High temperature coatings from post processing Fe-based chips and Ni-based alloys as a solution for critical raw materials

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Abstract

Due to shortage of natural resources worldwide, it is a need to develop innovative technologies, to save natural resources and secure Critical Raw Materials (CRM). On the other hand, these new technologies should move forward materials engineering in order to develop better materials for extreme conditions. One way to develop new materials is to use post processing chips of austenitic steels (i.e. 304L stainless steel: 18/10 Cr/Ni) and other materials such as Ni-based alloy with high Cr content. In this work, the results of the preliminary study on the High Velocity Oxy Fuel (HVOF) coatings developed from 304L stainless steel chips and Haynes® 282® Ni-based alloys are shown. The study obeys development of the powder for HVOF technology. The produced coatings were exposed at high temperature at 500 and 700 °C for 100 and 300 hours respectively to assess corrosion behaviour.

Keywords: recycling, coatings, high temperature, steel, Ni-based alloy

1. Introduction

Corrosion represents a significant cost and technical challenges for developed economies affecting mostly constructions made of plain carbon steels or low alloyed steels: the materials often used in power plant, automotive, and other sectors of industry. Under ambient conditions, these quickly undergo corrosion processes leading to significant material loss that contribute strongly in economic losses providing high costs of repair or replacement [1]. Cost of boiler tube repair includes as well cost return to service and cost of lost production are generally in range of $10,000 – $100,000 depending of damage and difficulty accessing to the failure location, average costs reach around $10,000 per day. Overall, industrial boilers is one of the prominent features in fossil fuel fired power plants. The boilers constructed from low alloyed steel (T22) show failures mostly due to fuel ash corrosion, overheating, hydrogen attack, carburization and decarburization, corrosion fatigue cracking, stress corrosion cracking, caustic embrittlement, erosion, and steam oxidation. The failures are closely linked with wall thinning effect due to corrosion called metal loss effect [2, 3]. The majority of forced outages of power boilers are due to premature failure of boiler components [4, 5]. Boiler tube failures are the main cause of forced outages of power generating units. In the United States (US), the cost penalty is estimated to be in excess of 5 billion dollars a year in replacement power charges and maintenance costs [6]. The contribution of total tube failures can be grouped as: furnace water wall tubing 40%, super heater...
tubes 30%, re-heater (RH) tubes 15%, economizer tubes 10% and burner tubes 5% [7]. Hence, it can be assumed that around 3.14% GDP of the European Union (EU) may end up with direct costs of corrosion reaching 250 billion of € [8,9]. The mentioned costs showing, high impact of corrosion in different fields for GDP of EU, therefore it is extremely important to perform more scientific research in order to reduce provided corrosion costs. The highest, most accelerated corrosion degradation is observed at high temperatures as mentioned earlier: corrosion as a process is activated by temperature; as shown in Figure 1. The highest corrosion rate (metal loss) is met in low alloyed steels such as 15Mo3, T22, and T23 (blue stripe in Figure 1); the steels are unable to promote development of a stable, thin protective oxide scale. On the other hand, low alloyed steels cannot be replaced in full in power industry by expensive highly alloyed steels and Ni-based alloys, because low alloyed steels must be used in boiler walls due to much higher coefficient of thermal conductivity (CCT) and lower coefficient of thermal expansion (CTE) than highly alloyed steels (austenitic steels) and Ni-based alloys [10].

**Figure 1** Material limits at high temperature for power plant industry

In order to reduce corrosion costs in low alloyed steels in power plant industry and in other sectors where such steels are used, increase efficiency due to higher operating temperature (Figure 2), enhance performance, reduce metal loss, a protective coating with a tailored chemical composition ensuring development of stable, thin, and adherent oxide scale have to be applied.

**Figure 2** Efficiency and CO₂ emission in function of temperature and technology
Furthermore in nowadays economically and strategically important for the European economy, is secure of Critical Raw Materials (CRM). The materials such as Antimony, Beryllium, Borates, Chromium, Cobalt, Cooking Coal, Fluorospars, Gallium, Magnesite, Magnesium, Natural Graphite, Niobium, Phosphate Rock, Platinum Group Metals (PGMS): Palladium, Platinum, Rhodium, Iridium, Osmium, Ruthenium, are often in use for environmental technologies, consumer electronics, health, steel-making, defence, space exploration, and aviation. These materials are not only ‘critical’ for key industry sectors and future applications, but also for the sustainable functioning of the European economy. Hence, it is crucial to find a way in order to secure concentration of CRM. One of the directions postulated in this paper is to produce high temperature coatings using thermal spray technique like High Velocity Oxy Fuel (HVOF) for harsh application based on recycling technology that consumes post machined chips out of austenitic steels and Ni-based alloys with more than 15 wt% of Cr in metal matrix.

Currently one of the leading thermal spray processes to use in order to enhance corrosion resistance of low alloyed steels is HVOF process [11]. The technology produces coatings with high thickness (> 50 µm) with good bonding structure to the metallic core [12]. Nevertheless, the powder used to a coating production originates throughout expensive long term technological processes from natural resources (metal ores) leading to deplete of those resources extensively, hence development of powders for coatings is extremely costly and resource intensive. Moreover, each individual thermal spray process needs a high quantity of powder to deposit a 1 m² area. Sadly, thermal spray processes are not efficient as should be i.e. for deposition of WC/Co 200 – 300 µm thick coating on 1 m² area at least 12 – 14 kg of powder is needed, to deposit 100 µm thick coating based on austenitic steel (FeCrNi powder) on 1 m² area at least 3 kg of powder is needed. It is important to note, that powder usage in thermal spray processes is dictated by individual factors such as density of powder, thickness of coating to be deposited, torch design, temperature, distance from torch to the substrate and more, hence it is difficult to measure exact amount of powder needed for a coating deposition. Hence, in this study an idea is to produce, deposit and test at high temperatures the coatings produced from metallic chips of 304L and Haynes® 282® Ni-based alloy. Oxidation tests in static air under atmospheric pressure were conducted at 500 °C for plain steel with 304L based coating and at 700 °C for Haynes® 282® coating type deposited on 304L steel surface. Prior and post examinations were carried out by standard analytical equipment using: single lens digital camera Canon 70D coupled with Canon MP-E 65 mm f/2.8 macro lens, Optical Microscope, Scanning Electron Microscope (SEM) Hitachi TM3000 equipped with Energy Dispersive X-Ray Spectrometry (EDS) Quantax 70 analyser from Bruker.

2. Experimental procedure

In this work two main coating systems were produced by HVOF technology and tested under air oxidation conditions: 304L and Haynes® 282® type coatings with the following composition.

| (wt%) | Fe | Cr | Ni | Mn | S    | P    | C    | N  | Si |
|-------|----|----|----|----|------|------|------|----|----|
| 304L steel | Bal. | 19 | 10 | 2 | 0.003 | 0.045 | 0.03 | 0.1 | 0.75 |
Table 2 Chemical composition of Haynes® 282® steel chips used for coating production

| (wt%) | Ni | Fe | Cr | Co | Mo | Si | Mn | Cu | La | Ti | Al | C | W | B |
|-------|----|----|----|----|----|----|----|----|----|----|----|   |   |   |
| Haynes® 282® | Bal. | 1.5 | 20 | 10 | 8.5 | 0.15 | 0.3 | - | - | 2.1 | 1.5 | 0.06 | - | 0.05 |

The fine grain powders were produced using liquid-assisted process for consolidation of metallic chips by melting and casting into the ingots. The processes are described in details under two application patents entitled: Development route in order to form fine grain powder using recycling technology of Fe-based chips and Development route in order to form fine grain powder using recycling technology of Ni-based chips. Patent application numbers: P. 417489, P. 417490. The presented technology roughly is presented below:

- Post processing chips delivery,
- Degreasing process using available ultrasonic bath at 40 °C for at least 40 minutes (x3 times), chemical composition analyses by X-ray Fluorescence (XRF) and Energy-dispersive X-ray spectroscopy (EDS) analyses,
- Liquid-assisted process for consolidation of metallic chips by melting and casting into the ingots,
- Casting ingots formation, chemical composition analyses by X-ray Fluorescence (XRF) and Energy-dispersive X-ray spectroscopy (EDS) analyses,
- Atomisation of the produced ingots into fine grain powder, chemical composition analyses by X-ray Fluorescence (XRF) and Energy-dispersive X-ray spectroscopy (EDS) analyses,
- Development of coating by HVOF process.

The process shown above is described in Figure 1 for better understanding.
The produced powders were chemically analysed in order to investigate chemical composition changes after liquid-assisted process for consolidation of metallic chips by melting and casting into the ingots. The results for 304L and Haynes® 282® are presented in Table 3 and Table 4 respectively.
Table 3 Chemical composition performed using EDS analyser of the as deposited coating based on 304L chips powder

| Spectrum: Point | Element  | AN Series | unn. C | norm. C | Atom. C | Error |
|-----------------|----------|-----------|--------|---------|---------|-------|
|                 | Iron     | 26 K-series | 27.29  | 39.25   | 25.23   | 0.8   |
|                 | Chromium | 24 K-series | 16.57  | 23.84   | 16.46   | 0.5   |
|                 | Oxygen   | 8 K-series  | 14.64  | 21.06   | 47.26   | 2.6   |
|                 | Nickel   | 28 K-series | 9.62   | 13.83   | 8.46    | 0.3   |
|                 | Silicon  | 14 K-series | 1.41   | 2.03    | 2.59    | 0.1   |
|                 | Total:   |            | 69.53  | 100.00  | 100.00  |       |

Table 4 Chemical composition performed using EDS analyser of the as deposited coating based on Haynes® 282® chips powder

| Spectrum: Point | Element   | AN Series | unn. C | norm. C | Atom. C | Error |
|-----------------|-----------|-----------|--------|---------|---------|-------|
|                 | Nickel    | 28 K-series | 30.01  | 35.10   | 21.51   | 0.9   |
|                 | Oxygen    | 8 K-series  | 18.67  | 21.83   | 49.08   | 3.1   |
|                 | Chromium  | 24 K-series | 18.24  | 21.34   | 14.76   | 0.5   |
|                 | Molybdenum| 42 L-series | 5.92   | 6.93    | 2.60    | 0.2   |
|                 | Cobalt    | 27 K-series | 5.84   | 6.83    | 4.17    | 0.2   |
|                 | Aluminium | 13 K-series | 2.96   | 3.47    | 4.62    | 0.2   |
|                 | Titanium  | 22 K-series | 2.96   | 3.47    | 2.60    | 0.1   |
|                 | Iron      | 26 K-series | 0.88   | 1.03    | 0.67    | 0.1   |
|                 | Total:    |            | 85.49  | 100.00  | 100.00  |       |

The results presented above clearly indicate, that both powders during fabrication underwent oxidation process, content of oxygen in both powders are quite high and reached up to 25 wt%. The powders showed high degree of oxidation during the liquid-assisted process for consolidation of metallic chips, perhaps due to easy access of oxygen from an ambient atmosphere. However, the problem can be avoided in the future when vacuum furnace with a protective atmosphere will be used. Nevertheless, it is important to mention that Cr content in both powders were high (over 20 wt%). High Cr content is crucial for development of a protective oxide scale in oxidising atmospheres, role of Cr in protective oxide formation is well known from many years [13, 14]. Finally fine grain powders that were produced via atomisation process under argon atmosphere [15] showed different dimensions ranging from 50 up to 300 µm. Both types of coatings were produced using High Velocity Oxy Fuel (HVOF) using certain facilities and under the following conditions:
Prior the coatings deposition, powders were preheated by propane and oxygen to plastic or semi liquid/liquid state, further the powders were mixed with flammable gases and air. The HVOF process used compressed air pressure of 0.55 MPa, with distance from the surface of steel: 200 mm. Prior deposition, surface was cleaned in organic solutions and grinded to obtain roughness of $R_{\text{y5}} = 45$ µm.

3. Results and discussion

3.1 As deposited coatings

Figure 4 shows 304L coatings deposited by HVOF process on plain steel with different coating thickness, whereas Figure 5 presents Haynes® 282® coatings that were deposited based on different fine grain powder dimensions deposited on 304L steel. The pictures were captured using single lens digital camera Canon 70D coupled with Canon MP-E 65 mm f/2.8 macro lens.

![Figure 4](image_url) As deposited coatings based on 304L steel chips by HVOF process on plain steel (with different thickness)
Figure 5 As deposited coatings based on Haynes® 282® steel chips by HVOF process on 304L steel: A) 45 µm, B) 45 – 100 µm, and C) 100 – 200 µm

The coatings showed in Figure 4 and Figure 5 respectively, present, no cracks of the deposited layers, suggesting good bond strength that formed between the substrate and the deposited coatings when HVOF process was used. Moreover, the analyses performed by EDS on as deposited coatings that were carried out shown no much difference between the chemical compositions of the powders that were used, suggesting that HVOF process showed no influence on chemical composition of the developed coatings.

3.2 Kinetic behaviour

The samples with dimension of approximately 1.5, 0.7 and 0.4 cm were decreased using organic solution and ultrasonic bath for 15 minutes at 40 °C and accurately weight using digital balance CPA 225D-0CE prior air oxidation test and during exposures. As mentioned previously air oxidation test for 304L coatings on plain steel was carried out for 100 hours at 500 °C, but coatings based on Haynes® 282® post machined chips deposited on 304L were exposed at 700 °C for 300 hours. Together with the coated materials, the uncoated plain steel and 304L steel was exposed as a reference sample. The kinetic data shown in Figure 6 and Figure 7 from high temperature tests showed that the coatings made of post machined scrap indicate some rate of protectiveness.
Figure 6 Kinetic data of the exposed 304L coating based on metallic chips deposited on plain steel at 500 °C for 100 hours
Figure 7 Kinetic data of the exposed Haynes® 282® coating based on metallic chips deposited on 304L steel at 700 °C for 300 hours

Kinetic data presented in Figure 6 shows, that plain steel coated by 304L based coating indicate some degree of protectiveness. The lowest mass gain was obtained by sample 2, the highest mass gain was found to be in the reference sample (plain steel). Its need to be pointed out that in the initial stages of oxidation, sample 6, showed higher mass gain than that observed in reference sample, but after longer exposure mass gain of the reference sample reached the highest values (4.5 mg/cm²). Enhanced corrosion resistance that was observed in this work for coated plain steel is related mainly to the higher Cr content in the deposited coating, that induces development of the oxide scale that possess higher corrosion resistance against oxidation atmosphere. Furthermore, the coated samples showed similar mass gain after 100 hours at 500 °C exposure that suggests that thickness of the deposited coatings show no much influence on the oxidation kinetics. In contrast to the data showed in Figure 6, in Figure 7 kinetic data of the exposed Haynes® 282® coating developed on the basis of post machined chips and deposited on 304L steel surface indicates that the coating with 45 µm grain dimension showed the highest mass gain. In contrast, two other coatings (45 - 100 µm and 100 – 200 µm grain size), indicated lower mass gain than that presented by reference material (the uncoated 304L steel). Finally, the kinetic curve that developed at 700 °C for 300 hours for the uncoated sample indicate constant weigh growth in contrast to two coatings (45 - 100 µm and 100 – 200 µm) where steady state oxidation process occurred.
3.3 Surface observations

Figure 8 shows macro images captured after exposure at 500 °C for 100 hours for plain steel coated with 304L based steel. Macro images shown in Figure 8 clearly indicate and confirms kinetic data showed in Figure 6, the higher mass gain of the samples is closely related to iron oxide formation, perhaps due to thin or inadequate coating process. As illustrated, samples 1 – 3 show no hematite formation (red colour), sample 4 is slightly affected by hematite formation, whereas sample 5 and sample 6 showed similar surface occurrence as the reference sample (plain steel), that is rich in red hematite phase on the surface [16]. It is well known that iron based oxides are less protective at high temperatures than the Cr based oxides where diffusion processes are much quicker due to high number of defects inducing higher kinetic growth [17]. Figure 9 shows macro images of the exposed Haynes® 282® coating based on metallic chips deposited on 304L steel exposed at 700 °C for 300 hours.
In contrast to observations for the coated plain steel, in current situation deposition of Haynes® 282® coating on 304L steel induced reduction in hematite development due to higher Cr content in the coating and in the substrate material. Under oxidising atmosphere rich Cr coating (Haynes® 282®) and substrate (304L) provoked higher rate of Cr outward diffusion, responsible for developing of highly resistant oxide scale that consisted: fraction of Cr$_2$O$_3$ oxide, FeCr$_2$O$_4$. Ni-Fe-Cr$_2$O$_4$ spinel. The formation of the mentioned phases in austenitic steels are broadly described by many authors in the past, therefore a reader is directed to the following papers [14, 18, 19, 20, 21].

3.4 Cross-section observations

Figure 10 shows cross-sectioned, optical microscope images of the exposed 304L coatings deposited on plain steel at 500 °C for 100 hours. As is, the samples 1 – 3 are covered by thick 300 µm coating based on 304L composition, the other 3 samples (4 – 6), are coated by a thin coatings, whereas 7 showed the uncoated plain steel. The coated materials showed no cracks formation, no detachment or delamination of the deposited coating. The results in this study suggest that even deposition of a thin coating is beneficiary for high temperature exposure in air conditions due to the formation of more protective oxide scale than that developed on the uncoated material. The mechanism of surface protection relays on Cr diffusion from the coating that contains 20 wt% of Cr to the external part of the coating and development of Cr$_2$O$_3$ rich oxide scale. The oxide in rich oxygen atmosphere (air) due to more negative value of Gibbs free energy formation for Cr$_2$O$_3$ than that for Fe-based oxide, is more thermodynamically stable and offers higher corrosion resistance than that obtainable by Fe-based oxide.
In case of Haynes® 282® coating, surprisingly, the thickest coating developed using 45 µm fine grain size showed the poorest corrosion resistance in terms of oxidation protection. The thick coating (>500 µm) that was applied on 304L steel according to EDS analyses, showed high iron content suggesting high diffusion rate of iron from the 304L substrate throughout the coating. The other two coatings on cross-section images presented in Figure 10 (sample 2 and samples 3) indicate that during deposition by HVOF, large powder (grain size) showed no adherence to the 304L steel surface suggesting that kinetic energy of the powder during deposition process was too high resulting that powder was ejected instead of adhered to the 304L steel substrate. The described process indicate effect of shot peening process, that is a cold working process that is often used in order to obtain a compressive residual stress layer and modify mechanical properties of alloys and composites. In addition some researchers proposed that shot peening improve corrosion resistance throughout the formation of protective layer on the surface of the material [22, 23] by diffusion of Cr ions from the metal matrix to the exposed surface, resulting development of Cr-rich region on the surface, that facilitate the formation of dense, protective, well adherent Cr2O3 film [24].
Figure 11 Cross-sectioned microstructures of the exposed Haynes® 282® coating on 304L steel exposed at 700 °C for 300 hours

The uncoated 304L steel developed under air oxidation process at 700 °C for 300 hours, a thin oxide scale that is composed mainly from FeCr₂O₄ spinel phase with some areas enriched in Cr suggesting the formation of Cr₂O₃ oxide. Nevertheless, the steel under relatively short exposure indicate some corrosion degradation due to brittle, fractured scale that formed (white circle). In overall, the corrosion resistance of the uncoated 304L steel can be compared to the materials that were coated by the coating with the thickest grains. Moreover, it can be suggested, based on the achieved results and cross-section images, that in the case of thick grain, effect of shot peening is stronger than influence of Haynes® 282® coating that was applied based on post machined scrap.
4. Conclusions

The aim of this paper was to show a solution for Critical Raw Materials (CRM) such as Cr by the development of fine grain powders derived from post machined chips rich in Cr.

Chromium (Cr) as a one of Critical Raw Material is often used as an alloying element to steels, Ni-based alloys and coatings for better corrosion protection; hence, concentration of Cr in earth is significantly reduced. Nevertheless, Cr can be regained to secure CRM by the simple process.

The chips may originate either from austenitic steels or Ni-based alloys. In general post machined chips are treated frequently as a scrap material with no value, especially when are contaminated by organic based lubricant. However, in this work post machined chips after liquid-assisted process for consolidation of metallic chips by melting and casting into the ingots, atomisation, and thermal spray HVOF process were deposited on two different materials.

The produced powders based on 304L stainless steel and Haynes® 282® Ni-based alloy post machined chips were deposited on a plain steel and 304L steel respectively. Both type of corrosion couples, where exposed in air oxidation tests for 100 and 300 hours at 500 and 700 °C respectively. The research carried out in this study showed, that coatings produced using thermal spray process exposed at high temperatures offer protection for plain steel, as well as for 304L steel. Nevertheless, it is need to pointed out, that powder size is crucial for coating deposition process. It was found that due to large grain size of powder, instead of deposition, ejection of powder appeared, leading to the formation of shot peening effect. Nevertheless, the presented results in this study, can be an excellent starting point for further work that can be carried out in the field of high temperature protection where post machined wastes can be re-used in order to secure Critical Raw Materials (CRM) like Cr. Furthermore, the produced powder can be used as well for Hot Isostatic Pressing (HIP) process and in 3D printing technology such as: SLM – Selective laser melting.
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