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Behavior of steels in flowing liquid PbBi eutectic alloy at 420–600 °C after 4000–7200 h

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Abstract

This paper presents the results of steel exposure up to 7200 h in flowing LBE at elevated temperatures and is a follow-up paper of that with results of an exposure of up to 2000 h. The examined AISI 316 L, 1.4970 austenitic and MANET 10Cr martensitic steels are suitable as a structural material in LBE (liquid eutectic $Pb_{45}Bi_{55}$) up to 550 °C, if 10^{-6} wt% of oxygen is dissolved in the LBE. The martensitic steel develops a thick magnetite and spinel layer while the austenites have thin spinel surface layers at 420 °C and thick oxide scales like the martensitic steel at 550 °C. The oxide scales protect the steels from dissolution attack by LBE during the whole test period of 7200 h. Oxide scales that spall off are replaced by new protective ones. At 600 °C severe attack occurs already after 2000 and 4000 h of exposure. Steels with 8–15 wt% Al alloyed into the surface suffer no corrosion attack at all experimental temperatures and exposure times.

1. Introduction

Perspective accelerator driven subcritical systems (ADS) employing liquid Pb and eutectic $Pb_{45}Bi_{55}$ (LBE) as a coolant and/or target [1] require investigation of corrosion effects of steels in such environment at relevant temperatures. Recently corrosion experiments with steel in stagnant liquid lead [2,3] and flowing LBE [4–6] were reported. The experiments confirmed results of earlier investigations [7] which showed that the control of an appropriate concentration of oxygen in the liquid metal is an inevitable measure to prevent the steel from dissolution attack. The oxygen potential must be high enough to form protective oxide layers. Therefore, the experiments in flowing LBE described here were carried out with an oxygen concentration of about 10^{-6} wt% in the liquid metal.

The present paper describes the continuation of the corrosion experiments up to 2000 h of exposure with AISI 316 L, 1.4970 and MANET steel in original state and with an Al alloyed surface (austenites only) [5]. The experiments which were planed up to an exposure time of 7200 h were interrupted for specimen examinations at 2000 and 4000 h. Test temperatures are 420, 550 and 600 °C as in the experiments reported previously [5]. As a result of these investigations the following conclusions are drawn.

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In general, the original steels without surface alloying are resistant against dissolution attack in liquid LBE up to temperatures of 550 °C and 2000 h exposure at oxygen concentrations of 10^{-6} wt%. The austenitic specimens surface alloyed with Al having FeAl at the surface, show no signs of any corrosion even at 600 °C. They are protected by a thin alumina layer which remains stable. However, in contact with liquid LBE the activity of Al at the surface of Al alloyed steel must be low enough to minimize the solution rate of Al in LBE and allow oxide scale formation. FeAl at the surface fulfills this requirement.

2. Experimental

2.1. Loops tests

The corrosion tests were carried out in two non-isothermal, forced lead–bismuth loops at IPPE, Obninsk and one at PROMETEY, St. Petersburg [5]. All three loops consist of a main heater, a cooler, a hot and a cold section, an electromechanical pump, a purification system, a flow meter and oxygen meters. The test sections of the two IPPE loops are at 420 and 600 °C. In case of the PROMETEY loop the experiments are performed in the hot test section at 550 °C. The volume of the LBE in both loops is about 60 l. The temperature is maintained by an electrical resistance heater which is passed just before entering the hot test section. A cooler controls the temperature of the cold test section. The oxygen activity in the liquid LBE containing 10^{-6} wt% oxygen is measured by electrochemical cells. To control the oxygen content two different circuits are foreseen; injection of ArH_2 to reduce and purify the LBE and supply of oxygen by dissolving solid PbO. The loop test parameters are given in Table 1.

Table 1
Loop test parameters

	IPPE	PROMETEY
Liquid medium	LBE	LBE
$T_{\text{loop 1}}$ (°C)	420	550
$T_{\text{loop 2}}$ (°C)	600	–
Duration (h)	2000, **4000**	2000, **4000**, **7200**
Velocity (m/s)	1.3	0.5
Oxygen (wt%)	1×10^{-6}	1×10^{-6}

The main difference between the two loops is in the flow velocities of the liquid metal, which is with 1.3 m/s three times higher in the IPPE loop.

2.2. Evaluation

LBE was washed off in 180 °C oil after exposure to remove residues from the specimen surface with exception of the specimens exposed at 550 °C. The analysis consisted of metallurgical examination by light and scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) on the cross section of the specimens. In addition, X-ray diffraction was performed to evaluate the phase composition of the steels and oxidation products.

2.3. Materials

Materials used in the experiments are cylindrical tubes of 1.4970 and rods of AISI 316 and MANET steel with 8 mm diameter. The chemical composition of the steels is listed in Table 2. The austenitic steels AISI 316 L and 1.4970 were employed in the long term exposures in an original state with polished surface and also with a surface alloyed with Al. The process of alloying by an Al-foil wrapped around the tube and rod, respectively, and the properties of the alloyed layer are described in [5]. MANET steel was used only in its original state with a polished surface.

3. Results

3.1. AISI 316 L specimens

The effect of LBE on the steel after 4000 h at the two temperatures employed is shown in Fig. 1. For the specimen at 420 °C nothing changed compared to the state after 2000 h. There is still a thin protective Cr_2O_3 rich layer on the surface. At 550 °C the whole surface is covered by a magnetite + spinel layer. This multilayer structure is well known for oxidation in air and liquid metals [2,3]. The spinel layer varies in thickness up to 12 μm and is inhomogeneous. The gap indicated between magnetite and spinel in the lower part of Fig. 1 may hint at starting spallation. At 600 °C no specimen was tested because it was completely destroyed after 2000 h.

Table 2
Chemical composition of steel in wt%

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Ti
316 L	0.02	0.35	1.8	0.19	0.0005	17.3	12.1	2.31	–
1.4970	0.46	0.89	1.91	0.012	0.009	16.5	13.8	0.66	0.43
MANET	0.11	–	0.78	0.003	–	10.3	0.68	0.61	–

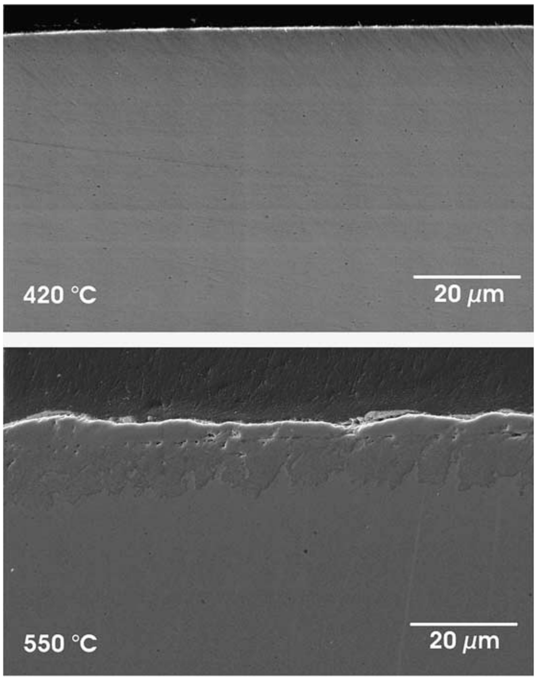

Fig. 1. SEM cross section of AISI 316 L specimens after 4000 h of exposure; an invisible thin protective Cr_2O_3 rich layer exists on top of the surface at 420 °C and a thick multilayered oxide scale at 550 °C.

The SEM of the specimen at 550 °C exposed for 7200 h (Fig. 2) indicates that the oxide layer spalled off and a new oxide layer was formed of varying thickness up to 5 μm. At some places LBE was enclosed between magnetite and spinel during the oxide growth. There is, however, no indication of a progressive dissolution attack.

3.2. 1.4970 Specimens

Specimens exposed to 420 °C did not show remarkable differences as compared to the 2000 h exposure and to the other austenite 316 L. The surface is still covered by a thin Cr_2O_3 rich scale. At 550 °C, the behavior changes, a thick scale of about 20 μm consisting of spinel and magnetite appears (Fig. 3). A gap exists between the two oxides that leads to some break away of the magnetite. There are at many places infiltrations of LBE into the spinel zone below the magnetite scale indicated by the small white areas. This bright grey spinel zone contains mainly Bi on the grain boundaries of the small textured grains formed by recrystallization during the tube production. The diameter of the grains is smaller than 1 μm and not resolved in this figure.

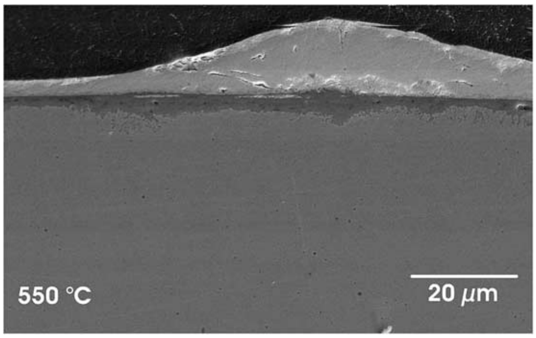

Fig. 2. SEM cross section of AISI 316 L specimen after 7200 h of exposure showing a renewed oxide layer of varying thickness.

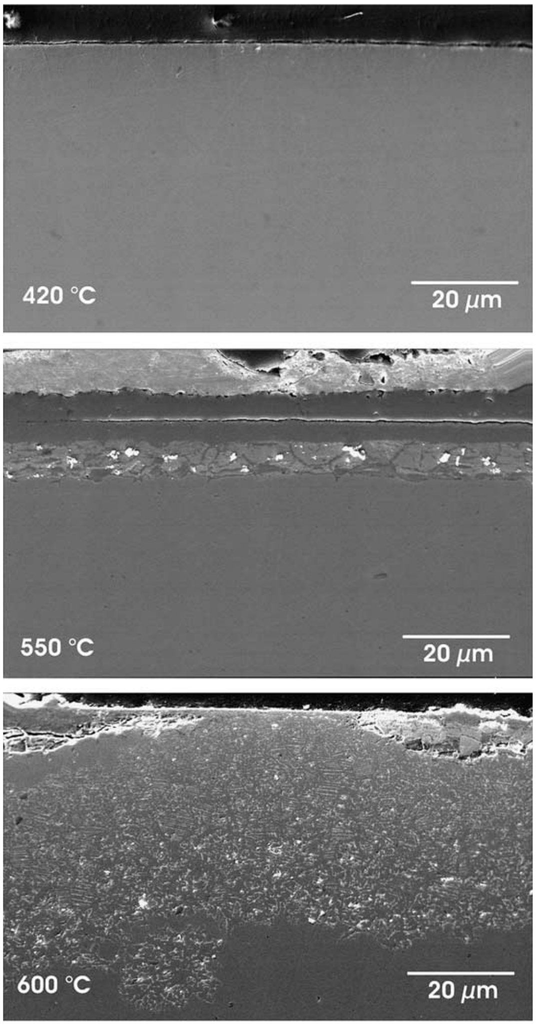

Fig. 3. Specimens of 1.4970 steel after 4000 h of exposure; an invisible thin protective Cr_2O_3 rich layer exists on top of surface at 420 °C and a magnetite and spinel layer partly infiltrated with LBE at 550 °C. At 600 °C severe dissolution attack occurs – bright spots consisting of LBE penetrated the steel matrix.

At 600 °C a severe dissolution attack is on the way with penetration depths of more than 100 μm. The bright lines are LBE inclusions embedded into the grain boundaries. The Ni is completely leached out in this region.

After 7200 h of exposure at 550 °C, Fig. 4, the 1.4970 steel specimen has still an appearance similar to that after 4000 h exposure. Only the number of white LBE inclusions is decreased and the diffusion zone of oxygen is extended into the substrate material. This indicates two facts. First, there is no more infiltration of LBE into the spinel zone and no progressive dissolution attack. A great part of the LBE is further taken up by the grain boundaries which are not resolved here. Second, oxygen still penetrates the oxide scale and enlarges the oxygen diffusion zone.

The lower part of Fig. 4 shows part of the 1.4970 steel tube that suffered from dissolution attack at the tube interior. Somewhere at the tube connections in the test rack LBE penetrated into the tube. Because oxygen inside the tube is quickly depleted from the melt and exchange with the melt outside the tube is to slow, a severe dissolution attack occurs inside the tube wall.

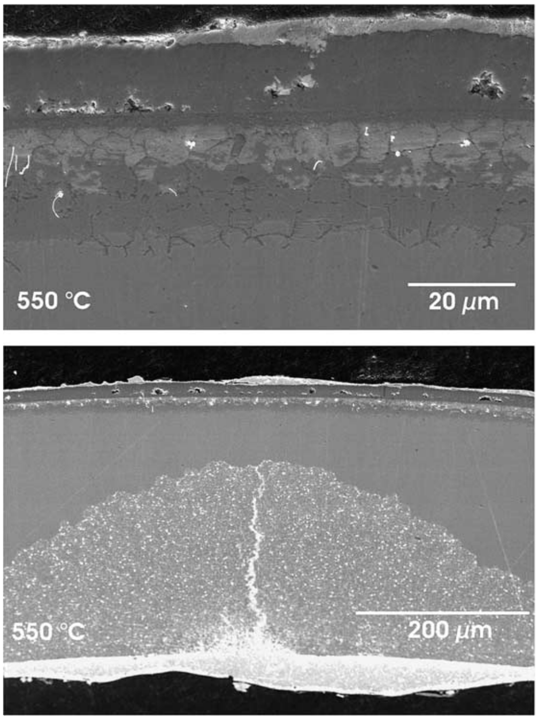

Fig. 4. Specimens of 1.4970 steel after 7200 h of exposure to 550 °C; above – tube outside showing no change compared to the 4000 h sample; below – tube inside showing severe dissolution attack – bright spots consist of LBE penetrated the steel matrix.

3.3. MANET specimens

As opposed to the austenitic specimens a thick oxide scale of 10 μm develops on MANET steel already at 420 °C that protects the surface from dissolution attack, Fig. 5. At 550 °C the magnetite layer spalls off between 2000 and 4000 h and also part of the spinel layer. A thin oxide layer and at some places a thicker one which may have been formed again protects the surface. There was no specimen tested at 600 °C because this is above the temperature at which MANET can be employed.

After 7200 h of exposure at 550 °C a new oxide layer is formed also on MANET consisting of spinel and magnetite which is partly up to 20 μm thick and contains LBE inclusions in the spinel region like in the austenites with no indication of progressing dissolution attack, Fig. 6. The substrate adjacent to the oxide layer shows Cr depletion because of its migration into the spinel.

3.4. Austenites surface alloyed with Al

Like after 2000 h of exposure, there is no attack on the surface of Al alloyed austenitic specimens at all temperatures and exposure times. As an example, Fig. 7 shows the cross section through the specimen exposed

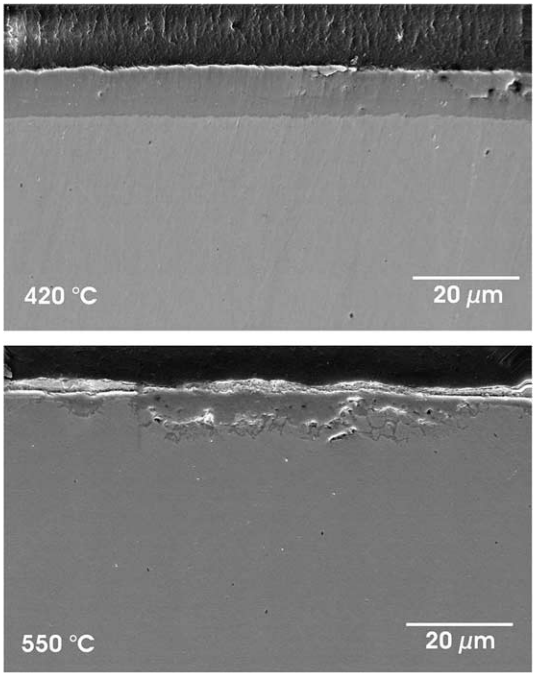

Fig. 5. SEM cross section of MANET steel after 4300 h of exposure; at 420 °C a thick oxide scale protects the surface, at 550 °C only residues of former thick oxide scale are visible.

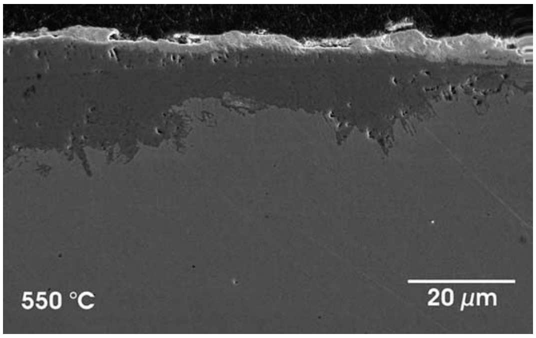

Fig. 6. SEM cross section of MANET steel after 7200 h of exposure showing renewed oxide layer of varying thickness.

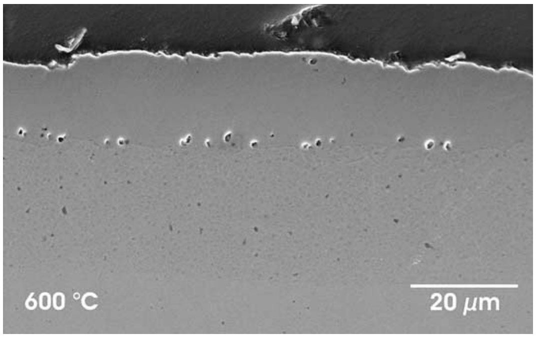

Fig. 7. SEM cross section of surface alloyed austenitic AISI 316 L exposed at 600 °C for 4000 h; there is no corrosion attack and no change in microstructure and elemental distribution.

at 600 °C for 4000 h. Since exposure was stopped in the IPPE loop there are no examinations at 600 °C with more than 4000 h. Even after 4000 h of exposure to LBE at 600 °C no changes in microstructure and elemental distribution can be observed.

4. Discussion

There is still sufficient protection of the steel surface against the dissolution attack of liquid LBE at temperatures up to 550 °C and up to 7200 h of exposure. Important parameter in the experiments is the concentration of oxygen in LBE that is controlled at 10^{-6} wt%.

While thick oxide layers develop after 4000 h on the surface of the martensitic MANET steel at 420 and 550 °C, the very thin layers on austenitic steel consist at 420 °C of chromia only. The austenites produce thick layers of magnetite and spinel also, if a temperature of 550 °C is applied. After 4000 h the 1.4970 austenitic steel shows inclusions of LBE in the spinel layer, not however, in the magnetite scale. These inclusions indicate a dissolution attack before or during the formation of the new magnetite scale after spalling off between 2000 and 4000 h. Indeed, there is no further penetration of LBE into the spinel zone during extension of exposure to 7200 h. The magnetite scale on top of the surface is dense enough to seal it against the LBE. It does, however, not hinder the oxygen to migrate to the spinel zone and to diffuse into the metallic matrix. This is indicated by the good visible extended oxygen diffusion zone after 7200 h.

The other austenite AISI 316 L shows a different behavior. Its oxide layers spall off between 4000 and 7200 h and a new oxide scale develops with minor dissolution attack in its transient state. Only few inclusions of LBE are observed between the spinel and magnetite zone. The different behavior can be founded by the different structures of both austenites. The AISI 316 L rod specimen is coarse grained, while the 1.4970 tube specimen has a fine grained, plate like structure (<1 μm thick) that is oriented parallel to the surface. This latter structure may favor the LBE penetration in the first stage of oxide scale formation.

The example of LBE attack from the inside of the 1.4970 tube in Fig. 4 shows what happens, if oxygen is not sufficiently delivered to the steel surface. There is no protective oxide formation and after 7200 h a dissolution zone extends almost through the whole tube wall. In loops care has to be taken that there are no positions with temperatures above 500 °C that have larger areas with bad oxygen exchange. This may happen in places where LBE is stagnant.

Austenitic steels which are alloyed with 8–15 wt% Al do not have any dissolution attack at all temperatures and exposure times. They keep their thin protective alumina scales unchanged.

Table 3 shows the suitability of the steels as structural material. It looks not much different from that after 2000 h of exposure. The only change is the (–) for 1.4970 at 600 °C after 4000 h because the specimen failed under this conditions. All the 7200 h specimens, with exception of those having an Al alloy at the surface, suffer from infiltration of LBE into the magnetite and/or spinel layer (* in Table 3). It is questionable whether this constellation keeps stable for exposures far beyond 7200 h. Experiments with AISI 316 L in stagnant LBE up to

Table 3
Suitability of steels for LBE loops

	4000 h			7200 h
Steel (°C)	420	550	600	550
AISI 316 L	+	+	–	+*
1.4970	+	+	–	+*
MANET	+	+		+*
Al-all. aust.	+	+	+	+

* LBE infiltrations in the spinel and/or magnetite layer.

10 000 h of exposure give an indication that destabilization occurs above 7200 h. The steel suffered severe dissolution attack up to a depth of several 100 μm [8].

5. Conclusions

In general, original steels without surface alloying are suitable for application in LBE up to temperatures of 550 °C and exposure times of up to 7200 h. Although oxide scales spall off after some 1000 h, no proceeding dissolution attack takes place, since new oxide scales are developed that protect the steel from interaction with LBE. At 600 °C all of the steels fail after at least 4000 h because of severe dissolution attack.

Only if Al is alloyed and FeAl is formed at the surface there is no corrosion attack at all. These surface alloyed steels are suitable as structural materials in LBE environment at least up to 600 °C for long exposure times.

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