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Journal of Nuclear Materials 301 (2002) 40–46

journal of nuclear materials

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Results of steel corrosion tests in flowing liquid Pb/Bi at 420–600 °C after 2000 h

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Abstract

Corrosion tests were carried out on austenitic AISI 316L and 1.4970 steels and on MANET steel up to 2000 h of exposure to flowing (up to 2 m/s) Pb/Bi. The concentration of oxygen in the liquid alloy was controlled at 10^{-6} wt%. Specimens consisted of tube and rod sections in original state and after alloying of Al into the surface. After 2000 h of exposure at 420 and 550 °C the specimen surfaces were covered with an intact oxide layer which provided a good protection against corrosion attack of the liquid Pb/Bi alloy. After the same time corrosion attack at 600 °C was severe at the original AISI 316L steel specimens. The alloyed specimens containing FeAl on the surface of the alloyed layer still maintained an intact oxide layer with good corrosion protection up to 600 °C.

1. Introduction

Steel corrosion by the eutectic liquid Pb/Bi alloy is one of the problems that appear in accelerator driven subcritical systems (ADS) [1] where the eutectic alloy is intended to be used as a coolant and target material. Corrosion effects in the 100 μm range are reported on ferritic Fe–Cr steels between 575 and 750 °C after 3250 h exposure to liquid lead [2]. Steel components are soluble in liquid lead in the range of 10^{-3}–0.1 at.% in this temperature region [3]. An exception exists for Ni, which has a solubility of 2 at.% at 600 °C in lead [4].

Since all the solubilities vary with temperature, transport processes will take place which live from the higher solubility at high temperatures and precipitation at low temperatures. A temperature difference of about 150 °C is typical for lead cooling loops. Therefore already small solubilities can lead to heavy corrosion effects with high flow velocities, in the range of 1 m/s, and long in pile times.

These problems are increased by using the eutectic Pb/Bi alloy instead of Pb. Table 1 shows a comparison of solubilities in Pb and Bi. It is to be expected that Pb/Bi alloys are much more corrosive than Pb.

Early experiments with liquid Pb and Pb/Bi revealed that stable oxide scales on steel surfaces, consisting of magnetite and FeCr-spinels, prevent the dissolution attack if oxygen is dissolved in the liquid metal with a concentration of 10^{-6} at.% [6,7]. Recent investigations of corrosion effects in stagnant liquid lead give an overview on the corrosion processes and its prevention by oxide scale formation on steel [8,9]. Stable oxide layers are formed in liquid lead at 550 °C with a controlled oxygen concentration of 8×10^{-6} at.% [8] as well as with saturated oxygen concentration of 3×10^{-3} at.% [9]. The scale thickness including a magnetite layer on top and a spinel layer underneath amounts to 20–30 μm

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PII: S0022-3115(01)00725-5

Table 1
Solubilities in Pb and Bi at 600 °C [4,5]

	Pb (at.%)	Bi (at.%)
Ni	2	17
Al	1	11
Cr	0.02	0.56
Fe	0.01	0.017

after 3000 h of exposure. This may impose a new problem at much longer time scales because the corrosion on steel turns from the dissolution attack to that of oxidation. A way out of this dilemma is alloying of Al into the steel surface. The alloyed Al causes formation of a thin protective alumina layer that grows very slowly and prevents also extensive oxidation of the steel [8,9]. Earlier experiments on Fe–Cr alloys containing 8 at.% Al show also alumina scale formation in liquid lead at low oxygen potential [10].

Other experiments [11] employing a Fe-aluminide layer on MANET steel, which was oxidized before the experiment, resulted in no corrosion attack in liquid Pb–17Li after 10 000 h at 450 °C. Thermodynamic investigation of Al–Fe alloys [12] showed that a self-healing of the alumina scale can take place in Pb–17Li if the kinetics of the process are high enough.

Although the temperatures of Pb/Bi in a proposed DEMO-ADS [13] can be kept below 400 °C because of the low melting point of the eutectic alloy, it must be expected that at some places like at the beam window or in the core (on the claddings) the temperatures increase well above this value. Therefore, in the experiments the requirements of a real energy amplifier with high energy fluxes have to be considered. There, surface temperatures in the range of 600 °C can occur. Thus the experiments conducted in this work are extended up to 600 °C. To examine the influence of Bi in the alloy the Pb/Bi eutectic alloy is used in the experiments conducted in the liquid metal loops of IPPE, Obninsk and PROMETEY, St. Petersburg in Russia.

2. Experimental

2.1. Loop tests

The corrosion tests were carried out in two different non-isothermal forced lead–bismuth loops at IPPE, Obninsk and at PROMETEY, St. Petersburg. Both 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. In the IPPE loop two test sections are available, one at 420 °C the other at 600 °C. In case of the PROMETEY loop the experiments are performed in the hot test section at 550 °C.

Table 2
Loop test parameters

	IPPE	PROMETEY
Liquid medium	Pb/Bi	Pb/Bi
$T_{\mathrm{cold\,leg}}$ (°C)	420	–
$T_{\mathrm{hot\,leg}}$ (°C)	600	550
Duration (h)	1000, 2000, 5000	1000, 2000, 5000
Velocity (m/s)	2	0.5
O_2 (wt%)	1×10^{-6}	1×10^{-6}

The volume of the liquid Pb/Bi in both loops is about 60 l. The temperature is maintained by an electrical resistance heater which is positioned just in front of the hot test section. A cooler is placed directly before the cold test section. The oxygen activity in the liquid Pb/Bi containing 10^6 at.% oxygen is measured by electrochemical cells. Test parameters for both loops are listed in Table 2.

The main difference between the two loops is in the flow velocities of the liquid metal, which is with 2 m/s four times higher in the IPPE loop. The still running corrosion experiments are foreseen for exposure times up to 5000 h. This paper deals with the results after the first stop of the loops at 2000 h.

2.2. Evaluation

Specimens were washed of in 180 °C oil after exposure to remove residues of lead–bismuth. 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.

2.3. Materials

Materials used in the experiments are cylindrical tubes and rods of AISI 316, 1.4970 and MANET steel of 8 mm diameter. The chemical composition of the steels is listed in Table 3.

A surface layer of 10–100 μm is alloyed with Al in one part of the specimens signed with the number 2, 3. The other part is just smoothened and signed with the number 1. The specimen signatures are listed in Table 4.

Al alloying was achieved by two different procedures. The first (2) was done by wrapping Al-foil around the tube and heating at 1040 °C for 0.5 h, the second by hot-dipping aluminization and annealing [14]. The hot-dipping process for the austenitic steels is performed in an Al-melt containing 12 at.% of Si and consecutive annealing at 550 °C for 0.5 h. The low annealing temperature for the austenitic steels was necessary because of severe embrittlement and crack formation in the aluminized layer on this steels.

Table 3
Chemical composition of steels in wt%

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

Table 4
Specimen signatures

Steel	Surface smoothed	Surface alloyed	
		Al-foil	Al-melt dipping
AISI 316L	A1	A2 (1040)	A3 (550)
1.4970	B1	B2 (1040)	B3 (550)
MANET	C1	–	–

Numerals in parentheses indicate annealing temperature of alloyed steels in °C.

A typical cross-section of an Al alloy layer obtained by wrapping the tube sample and annealing is shown in Fig. 1. On top of the original surface there is a FeAl layer which forms by diffusion of iron into the liquid Al layer during annealing. The diffusion zone of 25 μm depth below the surface contains Al dissolved in Fe and NiAl precipitations, while the interface some μm thick contains NiAl created by Ni diffusion.

The hot-dipped austenitic specimens A3 and B3 have a 50 μm layer consisting of Al with 12 at.% of Si. The cross-section of the layer on specimen A3 is shown in Fig. 2. This layer contains only a small amount of dissolved Fe because the annealing temperature was to low for a sufficient interdiffusion of Fe and Al. Silicon is not homogeneously distributed throughout the whole layer, it appears mainly in silicon rich precipitations with up to 65 wt% Si.

The specimens were stacked together and fixed by an internal rod. The arrangement is completely immersed in the test sections of the loops.

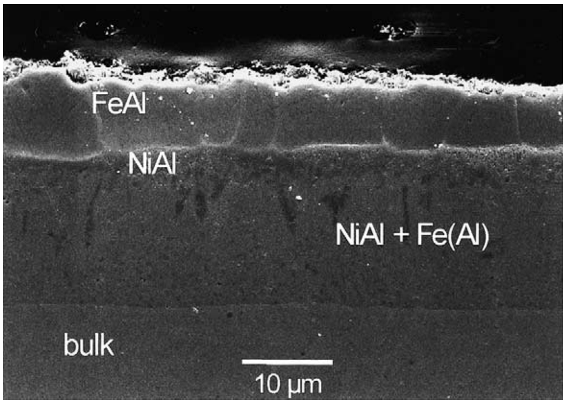

Fig. 1. SEM cross-section of 1.4970 specimen B2 after alloying by Al-foil wrapping and annealed at 1040 °C for 0.5 h.

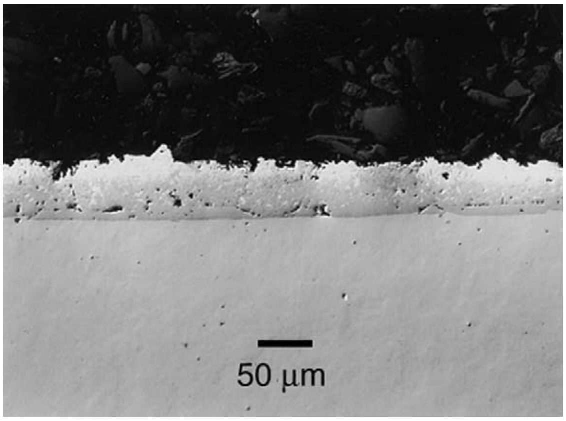

Fig. 2. SEM cross-section of AISI 316L specimen A3 dipped in AlSi10 at 700 °C and annealed at 550 °C for 2 h.

3. Results

All the reported results are obtained from specimens which were taken out of the loop test sections after 2000 h at 420, 550 and 600 °C. In the following, the results of the examinations are described in a separate chapter for each one of the specimen types listed in Table 4. The behavior of the austenitic steel specimens A2 and B2 is described by the example of the AISI 316L specimen A2 only, because there is no significant difference visible for both specimens.

3.1. AISI 316L specimen A1

The effect of liquid Pb/Bi on the steel specimen of type A1 after 2000 h of exposure is shown in Fig. 3. No attack on the surface can be seen at the SEM cross-section of specimen A1 after exposure to 420 °C. The EDX analysis indicates that the steel composition is not changed in the vicinity of the surface. This points out that no dissolution took place. Probably, a thin oxide scale protects the material from dissolution attack.

During exposure to 550 °C specimen A1 develops partly thick oxide scales consisting of a magnetite and a spinel zone underneath. The thin oxide layer observed after exposure to 420 °C is maintained on the other parts of the surface. In any case no dissolution attack took place. The concentration of the steel components below the oxide layer is also not changed.

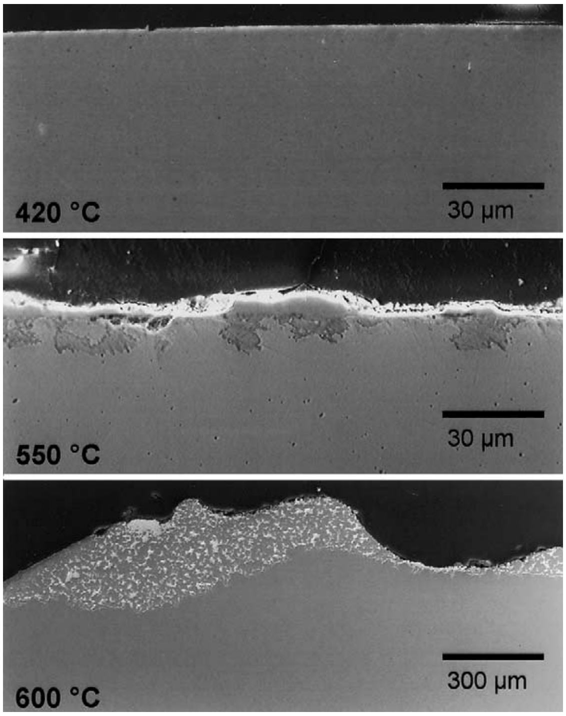

Fig. 3. SEM cross-section of AISI 316L specimens A1 after 2000 h of exposure.

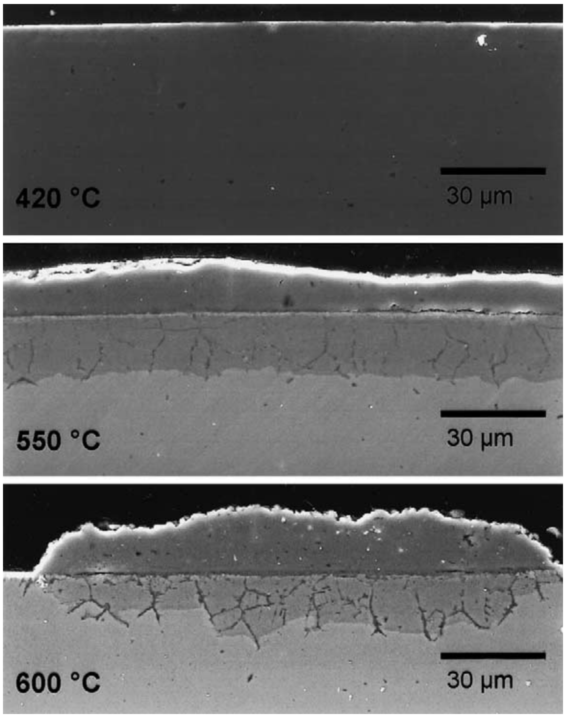

Fig. 4. SEM cross-section of 1.4970 specimens B1 after 2000 h of exposure.

Deep liquid metal penetration and massive ablation of material by erosion is observed at 600 °C on steel specimen A1 in the lower part of Fig. 3. Bright inclusions consist of Pb/Bi alloy enriched in Bi. The penetration zone is depleted in Ni down to 1 at.%.

3.2. 1.4970 specimen B1

Corrosion effects of liquid Pb/Bi on the steel specimen of type B1 after 2000 h of exposure are shown in Fig. 4. The specimen has the same appearance at 420 °C like specimen A1 with no signs of corrosion attack. At 550 °C, however, large parts of the surface are covered by a continuous magnetite scale with a spinel zone underneath. On about half of the specimen the thin oxide layer observed for 420 °C is, however, still maintained. This behavior did not change at 600 °C. At 550 and 600 °C precipitation of chromium oxide is observed in the grain boundaries of the spinel zone represented by the dark network in the bulk material.

3.3. MANET specimen C1

The behavior of the MANET specimen C1 was examined at 420 and 550 °C only because this steel is not designed for higher temperatures. As expected from earlier experiments in stagnant lead [8] on martensitic steels a protective oxide formation takes place with a magnetite scale on top and a spinel layer below the specimen surface. It grows strongly with increasing temperatures.

3.4. Austenitic specimens A2 and B2, diffusion alloyed by Al-foil wrapping

The specimens show good corrosion resistance at all temperatures. This is demonstrated by the SEM cross-sections for the example of AISI 316L specimen A2 in Fig. 5. The only difference between the specimens is the appearance of some pores in the NiAl interface layer between the FeAl and the Fe(Al) dissolved region of 316L on specimens exposed to 550 and 600 °C because of outward diffusion of iron into Fe(Al) layer. Specimen B2 consisting of 1.4970 steel has a dense NiAl interface layer. The FeAl layer on top of the specimens is maintained with the original thickness. No dissolution attack or liquid metal penetration is visible also at 600 °C on both specimens.

3.5. AISI 316L specimen A3, diffusion alloyed by Al hot dipping

Severe attack and penetration of the liquid metal is observed in the upper part of the Al layer already at

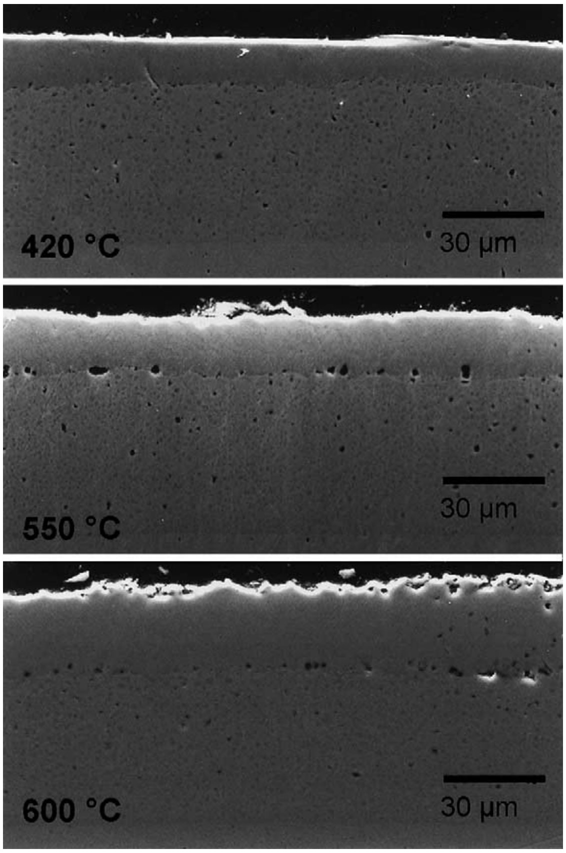

Fig. 5. SEM cross-section of AISI 316L specimens A2 after 2000 h of exposure.

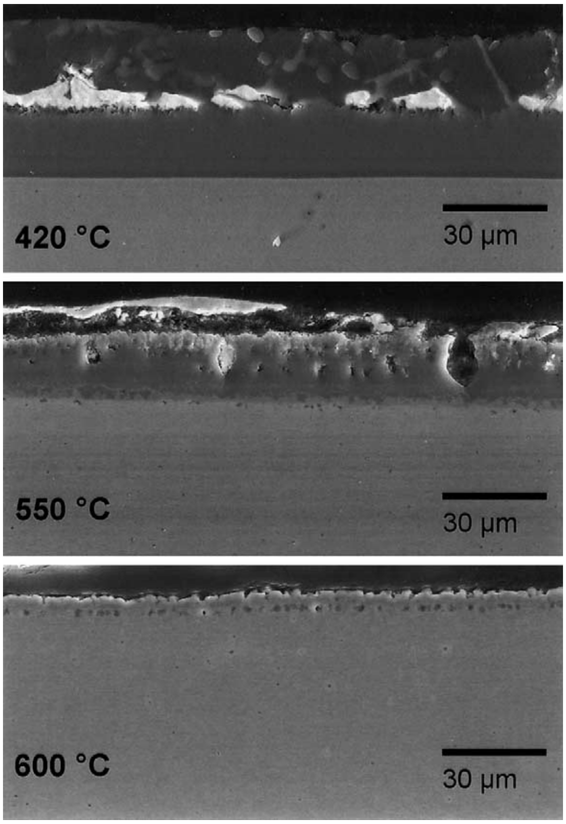

Fig. 6. SEM cross-section of AISI 316L specimens A3 alloyed by Al-hot-dipping after 2000 h of exposure.

420 °C after 2000 h as shown in Fig. 6. This part consists only of Al Si rich precipitations which appear as slightly brighter inclusions. The lower part of the layer contains additionally up to 10 at.% iron. The sharp line represents the original steel surface. At 550 °C also the lower part of the Al layer containing some iron is corroded and penetrated by liquid metal. The specimen exposed to 600 °C has no Al layer any more. A small protective layer of a few microns only is observed on the surface. This layer consists now of FeAl. Since this phase was not existent in the beginning it must have been formed during the tests.

3.6. 1.4970 specimen B3, diffusion alloyed by Al hot dipping

The layer on specimen B3 shows a similar structure like that on A3. At 420 and 550 °C, Fig. 7, in principle the same type of attack occurs as observed for the hot-dipped 316L specimen A3. However at 600 °C the remaining small interdiffusion zone has no protective behavior. This zone contains less than 8 at.% Al. The liquid metal penetrated the steel surface and caused dissolution on Ni partly through the whole tube wall of 400-μm thickness. By looking at the specimen surface it is noticed that large parts of the tube wall disappeared.

3.7. Summary of the results after 2000 h of exposure

Because of the large variety of the results described above, these are summarized in Table 5 to allow an overview.

4. Discussion

The formation of stable dense oxide layers protects steel from dissolution attack by liquid Pb/Bi at temperature below 600 °C. It is necessary therefore, to add oxygen and control its concentration in the liquid metal alloy to prevent oxide degradation. The oxygen concentration of 10^{-6} at.% applied in the loop test is sufficient for formation of oxide scales [8].

The austenitic and martensitic steels develop and maintain protective oxides at the surface that avoid the contact between the liquid metal alloy and the metallic

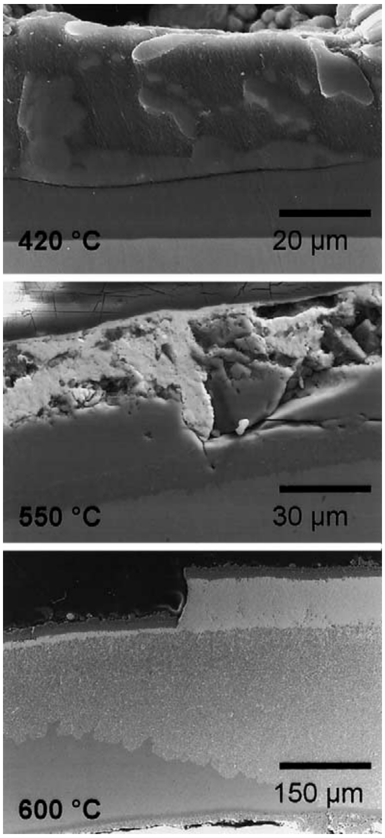

Fig. 7. SEM cross-section of 1.4970 specimens B3 alloyed by Al-hot-dipping after 2000 h of exposure.

Table 5
Summary of the results

Steel	420 °C	550 °C	600 °C
AISI 316L original	+	+	−
AISI 316L Al-wrapped	+	+	+
AISI 316L Al-hot-dipped	−	−	−
1.4970 original	+	+	+
1.4970 Al-wrapped	+	+	+
1.4970 Al-hot-dipped	−	−	−
MANET original	+	+	

(+) = sufficient protection; (−) = insufficient protection.

steel. However, locally disintegration of the protective scale starts at 600 °C. This is the reason for onset of a partially severe solution attack, as observed for the AISI 316L specimen A1. Once the liquid metal permeates the protective scale, its oxygen supply out of the liquid metal bulk is strongly reduced and with it the possibility of oxide formation at the front of penetrating Pb/Bi. The liquid metal inside the deep reaction zone in specimen A1 after exposure to 600 °C for 2000 h is highly enriched in Bi, represented by the bright phase. The remaining steel structures in this zone are highly reduced in Ni to <1 at.%. The other austenitic specimen B1 of 1.4970 steel does not show this severe dissolution attack. The reason for this different behavior is not yet clear. The oxide layer on 1.4970 should be more stable than that one on 316L.

The oxide scale on MANET steel specimen C1 has a continuous protective oxide layer up to 550 °C. However, further increased oxide layer thickness during longer exposure times could impose a problem as well. A consideration of corrosion effects of this steel at 600 °C is not useful because of the insufficient mechanical stability at this temperature.

Steels with alloy formation at the surface have a good resistance against dissolution attack of liquid Pb/Bi up to 600 °C on condition that the Al and Fe concentration is high enough to allow FeAl formation at the surface. Both austenitic steels alloyed by Al-foil wrapping and annealing have an about 15-μm thick FeAl layer on top of the steel surface which is created by diffusion of iron into the liquid Al layer during annealing at 1040 °C. On the other hand Al diffuses into the bulk steel body, such forming a Fe(Al) solution zone. The surface layer develops a stable thin alumina layer in oxygenated liquid Pb/Bi which constitutes an effective barrier against dissolution and further oxidation. The same positive result is obtained in an earlier work with stagnant lead [8] by alloying Al into the steel surface using the GESA facility [15].

Specimens A3 and B3 are alloyed by hot-dipping of austenitic steel into liquid Al and subsequent annealing. The steels examined have no stable surface alloy. It consists of Al with 12 at.% Si and a few at.% of iron only, because the annealing temperature is as low as 550 °C in this case. The silicon is an addition to the Al bath. Already at 420 °C the dissolution of the Al layer starts and is completed at 600 °C. After 2000 h of exposure only a few μm thick FeAl layer in the interdiffusion zone at the AISI 316L steel surface still hinders the penetration of Pb/Bi at 600 °C. On the 1.4970 specimen B3, this barrier is already broken after 2000 h at 600 °C with a catastrophic dissolution attack as a consequence. The high carbon content in 1.4970 and observed precipitations of TiC and other impurities, mainly sulfur of up to 5-μm extension may be the reason for a forced penetration through the steel surface.

The fact that FeAl layers form stable oxide scales and Al layers get dissolved shows the important role of the activity of Al in protective layer formation. The activity of Al must be drastically lowered e.g. by FeAl formation to favor oxide formation against the dissolution attack. Because of the high solubility of Al in Bi the dissolution attack of Pb/Bi on Al is so fast that no oxide scale can be formed. Therefore an Al compound is required at the surface which is stable enough to minimize the high dissolution attack of Bi. This problem does not appear with pure Pb melts in which the solubility is much lower [8].

5. Conclusions

In general, the original steels without surface alloying are suitable for application in liquid Pb/Bi up to temperatures of 550 °C at oxygen concentrations of 10^{-6} at.% and higher. The austenitic A2 and B2 specimens, surface alloyed by Al with formation of FeAl at the surface, have no signs of any corrosion even at 600 °C. They are protected by a thin alumina layer which remains stable.

Austenitic specimens A3 and B3 hot dipped in Al and annealed at 550 °C only, with no FeAl formation at the surface, are not able to develop protective oxide scales.

In liquid Pb/Bi the activity of Al at the surface must be low enough to minimize the solution rate of Al in Pb/Bi and allow oxide scale formation. FeAl at the surface fulfills this requirement.

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