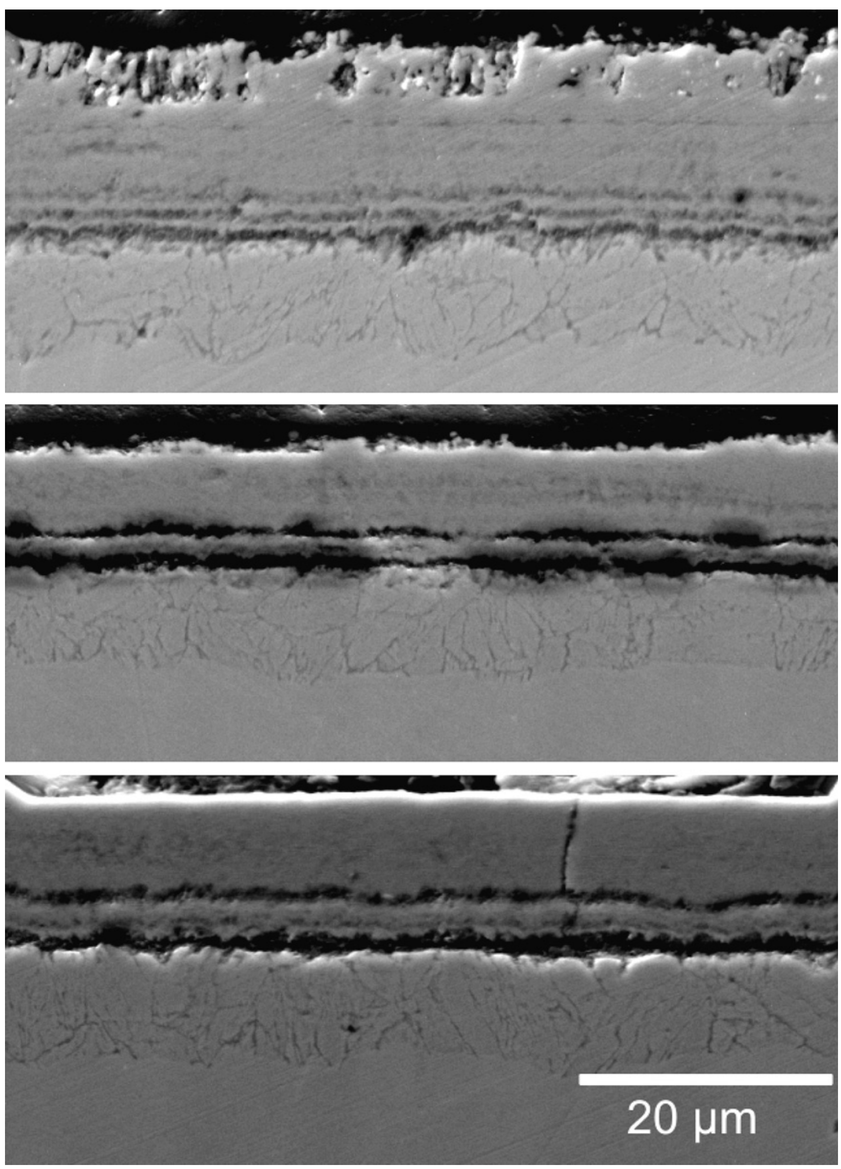

Fig. 9. SEM's of the T91 steel tube specimens exposed 2000 h at 550 °C to LBE with a flow velocity of 1 (above), 2 (middle) and 3 m/s (below). At 1 m/s magnetite is still visible, at 3 m/s only the spinel layer remains on top.

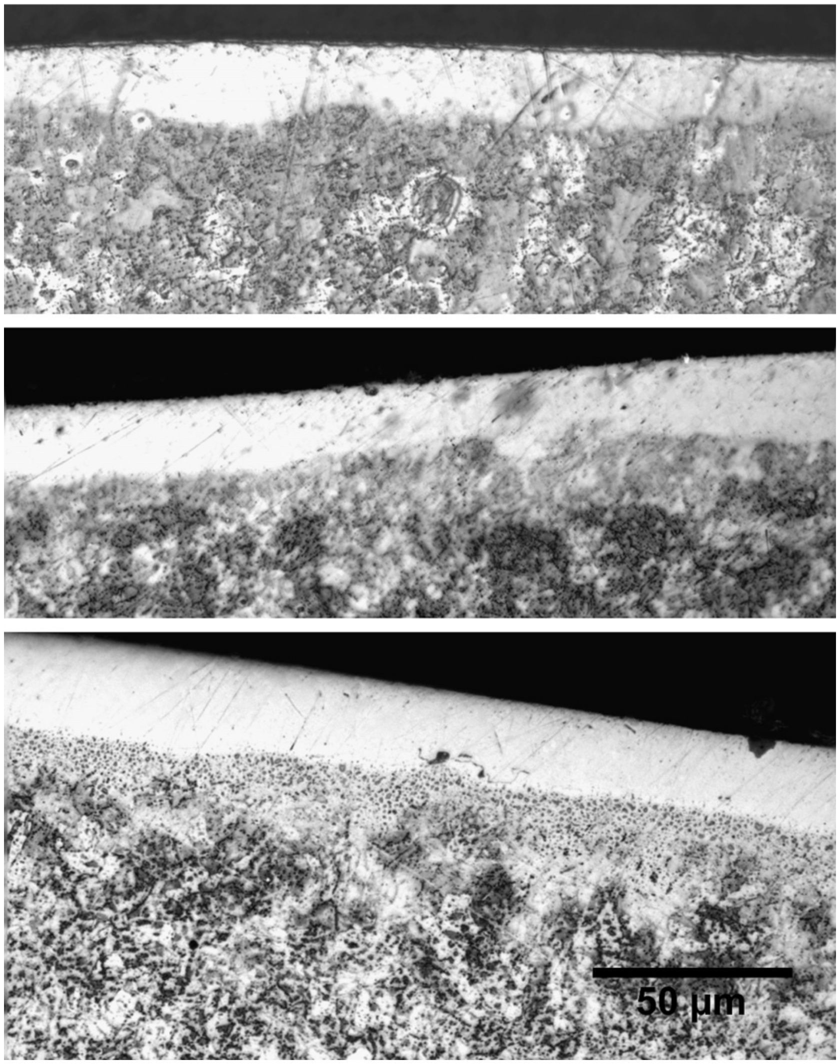

Fig. 10. LM's of the coated T91 steel tube specimens exposed 2000 °C at 550 °C to LBE with a flow velocity of 1 (above), 2 (middle) and 3 m/s (below). No influence of such flow velocities is visible.

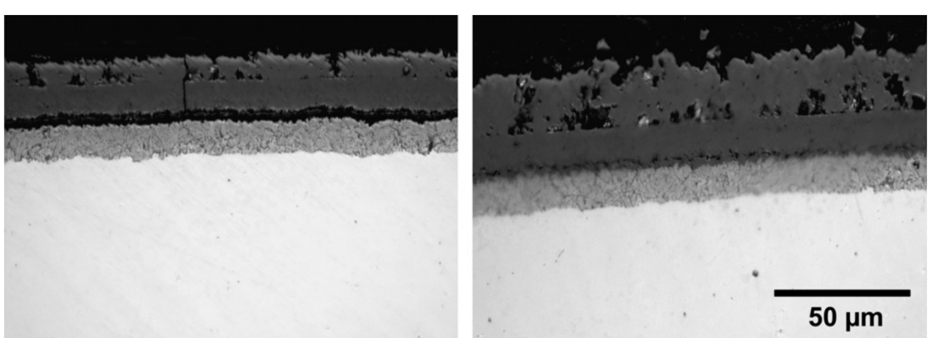

Fig. 11. LM's of the cross section through the wall of a T91 steel tube without (left) and with (right) internal pressure of 150 bar after 2000 h exposure to 550 °C in LBE with the flow velocity of 1 m/s. The magnetite layer of the tube with internal pressure grows significant thicker.

results in a new surface area of the cladding with an Al content between 4 and 5 wt% that will be sufficient high to grow thin stable oxide scales. This concept is proven for T91 steel tubes examined with the experiments described here. No negative response of such a modified coating on the mechanical properties and the stability under irradiation was observed up to now [11].

The difference between the original and FeCrAlY coated tube specimens is the very thin alumina scale on top of the FeCrAlY surface which is stable also at higher temperatures like 600 °C and has a much better thermal conductivity than the thick oxide layers that develop on original T91 surfaces. The thickness of oxide layers on original steel grows with temperature and is no effective barrier for oxygen diffusion into the bulk and for Fe diffusion through the surface that leads to a formation of magnetite on top of the surface. There are, however, some places on the FeCrAlY coated tube specimen where also oxide scales grow like on the original material. They are caused by failures in the LPPS process which lead there to Al concentrations below 4 wt%. The Cr rich precipitations stem certainly from uncomplete mixing of the bulk material and the FeCrAlY. The latter one has twice as much Cr. The Al increase at the end of the melting zone may be due to Fe_3Al formation in the border to the bulk material.

The tests at three different flow velocities of liquid LBE show clearly that at high flow velocities (>2 m/s) the Fe that diffuses through the spinel surface and gets oxidized is washed off by the passing liquid. Therefore, the tube specimen of the 3 m/s test develops no magnetite scale on the surface and has a shiny smooth appearance. Some small remains are observed on the surface of the 2 m/s specimen while the magnetite on the 1 m/s specimen has a magnetite layer of a thickness that is normally observed on ferritic steels under equivalent conditions [12]. The FeCrAlY coated tubes that were restructured by GESA pulses show no influence of the flow speed. All specimens have the same undisturbed, thin, protective alumina surface scale.

Pressure inside the tube specimens that exposes the tubes to mechanical stress causes some creep in the tube wall which reaches a strain of 0.7%. But this is not the only effect. Besides this the strain obviously increases Fe diffusion that leads to an enhanced growth of the magnetite layer which will not occur with the coated specimens that have no magnetite layer. This is another advantage of the coating applied.

The magnetite layers are in any case not desired. They tend to spall off, decrease the heat conductivity and have no major influence on the prevention of liquid LBE attack.

7. Conclusions

Unprotected T91 steel in the as received condition is not suitable for the use with liquid LBE at temperatures above 500 °C because it develops thick oxide scales including magnetite and spinel with low thermal conductivity. The magnetite tends to spall off.

Coating the surface with FeCrAlY after homogenization by melting with the GESA pulse avoids this disadvantage because this coating develops a thin protecting alumina scale with good thermal conductivity.

The coating process needs some improvement to avoid coating regions which have aluminium concentrations below 4 wt%. Measures are use of finer powder particles and cleaner preparation procedures and coating atmospheres.

There is an upper limit of LBE flow velocity of 2 m/s above which no magnetite scale appears because it gets instantly removed.

Tangential wall stress of about 112.5 MPa induced by an internal tube pressure of 15 MPa increase the Fe diffusion and lead to enhanced magnetite scale growth.

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