

NEWS4CSP Project – New Coatings Approaches to Protect Metallic Materials From Heat Transfer Fluids

Teresa C. Diamantino^{1,*} , Fátima Pedrosa¹ , Teresa Paiva¹ , Eduardo Silva² ,
Francisco Gonçalves² , Renato Monteiro² , and João P. Cardoso¹ 

¹Laboratório Nacional de Energia e Geologia (LNEG), Portugal

²TeandM – Tecnologia, Engenharia e Materiais, S.A., Portugal

*Correspondence: Teresa C. Diamantino, teresa.diamantino@lneg.pt

Abstract. The efficiency of Concentrated Solar Power technologies increases with the operation temperature of the power block, which can be achieved using advanced power cycles operating at temperatures $\geq 650^{\circ}\text{C}$. Molten Salt (MS) based HTF have been facing critical challenging issues of severe corrosion and lower specific heat capacity. This paper aims to present the NEWS4CSP project to the CSP scientific community, highlighting the main concepts being pursued and the preliminary results obtained regarding the application of new coatings to increase the anticorrosive protection of structural materials in contact with MS. Two different types of powder coatings (nickel and cobalt alloys) were applied to AISI 430 stainless steel using two coating technologies: High Velocity Oxy-Fuel (HVOF) and Laser Cladding (LC). LC proved to be the most suitable technique of these two coating application technologies. The Co-Cr coating alloy showed good anticorrosive behaviour even after 3000 h of testing. The obtained results are very promising, nevertheless, more studies are needed to optimise its application by LC. These include optimizing the thickness and chemical composition, as well as gaining a deeper understanding of the degradation mechanisms and whether this behaviour is maintained over longer periods.

Keywords: Corrosion, Metallic Coatings, Laser Cladding, Molten Salts

1. Introduction

Molten salts (MS) have been widely used as heat transfer fluids (HTF) and thermal energy storage (TES) media in concentrated solar power (CSP) plants. They are the most used TES fluids in commercial CSP plants, particularly the so-called Solar Salt, composed of 60wt.% NaNO_3 and 40wt.% KNO_3 , whose application is limited to temperatures below 600°C . To remain competitive against other renewable energy sources, CSP plant's Levelized Cost of Electricity (LCOE) needs to be reduced. This can be achieved by lowering CAPEX and OPEX costs and/or increasing solar-to-electricity efficiency. The latter can be achieved using advanced power cycles operating at temperatures $\geq 650^{\circ}\text{C}$, which will require new MS mixtures [1] such as halides [2] [3] or carbonates [4]. However, MS-based HTF and/or TES media have been facing critical challenging issues of severe corrosion and lower specific heat capacity. Considering these problems, more effective studies should be conducted to lower corrosion rates and explore alternative MS focusing on widening the thermal stability range and enhancing thermophysical properties [5].

The promise of MS-based technologies can only be realized if structural materials that can withstand long-term operation in demanding extreme environments are developed and become available. Employment of cheaper alloys (low alloys steels) as structural materials can be a very efficient method to reduce costs in CSP plants. The development of protective coatings for low alloyed steels (e.g. ferritic stainless steels) could be an economical alternative for increasing the lifetime of CSP plants against MS corrosion [6]. Some coating technologies (dip coating, diffusion, electroless, electrodeposition and thermal spray) have been studied to increase corrosion protection of structural materials at lower costs [6] [7]. However, coatings applied by High Velocity Oxygen Fuel (HVOF) or Laser Cladding (LC), used in industries due to higher performance and lower cost of maintenance, have not yet been investigated for corrosion protection of metallic materials in contact with MS.

HVOF technique is the surfacing method of choice when high-density coatings are required. With high-velocity flame spraying, a fuel/oxygen mixture is continuously combusted at very high pressure. A powdery spray-additive is injected into the central axis. The pressure created by the gas/oxygen mixture in the combustion chamber and the downstream expansion nozzle creates a very high flow velocity. This way the spray particles are accelerated to supersonic speed and applied to the workpiece. This process provides a very dense coating and is especially designed for the application of high-quality coating, which is characterised by high hardness, intrinsic porosity and high adhesion to the substrate. With Laser Cladding (LC) the surface of the workpiece is melted locally. Motion of the laser optics and powder nozzle create weld-beads on the workpiece to be coated. The laser creates a weld pool on its surface. Metal powder is automatically inserted through a nozzle. Coatings with strong metallurgical bonding, low dilution and virtually no porosity can be obtained by LC. Applied side-by-side, defined areas can be functionally coated and applied on top of each other to increase layer thickness so that part shapes can be created or repaired.

The NEWS4CSP project (*New materials approaches for concentrating solar power (CSP): Molten salts and corrosion protection*) is an ongoing project, with the following main objectives:

1. obtain new LiNaK carbonate molten salts mixtures (doped with micro/nanoparticles) with enhanced thermophysical properties and low corrosivity;
2. obtain new coatings to increase the anticorrosive protection of structural materials;
3. clarify the influence of cyclic thermal conditions, dynamic conditions and atmosphere in the corrosion behaviour and corrosion rate of stainless-steel materials;
4. understand the impact of these new materials (new molten salt mixtures and coatings) on the energetic and economic performance of a solar tower power plant.

This work highlights the main concepts being pursued within the project's second objective and the preliminary results already obtained, namely, the characterisation of AISI 430 in contact with LiNaK carbonate molten salt mixtures with the application of two different types of powder coatings using two different technologies: Laser Cladding (LC) and High Velocity Oxygen Fuel (HVOF).

2. Methodology

2.1 Material samples and application of coatings

AISI 430 ferritic steel was used and its chemical composition is shown in the table 1.

Table 1. Elemental chemical composition (wt. %) of ferritic steel AISI 430

C	Mn	Si	P	S	Cr	Ni	Mo	N	Cu	Co	Fe
0.037	0.310	0.350	0.028	0.001	16.260	0.270	0.020	0.048	0.160	0.020	Bal.

Rectangular coupons of AISI 430 measuring 30 mm × 40 mm with a thickness of 4 mm are coated with two different types of powder alloys (Ni-Co-Mo and Co-Cr alloys) using two coating technologies: High Velocity Oxy-Fuel (HVOF) and Laser Cladding (LC).

In the case of HVOF, before coating application, the samples were blasted with an alumina-based compound to remove surface impurities, as well as to create roughness and activate the surface to promote better coating adhesion. This procedure is not required for LC and the samples are only cleaned with ethanol to remove organic impurities.

Two different gas atomized powders were used for the application of the coatings by HVOF and LC: Ni-Cr-Mo and Co-Cr. The main characteristics of these powders are described in Tables 2 and 3, respectively. These characteristics were provided by the powder supplier (Oerlikon) and coating supplier (Durit Coatings).

Table 2. Nominal Composition (Mass %) and Physical Properties of Ni-Cr-Mo base powder

Ni	Mo	Cr	Fe	W	Co	Others	Hardness	Density
Remainder	15-17	14.5-16.5	4-7	3.0-4.5	2.5 (max)	Mn, C, V, P, S, Si	240-260 HV0.1 (min)	8.89 g/cm ³

Table 3. Nominal Composition (Mass %) and Physical Properties of Co-Cr base powder

Co	Cr	W	C	Others	Hardness	Density
Base	27-32	3-6	0.9-1.4	Ni, Fe, Si, Mn, Mo	460-550 HV0.1	7 g/cm ³

2.2 Corrosion Testing Conditions

The corrosion tests on the coated AISI 430 samples were carried out in alumina crucibles, in a muffle furnace at 650 °C, for up to 3000 h, in direct contact with a ternary mixture of molten salts containing 32.1% Li₂CO₃, 33.4% Na₂CO₃ and 34.5% K₂CO₃ (LiKNa carbonate salts), under static conditions in an air atmosphere. After each dwell time, the samples were removed from the salt, cooled and washed in distilled water to remove the salts.

2.3 Characterization techniques

The Phillips Scanning Electron Microscope, Model XL 30 FEG, in conjunction with X-ray microanalysis, permitted the morphological and the elemental chemical composition (semi-quantitative) of the coatings to be analysed before and after the contact with LiNaK carbonate molten salt mixtures at 650°C. Images were captured utilising secondary and backscattered electrons, with an applied energy of 15 keV. In the cross-sectional analysis, the test specimens were metallographically mounted in Polyfast resin (a conductive resin suitable for hot mounting). The samples were wet ground with sandpaper of different grain sizes (220, 320, 500, 800, 1000, 2500), followed by fine polishing using diamond pastes (1, 3, 6 µm).

3. Results

3.1 Characterization of coatings before exposure to molten salts

After optimizing the surface preparation and application, the coatings were obtained by HVOF and LC (Figure 1).

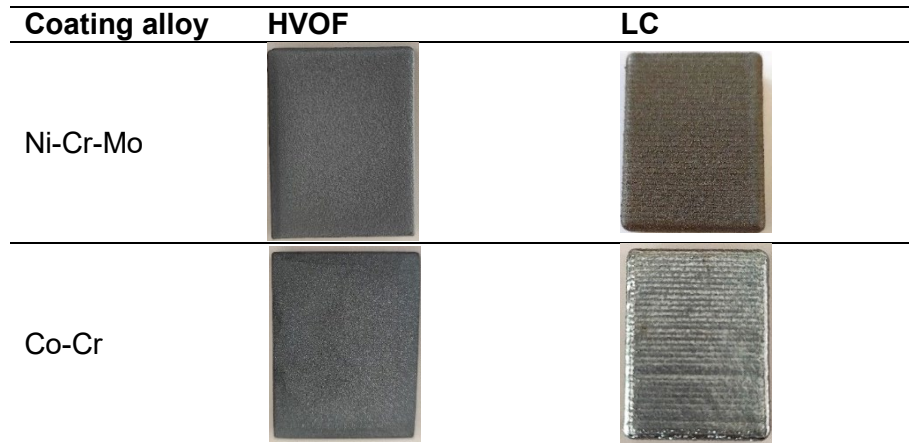


Figure 1. Images of the samples after the application of the coatings by HVOF and LC

SEM/EDS evaluation of the coatings obtained by HVOF, both with Co-Cr and Ni-Cr-Co powders, revealed adhesion problems, namely in the areas closest to the edges. Coating thicknesses between 200-260 μm were obtained for both alloys. However, in the edge zone, the thickness is slightly lower. Figure 2 shows SEM cross-section images and EDS spectra obtained in the centre and on the edges of the coatings applied by HVOF where it is possible to observe low interfacial adhesion. Even though the origin of such behaviour could not be precisely determined, it was considered that the level of porosity and probability of coating spallation would present significant limitations towards high temperature corrosion resistance. Therefore, these coatings were deemed unsuitable until further optimization of coating application.

When using laser cladding (LC), very uniform and thick coatings were obtained with both powders, in some cases exceeding 1 mm. However, in the edge zone, the thickness is lower. Both coatings showed good adhesion. Some metallic residues from the coating can be seen on the surface (Figures 3 and 4).

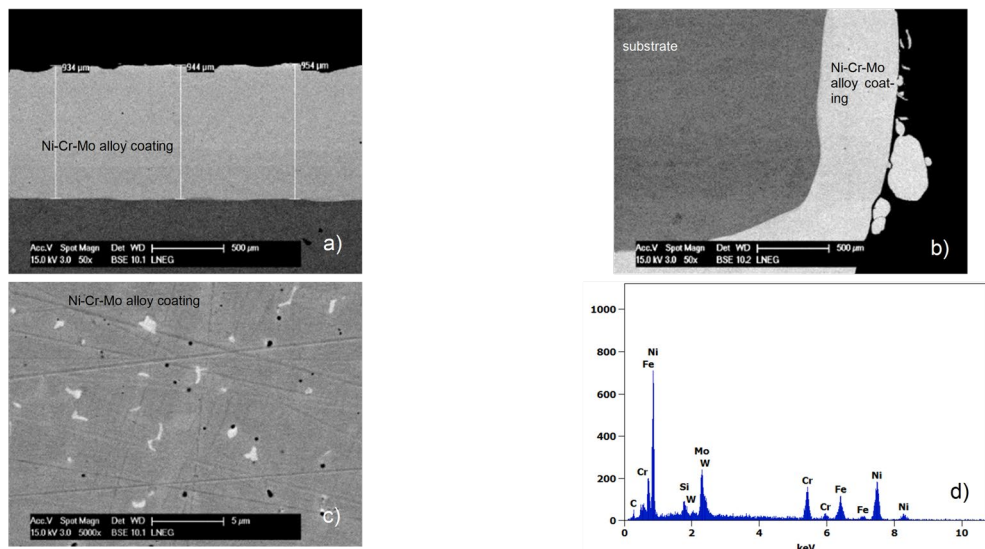


Figure 2. SEM cross-section images (scale bar is 100 μm) and EDS spectra obtained in the centre of Ni-Cr-Mo coating (a - c) and Co-Cr coating (d - f) applied by HVOF on AISI 430.

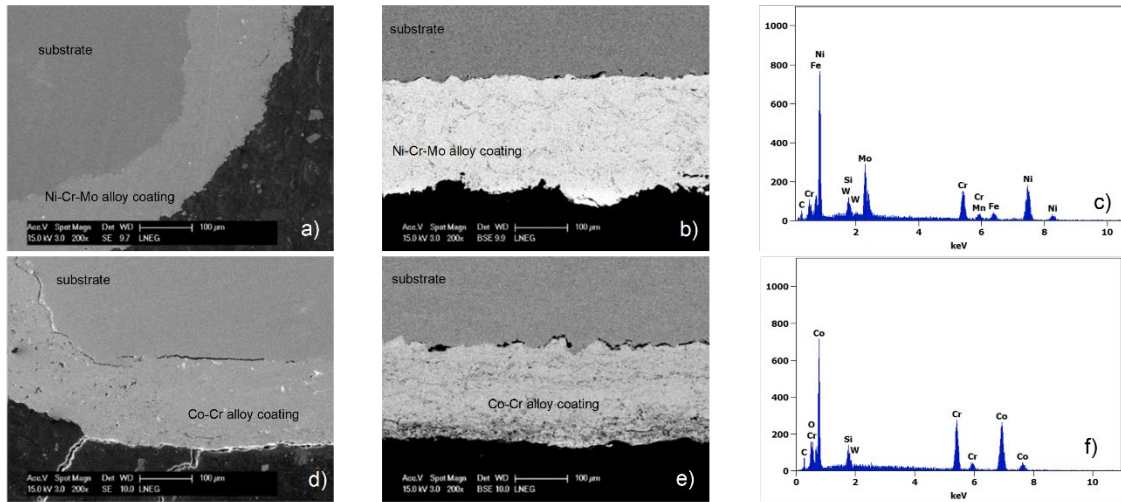


Figure 3. SEM images of AISI 430 with Ni-Cr-Mo coating applied by LC in the face of the sample (a) and in the edge area (b) (scale bar is 500 μm), as well as a magnification of the coating (scale bar is 5 μm) (c) with the corresponding EDS spectrum (d)

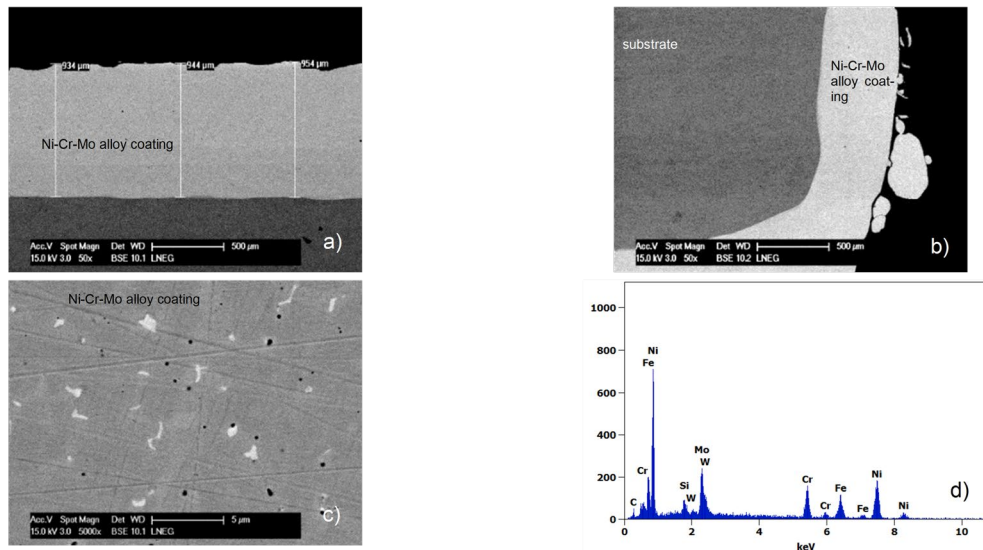


Figure 4. SEM images of AISI 430 with Co-Cr coating applied by LC in the face of the sample (a) and in the edge area (b) (scale bar is 500 μm and 1mm, respectively), as well as a magnification of the coating (scale bar is 2 μm) (c) with the corresponding EDS spectrum (d)

3.2 Characterization of coatings after exposure to molten salts

Figure 5 shows the images of the samples with the Ni-Cr-Mo coating alloy, applied by LC, before and after contact with LiKNa carbonate salts at 650 $^{\circ}\text{C}$ during 480h and 1000 hours. Visually, after 480 hours, there were few changes. However, at 1000h a very significant change is visible in the samples.

When analysing these samples using SEM/EDS after the contact with molten salts for 480 hours, oxides are visible on the surface of the Ni-Cr-Mo coating with a very heterogeneous thickness, as shown in Figures 6 a) to c). Some fissures in the coating are also visible (Figure

6 b)). The oxide layer is quite stratified, exhibiting low internal cohesion. After 1000 hours of exposure, the stratified layer became even thicker and less cohesive, being composed by metallic oxides interspersed with molten salts (Figure 6 d) to f)). The thickness of the coating was reduced by almost 50%. It should be noted that the elemental chemical composition shown in Figure 6 f) is semi-quantitative and has a high uncertainty associated, since the characteristics of this layer can include some resin from the metallographic preparation, particularly in terms of carbon and oxygen content. Given these results after 1000 hours of testing, it can be seen that this coating is not suitable for use with this salt mixture at 650°C.

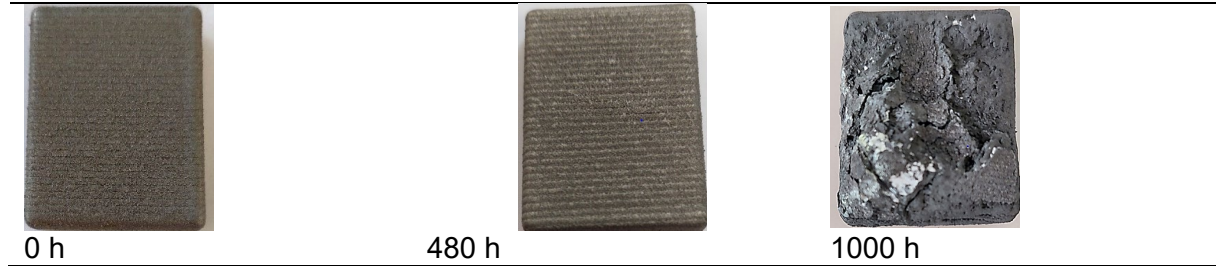


Figure 5. Images of the samples with the Ni-Cr-Mo coating alloy, applied by LC, before and after contact with LiKNa carbonate salts at 650 °C during 1000 h

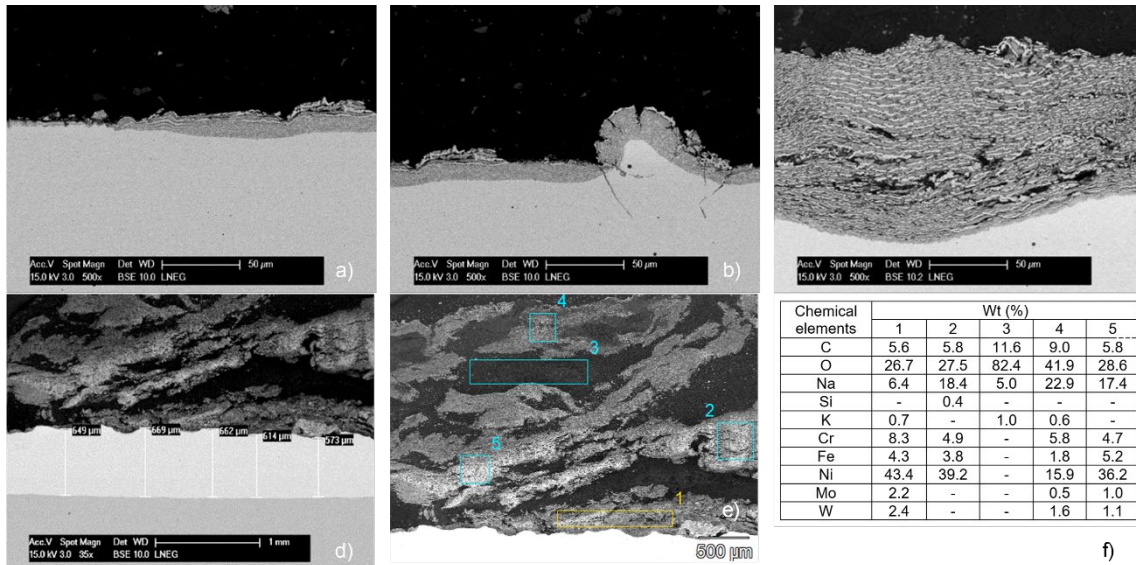


Figure 6. SEM images of AISI 430 with Ni-Cr-Mo alloy coating applied by LC after the contact with LiKNa carbonate salts at 650°C (scale bar is 500 µm) during 480 hours (a) to c)) and 1000 h (d) to e)) (scale bar is 1 mm and 500 µm, respectively) and EDS results obtained in the areas indicated (f))

Figure 7 shows the images of the samples with the Co-Cr coating alloy, applied by LC, before and after contact with LiKNa carbonate salts at 650 °C for 480, 1000 and 3000 hours. Visually, there were few changes.

SEM/EDS shows that after 3000 hours of exposure to molten salts, a layer constituted by several sublayers ($\approx 43 \mu\text{m} \pm 11 \mu\text{m}$) is formed on top of the coating, being relatively adherent and uniform, including in the edge areas (Figure 8). The coating also remains adherent to the substrate without any fissures. EDS analyses show the presence of Co, Fe, Mn and O in the outer sublayers, more porous, and the presence of O and Cr in an adherent inner sublayer, probably Cr_2O_3 . The good corrosion behaviour displayed by the Co-Cr base alloy is most probably related to the passivation effect of the chromium oxide layer covering the surface (Figure

9). However, more studies are needed to better understand the corrosion mechanism and the protection of this coating when in contact with LiKNa carbonate salts at 650°C.

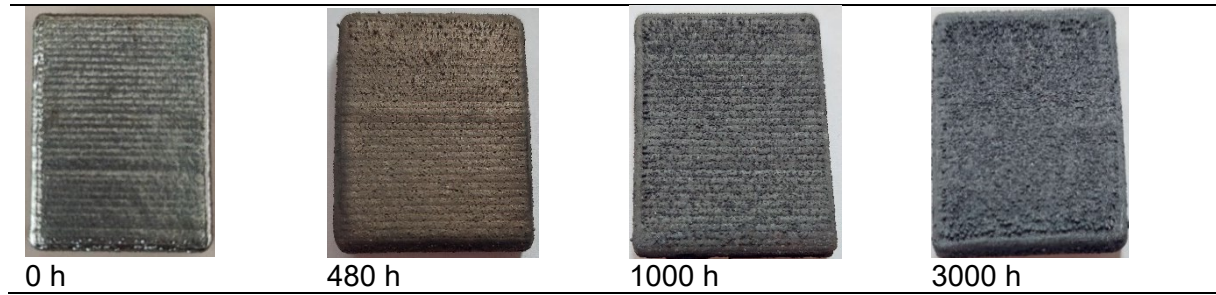


Figure 7. Images of the samples with the Co-Cr coating alloy, applied by LC, before and after contact with LiKNa carbonate salts at 650 °C during 3000 h

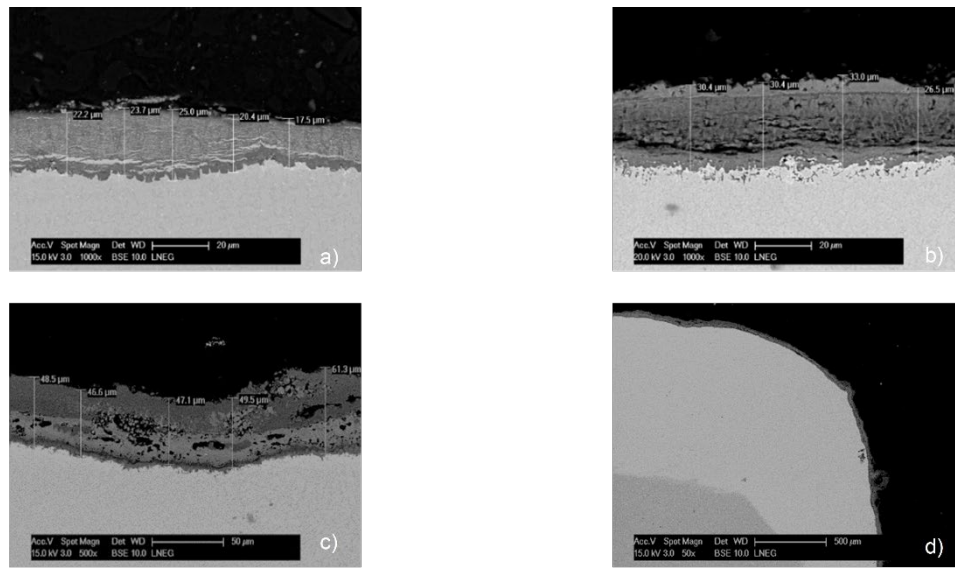


Figure 8. SEM images of AISI 430 with Co-Cr alloy coating applied by LC after the contact with LiKNa carbonate salts at 650°C after 480 hours (scale bar is 20 μm) (a), after 1000 hours (scale bar is 20 μm) (b)) and after 3000 hours (c) and d)) (scale bar is 50 μm and 500 μm, respectively)

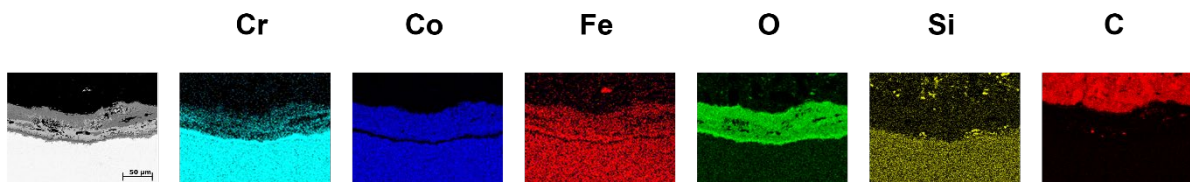


Figure 9. Backscattered electrons image and corresponding EDS maps for the AISI 430 with Co-Cr alloy coating applied by LC after the contact with LiKNa carbonate salts at 650°C during 3000 hours (scale bar is 50 μm)

4. Conclusions

AISI 430 ferritic steel is a ferritic steel with good characteristics for use with coatings for higher temperatures. Of the two coating application technologies studied (HVOF and LC), LC proved to be the most suitable technique. However, the Ni-Cr-Mo coating alloy, even when applied by LC, proved not to be appropriate for this application. The Co-Cr coating alloy showed good

anticorrosive behaviour, even after 3000 h of testing. Before considering these coatings for use in CSP, in contact with high temperature molten salts, further studies are needed to optimise the application of these Co-Cr alloys coatings by LC, particularly in terms of thickness and chemical composition, as well as to better understand the degradation mechanisms and whether this good behaviour is maintained over longer periods.

Author contributions

Teresa C. Diamantino: Project administration, Conceptualization, Investigation, Data curation, Writing, Supervision. Fátima Pedrosa: Methodology, Data collection, Data curation, Writing. Teresa Paiva: SEM-EDX analysis. Eduardo Silva: Methodology; Coating of Samples, Writing. Francisco Gonçalves: Coating of samples. Renato Monteiro: Methodology; Coating of Samples. João P. Cardoso: Conceptualization; Writing; Proof-reading.

Competing interests

The authors declare that they have no competing interests.

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