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# 10,000 h Molten Salt Corrosion Testing on IN617, Uncoated and Aluminide Ferritic Steels at 580 °C

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**Abstract.** Long term testing of two ferritic-martensitic steels (P91 and VM12-SHC) with and without slurry deposited aluminide coatings containing 20 wt.% of Al at the surface was carried out by exposing these materials to the Solar Salt, a eutectic mixture composed of 60 % NaNO<sub>3</sub> - 40 % KNO<sub>3</sub> at 580°C. This salt is currently used in operating thermal solar power plants as heat transfer and storage fluid. Tubes made of expensive Ni based alloys are employed to mitigate corrosion. The tested uncoated ferritic materials exhibited very high corrosion rates developing thick, easily detached scales. IN617 was also tested as a reference and experienced very low corrosion up to 5,000 h, but after 10,000 h a 50 µm thick, mostly NiO scale had developed with Na<sub>0.6</sub>CoO<sub>2</sub> crystals deposited on top. There was also evidence of significant Cr depletion at the alloy surface. Carcinogenic CrVI was found in the Solar Salt melt in which the three uncoated alloys were immersed. In contrast, the two coated ferritic steels did not show evidence of degradation after 10,000 h and the most significant microstructural change was the development of a very thin protective NaAlO<sub>2</sub> layer on their surface. An industrial process to deposit these coatings on the inner surfaces of pipes has already been developed.

## INTRODUCTION

Concentrating solar power (CSP) plants represent a valuable technology in terms of baseload and dispatchable renewable energy. However, it still needs to become an economically viable technology to gain the upper hand over solar photovoltaic and wind power. To overcome the main drawback of intermittency, improving the heat storage system by targeting 15 h to 24 h storage in the mid- or long-term brings added-value to CSP. In that sense, molten salts used as a heat transfer and storage fluids are investigated, but corrosion issues for tubes and tanks materials in contact with them are of concern. Protecting base materials with coatings can resolve or moderate corrosion degradation and therefore improve the plant efficiency. This alternative also allows reducing capital expenditure when designing a new plant because coatings can be applied on lower cost ferritic-martensitic or even carbon steels instead of expensive Ni-base alloys.

Slurry aluminide coatings have already demonstrated high corrosion resistance to molten salt after short term exposure (2,000 h) [1]. However, the protection mechanism still remains under investigation and long-term exposure is required to confirm the lifetime gain brought by these coatings. Presently, plants operating with the Solar Salt employ Ni base alloys tubes. These alloys have been studied under different conditions and with different salt mixtures to observe their corrosion behavior. Dorcheh et al. analyzed the behavior of IN625 and other ferritic and austenitic steels in molten nitrate salt at 600°C up to 5,000 h [2]. IN625 showed the best corrosion resistance with a linear and very slow weight loss, forming a layer of NiO that remains protective during the immersion time. No longer exposure results were found in the literature.

This study focuses on the corrosion resistance of slurry aluminide coatings after long-term exposure in contact with the most currently employed heat storage system, the so-called Solar Salt (60 % NaNO<sub>3</sub> - 40 % KNO<sub>3</sub>). To do that, slurry applied aluminides to 9 wt.% Cr P91 and 11.5 wt.% Cr VM12-SHC alloys have been deposited, heat treated at high temperature and both systems have been tested at 580°C in contact with the Solar Salt under static

isothermal conditions. In addition IN617 has also been tested as the material currently chosen by the industrial sector for tubes [3].

## EXPERIMENTAL PROCEDURE

### Substrate Materials

Sample coupons (20 x 10 x 3 mm) of ferritic-martensitic steels P91 and VM12-SHC as well as nickel-based alloy IN617 (all supplied by Vallourec) were machined from tubular sections and ground with P180 SiC papers before coating and/or testing. The substrate compositions are given on TABLE 1.

TABLE 1. Alloys composition (wt. %)

Alloy	Fe	Cr	Co	N	Ni	Si	V	Mo	C	Mn	W	Nb	Cu	Al	Ti
P91	Bal.	8.6	-	0.03	0.08	0.40	0.20	0.95	0.10	0.50	1.80	0.08	-	0.04	-
VM12-SHC	Bal.	11.5	1.60	0.05	0.25	0.50	0.25	0.30	0.12	0.30	1.50	0.08	0.25	0.02	-
IN617	1.40	22.5	12.5	-	Bal.	0.20	-	8.20	0.10	0.10	-	-	0.40	1.20	0.40

### Slurry Coatings

Prior to coating, the ground samples were degreased in ethanol in an ultrasonic bath. The samples were spray coated with an environmentally friendly Cr<sup>+6</sup>free, water based Al slurry developed by INTA. The slurry was produced by mixing Al powder ( $\varnothing$ : ~ 5  $\mu$ m, 99 wt.% obtained from Poudres Hermillon) with water and a proprietary binder constituted by a mixture of inorganic compounds. The slurry was homogenized by magnetic stirring and was sprayed with a 475 Xtech spraying gun. Then, the samples were left to dry under laboratory air during 3 h. Subsequently, a diffusion heat treatment was performed under argon flow at 1050°C for 35 min to produce the coating. After heat treatment, undiffused slurry residues (“bisque”) were removed by softly grinding.

### Corrosion Testing

Both coated and uncoated samples were isothermally tested by immersion in Solar Salt (eutectic mixture of 60 % NaNO<sub>3</sub> – 40 % KNO<sub>3</sub>, industrial quality) at 580°C. The salts were provided by BASF and Haifa Chemical respectively. Both salts came from batches currently employed by BrightSource Industries Israel LTD in CSP plants.

The corrosion tests were performed under static conditions. Before beginning the test, the salts were kept in the oven at 110°C for 2 h in order to remove humidity, and then cooled down to room temperature. Then, each test specimen was fully immersed in a 30 ml alumina crucible with 30 g of salt and placed in a Carbolite CWF12/23 furnace at the corresponding temperature, which was constantly measured during the tests. Samples were removed from the oven at different time intervals to be weighted by taking them out from the crucible, leaving them in laboratory air during a few minutes followed by immersion in hot distilled water ( $\approx$  80°C) in order to remove the salt residues. As the Solar Salt slightly evaporated at the test temperature, crucibles were replenished with 10 g of the salt mixture every week.

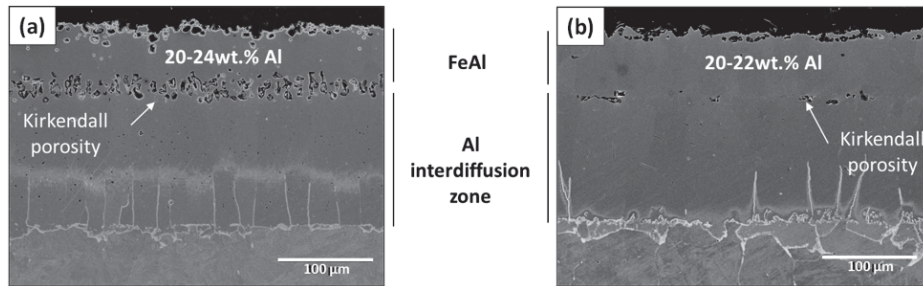
### Characterization

The exposed samples were characterized by light optical microscopy (Leica MEF 4), scanning electron microscopy (HITACHI S3000N) coupled with an energy dispersive X-ray spectrometer (EDS BRUKER QUANTAX) and by Field Emission scanning electron microscopy (JEOL JSM 6500F). X-ray diffraction (XRD) analysis (Panalytical X’Pert, Cu K $\alpha$  line) was also performed in order to determine the corrosion products and the coating phases.

## RESULTS AND DISCUSSION

### Coating Microstructure before Exposure

The coatings were applied on both ferritic-martensitic grades and their microstructures are quite similar as shown in Fig. 1.a and b, with the FeAl phase at the surface containing 20-24 wt.% of Al and progressively lower Al content as a function of coating depth on which the coatings deposited on P91 and VM12-SHC are shown respectively. A significantly lower degree of Kirkendall porosity on VM12-SHC is the only noteworthy difference between the two coating's microstructure.

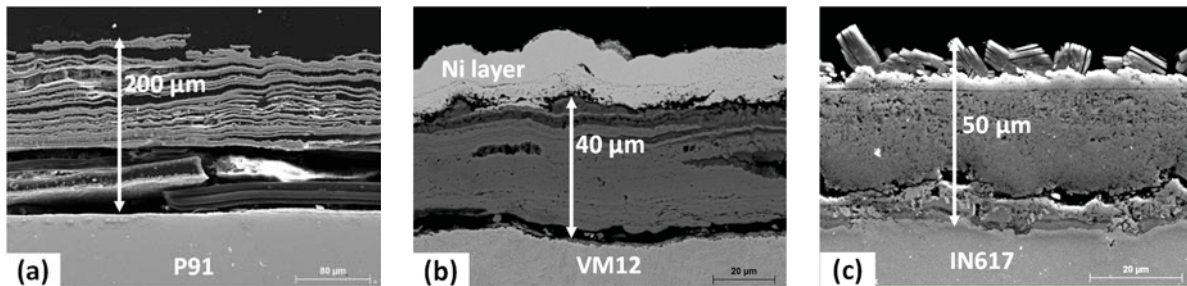


**FIGURE 1.** Slurry aluminide coating on a) P91 and b) VM12-SHC after heat treatment at 1050°C for 30 min.

### Uncoated Substrates after Isothermal Corrosion Testing

After 10,000 h of exposure uncoated P91 and VM12-SHC steels developed a multi-layered oxide with little cohesion and also experienced spallation throughout the whole test period (Fig. 2.a and b). As already shown by Audigié et al. [1] for ferritic-martensitic steels, a thin  $\text{NaFeO}_2$  formed on top of thick Fe,Cr oxides. Due to spallation,  $\text{NaFeO}_2$  is not always observed but when it is present, it is easily recognizable as a thin layer on top of the scale and by its columnar structure. Na can be detected inside the scale, probably penetrating throughout the cracks and pores, leading to the formation of  $\text{NaFeO}_2$  inside the oxide scale as well.

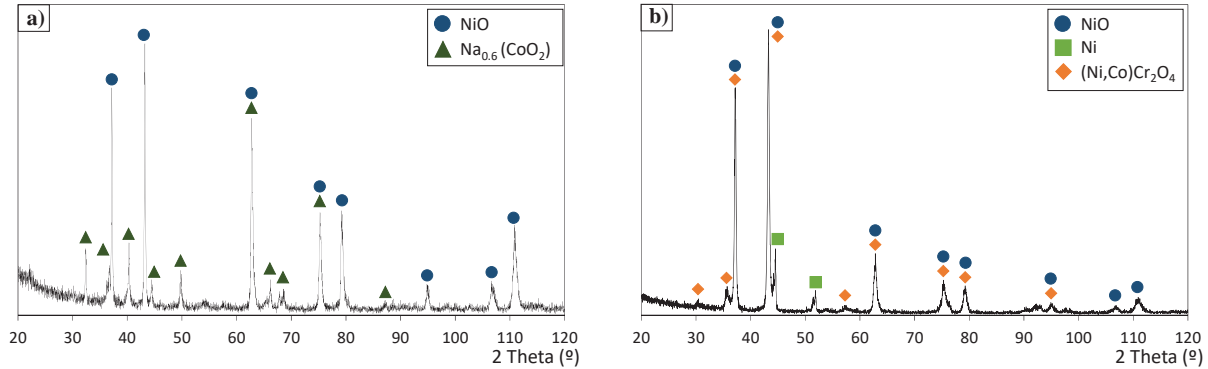
The IN617 nickel-based alloy exhibited much lower corrosion attack up to 5,000 h of exposure by forming a very thin oxide (5  $\mu\text{m}$  thick). Slight pitting as well as dissolution of Ni and Co occurred confirming the results of Spiegel et al. [4] as well as Audigié et al. [5] after only 500 h and 1,000 h at 600°C and 580°C in Solar Salt, respectively. However, in the present study, after 10,000 h of exposure, there was evidence of breakaway corrosion with a 50  $\mu\text{m}$  thick oxide (Fig. 2.c). A thick scale was observed on the alloy surface seemingly indicating that a more uniform degradation took place after longer exposure. Similar scales were observed after 120 h of corrosion of IN601 in molten ternary carbonate at 450°C [6].



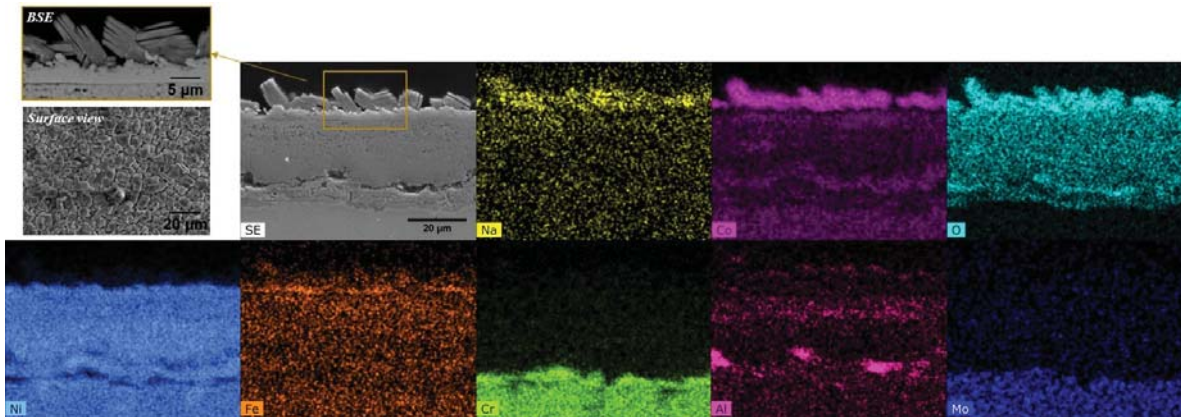
**FIGURE 2.** Oxide scales on a) P91, b) VM12-SHC and c) IN617 after 10,000 hours at 580°C with molten Solar Salt.

Figure 3.a shows the XRD pattern of IN617 after 10,000 h of exposure at 580°C.  $\text{NiO}$  and  $\text{Na}_{0.6}(\text{CoO})_2$  appeared as the only corrosion products. After removal of some of the oxide scale,  $\text{NiO}$  appeared again and  $(\text{Ni},\text{Co})\text{Cr}_2\text{O}_4$  spinel could be observed as well as peaks attributed to the substrate (Fig. 3.b). The presence of these phases was confirmed by EDS mapping of the cross section as shown on Fig. 4. Most of the scale was formed by  $\text{NiO}$  with some Co, Al and

Fe coming from the substrate (but little or no Cr). As already described for instance by Khorsand et al. for IN625, a non-protective NiO oxide formed on exposure to Solar Salt at 500 and 600°C after short exposures [7], while Dorcheh et al. observed a seemingly protective NiO scale after 5,000 h at 600°C [2]. Some needle-like crystals were also observed on top but only after 10,000 h, and according to their composition, they can be identified as  $\text{Na}_{0.6}\text{CoO}_2$ .  $\text{Na}_x\text{CoO}_2$  is a layered oxide, well known for its thermoelectric properties with low thermal conductivity as well as resistivity [8, 9]. It exhibits a multilayered structure with  $\text{CoO}_2$  blocks and intercalated Na atoms.  $\text{Na}_{0.6}\text{CoO}_2$  is a high temperature stable phase [10]. To develop these crystals, Co from the alloy has diffused outward through the thick NiO scale.



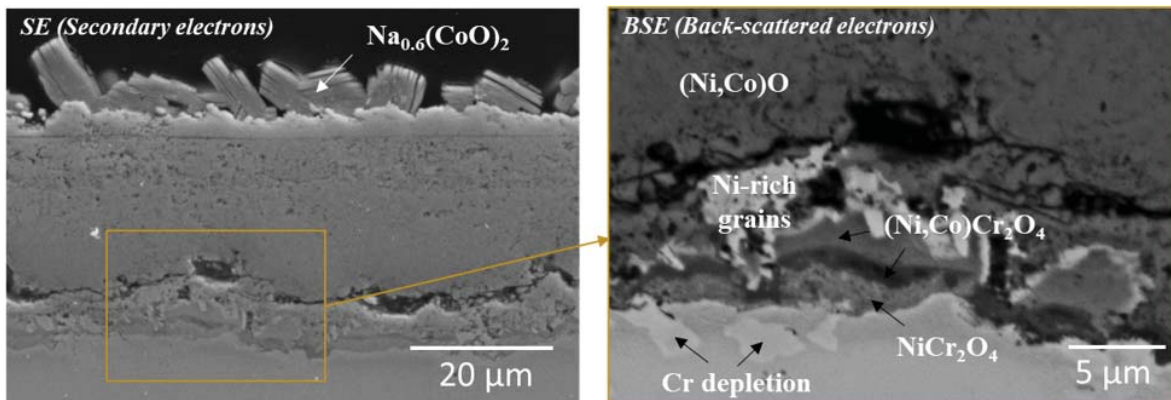
**FIGURE 3.** X-ray diffraction patterns of the uncoated IN617 after 10,000 hours at 580°C with molten Solar Salt a) after exposure, b) after removing part of the corrosion products.



**FIGURE 4.** EDS Mapping of uncoated IN617 after 10,000 hours at 580°C with molten Solar Salt.

According to the EDS mapping (Fig. 4), Co is also present in significant amounts within the NiO layer and the peaks in the XRD pattern taken after grinding (Fig. 5) some of the oxide correspond to  $(\text{Ni,Co})\text{Cr}_2\text{O}_4$ , and can perhaps be attributed to Ni, Co and Cr rich layers with variable contents of Ni and Co at the interface with the substrate below the  $(\text{Ni,Co})\text{O}$  layer. An observed lighter grey layer directly in contact with the substrate does not have Co and could be identified as  $\text{NiCr}_2\text{O}_4$  whereas the darker layer on top is  $(\text{Ni,Co})\text{Cr}_2\text{O}_4$  (Fig. 5). Cr depletion was observed in Fig. 5 below the oxide scale in some grains. Co and Ni have similar physical properties, so both elements can substitute each other, this explains why Ni and Co co-exist in the corrosion products like  $(\text{Ni,Co})\text{O}$  and  $(\text{Ni,Co})\text{Cr}_2\text{O}_4$ . This Ni-Co substitution has already been detected in the oxides formed on Ni-Co based alloys after exposure in  $\text{LiCl-Li}_2\text{O}$  molten salt at 650°C up to 216 h under argon atmosphere [11].

The absence of Cr on the top oxide scale can be explained by Cr dissolution into the Solar Salt melt. Indeed, evidence was found by the yellow-green color of the salts after exposure and Cr was found in the salt melt corresponding to the three tested alloys by inductively coupled plasma (ICP). CrVI was also identified by spectrophotometry and results from the reaction  $\text{Cr}_2\text{O}_3 + 5\text{O}^{2-} \rightarrow 2\text{CrO}_4^{2-}$  as a result of a basic fluxing mechanism typical of molten salt corrosion as described by Rapp [12].

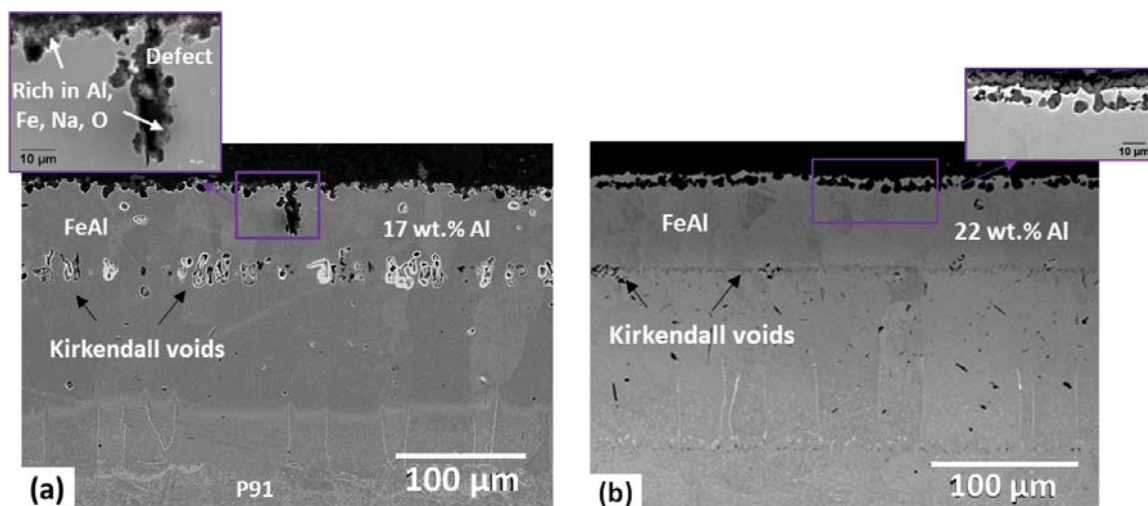


**FIGURE 5.** Oxide formed on the uncoated IN617 after 10,000 hours at 580°C with molten Solar Salt.

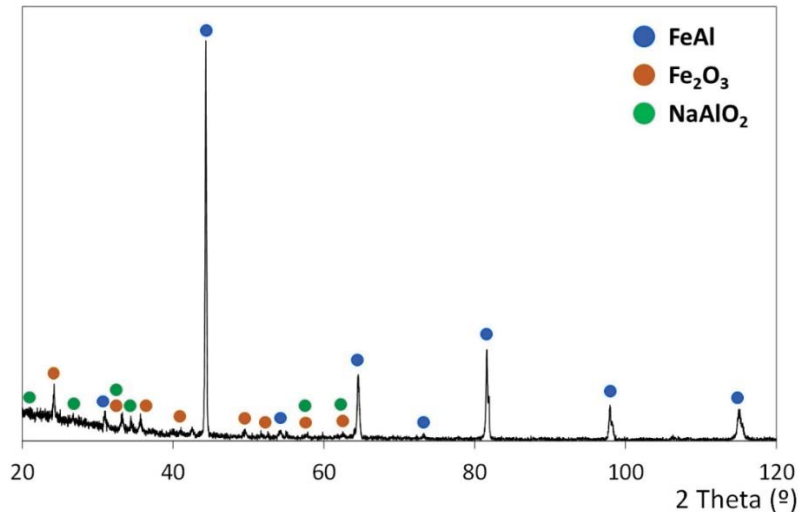
### Coated Steels after Isothermal Corrosion Testing

In contrast with the uncoated substrates after 10,000 h of exposure of both aluminide coated P91 and VM12-SHC, there was no evidence of corrosion attack (Fig. 6). Their morphology and composition were essentially the same as that of the as deposited coatings (Fig. 1.a and b). On top of these samples or on the surface of some fabrication defects, a thin layer of  $\text{NaAlO}_2$  was found as well as a small proportion of  $\text{Fe}_2\text{O}_3$  according to XRD analysis (Fig. 7). Other authors have seen this phase and have claimed that it is stable in the melt and also protective [13]. In addition, it has been shown that it can be used as a sealant to protect Al and Mg alloys from atmospheric corrosion [14, 15]. Moreover, more than 17 wt.% of Al was still available below the surface which indicates that both coatings can sustain the growth of a protective oxide for a long time under the present conditions.

Interestingly, very few Kirkendall voids could still be observed on the coated VM12-SHC specimen despite the 10,000 h of exposure at 580°C. This indicates that the composition of this aluminide coated alloy favors an equilibrium between inwards going Al and outwards diffusing Fe when comparing its behavior to that of P91. A higher content of Cr when comparing with P91 in addition to the presence of Co, may be related to this observed behavior. An industrial process for the deposition of this coating on the inner surface of ferritic steels pipes is already available.



**FIGURE 6.** Aluminide coating on a) P91 and b) VM12-SHC after 10,000 hours at 580°C with molten Solar Salt.



**FIGURE 7.** X-ray diffraction pattern of the aluminide coated P91 after 10,000 hours at 580°C with molten Solar Salt.

## CONCLUSIONS

Two ferritic-martensitic steels and one nickel-based alloy were isothermally tested at 580°C in contact with molten Solar Salt (60 % NaNO<sub>3</sub> – 40 % KNO<sub>3</sub>) under static conditions up to 10,000 hours. P91 and VM12-SHC Fe-based alloys showed extensive corrosion attack and spallation. They formed a fast-growing stratified oxide including columnar NaFeO<sub>2</sub> as well as Fe,Cr thick oxides. If the multi-layered oxide is not dense, Na can be detected inside the scale, probably penetrating through cracks and pores, leading to the formation of NaFeO<sub>2</sub> between the strata observed within the oxide as well. IN617 Ni-based alloy was little attacked by the melt up to 5,000 hours but after 10,000 hours at 580°C, IN617 suffered uniform degradation to a larger extent since a 50 µm thick oxide was observed on the surface. Na<sub>0.6</sub>(CoO)<sub>2</sub>, NiO, and (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> were detected as the main corrosion products. Therefore, long term testing of materials and coatings in contact with molten Solar Salt needs to be carried out systematically as materials that exhibit excellent behavior after 5,000 h such as IN617 suffer degradation after longer exposure at 580°C. All tested Cr containing alloys resulted in chromate formation and dissolution into the molten salt. CrVI is a carcinogenic species that must be removed from the salt after the end of its useful life.

Aluminide slurry coatings deposited on P91 and VM12-SHC ferritic steels behaved very well, were very stable and did not suffer any corrosion attack after 10,000 h. Only a thin layer of NaAlO<sub>2</sub> which appears to be very protective was found as well as a small proportion of Fe<sub>2</sub>O<sub>3</sub> as the main corrosion products.

Coated ferritic steels are significantly lower in cost than the Ni based alloy (4 to 10 times, depending on the material) and according to the present results will have a longer useful life contributing to CSP cost reduction and therefore will increase competitiveness with other sustainable sources of energy. If higher operating temperatures (> 650° C) are required, instead of ferritic steels, coated austenitic steels would still be significantly lower in cost than Ni based alloys.

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## REFERENCES

1. P. Audigié, V. Encinas-Sánchez, M. Juez-Lorenzo, S. Rodríguez, M. Gutiérrez, F.J. Pérez and A. Agüero, *Surf. Coat. Technol.* **349**, 1148-1157 (2018).
2. A. S. Dorcheh, R.N. Durham and M.C. Galetz, *Sol. Energy Mater. Sol. Cells* **144**, 109–116 (2016).
3. G. McConohy and A. Kruiženga, *Sol. Energy* **103**, 242-252 (2014).
4. M. Spiegel and J. Mentz, *Mater. Corros.* **65**, 276–281 (2014).
5. P. Audigié and A. Agüero, “Comparative Behavior of Fe-based and Ni-based alloys Exposed to Molten Salt Corrosion for Concentrating Solar Power Technologies”, in *International Symposium On High-Temperature Oxidation And Corrosion 2018*, edited by The Iron and Steel Institute of Japan, Matsue, Shimane (2018), pp. 58-61.
6. M. Sarvghad, G. Will and T. A. Steinberg, *Sol. Energy Mater. Sol. Cells* **172**, 220-229 (2017)
7. S. Khorsand, A. Sheikhi, K. Raeissi and M. A. Golozar, *Sol. Energy* **90**, 169-186 (2018).
8. I. Terasaki, Y. Sasago and K. Uchinokura, *Phys. Rev. B* **56**, 12685-12687 (1997).
9. H. Yakabe, K. Kikuchi, I. Terasaki, Y. Sasago and K. Uchinokura, “Thermoelectric properties of transition-metal oxide  $\text{NaCo}_2\text{O}_4$  system” in Proceedings of the 16th International Conference on Thermoelectrics (ICT 97), Dresdesn, Germany, (IEEE, Piscataway, NJ, 1997), pp. 523-527.
10. M. Miclau, K. Bokinala, N. Miclau, *Mater. Res. Bull.* **54**, 1-5 (2014).
11. S. H. Cho, S. C. Kwon, D. Y. Kim, W. S. Choi, Y. Kim and J. H. Lee, *Corros. Sci.* **151**, 20-26 (2019).
12. A. Rapp, *Corros. Sci.* **44**, 209-221 (2002).
13. A. Soleimani Dorcheh and M.C. Galetz, *Sol. Energy Mater. Sol. Cells* **146**, 8-15 (2016).
14. Y. Yang, J. Cheng, S. Liu, H. Wang and P. Dong, *Mater. Corros.* **70**, 120-127 (2019).
15. J. Liang, B. Guo, J. Tian, H. Liu, J. Zhou, W. Liu and T. Xu, *Surf. Coat. Technol.* **199**, 121-126 (2005).