

Coatings on Steels T91 and 316L in Lead-Bismuth Eutectic Environment

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Abstract. The work is aimed on the coatings used as a barrier against Heavy Liquid Metal (HLM) influence and coated material behaviour under mechanical loading. The comparison of two kinds of coatings deposited on two different steels is examined: ferritic-martensitic steel T91 coated with AlTiN and austenitic steel 316L coated with Al₂O₃. Both samples underwent tensile tests with constant extension rate in the HLM autoclave-cell for material testing. The testing environment in the cell was liquid PbBi eutectic at the temperature of 550 °C. The examination by Scanning electron microscopy and Energy-dispersive X-ray spectroscopy followed after exposure. The yield strength of the steel was exceeded in both cases, cracks and adhesion were studied in depth to characterize their resistance to the simultaneous effect of load and environment. Both coatings offered protection against corrosion; however, localized cracking gave rise to the damage of the substrate. These coatings provided a corrosion barrier, which once damaged is not able of self-healing.

1 Introduction

Heavy liquid metals (HLM) are being studied as candidate coolants for Generation IV fast reactors. The nuclear industry remains generally conservative in terms of using new materials and qualification under irradiation. Thus the use of coatings as protective barriers is being investigated [1-3] as a response to the issue of material dissolution in HLM environment [3-5]. The main adopted principle is the use of Al₂O₃ forming materials, as the oxide is fairly stable and resistant to high temperature exposure [1, 6 and 7].

The main candidates among structural materials proposed for HLM applications include ferritic-martensitic steel T91 and austenitic steel 316L, mainly because of their qualified properties under irradiation and the existence of a large database for their corrosion behaviour in environment [4].

AlTiN coatings as a perspective solution for HLM application are proposed due to the suitable mechanical properties and chemical stability. Pure Al₂O₃ has a potential due to substantially insolubility in lead and compatibility from the chemical point of view [8, 9].

Experiments in the frame of the FP7-MATISSE project were aimed to compare the performance of two coatings under loading condition in lead-bismuth eutectic (LBE). Moreover, the characterisation of the corrosion resistance of coatings was carried out, due to insufficiency of literature data on the stability and overall performance of coatings under loading conditions.

2 Experiments

2.1 Materials



The coating-substrate combinations were chosen according to the agreement of the project (FP7 MATISSE) members. The selection was limited on a small amount due to the project schedule.

2.1.1 Ferritic-martensitic steel T91. (Grade 91 Class 2/S50460) of nominal composition (wt. %) Fe-8.9Cr-0.9Mo-0.4Mn-0.2Si-0.2V was produced by Industeel, Arcelor Mittal group. The material as 15 mm thick plate was normalized at 1050°C with a holding time of 1 min/mm followed by water quenching to room temperature and then annealed at 770°C with a holding time of 3 min/mm followed by air cooling. T91 steel was used as a substrate for application of AlTiN coating.

2.1.2 Austenitic steel 316L. (ASTM A240-Ed02) was produced by Industeel, Arcelor Mittal group. The austenitic stainless steel was received as hot rolled and heat treated plates with a thickness of 15 mm. The solution annealing was done at 1050-1100 °C. The microstructure obtained was fully austenitic with a small fraction of delta ferrite. 316L stainless steel was used as a substrate for application of Al₂O₃ coating.

2.2 Coatings

2.2.1 AlTiN. (more than 50% of Al) coating normally used for abrasive and high temperature applications (>800 °C) was deposited on the steel T91 tensile specimens by using combination of reactive HiPIMS (High Power Impulse Magnetron Sputtering) and pulsed-DCMS (Direct Current Magnetron Sputtering) technologies in the CNR (Centro Nazionale Ricerca) in Italy. The thickness of the layer was about 7 μm.

2.2.2 Al₂O₃. Coating for wide range of applications naturally provides a passivation layer, which prevents the direct interaction between the steel and the environment. The coating was deposited on the austenitic 316L steel by detonation gun (a high-velocity thermal spray process with an extremely good adhesive strength, usually low porosity and coating surface with compressive residual stresses).

2.3 Specimen

Rod tensile specimens (figure 1) with 4 mm diameter were fabricated in longitudinal direction of the plates. The shape of the specimen was designed to fit in alignment system in HLM.

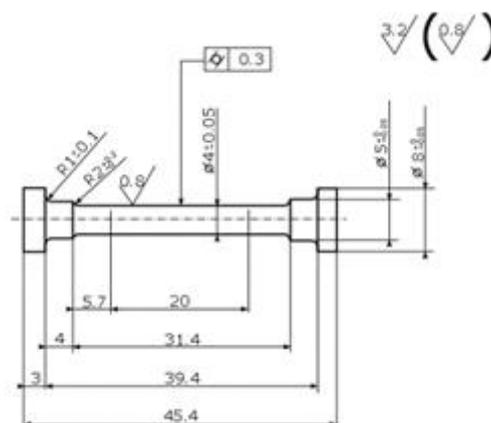


Figure 1. Rod tensile specimen with coating for HLM environment.

2.4 Experimental procedure

The tensile tests were performed in LBE medium at 550 °C in order to characterize the thermo-mechanical behavior of materials' coatings. As a testing equipment, the autoclave cell built on the Kappa 50DS Electromechanical Creep Testing machine was used. The testing system is based on 2-

tank concept, where the first tank is for medium preliminary preparation and the medium is subsequently transferred to the second tank with the specimen and holders, where the oxygen dosing is regulated to obtain required environmental conditions. The test is then initialized after reaching the precise conditions (table 1) and performed at the constant extension rate. One of the specimens with Al_2O_3 coating was firstly tested in air environment to quickly verify the adhesive properties of the coating. The test was performed due to previous insufficient preparation of another Al_2O_3 coating.

Table 1. Conditions of performed tensile tests.

Sample design.	Environment	Temperature [°C]	Extension rate [s^{-1}]	C_{O_2} wt.%
AlTiN 1	LBE	550	10^{-4}	10^{-8}
AlTiN 2	LBE	550	10^{-4}	10^{-8}
Al_2O_3 1	Air	550	10^{-6}	-
Al_2O_3 2	LBE	550	10^{-6}	10^{-13}

2.5 Post-test evaluation

After exposure, the samples were cleaned in a solution H_2O_2 , CH_3COOH and $\text{CH}_3\text{CH}_2\text{OH}$, in the ratio 1:1:1, in order to remove residuals of LBE from the surface. Samples were subjected to the surface analysis using Scanning electron microscopy (SEM) LYRA 3, TESCAN. Subsequently, samples were embedded in the acrylic resin and their cross-section polished for SEM analysis, followed by Energy-dispersive X-ray (EDX) spectrometer. The integrity of the coatings and their adhesions were examined.

3 Results

Figure 2 summarizes the stress-deformation results from both materials at 550 °C. Due to very thin layer thickness the effect of the coatings to material stress-dependence is being considered as negligible. Thus the maximum stress thresholds can be evaluated as approximate Ultimate tensile strength (UTS) of steels T91 and 316L at the given temperature and extension rate.

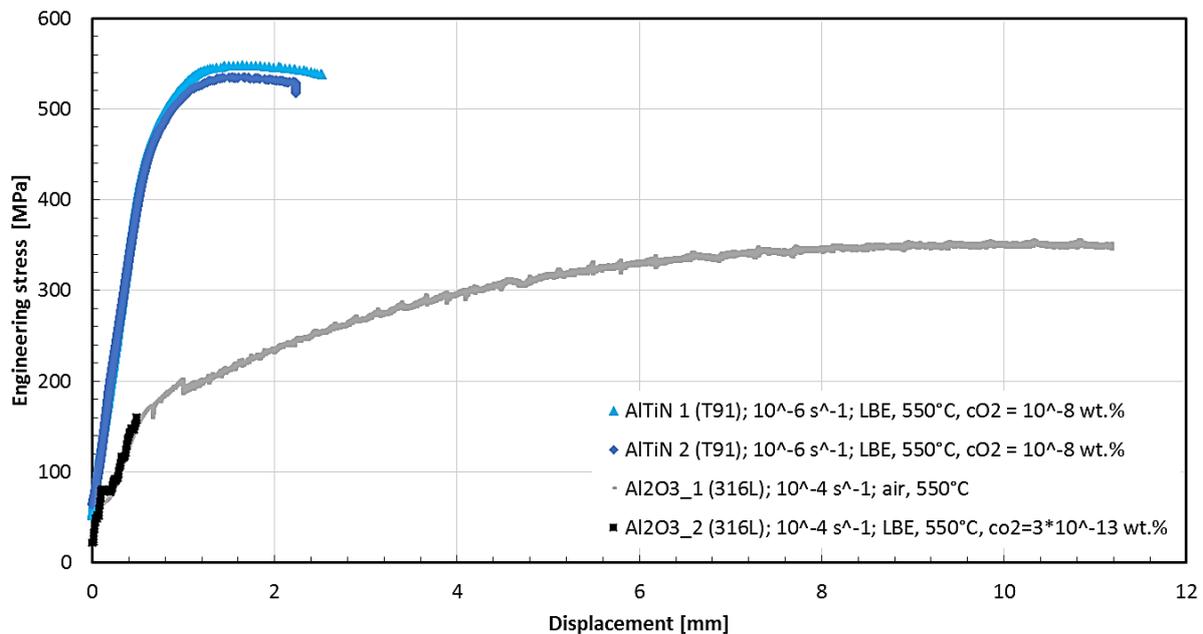


Figure 2. Tensile test with constant extension rate at 550°C on the steels with coatings.

The 316L specimen with Al_2O_3 coating was loaded in air up to UTS, as a reference test. However, 316L steel has significant plastic deformation up to the UTS (approx. 11 mm extension), therefore it was decided to load the specimen in LBE up to Yield stress (YS) of the material at 550 °C.

3.1 AlTiN

AlTiN surface layer on the sample showed cracks of regular rhomboidal shapes (Figure 3a). The cracks are distributed over the coating surface, though without signs of significant delamination. Cross-section examination indicates that the process of corrosion immediately started due to the contact of LBE with substrate through the cracking (figure 3b, c). The direct contact between the T91 and LBE at 550°C, with 10^{-8} wt. % of oxygen amount, induce a fast reaction which is driving the Fe and Cr out into the liquid metal and make space for the LBE to penetrate quickly into the steel.

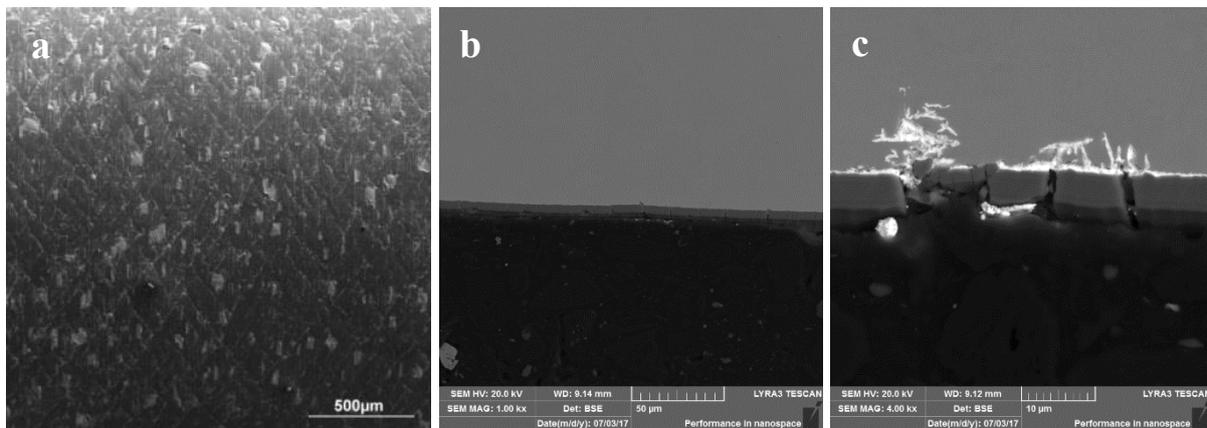


Figure 3. a) Surface of the T91 steel + AlTiN coating with homogeneously distributed cracks; b) detail of cross-section area; c) detail of cracks in the coating and the underneath damage.

3.2 Al_2O_3 in Air environment

Post-test surface examination did not show any changes of the coating morphology. Several superficial cracks of the coating can be observed and the coating is locally delaminated (figure 4b, c). The concentration of the coating loss was observed in the middle of the sample with the highest stress concentration. Considering the extension of the specimen, the coating remain mostly intact and adherent on the majority of the surface.

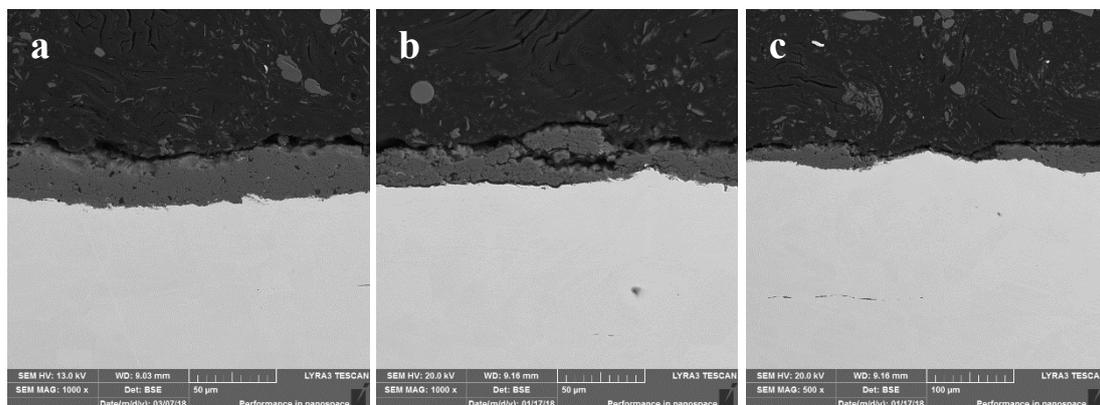


Figure 4. Cross-section of steel 316L + Al_2O_3 coating after test in air at 550 °C; a) The intact Al_2O_3 coating layer, b) detailed cracked layer of Al_2O_3 ; c) detail of delaminated coating layer.

3.3 Al_2O_3 in LBE environment

The cracking of Al_2O_3 coating after LBE exposition differs from AlTiN coating. Al_2O_3 coating is partly delaminated and LBE came to contact with the substrate 316L (figure 5c). The process of corrosion in the steel 316L started as well, though with the minor effect compared to the T91 steel.

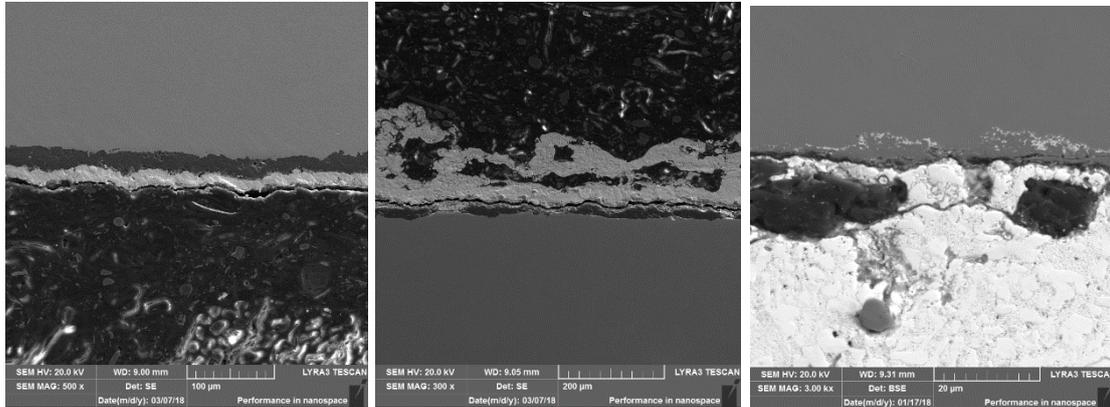


Figure 5. Cross-section of steel 316L + Al_2O_3 coating after test in LBE at 550 °C;

- a) the coating layer with the LBE layer on it; b) cracked and partly delaminated coating layer; c) detail of cracks in the coating and the LBE-substrate contact

4 Discussion

The difference in depths of penetration in the steels is possibly due to the different steel-LBE contact time. This may indicate earlier failure of the AlTiN coating and the LBE had more time to interact with the steel. In fact, the strain rates are very different: the AlTiN was tested at faster rate, therefore it can be assumed, that the coating failed very early in the loading process. On the other hand, the Al_2O_3 coated specimens were tested at lower strain rates, but at much lower YS. Therefore it could be assumed that this coating failed at a much later stage, since the test was also very slow and the steel-LBE contact was only shortly before stopping the test.

The T91 and 316L steels are different with different mechanical properties: the T91 has significantly higher YS than the 316L; moreover the extension necessary to reach the UTS is significantly different too, very short for T91 (0.5 mm) and very long for the 316L (10 mm). However, both reached the YS after about 0.5 mm of deformation. These parameters have a different effect on the coating and in this case it is difficult to compare. However, the main observation was that both coatings failed in the loading conditions and the LBE was in direct contact with the substrate and consequently, interacted with the steel.

5 Conclusion

- We may say that the methods used for application of the AlTiN coating and for Al_2O_3 was chosen correctly because of the great adhesion of both coatings to the substrates.
- The coatings in combination with the structural materials (AlTiN with ferritic-martensitic steel T91; Al_2O_3 with stainless steel 316L) had not only good adhesions but also high hardness, corrosion resistances in contact with liquid metals.
- In both cases (AlTiN and Al_2O_3), the coatings in atmosphere and also in LBE were very stable at testing temperature and no chemical reactions occurred.
- These kinds of coatings provide a corrosion barrier, which once damaged is not able of self-healing.
- Coatings are a valuable solutions for high temperature HLM, however, application limits have to be established and quantified by a wider experimental campaign.

Acknowledgments

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