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Short Communication

Advanced Al_2O_3 coatings for high temperature operation of steels in heavy liquid metals: a preliminary study

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ABSTRACT

In this work, we propose a nanocrystalline Al_2O_3/amorphous Al_2O_3 composite coating for protecting steels operating in heavy liquid metals (HLMs) at high temperature. The coating is grown by Pulsed Laser Deposition (PLD). Previous work by García Ferré et al. [27] has shown that PLD-grown Al_2O_3 attains an unusual ensemble of metal-like mechanical properties and strong interfacial bonding, all combined with the chemical stability and resistance to wear of ceramics. In a short term corrosion test (500 h), 9Cr1Mo steel samples were coated and exposed to stagnant lead at 550 °C. Cross-sectional SEM and EDX analysis revealed no signs of corrosion.

1. Introduction

Heavy liquid metals (HLMs), namely lead or lead–bismuth eutectic (LBE), have been selected as candidate coolant materials for future generation nuclear reactors due to their favorable thermo-physical and neutronic properties [1,2]. Nevertheless, corrosion and erosion of structural steels by HLMs stand as a major bottleneck for the deployment of HLM-cooled nuclear systems.

One of the main approaches to mitigate HLM corrosion is to favor the *in situ* formation of a stable and protective layer of iron and chromium oxides on the surface of steels [3,4]. This can be achieved by injecting oxygen into the liquid metal and maintaining its concentration in the melt within an appropriate range [4]. Nevertheless, such a method is not viable for temperatures above ≈500 °C [5,6], mainly due to the fast kinetics of oxide growth and the considerable reduction of thermal conductivity. Furthermore, although the oxygen injection approach may provide satisfying protection for temperatures below 500 °C, there is a number of technical issues with the strategy, including oxide spallation and channel plugging, as well as difficulties in attaining a homogeneous concentration of oxygen throughout the whole system.

A significant amount of work has been carried out on high-temperature corrosion mechanisms and protection methods for the foreseen structural materials for Generation IV HLM-cooled systems. Many relevant experimental investigations have focused on corrosion modes and oxygen control techniques [4,7–12], as well as on the development of other approaches for providing corrosion protection, such as aluminizing surface treatments [13,14], electron beam-treated FeCrAl and FeCrAlY coatings [15,16], or even new alloys, including Fe–12Cr–2Si [17] and oxide dispersion strengthened (ODS) steels [18–20]. Despite these efforts, the protection of structural steels from HLM corrosion at high temperature is still an open issue.

The difficulties in developing a *fully reliable and viable* technology are leading to the reconsideration of ceramic coatings [21–24], which are an interesting option owing to their chemical inertness. One of the most attractive features of ceramic barriers is the possibility of decoupling oxygen control strategies for steel passivation at *low temperature* (i.e. <500 °C) from protection of parts that operate at *high temperature* (i.e. above 500 °C), such as fuel cladding or other in-core components. In spite of this advantage, ceramic coatings have been considered as a *taboo* in the past, mainly due to the lack of *self-healing* properties, and to the extremely harsh conditions to which fuel cladding will be exposed. Indeed, apart from corrosion, typical materials degradation modes will include fatigue and creep- which can be both enhanced *and* induced by intense radiation fields, as well as many irradiation-induced phenomena, including amorphization, high temperature helium embrittlement and void swelling, among others [25]. Other limitations for coatings come from the high temperatures that several deposition processes or pre-treatments require (up to over 1000 °C, which may

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induce microstructural changes in the substrate material), and from intrinsic drawbacks including brittleness, non-uniform density, micro-cracks and porosity, and poor adhesive strength. In other words, while the use of ceramic coatings in the extreme environment of a HLM-cooled nuclear reactor would require chemical stability, full density and compactness, toughness, high wear resistance, strong adhesion, and a close match of mechanical properties with steels, such requirements haven't been attained yet *altogether* with standard industrial techniques, especially at low process temperatures.

Pulsed Laser Deposition (PLD) is a relatively simple technology that allows growing thin films of a wide range of materials. The deposition conditions can be adjusted to obtain different coating microstructures, varying from fully dense and compact to columnar and porous [26]. In this work, a fully dense and compact Al_2O_3 coating is grown by PLD on 9Cr1Mo grade steel. The deposition process is tailored according to the results from a separate study so as to attain an advanced nanocomposite with metal-like mechanical properties, strong interfacial bonding and outstanding wear resistance [27]. All these features are desirable for long-term operation of the ceramic coating-alloy substrate system in HLMs at high temperature.

The aim of this work is to provide a preliminary statement, based on short term corrosion tests, concerning the viability of PLD as a coating technology for protecting steels in HLM environment. The chemical stability of the coatings was investigated by the exposure of coated steel samples to molten lead at 550 °C for 500 h, followed by SEM and EDX analysis.

2. Experimental

Steel substrates were prepared by cutting $10 \times 20 \times 1\ mm^3$ plates from as received Cr9Mo1 grade steel. The composition of the alloy is listed in Table 1. Samples were ground using SiC paper with increasing grits (600, 800, 1000, 1200 and 2000), properly chamfered, cleaned with an ultrasonic device in acetone and isopropanol, and rinsed in isopropanol.

The Al_2O_3 coatings were grown by PLD in a stainless steel vacuum chamber at low oxygen pressure on just one face of the steel samples, at room temperature, 400 °C and 600 °C. The pulse energy was fixed at 250 mJ, whereas the focus was adjusted to a fluence of $2.38\ J/cm^2$, with a repetition rate of 20 Hz. The thickness of the coatings was in the range 2–8 μm depending on the number of laser pulses, with a deposition rate of roughly 1 nm/s over an area of $50\ cm^2$. Incidentally, it is worth pointing out that higher deposition rates can be obtained over larger areas by employing industrial lasers, which can work with pulse frequencies up to 600 Hz.

One single corrosion test was carried out in a tubular furnace for 500 h in an extra-pure N_2 atmosphere (nominal gas bottle concentrations: <1 ppm_v H_2O and <0.5 ppm_v O_2), with no active oxygen control. The temperature was set at 550 °C. Under these conditions, the atmosphere can be considered as *oxidizing*, in the sense that the formation of chromium, iron and lead oxides is thermodynamically favoured according to the Ellingham diagram (Fig. 1). This diagram shows the stability lines for several oxides as a function of temperature, in terms of Gibbs free energy of formation. A test condition of 550 °C and a partial pressure of oxygen of 10^{-16} atm falls above the stability line for these oxides; an oxygen concentration of around 0.5 ppm is already enough to exceed such partial pressure in the gas phase, H_2O left apart. The gaseous oxygen is dissolved in the liquid metal by mass transfer and reaches an equilibrium concentration in the melt.

Table 1
Composition of the martensitic steel substrates in wt%.

Cr	Mo	Si	Mn	V	Ni	Cu	Nb	C	Fe
9.21	0.9	0.35	0.33	0.2	0.12	0.07	0.06	0.105	Balance

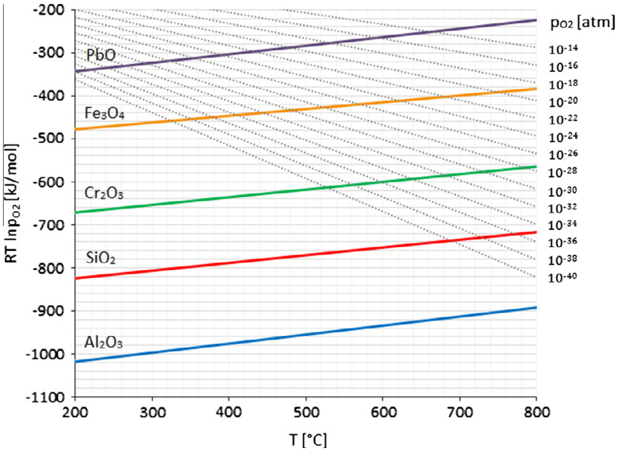

Fig. 1. Ellingham diagram reporting the Gibbs free energy of formation for PbO, Fe_3O_4, Cr_2O_3, SiO_2 and Al_2O_3 as a function of temperature. The iso-lines of oxygen partial pressure are also shown.

Three uncoated samples and twelve coated substrates (six coatings grown at room temperature, three of which 2 μm thick, the rest being 8 μm; three coatings grown at 400 °C and three coatings grown 600 °C, all 8 μm thick) were held in fifteen different 10 ml sintered alumina crucibles by steel holders. The crucibles were filled with lead grains, that were cut from an as-received pure lead slab (99.99%), and loaded into the furnace. The melting of the lead grains occurred during the temperature ramp of the furnace in the extra-pure N_2 atmosphere. The amount of molten lead in each of the crucibles was ~5 ml.

After 500 h, the molten lead was directly poured out from the crucibles and the specimens were left to cool down in air. PbO was observed on the surface of the melt before pouring, suggesting that the liquid metal reached oxygen saturation during the test. The remaining adherent melt on the uncoated faces was not removed, but left to solidify. Transversal and longitudinal cross-sections were cut using a SiC rotating blade. Samples were prepared following standard procedures for SEM analysis. The surface morphology and cross-sections were examined by means of a field emission (FE) SEM microscope (Zeiss Supra 40), equipped with an EDX spectrometer (Oxford Instruments INCA). The electron voltage was set at 2 kV for imaging and at 10 kV for the elemental analysis.

3. Results and discussion

The main goal of the experiment was to verify by the available means that the PLD-coating technology is able to provide protection of steels in HLM environment. SEM analysis revealed that the surface of the *as-deposited* coatings is smooth, with very low droplet density (figures not shown). A picture of the coated face of a sample before exposure to molten lead at 550 °C is shown in Fig. 2a. The color fringes are due to interference phenomena, owing to a small gradient of thickness of the coating. In some cases, the upper part of the substrates was not coated, since it was shadowed during the deposition process, due to sample holding. After exposure to HLMs, the uncoated face of the samples was visibly corroded (Fig. 2b), while the coated face was protected from corrosion (Fig. 2c). The immersed surface was nearly $1 \times 1\ cm^2$. Fig. 3a shows that the specific conditions of the melt (550 °C, saturation of oxygen) led to the formation of a duplex oxide layer