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Temperature effect on the corrosion mechanism of austenitic and martensitic steels in lead–bismuth

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Abstract

Compatibility tests on the austenitic AISI 316L and the martensitic MANET II steels in stagnant PbBi were performed at 573, 673 and 823 K with exposures up to 5000 h. The change of the corrosion mechanism with increasing temperature has been evaluated. The results showed that at 573 and 673 K a thin oxide layer growth on the surface of both steels. By increasing the temperature to 823 K both types of steels were attacked by the liquid metal and dissolution of the steel alloying elements has been observed. The herein-reported experimental activities were performed in collaboration with the IPPE of Obninsk, where preliminary dynamic tests were performed in the experimental facility CU-2. The Russian ferritic–martensitic steel EP823 has been exposed to flowing PbBi at 623, 723 and 823 K for 700 h. After 700 h of testing, the surface of the EP823 samples showed for the three temperatures a compact oxide layer.

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1. Introduction

The accelerator driven systems concept studied for treatment of nuclear fuel waste is reported in Ref. [1]. Several research projects are ongoing in order to demonstrate the feasibility of those systems [2,3]. In these projects the use of eutectic PbBi as a cooling mean and target is foreseen and for the radioactive waste incinerator, austenitic steels and martensitic steels of the 9–12 Cr class are considered as candidate structural materials. It is well known that from a physical and nuclear point of view, the PbBi alloy is a valid target and coolant candidate, but on the other hand the compatibility with the structural materials seems to be a critical issue. Several compatibility studies of structural materials with Pb and PbBi alloy has been performed in the near past [4–7]. A background knowledge of compatibility of steels with PbBi was obtained from tests during the sixties [8].

These works showed that the temperature and the oxygen content in the molten metal plays an important role in the definition of the corrosion mechanism. For instance, tests conducted on the refractory metals Mo and W, in stagnant oxygen saturated molten Lead, showed that these two metals are strongly oxidized [9]. Oxidation of the martensitic steels, F82H and MANET II, exposed to molten lead and lead–bismuth, both bath oxygen saturated, in the temperature range between 573 and 749 K was observed [4]. With regard to corrosion phenomena that could occur in presence of liquid metal, further works showed that the surfaces of a Fe–9Cr martensitic steel, exposed to molten lead under oxygen control, up to 3000 h and at 823 K, are also oxidized [5]. Moreover, in the steel–liquid PbBi system an oxide layer on the steel surface could be beneficial as far as the prevention of the dissolution of the steel elements in the liquid metal is concerned. In fact it has been discussed that oxides acts as corrosion barrier against the liquid metal attack, given that the oxide growth that occurs on the steels when exposed to liquid metal could be controlled [10].

The herein-reported results concern long-term compatibility static tests performed at 873 K and up to 5000 h

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on AISI 316L and MANET II steels in molten Pb–Bi eutectic. In a previous work [4] results on compatibility tests performed in stagnant Pb–Bi eutectic on the AISI 316L and the MANET II steels for 1500 h and 5000 h at 573 and 673 K have been discussed. In that work it was shown that at 573 K on both steels a thin oxide layer grown in situ protected both steels against liquid metal attack, even after 5000 h exposure [4]. At 673 K and after 5000 h of exposure, the austenitic AISI 316L steel exhibited still a protective thin oxide layer (1 μm) of Fe, Cr spinel oxide [4]. On the other hand the martensitic MANET II samples exhibited after 5000 h an oxide layer with two sublayers and a thickness of about 5 μm. The composition of the outer sub-layer was comparable to the Fe_3O_4 oxide and the one of the inner sub-layer was comparable to the $Fe(Fe_{1-x},Cr_x)_2O_3$ oxide [4]. The outline was that the corrosion–oxidation resistance of the two steels exposed to PbBi eutectic at 573 and 673 K up to 5000 h seemed to be reasonably good.

In the present work, besides the results obtained at the testing temperature of 873 K, the results given in Ref. [4] are taken into account, in order to give a complete frame of the corrosion–oxidation resistance of the AISI 316L and MANET II steels in the temperature range of 573–873 K.

The herein-reported experimental activities were performed in collaboration with the Institute of Physics and Power Engineering (IPPE) of Obninsk. Beneath the results obtained from the stagnant tests, preliminary results obtained from dynamic tests were also discussed. The dynamic tests were performed in the experimental facility of IPPE called CU-2 loop. The material tested was the Russian ferritic–martensitic EP823 and the testing temperatures were 623, 723 and 823 K. The tests were performed in oxygen controlled conditions.

2. Experimental

2.1. Materials

The chemical composition of the two steels MANET II and AISI 316L tested in stagnant conditions and of the Russian steel EP823 tested in flowing conditions are given in Table 1. For the stagnant test the Stachow GMbH firm (Germany) supplied the eutectic Pb–55.5Bi (44.8 wt% Pb and 55.2 wt% Bi). The alloy contained a few ppm of impurities (Ag 4; Zn < 0.2; Cu < 0.5; Sb < 3; Sn 9.5; Mg < 1; Cd 0.2; Fe < 0.6; Ni < 0.9 wppm). The eutectic alloy used for the dynamic test has the following composition: 44.4 wt% Pb and 55.6 wt% Bi with Fe, Cr and Ni as impurities.

2.2. Testing

The stagnant tests were performed by exposing the MANET II and the AISI 316L steels to molten Pb–55.5Bi at the temperatures of 573, 673 and 823 K using alumina crucibles, in a glove-box as described in a former work [4]. For each temperature and each type of steel the immersion times were 1500, 3000 and 5000 h. Due to the presence of oxides floating on the free surfaces of the bathes at the three testing temperatures, it was assumed that the liquid metal was oxygen saturated. The oxygen content in the liquid metal, supposing a thermodynamic equilibrium and using the solubility equation estimated by Orlov et al. [10], was 1.84×10^{-5} wt% at 573 K, 1.41×10^{-4} wt% at 673 K and 1.17×10^{-3} wt% at 823 K.

The tests in dynamic conditions were performed in the CU-2 loop at IPPE. The description of the loop is reported elsewhere [11]. The EP823 steel samples were exposed to flowing PbBi at 623, 723 and 823 K for 700 h. The liquid metal velocity was 2 m/s and the oxygen content in the flowing liquid metal was maintained constant at 4×10^{-6} wt%. After extracting the specimens from the loop they were cleaned with glycerine at 150–180 °C in order to remove the traces of PbBi from the surfaces.

Metallographic examinations of all the tested samples were accomplished by optical microscopy (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Chemical analyses were carried out by energy dispersive X-ray spectroscopy, EDS, using the ZAF-correction procedure.

3. Results

3.1. Stagnant tests

As far as the wetting of the steel surfaces is concerned, it was observed by visual inspections after the tests that both steels, the AISI 316L and the MANET II, tested at 573 K did not exhibit traces of PbBi alloy after

Table 1
Chemical composition (wt%) of the steels

	Cr	Ni	Mo	Mn	V	Nb	W	Si	C
AISI 316L	17.3	12.1	2.31	1.8	–	–	–	0.35	0.02
MANET II	10.3	0.68	0.61	0.78	0.20	0.14	–	–	0.1
EP823	12	0.89	0.7	0.67	0.43	0.4	1.2	1.8	0.14

1500 and 3000 h immersion. At the same temperature and after 5000 h on the MANET II sample surface traces of PbBi alloy were present. At 673 K the three MANET II samples exposed for 1500, 3000 and 5000 h were almost completely covered by the PbBi alloy, while on the surface of the AISI 316L samples only traces of PbBi were detected. At the highest testing temperature, 823 K, the PbBi alloy covered all the samples extracted from the bathes.

The metallurgical analysis showed that the austenitic steel tested at 573 and 673 K did not suffer any corrosive attack and on the steel surface a thin oxide layer could be detected as described in Ref. [4]. Moreover, the behaviour of the martensitic steel tested at 573 K was comparable to that of the austenitic [4]. At 673 K after 1500 and 3000 h still a thin oxide scale was observed on the surface of the MANET II samples while after 5000 h exposure to PbBi the martensitic steel exhibited a double layered oxide with a higher thickness [4].

At 823 K the corrosive behaviour of both steels changed completely. The AISI 316L sample exposed for 1500 h at 823 K to PbBi presents in few areas a thin oxide scale on the surface. The cross-section of the specimen showed that the most parts of the edge has a spongy appearance, as shown in the SEM-micrograph in Fig. 1. EDS point analysis performed on this spongy layer showed that it was mainly composed of Fe and O. The Cr and Ni content in this layer was about 5 and 2 wt% respectively.

After 3000 h of exposure the spongy layer was detected on the cross section of the sample and beneath of this layer, PbBi penetration was observed, as reported in the SEM-micrograph of Fig. 2. The corrosion mechanism observed was the dissolution of steel elements in the liquid metal. It could be supposed that by increasing the exposure time together with the dissolution of Ni and Cr, observed after 1500 h immersion, also the dissolution of Fe starts to be active. The behaviour of the AISI 316L sample exposed for 5000 h was comparable to that one exposed for 3000 h and it could be observed that, by increasing the exposure time to the liquid metal, the deepness of liquid metal penetration increased.

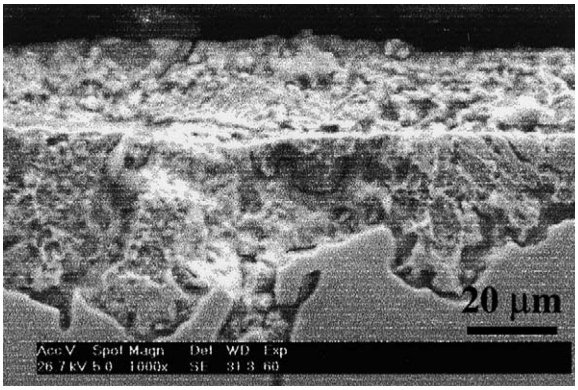

Fig. 1. SEM-micrograph, cross-section of the AISI 316L steel exposed to PbBi at 823 K for 1500 h.

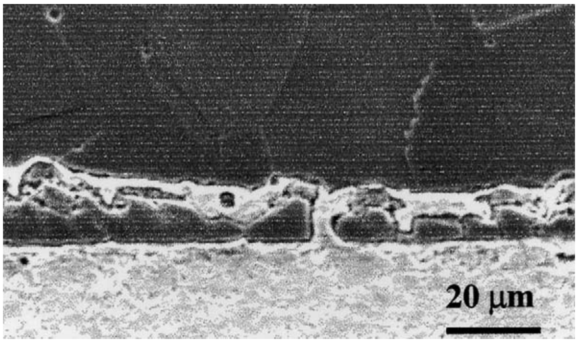

Fig. 2. SEM-micrograph, cross-section of the AISI 316L steel exposed to PbBi at 823 K for 3000 h.

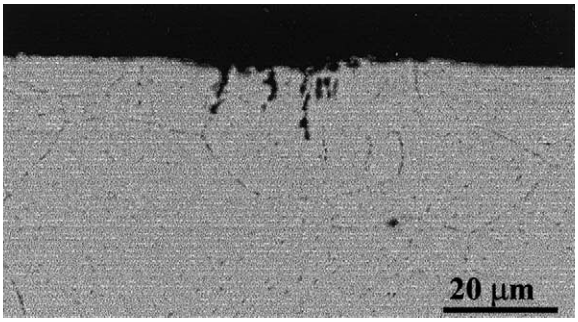

Fig. 3. SEM-micrograph, cross-section of the MANET II steel exposed to PbBi at 823 K for 1500 h.

The MANET II steel exposed to PbBi at 823 K for 1500 h exhibited liquid metal corrosion as shown in the micrograph of the transversal section reported in Fig. 3. Inter- and trans granular attack of the liquid metal could be observed. Besides the liquid metal penetration, it was still possible to detect in some area a thin oxide layer composed of oxygen, chromium and iron.

By increasing the testing time to 3000 and 5000 h the liquid metal penetration within the bulk of the steel was more severe, as shown in the SEM-micrograph of Fig. 4 where the cross-section of the 5000 h tested sample is presented. The main corrosion mechanism that has been supposed for the MANET II steel, as well as for the AISI 316L steel, is the dissolution of the steel elements. Nevertheless, on the MANET II samples tested at 3000 and 5000 h, besides the liquid metal penetration also thin oxide scales could be detected on a few surface

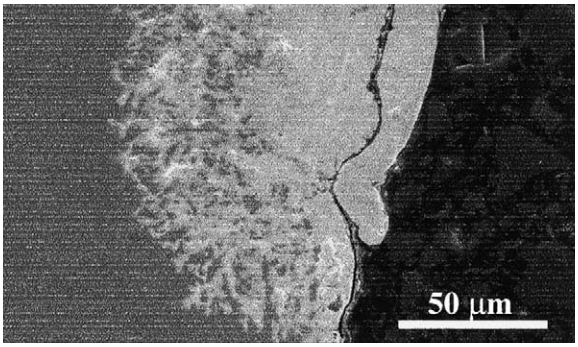

Fig. 4. SEM-micrograph, cross-section of the MANET II steel exposed to PbBi at 823 K for 5000 h.

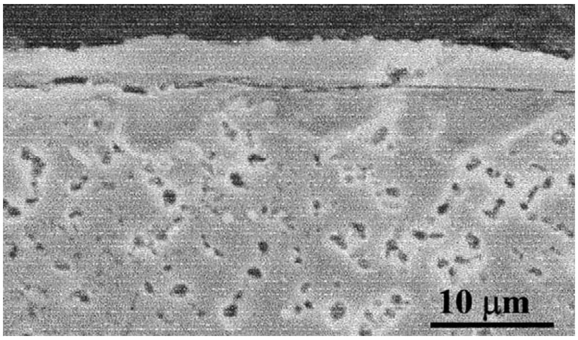

Fig. 5. SEM-micrograph, cross-section of the EP823 steel exposed to flowing PbBi at 823 K for 700 h.

parts. The EDS analysis performed showed that the oxide scales were composed mainly of Fe, Cr and O.

3.2. Dynamic tests

The three samples extracted from the CU-2 loop tested for 700 h at 723 and 823 K exhibited an oxide scale on their surfaces, while on the surface of the sample tested at 623 K no oxide scale could be observed with the herein used analytical techniques. Nevertheless, as the surface of this latter sample appeared to be smooth it could be reasonably deduced that a very thin scale is grown also on this sample. The oxide layers that were observed on the other two samples were not uniform in terms of thickness. The oxide thickness measured on the sample tested at 723 K ranged from 0.2 to 6.5 μm and those measured on the sample tested at 823 K ranged from 0.6 to 11.5 μm. These large ranges could be due to the preparing procedures for the metallurgical analysis.

The oxide grown at 723 K was made by two layers and EDS analysis performed on the oxide showed that the internal layer, about 4-μm thick, was composed of oxygen, chromium, iron and about 3 wt% of silicon. The outer layer was about 3-μm thick and composed mainly of iron and oxygen. In comparing the composition and the morphology of the oxide grown at this temperature, with the one grown on the same steel as reported in a previous work [7], it could be supposed that the outer layer of the oxide is a magnetite and the internal part a Fe, Cr spinel oxide with Si in solution.

The morphology of the oxide grown on the EP823 steel at 823 K is reported in the SEM-micorgraph of Fig. 5. The oxide consists mainly of one layer, and from the EDS analysis it was possible to establish that the composition of this layer was the same as that of the inner layer of the oxide grown at 723 K. In some surface parts of this sample it was possible to detect also an outer oxide layer with a thickness less than 1 μm composed of magnetite.

4. Discussion

With regard to the earlier static tests it was noticed that the surfaces of the AISI 316L and the MANET II samples tested at 573 K up to 5000 h were only partially wetted and on both the type of steels a very thin ($\leqslant 1$ μm) oxide scale could be detected [4]. At 673 K after 5000 h, the surfaces of the MANET II samples was wetted completely and a double layer oxide with a thickness of about 5 μm was detected. The surface of the AISI 316L sample was only partially covered and a thin single layer oxide was observed.

At 823 K the behaviour of the two type of steels changed completely. The austenitic samples showed the dissolution of the steel elements into the liquid metal, and that phenomenon became more severe by increasing the testing time. In fact after 1500 h a ferritization of the austenitic steel was observed, where a spongy like ferrite layer was oxidized. By increasing the immersion time also this ferrite layer was partially dissolved into the liquid metal and liquid metal penetration into the bulk was observed. On the other hand the martensitic steel exhibited at this temperature on some part of the surface oxide scales for each immersion time, but the main corrosion mechanism was also for this type of steel the dissolution.

From the herein reported results and by taking also into account the results reported in Refs. [4,6,7], it could be assumed that the AISI 316L steel, exposed to oxygenated PbBi from 573 to 750 K underwent an oxidation following probably a logarithmic kinetic, as reported for gas-phase oxidation when only film oxides are formed [12]. Since at 823 K the corrosion mode active on the austenitic steel seems to be the dissolution of the steel element into the melt, it could be assumed that in between 750 and 823 K a transition temperature or temperature range occurs where a change of the corrosion mechanism from oxidation to dissolution is expected.

Similarly to the austenitic steel, the martensitic steel MANET II exhibited an oxidation following a logarithmic kinetics in the temperature range between 573 and 623 K. At temperatures up to 753 K it was observed that the oxidation of martensitic steels follows a parabolic law [7]; this observation is also in accordance with the oxidation kinetic observed in gas phase at higher temperatures [12]. Also for the MANET II steel, as for the AISI 316L steel, it seems reasonable to assume that in between 750 and 823 K a transition temperature or temperature range occurs, where the corrosion mechanism changes from oxidation to dissolution.

As far as the EP823 steel is concerned, the results indicate that at 723 K the oxidation of steel occurred and a double layer oxide was detected. The outer layer was magnetite and the inner Fe, Cr oxide with Si dissolved inside. At 823 K the steel exhibited still an oxide layer, but it was noticeable that the oxide was composed mainly of Fe, Cr oxide with 3 wt% Si, while only in some parts of the surface a thin magnetite layer was detected. From these results it appeared evident that at 823 K the spinel oxide is still resistant and acts as a barrier against the dissolution of the steel elements into the liquid metal. On the other hand by comparing the behaviour of the MANET II and the EP823 steels, it appeared evident that the presence of Si in the spinel oxide improves its resistance at 823 K. It is thus expected that the transition temperature from oxidation to steel element dissolution for the EP823 steel should occur at a higher temperature as compared to the one of the MANET II and the AISI 316L steels.

5. Conclusions

The conclusions that can be drawn are: at 573 and 673 K the austenitic and martensitic steels immersed in PbBi exhibited oxide layer on their surfaces and these oxides seem to be protective against dissolution of the steel elements into the liquid metal. At 823 K, even if the PbBi bathes were oxygen saturated, the MANET II and the AISI 316L steels suffer a severe liquid metal corrosive attack and the dissolution of the steel elements occurred. These results indicate that the two steels are resistant in PbBi up to 750 K and that between 750 and 823 K a transition temperature or temperature range occurs in which the corrosion mechanism changes from oxidation to dissolution. The results obtained for the EP823 steel showed that the resistance of the Fe, Cr oxide layer depends upon the composition and in particular Si improves the resistance of the oxide.

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