MORPHOLOGY AND CHEMICAL COMPOSITION OF INCONEL 686 AFTER HIGH-TEMPERATURE CORROSION

Damian KOCLĘGA [1], Agnieszka RADZISZEWSKA [1], Axel KRANZMANN [2], Przemysław MARYNOWSKI [1], Krzysztof WOŹNY [1]

[1] *AGH University of Science and Technology, Cracow, Poland, EU*
dkoclega@agh.edu.pl

[2] *Federal Institute for Materials Research and Testing - BAM, Berin, Germany, EU*
axel.kranzmann@bam.de

Abstract

The work presents the microstructure, chemical composition and mechanical properties of Inconel 686 coatings after high - temperature corrosion in environment of aggressive gases and ashes.To produce the Ni - based coatings the QS Nd:YAG laser cladding process was carried out. As the substrate used 13CrMo4-5 boilers plate steel. Ni - base alloys characterize the excellent high-temperature corrosion resistance, good strength and ability to work in aggressive environments. Formed clad were characterized by high quality of metallurgical bonding with the substrate material and sufficiently low amount of the iron close to the clad layer surface. After corrosion experiment the oxide scale on the substrate and clad created. The scale on 13CrMo4-5 steel had 70 µm thickness while the scale of the clad had less than 10 µm. The microstructure, chemical composition of the obtained clad and scales were investigated by scanning electron microscope (SEM) and electron probe microanalyzer (EPMA) equipped with the EDS detectors.

Keywords: Laser cladding, Inconel 686, high - temperature corrosion, aggressive environment, oxide scale

INTRODUCTION

The increasing emission standards are forcing the energy industry to continuous quest for constructing and building power boilers for maximum efficiency, while maintaining the lowest possible emission of dangerous combustion products to the environment [1]. It forces to develop new technologies of fuel combustion energy such as: gradual combustion, which contributes to the formation in the power plant boilers, places with various corrosive environments, like: reducing or oxidizing. As a result, the construction boilers materials work in a completely different condition depending on the location. Changes in condition have a decisive influence on the corrosion, resulting in the life of the power plants. The level of corrosion becomes stronger when the plant fuel is switched to alternative fuels such as: biomass and municipal waste. The result of their combustion are very aggressive chlorine compounds which become a catalyst for corrosion processes due to low melting eutectic composition or closed transport cycles of chlorine. Therefore, it is necessary to develop resistant materials and coatings for high efficient power units able to work under these difficult conditions [2]. Low price construction steel like 13CrMo4-5 covered by high corrosion resistance material like nickel-base alloy such Inconel 686 (Ni-Cr-Mo-W) offering an excellent high-temperature corrosion resistance in oxidation and reduction environments, good strength and creep resistance in elevated temperatures [3]. On the top of Inconel 686 the corrosion processes could create the Cr_2O_3 and NiO_2 scales which are a barrier against further oxidation of material [4,5]. The investigation confirm that alloying elements like Mo and W diffuse to grain boundaries places which are particularly exposed to corrosion [6]. However those elements are high resistance on corrosion and their higher content in grain boundaries should be barrier against further degradation of material. Therefore the samples were subjected to high temperature corrosion experiments in environments similar to coal combustion power plants with atmosphere of gases: CO_2, H_2O, N_2, O_2, SO_2 and ashes: Fe, O, Si, Ca, Cl, Na, C, Al, K, Mg, S at time 240 h.

There are papers available in the literature about high temperature corrosion of the Ni-base alloys in oxidizing atmosphere simulating work environment of turbine engines for aircraft [8,9]. However, there are carried out research about behavior of Ni - base alloys during high temperature corrosion in aggressive gases atmospheres and ash environment occurring combustion process of coal and municipal waste [10,11]. Therefore there is no information about the Inconel 686 clad layers obtained using laser cladding process. Therefore the motivation and importance of this study is the investigation of the influence of Ni-base coatings on the 13CrMo4-5 iron alloy's high temperature resistance. The aim of the present work was the high-temperature corrosion of Inconel 686 coatings clad on 13CrMo4-5 steel exposed to aggressive environment containing harmful gases and ashes as well as the characterization of the microstructure and the changes in chemical composition of scales. Therefore we have used scanning electron microscopy (SEM) and electron probe microanalyzer (EPMA) to investigate chemical composition of coatings and scales.

1. MATERIALS AND EXPERIMENTAL METHODS

The samples were performed by the laser cladding process described in previous author's work [7]. The low carbon steel 13CrMo4-5 was covered by Ni - base alloy Inconel 686. The powder of Inconel 686 was deposited on steel by a Q-Switch Nd:YAG JK System 5000 laser .The chemical composition of both metals are presented in **Table 1**. The substrate material is widely used in the power industry owing to its good properties of strength and plasticity, as well as good welding property compare to volume of price / tone. The Inconel 686 is known as material with excellent high - temperature corrosion resistance in aggressive environments.

Table 1 Chemical composition of the base material - steel Cr13Mo4-5 and the Inconel 686 powder

13CrMo4-5 steel - Base material (BM)									
C	Si	Mn	P	S	Cr	Mo	N	Cu	Fe
0.08 - 0.18	0.35	0.4 - 1	0.025	0.01	0.7 - 1.15	0.4 - 0.6	0.012	0.3	Balance
Inconel 686 - Powder									
Cr	Mo	Fe	W	Mn	P	S	Ti	C	Ni
19-23	15-17	<5	3-4.4	<0.75	<0.04	<0.02	0.02-0.25	0.01	Balance

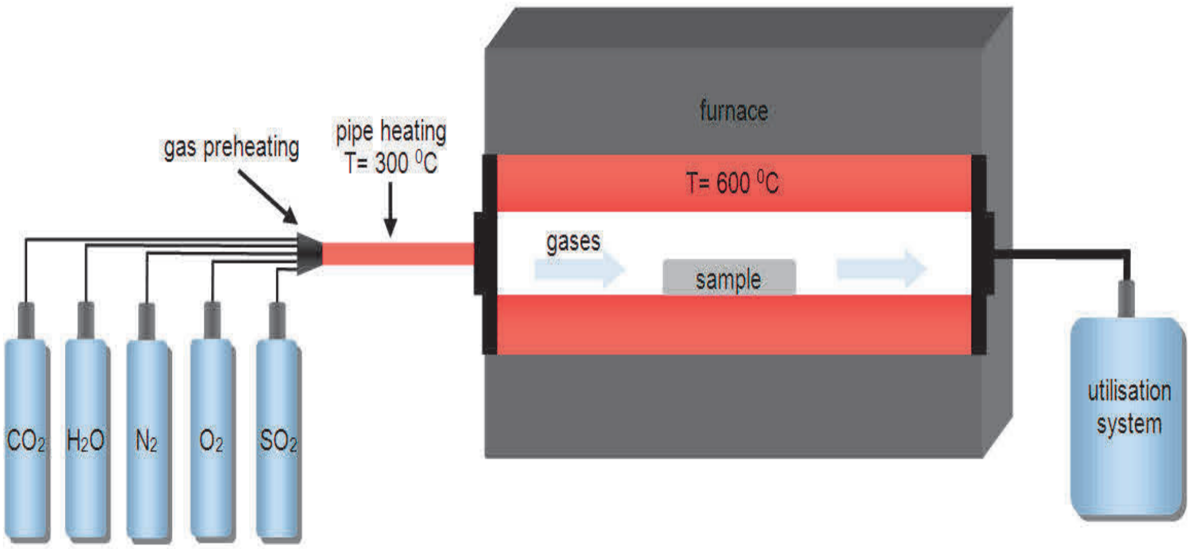


Figure 1 Apparatus for conducting a high temperature corrosion experiment

The corrosion tests were performed in typically coal combustion atmosphere The samples were set into the furnace chamber where the gas mixture (CO_2, H_2O, N_2, O_2, SO_2) was injected after preheating (**Figure 1**). The temperature in chamber was 600 ^{0}C which is enough to obtain into chamber the atmospheres with very aggressive sulfur compounds and low temperature chloride eutectics. The gases flow through the chamber to the utilization system, which ensures the same condition throughout the duration of the experiment. The tests were made in two parallel running variations; first: only in gas atmospheres and second: samples in gas atmospheres covered by ash with elements typically for coal combustion process such like: Fe, O, Si, Ca, Cl, Na, C, Al, K, Mg, S. The **Figure 2** presents energy dispersive X- ray spectroscopy of ash investigation before corrosion process. The duration time under described above condition was 240 hours. SEM investigation was performed using an FEI Nova NanoSEM 450 micro equipped with an EDS spectrometer of EDAX company while chemical composition analysis were supported by electron probe microanalyzer (EPMA) contain three EDS detectors which collect information from different electron shell lines.

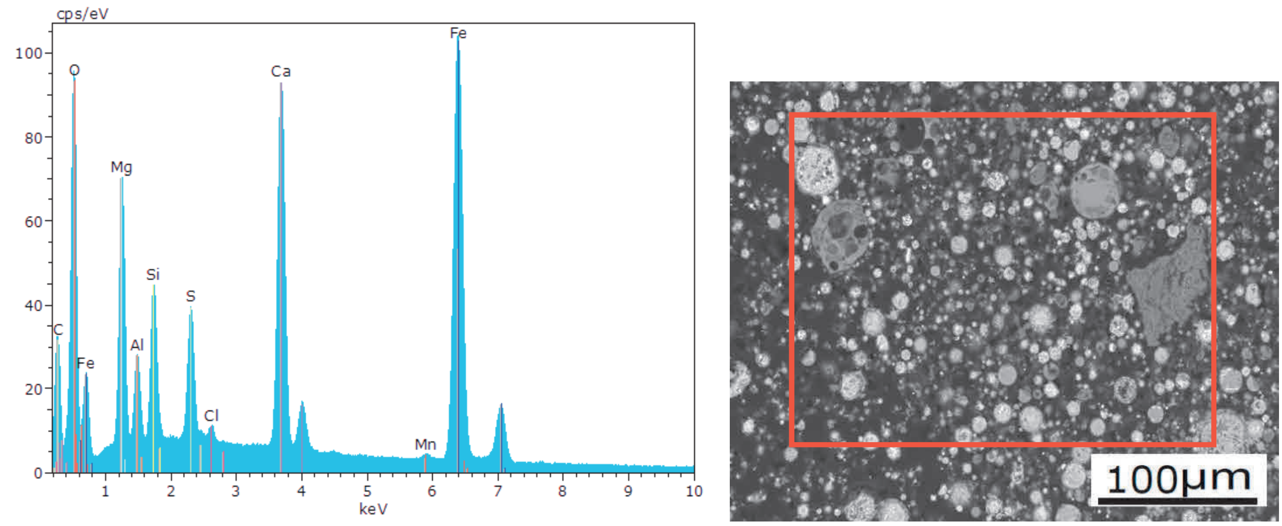
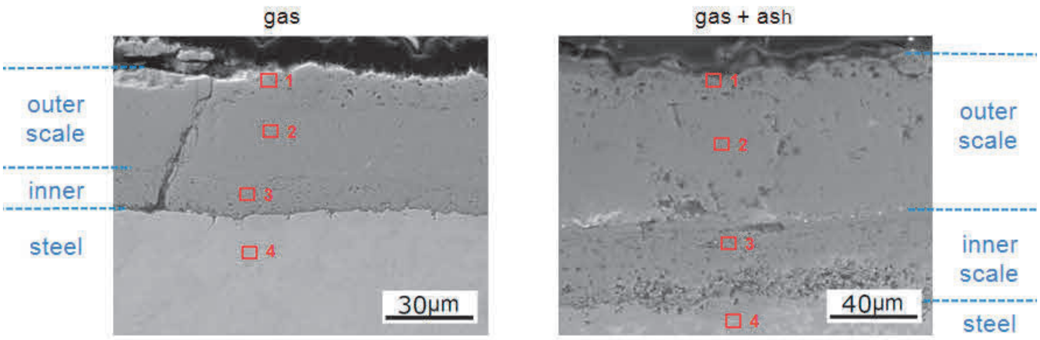


Figure 2 EDS spectrum of the ash used in high - temperature corrosion experiment

2. RESULTS AND DISCUSSION

2.1. Scanning Electron Microscope investigation of the scales

As a result of carrying out the corrosion experiment the oxide scales were created on substrate material steel 13CrMo4-5 and on Inconel 686 clad layer. The scale of the steel had average 70 µm thickness while the scale which grew on the overlay weld had less than 10 µm thickness. In the **Figure 3** are present the oxide scales observed on base material after corrosion in gas and gas + ash atmosphere. The formed scale is composed of two parts: outer and inner scale. After gas + ash corrosion process the created scale on steel is thicker (about 90 µm) then obtained after gas interaction (about 40 µm). For coating, scale in similar for both cases of corrosion test. The inner scale were created during inner diffusion of corrosive elements, which is confirmed by chemical composition analysis in area 3 for gas corrosion and area 3 and 4 for gas + ash corrosion conditions (**Figure 3**). The scales are characterized by occurrence of many pores and brittle structure. As a result, it does not constitute a barrier against further oxidation of the substrate material. The chemical analysis of the outer scale revealed, the presence of iron and oxygen and additional elements like: sulfur, silicone and manganese.

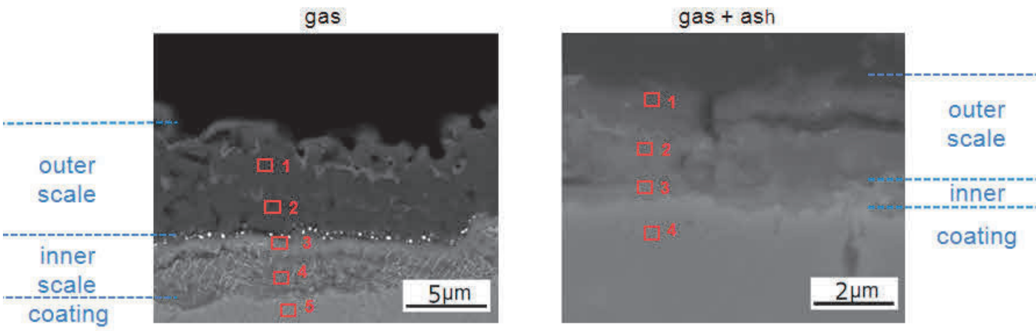


Element	1	2	3	4
	Wt, %			
Fe-$K_α$	81.8	79	69.4	97.8
O-$K_α$	18.2	17.7	18.6	-
Cr-$K_α$	-	-	3.8	1.2
Mo-$L_α$	-	1	3.6	1
S-$K_α$		2.3	4	-
Mn-$K_α$	-	-	0.6	-

Element	1	2	3	4
	Wt, %			
Fe-$K_α$	85.1	91.3	80.9	95.1
O-$K_α$	9.9	6.7	8.3	0.7
Cr-$K_α$	-	-	2.6	1.2
Mo-$L_α$	-	-	6.3	2.3
S-$K_α$	2.4	0.3	0.5	-
Mn-$K_α$	1.9	1.1	1.4	0.7
Si-$K_α$	0.7	0.6	-	-

Figure 3 The chemical composition of oxide scales created on the top of substrate from steel 13CrMo4-5

In **Figure 4** on the left-hand side is visible a marker (as white gold dots) which was applied to distinguish inner and outer scale. The chemical composition analysis showed that in the case of the gas condition on the surface of coating were created outer scale which contained higher amount of oxygen, nickel (44.3-47.6 wt%) and sulfur (23.2-24 wt%) (**Figure 4**, area 1 and 2). While in the inner scale (**Figure 4** - areas 3 and 4) were observed outward diffusion of nickel, chromium, molibdenium and tungsten from the Ni-base clad layer which might create the protective oxide scale. However, the amount of sulfur decreases towards to cladding material core. **Figure 4** on the right-hand side shows the scale created after gas + ash corrosion. This scale is characterized by higher amount of silicon which is one of the ash element and can change the character of corrosion mechanism, which will be proven by investigation after a longer period of corrosion tests. Additionally, EDS analysis confirmed the occurrence of oxygen and nickel (29.7 wt%) in the surface layer of scale. While higher concentration of chromium (18.4 wt%) and molybdenum (16.2 wt%) were analyzed in the area close to the clad layer surface.



Element	1	2	3	4	5
	Wt, %				
Cr-$K_α$	0.8	1	30.3	23.4	15
Fe-$K_α$	3.1	3.2	2.5	3.2	5.8
S-$K_α$	24	23.2	7.7	4.4	0.2
Ni-$K_α$	47.6	44.3	8.2	28.3	56.1
Mn-$K_α$	1.7	1	1.9	0.8	1.1
O-$K_α$	20.8	25,6	-	-	-
W-$M_α$	0.8	0.2	16.9	14.6	7.5
Mo-$L_α$	1.2	1.5	32.5	25.3	14.3

Element	1	2	3	4
	Wt, %			
Cr-$K_α$	1	18.4	14	14.8
Fe-$K_α$	4.4	4.3	3.7	4.5
S-$K_α$	5.4	5.5	1	-
Ni-$K_α$	29.7	22	56.5	60.2
Si-$K_α$	19.8	4.8	2.3	2.1
O-$K_α$	38.7	22.4	3.6	-
W-$M_α$	-	6.4	3.7	3.5
Mo-$L_α$	1	16.2	15.2	14.9

Figure 4 The chemical composition of oxide scales created on the surface of Inconel 686 coatings

2.2. Electron probe micro - analysis of the scales

To improve the changes in the elements concentration in the created oxide scales the microprobe (EMPA) technique was used. According to the colors of the scale - the warmer color presents a higher amount of the study elements. **Figure 5** presents microprobe analysis for coating surface after corrosion in gas and ash environments. The analysis showed that there occurred the outward diffusion of chromium and molybdenum towards to the surface of Ni-base coating. It should be noted that starts the creation of an inner scale with inward diffusion of sulfur and oxygen from the outside environment.

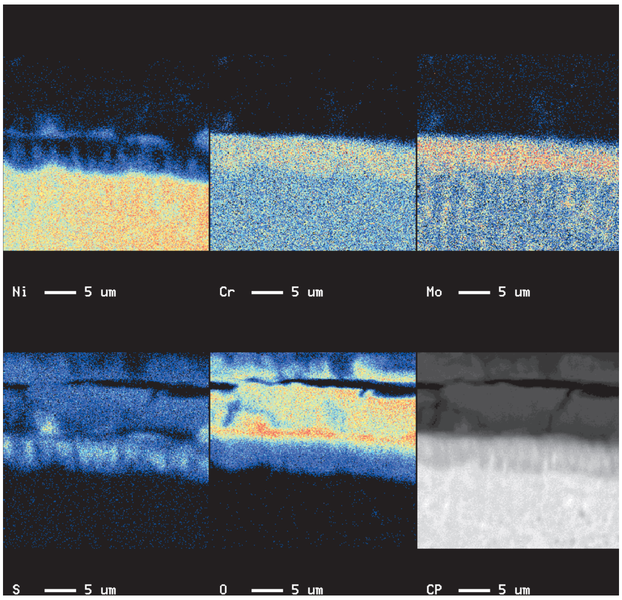


Figure 5 Microprobe (EPMA) analysis of Inconel 686 coating after corrosion test in gas and ash atmosphere

In the **Figure 6** the contact between three areas: steel, clad layer and oxide scale created on the top of material substrate steel 13CrMo4-5. The analysis confirmed the diffusion of such element like: chromium and molybdenum direct to the surface of the coating. It showed also diffusion of very small amount of sulfur towards to the coating material.

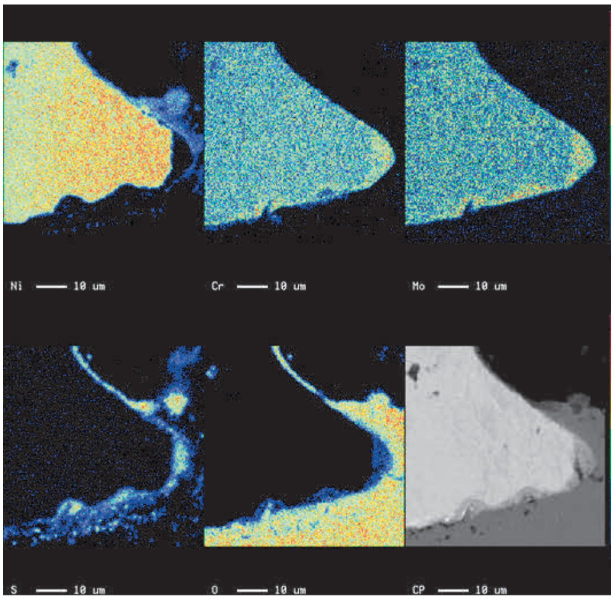


Figure 6 Microprobe (EPMA) analysis of Inconel 686 coating after corrosion test in gas atmosphere

CONCLUSIONS

The corrosion processes in gas and ashes atmospheres lead to create oxide scales on carbon steel 13CrMo4-5 and overlay weld material Inconel 686. The scale of the steel had 70 µm thickness while the scale of the overlay weld had less than 10 µm thickness. Study of the scales formed on the Ni-Cr-Mo-W allow to determine inward diffusion of nickel, chromium, molybdenum and manganese. Also it was observed the outward diffusion of the oxygen and increased quantity of sulfur into the scales.. After corrosion experiments the formation of scale with higher amount of: Ni, O, Mo, W and Cr were began, however, time was too short to form an uniform scale over the entire surface of the overlay weld. Therefore the long term corrosion experiments are needed to investigate the mechanism of corrosion in aggressive environments ofr Ni - base coatings like Inconel 686.

ACKNOWLEDGEMENTS

The authors would like to thank BAM - Federal Institute for Materials Research and Testing in Berlin for founding. The work was supported also by the Ministry of Science and Higher Education of Poland under contract No. 11.11.110.295

REFERENCES

[1] M. A. UUSITALO, P. M. J. VUORISTO, *Hot corrosion behavior of HVOF - sprayed Cr_3C_2 - NiCrMoNbAl coating,* Surf. Coat. Tech. 161 (2002) 275-285

[2] I. KLEVTSOV, H. TALLERMO, T. BOJARINOVA, *High Temperature of Boiler Steels Under Chlorine - Containing Surface Deposits*, J. of Pres. Ves. Tech., 127 (2005) 106 - 112

[3] J. N. DUPONT, J.C. LIPPOLD, S. D. KISER, *Welding metallurgy and weldability of nickel - base alloys, A J. Wiley &Sons 2009,*

[4] M. SOLECKA, J. KUSINSKI, A. KOPIA, M. ROZMUS - Górlikowska, A. Radziszewska, *High - temperature corrosion of Ni - Base alloys by waste incineration ashes*, A. Physica Polonica A, Vol. 130, 2016,

[5] J. ADAMIEC, *High temperature corrosion of power boiler components cladded with nickel alloys,* Materials Characterization, 2009, no. 60, pp. 1093 - 1099,

[6] CH. E. THORNTON, C. COOPER, *Welding and corrosion performance of Inco- weld 686CTP filler metal in waste to energy power plants,* Special Metals Welding Products Company, Canada House,

[7] KOCLĘGA D., DYMEK S. , Radziszewska A, Huebner J. *„ Laser cladding of Inconel 686 overlay weld on low carbon steel”*, METAL BRNO, 2017, accepted to publish in Thomson Reuters data

[8] SABER, D., EMAM, I. S., ABDEL-KARIM, R., High temperature cyclic oxidation of Ni based superalloys at different temperatures in air, Journal of Alloys and Compounds, 2017, no. 719, pp. 133-141

[9] CHO, S.-H., OH, S.-C., PARK, S.-B., KU, K.-M., LEE, J.-H., HUR, J.-M., & LEE, H.-S., *High temperature corrosion behavior of Ni-based alloys. Metals and Materials International*, 2012, no. 18(6), pp. 939-949

[10] ZAHRANI, E. M., & ALFANTAZI, A. M., *Hot Corrosion of Inconel 625 Overlay Weld Cladding in Smelting Off-Gas Environment*, *The Minerals, Metals & Materials Society and ASM International* 2013, no. 44(October)

[11] OKSA, M., AUERKARI, P., SALONEN, J., & VARIS, T. (2014). *Nickel-based HVOF coatings promoting high temperature corrosion resistance of biomass- fi red power plant boilers, Fuel Processing Technology*, 2014, no. *125*, pp. 236-245.