FeCrAI-based corrosion barriers for HLM-cooled systems

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Abstract

A key problem in development of heavy liquid metal cooled nuclear energy and transmutation reactors (ADS) is the corrosion of structural and fuel cladding materials in contact with the liquid metal. Lead and lead-bismuth, which are preferred as a heavy liquid metal coolant, attack unprotected steel surfaces by dissolution of the metallic components into the liquid metal.

During the last years the corrosion behaviour of austenitic and martensitic steels in liquid eutectic lead-bismuth alloy (LBE) was investigated in many laboratories around the world. It was found that oxide scales on the surface provide the best protection against dissolution attack. Therefore, oxygen is dissolved in the LBE to enable the steel to form an oxide scale on the surface and to support the self healing process in case of damage in the protective scale. However, at temperatures above 500°C austenitic steels suffer from severe dissolution attack, while martensitic steels form thick oxide scales which hinder heat transfer from the fuel pins and which may break off and eventually lead to a blocking of the coolant channel.

Above 500°C steels have to be protected by stable, thin oxide scales. A well understood measure is alloying of stable oxide formers into the surface. Al has shown its ability to form such oxide scales. In the range of 4-10 wt.% Al on the surface a stable thin alumina scale is formed by Al diffusion to the surface and selective oxidation. The alumina scale grows only very slowly and prevents migration of oxygen into the steel as well as migration of steel components onto the surface. Alloying Al into the surface was done by pulsed electron beam (GESA) melting of a thin layer on the surface on which Al was precipitated before. Another method to modify the surface properties is coating with an alloy that contains Al in the required concentration range. An overview on the behaviour of steels in HLM environment and their respective application ranges are described. The barrier development on the steel surface by alloying of Al and its positive effect on the corrosion resistance is presented. Furthermore the influence of HLM on mechanical properties, e.g. creep behaviour, is discussed.

Introduction

Heavy liquid metals like Pb and Pb45 Bi55 – lead-bismuth eutectic (LBE) – are foreseen as coolants in future fast breeder reactors like the LFR and or as a coolant and a target of an accelerator-driven system (ADS) [1]. One of the main problems in the development of such systems is the compatibility of the steels with the LBE. During the last years researchers in many different laboratories world wide examined the suitability of austenitic, ferritic and ferritic/martensitic (f/m) steels as structural and cladding material in lead alloy corrosion test systems [2-9]. At low oxygen content most steels tested show dissolution attack. Therefore most experiments are performed at higher oxygen concentration in the LBE of about 10⁻⁶ wt.% that allows 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 f/m steels form thick oxide scales impede 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 4-10 wt.% [2]. Stable thin alumina scales formed in this case protect the steel from dissolution attack and from internal oxidation as well as from Fe diffusion through the surface. Most of the work reported so far deals with corrosion resistance of steels at relevant LBE temperatures. However, it is expected that any stress applied to materials will result in a change of corrosion and oxidation behaviour and that any oxidation or corrosion scale at the surface might influence the mechanical behaviour. At lower temperatures liquid metal embrittlement is of concern for steels in liquid metals [10]. For example low cycle fatigue (LCF) life of ferritic/martensitic (f/m) steels like T91 and Manet II in contact with LBE is significant lower at 260 and 300°C [11,12].

This paper focuses, after a general overview on the compatibility of steels with lead alloys, on the corrosion barrier development accomplished in the laboratories of KIT in collaboration with IPPE Obninsk and Prometey St. Petersburg. Corrosion and oxidation tests especially of surface modified steels, the surface modification process and selected mechanical tests (creep) in liquid lead-bismuth will be discussed.

Experimental

Corrosion and mechanical test facilities

Facilities with stagnant and flowing lead and lead-bismuth were used for the experimental work within the last years. At KIT the COSTA [13] test stand is especially suited as screening test facility of materials in contact with stagnant lead alloys at temperatures varying from 450° C up to 750° C and oxygen concentrations in the liquid PbBi from 10^{-8} to 10^{-4} wt.%. At IPPE Obninsk several loops [2] are operated with Pb and lead alloys between 480 and 600°C and an oxygen concentration controlled at around 10^{-6} wt.%. The flow velocity of the lead alloys varies between 1 and 1.2 m/s. A specific test section can be used for pressurised tube experiments. At Prometey St. Petersburg [14] several heavy liquid metal loops especially designed for mechanical tests like LCF and creep to rupture are operated. Mechanical tests were performed up to now under oxygen control (10^{-6} wt.% oxygen) at temperatures of 550°C.

Compatibility of steels with lead alloys - corrosion, oxidation - mechanical behaviour

Compatibility of steels with HLM

Corrosion tests in static and flowing LBE covered the temperature range from 400 to 650° C. In most cases the HLM contained around 10^{-6} wt.% of oxygen to allow formation of protective

oxide scales on the steel surface. But also low oxygen concentration $<10^{-8}$ wt.% and high oxygen concentrations of 10^{-4} wt.% were considered. Below temperatures of 500°C no difficulties arise with the protection of steel surfaces by formation of oxide scales. Martensitic steels develop thick multi-layer oxide scales growing with exposure time. Austenitic steels have thin, stable, protective spinel scales on the surface. Experimental results of corrosion tests at 500°C in stagnant LBE with 10^{-6} wt.% oxygen up to 10 000 h exposure [15] show clearly the limits for the application of such steels. The austenitic steel AISI 316 FR (17.3Cr, 12.1Ni) in Figure 1(a), shows satisfying protection up to 2 000 h of exposure by a thin oxide scale with occasionally thicker oxide nodes like depicted in Figure 1(a). However, dissolution attack starts after 10 000 h where the oxide scale is penetrated by LBE in some places as shown in Figure 1(b). A different result was obtained for the martensitic steel HCM12a in Figure 1(c). The initially thin oxide scale in the upper right grows up to a thickness of more than 40 μ m after 10 000 h but still protects the surface from dissolution attack. At 550°C and higher, surface protection by oxidation of steel components fails because of scale penetration and subsequent dissolution attack on both steels after exposure times below 5 000 h already.

Figure 1: SEM of cross-sections of surface region after exposure to static LBE at 500°C with 10^{-6} wt.% oxygen



(a) Austenitic 316 steel after 2 000 h and (b) 10 000 h; c) Martensitic P122 steel after 800 h and (d) 10 000 h

Steels can be used in HLM with an oxygen concentration of 10^{-6} wt.% up to 500°C without any further measures. However, f/m steels form under such conditions already thick oxide scales. At parts of a reactor at which heat removal is a crucial point, like claddings or heat exchangers, formation of thick oxide scales is not acceptable.

Preliminary calculations of the inner clad temperatures [16] show a 10 K increase each 10 μ m of oxide scale considering a thermal conductivity of 1 W/mK, which is close to that of magnetite and spinel [17]. Considering the experimental evaluated oxide scale thickness a scale growth was extrapolated for T91 at different temperatures (Figure 2). Even at 450°C after two



Figure 2: Oxide scale growth of T91 in LBE at different temperatures

years the oxide scale reaches a thickness of about 30 μ m which is the just acceptable value for sufficient heat transfer at cladding tubes. A scale thickness of 50 μ m after 20 years for examples would require an increase of heat transfer surface of about 20% at a heat exchanger of a lead fast reactor. Therefore, only with a coating or surface alloy that ensures the protection against dissolution and oxidation attack, austenitic and f/m steels of T91 and 316-type can be employed in HLM environment above 500°C.

The protective layer has to fulfil following requirements:

- prevention of dissolution attack;
- tolerable oxidation rate;
- long-term high-temperature stability of the system also under abnormal conditions;
- long-term mechanical stability of the surface coating and alloy layer;
- tolerable influence of the coating and surface alloy on the mechanical properties of the steel;
- self-healing capability of the oxide scale;
- durability under irradiation;
- industrial feasibility.

Behaviour of steels with modified surface

Bulk Al containing alloys or thick coatings cannot be considered for the envisaged parts (e.g. cladding tubes) to be protected. Only the surface of steels should be enriched with Al. Two methods, alloying Al into the steel surface [4] and coating the surface with an Al alloy with subsequent GESA treatment [18] to form a surface graded material, were developed in our institute. The latter will be described in more detail.

Surface modification by the GESA process

The GESA process uses pulsed electron beams [18] with a kinetic energy in the range of 50 ± 400 keV a beam power density up to 6 MW/cm² at the target and a pulse duration up to $40 \ \mu$ s. The energy density adsorped at the target is up to $80 \ \text{J/cm}^2$, which is sufficient to melt metallic materials

adiabatically up to a depth of 10-50 μ m. Due to the high cooling rate in the order of 10⁷ K/s, very fine-grained structures develop during solidification of the molten surface layer. This is a suitable basis for the formation of protective oxide scales with good adhesion. The GESA facilities are designed and constructed together with NIIEFA (Efremov), St. Petersburg and are widely explored at KIT and NIIEFA. In the context of future fast reactors, the above-described surface modification process is mainly considered for cladding tubes and heat exchangers. Therefore a special GESA, the GESA IV (Figure 3), with a cylindrical cathode was designed. This facility allows the treatment of a tube segment of about 30 cm length with a single pulse.



Figure 3: Photograph of the GESA IV facility

Presently, GESA treatment of Al-alloy (FeCrAlY) coatings is the favourite process at KIT. The coating is applied using low pressure plasma spraying (LPPS) of powder having a mean diameter of about 33 μ m. Figure 4(a) shows a cross-section of a cladding tube with a ~20 μ m LPPS FeCrAlY coating. The coating has a rough surface because of the relatively large spray droplets, contains pores and also the adhesion on the bulk material is not sufficient for the application. To eliminate these inadequacies, the coatings are treated using the GESA surface melting process.

Figure 4: FeCrAIY coating on steel specimen



The GESA treatment parameters used to re-melt such coated samples are selected to melt the entire layer plus some μ m of the adjacent bulk material. A cross-section after GESA treatment of a FeCrAlY coated steel specimen is depicted in Figure 4(b). The surface of the specimen after GESA treatment is smooth and the pores are removed. Another important effect of the GESA treatment is interface mixing of the FeCrAlY layer with the steel. Due to the small layer thickness the melting zone reaches beyond the coating substrate interface and thus causes this mixing; the coating is "welded" to the bulk material.

Corrosion examinations on surface alloys

In long-term corrosion experiments austenitic AISI 316 FR and HCM12a and martensitic ODS steels with Al alloyed into the surface layer were exposed to LBE with 10⁻⁶ wt.% oxygen. The tests last over a period of 10 000 h at 550 and 650°C without any deterioration of the thin alumina scale that was developed during the initial exposure time [7]. Coating the surface with FeCrAlY leads to the same positive results as observed for surface alloyed steels. The coating behaves like an Al-alloyed surface layer after it is homogenised and smoothed by re-melting with GESA electron pulses. Coated T91 steel specimens were exposed 2 000h to LBE with 10⁻⁶ wt.% oxygen at 480, 550 and 600°C flowing at 1 m/s [19]. No dissolution attack, no scale damage and no severe oxide formation were observed after the experiments. The examination of the near surface region of the specimen exposed to LBE at 600°C is shown in Figure 5, which depicts the SEM (upper image) and the EDX scan (lower image). There is no oxide scale visible, but the EDX scan clearly shows an alumina peak (O and Al) at the surface followed by a Cr peak that seems to be in a metallic state. The EDX also shows the border between coating and steel, at which the

Figure 5: FeCrAlY-coated T91 tube specimen after 2 000 h exposure to LBE with 10⁻⁶ wt.% oxygen at 600°C

Above - SEM of the cross-section, below - EDX elemental scan of the respective region



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Al content drops down and some Cr precipitations in the grain boundaries of the coating. Experiments with FeCrAlY-coated steel 1.4970 support the suitability of this coating for high-temperature application. No corrosion attack could be observed in 5 000 h tests in LBE with 10^{-6} wt.% oxygen at 500, 550 and 600°C [20].

Corrosion experiments with alloyed steels show that 4 wt.% Al is necessary to achieve selective alumina scale formation. For concentrations above 20 wt.%, however, the Al activity gets too high and dissolution attack occurs [2].

From the experiments performed up to now prevention of dissolution attack, tolerable oxidation rate and long-term high-temperature stability seem to be fulfilled requirements a protective layer must meet, as discussed.

Mechanical tests

One necessary requirement for protective layers is a negligible influence on mechanical properties. This question about influence of LBE and steel coating was addressed in low cycle fatigue (LCF) [14], pressurised tube and creep to rupture tests. At LCF tests performed at Prometey at 550°C with 0.5 Hz and elongations $\Delta \epsilon_t$ between 0.3-2.0, no influence neither of the LBE with 10⁶ wt.% oxygen nor of the FeCrAlY coating could be observed.

The creep to rupture test of T91 is an ongoing experiment at Prometey. Tests of uncoated T91 in flowing PbBi at 550°C show a significant reduction in time to rupture of the specimens tested in the liquid metal compared to air for high stresses between 140 and 220 MPa (Figure 6). First creep to rupture tests with surface modified T91 clearly show that the negative influence of LBE is drastically reduced. At 200 and 220 MPa load the time to rupture is very similar to the values obtained with uncoated T91 in air.





Detailed examination showed the likely existence of a threshold stress above which LBE has significant influence on the creep strength of non-modified T91. Below 120 MPa load no significant difference in second creep rate could be observed. Below this threshold the creep data obtained in air can be most probably transferred to LBE.

Cross-sections of T91 non-modified tested at 160 MPa and surface-modified T91 tested at 220 MPa both in LBE are depicted in Figure 7. The upper cross-section shows cracks in the oxide scale of the non-modified T91. Due to the large strain values close to the rupture area the cracks are widened and reach the bulk T91. The opening angle of the cracks is large enough for LBE penetration that finally reduces the creep strength. The GESA modified samples tested at 220 MPa

Figure 7: Cross-section of T91 steels with and without surface modified layer after rupture

Above - non-modified T91 tested at 160 MPa, below - surface-modified T91 tested at 220 MPa



in LBE (lower part of Figure 7) do not show any cracks in the surface region. The thin scale, at this magnification invisible, is still protecting the steel from any influence of the LBE. Thin alumina scales formed on GESA treated FeCrAlY coated T91 are less sensitive to cracking due to the reduced brittleness and are therefore superior under constant loads in lead environment.

Summary and outlook

The application limits in liquid Pb or PbBi concerning temperature and oxygen concentration of f/m steels like T91 and austenitic steels like 316L were evaluated in many corrosion experiments. Oxidation of f/m steels (T91) above 450°C leads to insufficient heat transfer capability. Austenitic steels like 316L suffer from dissolution attack above 500°C. For temperatures higher than these, surface alloying of Al increase the temperature limit for both types of steel above 550°C, by selective Al₂O₃ formation. Such modified surface alloyed layers seem not to reduce the mechanical properties of the materials as shown in LCF experiments. In LCF tests no difference between samples tested in air and in LBE was found, either. The creep-to-rupture test shows a strong loss of creep strength of T91 non-modified in contact with liquid PbBi at 550°C. The GESA surface-modified specimens instead have at 550°C similar creep rupture strength as in air. The surface-alloyed layer improves drastically the behaviour in lead alloy environment.

The focus of future studies will be broadened to investigate more pure liquid lead systems and to intensify the material investigation to higher temperatures. In addition investigation of mechanical properties (e.g. fretting of cladding tubes), erosion resistance of pump materials and resistance to irradiation will be performed. Another issue will be the process development of surface alloying with GESA to industrial level and establishing methodologies for quality assurance of the processed cladding tubes.

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