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A DIRECT COMPARATIVE STUDY OF THE CORROSION BEHAVIOUR OF Si-FREE AND Si-RICH SLURRY ALUMINIDE COATINGS IN MOLTEN CARBONATE MELTS

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ABSTRACT

This study is focused on the evaluation of the hot corrosion behaviour of two low-cost slurry aluminide coatings with and without Si addition deposited on ferritic-martensitic steels, comparing them with uncoated steel, after 1000-h of exposure to Li, K, Na molten carbonates at 650°C, under static and dynamic conditions with a high linear velocity (1.3 m/s). Both coatings evidenced a high performance increase in comparison with uncoated substrates after exposure in both conditions. Both coatings behaved in a similar way according to the gravimetric results. However, after dynamic exposure, the Si-free aluminide maintained its morphology and composition after 1000 h with α -LiAlO₂ as the only corrosion product while the Si-rich coating showed a higher attack extent in the outer part and developed a large quantity of voids at the coating/substrate interface, leading to substrate corrosion.

Keywords: Concentrated solar power plants, Thermal energy storage, High-temperature corrosion, Coatings, Molten carbonates

1. INTRODUCTION

In recent years there has been a concern to improve the storage of thermal energy in the Concentrated Solar Power (CSP) plants and a great interest in employing molten salts. Currently, the most commonly used storage medium is composed by molten nitrates, particularly the eutectic mixture of 60% of NaNO₃ and 40% of KNO₃ (named as "Solar Salt") limited to 580°C because of its chemical decomposition. However to increase the efficiency of the plant, salts operating at higher temperatures are needed such as the carbonate mixtures based on Li, Na and K. The use of these new salt mixtures, together with the higher operating temperature, requires new studies to understand the behavior of the alloys with which it is in contact, as well as the study of coatings to avoid or mitigate corrosion phenomena that occur at high temperature. Aluminum coatings applied with slurry have already been studied in molten salts under static and dynamic conditions demonstrating a better performance than uncoated material [1, 2]. The discrepancies observed in the corrosion behaviour of aluminium slurry coatings after 1000 hours motivate this new study. The effect of

silicon, considered beneficial by other researchers [3] after exposure to molten nitrates was also investigated in this work.

2. DESCRIPTION

This work focuses on the study of the high temperature corrosion resistance of two coatings based on aluminides with and without addition of silicon deposited on ferritic-martensitic steels with a 9 wt.% Cr content. More precisely, the two coatings produced at INTA were slurry aluminide coatings with and without addition of silicon (hereinafter SiAl and Al coatings respectively) and were deposited onto T91 by spraying a Cr⁶⁺-free and water-based proprietary slurry formulation. After applying the same heat treatment at high temperature under inert atmosphere for both coatings, Fe-Al intermetallics formed and a high aluminium subsurface content (49 wt.%) was measured for both coatings (Fig. 1). A thinner coating was produced in the case of the Si-rich aluminide coating.

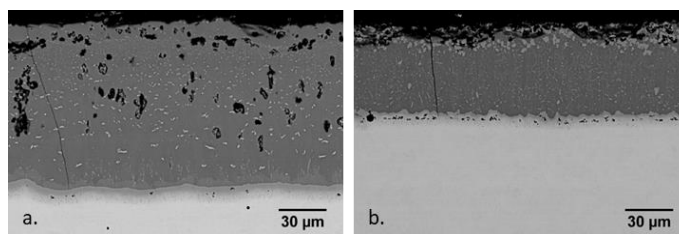


Fig. 1 – Microstructure of the as-tested coatings a. Slurry aluminide (Al) deposited onto T91 and b. Si-rich aluminide (SiAl) deposited onto T91.

The samples were then immersed in the ternary mixture of molten carbonates with 32% Li₂CO₃, 33% Na₂CO₃ and 35% K₂CO₃ at 650°C for 1000 hours under static and dynamic conditions. The static tests were conducted at INTA where samples were positioned in alumina crucibles with 30 g of salt mixture in a muffle furnace at constant temperature of 650°C. The dynamic tests were carried out at LNEG at the same temperature with 28 kg of salt and a linear velocity of 1.3 m/s. In both conditions, samples were removed to be characterized by gravimetry, scanning electron microscopy (SEM) and X-ray diffraction (XRD) after 250, 500 and 1000 h.

Gravimetric analysis (Fig. 2) showed that the uncoated T91 showed a very high weight gain reaching 30 mg/cm² after 1000 hours of exposure under dynamic conditions, while the coated showed very insignificant weight variations. After 1000 h, the uncoated T91 formed a dense and multilayered oxide of more than 150 µm thick, which explains the high weight gain of this material. According to the XRD analysis, oxides were rich in Li, Fe, Cr and O. Besides, the coated T91 showed no signs of attack during the test (Fig. 2). Under static conditions, a small layer of corrosion products was observed on the surface of the SiAl coating. According to XRD pattern, this scale may correspond to α -LiAlO₂ which appears as a protective oxide. The α -LiAlO₂ oxide was also detected by XRD on top of the Al coating. Under dynamic conditions, some changes in the morphology of both coatings were observed, exhibiting an increase in the FeAl phase to the detriment of Fe₂Al₅ due to substrate-coating interdiffusion. As in static conditions, α -LiAlO₂ was detected on the surface as the main corrosion product.

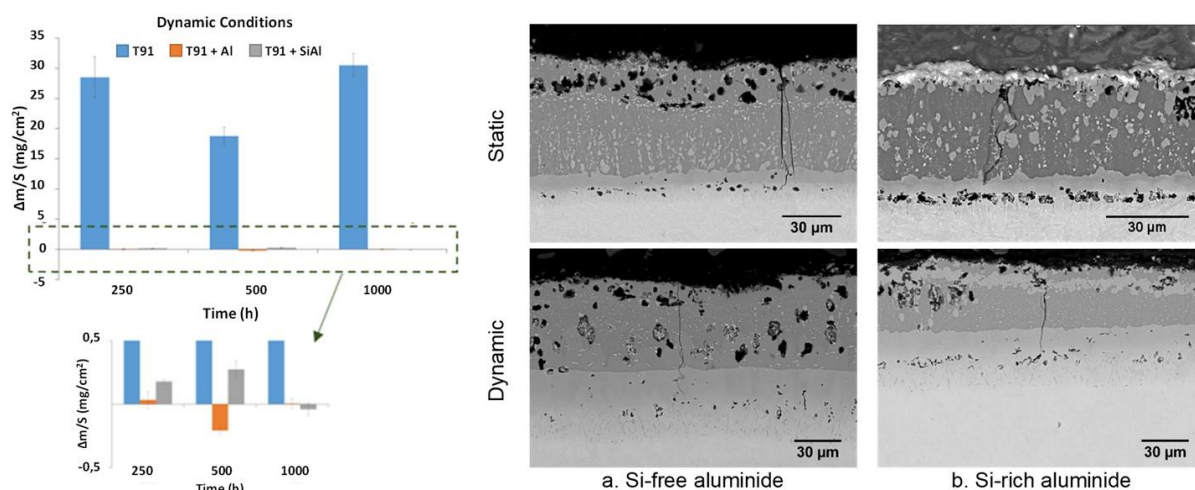


Fig. 2 – Gravimetric results after exposure under dynamic conditions and comparison of the microstructure after 1000 h of exposure in molten carbonates at 650°C under static and dynamic conditions of a. Si-free aluminide and b. Si-rich aluminide coatings.

3. CONCLUSIONS

Both Si-free and Si-rich slurry aluminide coatings evidenced a high performance increase in comparison with uncoated substrates after exposure in molten carbonates at 650°C under both static and dynamic conditions. The two coatings behaved in a similar way according to the gravimetric results. However, after dynamic exposure, the Si-free aluminide maintained its morphology and composition after 1000 h with α -LiAlO₂ as the only corrosion product while the Si-rich coating showed a higher attack extent in the outer part and developed a large quantity of voids at the coating/substrate interface, allowing substrate corrosion.

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