

CORROSION BEHAVIOR OF NICKEL-BASE ALLOYS IN HIGH-TEMPERATURE GAS ENVIRONMENTS FOR CCS TECHNOLOGIES

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<https://doi.org/10.37904/metal.2023.4729>

Abstract

Carbon dioxide is one of the possible working media for future advanced technologies in the power industry. Its use is possible in the supercritical state as a cooling medium in the nuclear power industry, as an extraction solvent, in the combustion of fossil fuels, in concentrating solar systems, or in CCS (Carbon Capture and Storage) processes. Important factors for these technologies will be the durability and compatibility of the construction materials in CO₂ and flue gas environments at high temperatures. This work describes the behavior of nickel-based alloys in a model flue gas environment and the condition of the surface layers after this exposition. The exposed samples were analyzed by XPS and by EDS detector on an electron scanning microscope (SEM). According to the exposure results, the nickel alloy samples are suitable for the model flue gas environment, and their suitability will be verified at 900 °C in further experiments. This project TK01030089 was co-financed with the state support of the Technology Agency of the Czech Republic within the Théta Programme.

Keywords: Nickel alloy, corrosion, CCS technology

1. INTRODUCTION AND DESCRIPTION OF THE EXPERIMENT

The constantly increasing demand for energy forces manufacturers to expand their production and increase the efficiency of their technologies, which can be achieved by increasing equipment parameters such as temperature, pressure, and media flow. Some parts of the equipment must therefore be replaced by more durable construction materials with higher creep strength and higher corrosion resistance. Examples could be superheaters and steam reheaters made of austenitic steels, which cannot meet the demanding material requirements in processes with increased steam parameters above 600 °C [1].

At the same time, there are increased material requirements and new technologies related to another closely monitored area of the industry, and that is ecological behavior. This paper focuses on the corrosion resistance of materials for CCS technology (Carbon Capture and Storage), which is an option to environmentally manage and store the greenhouse gas CO₂ for further use. The CO₂ capture and storage processes take place at temperatures above 600 °C in the corrosively aggressive flue gas environment. It is therefore essential to identify and test temperature and chemical resistant materials for these environments [2].

The main corrosion problems that are solved in the flue gas environment are corrosion in hot gases and corrosion in the dew point temperature region of the flue gas. This work deals with the behaviour of materials at high temperatures, therefore the effect of condensed H₂O on corrosion processes will not be described. The experiment presented in this paper is intended to illustrate the behaviour of materials in the environment of technologies operating with CO₂. CO₂ gas is considered a non-aggressive environment at temperatures up to 400 °C from a corrosion point of view. However, at higher temperatures, it can decompose into carbon atoms, which can form internal carbides in equipment alloys[3]. This can lead to significant changes in the mechanical properties of the materials.

Nitrogen can also cause problems in high-temperature combustion plants. NO formed by the reaction of N₂ and O₂ can oxidize a metal. Oxides can form on the surface of iron and nickel materials at high temperatures (specifically tested at temperatures of 580 °C - 780 °C), similar to the reaction with O₂. The surface layers are then mainly composed of Fe₃O₄ and NiO [3].

The aim of this work is to evaluate the corrosion behaviour of four nickel alloys of the composition shown in **Table 1**, to evaluate the most suitable material for a model flue gas environment at a temperature of 600 °C, or to recommend the most suitable material type for the given environment.

Table 1 Chemical composition of tested materials in (wt%) [4-7].

Alloy	Cr	Mo	Ni	Ti	Al	Co	Fe	Ta	Other(<0.50)
738	15.70-16.30	1.50-2.00	Balance	3.20-3.70	3.20-3.70	8.00-9.00	<0.50	1.50-2.00	W(2.40-2.80), C, B, Zr, Mn, Si, S
625	21.00	9.00	Balance	<0.40	<0.40	<1.00	<5.00	Nb+Ta (3.70)	C, Mn, Si
800H	19.00-23.00	-	30.00-35.00	0.15-0.60	0.15-0.60	-	>39.5	-	C
MoNiCr	6.82	15.81	Balance	0.26	0.26	-	2.32	-	Mn, W

1.1 Experiment

These results are part of a more complex project investigating the corrosion behavior of nickel-based alloys under the conditions of CO₂-based gaseous environments. The experiment presented here describes the exposure and behavior of 4 selected nickel-based alloys: 738, 625, MoNiCr, and 800H in a moisture-free model flue gas environment of 6 % O₂, 13 % CO₂, 81 % N₂ at 600 °C. The material samples were exposed in a high-temperature furnace (**Figure 1**) for 500 h with a heating rate to the desired temperature of 1°C/min and the same cooling rate to minimize the effect of temperature changes in the newly formed surface layers. After exposure, the chemical composition of the oxides on the surfaces was studied by XPS, and then the surface layers in the cross-sectional cut were analyzed by point analysis by EDS on SEM.

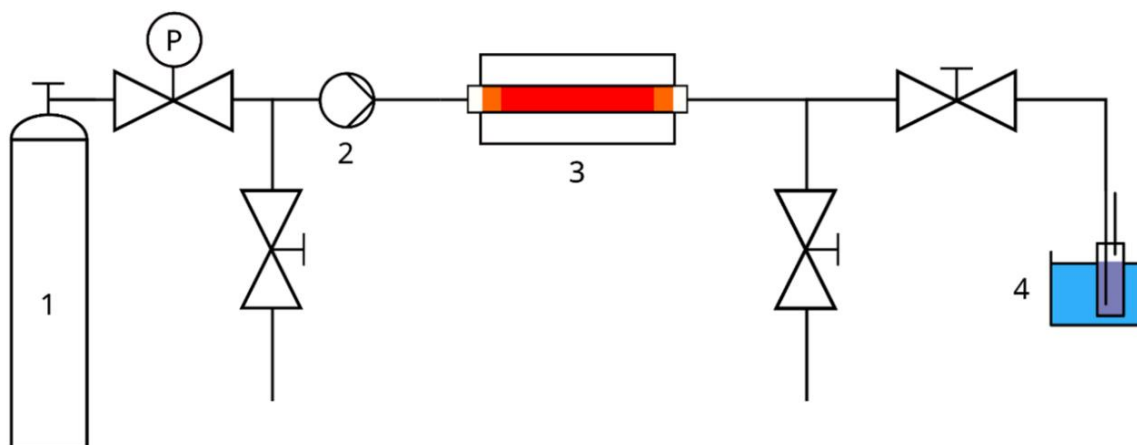


Figure 1 Scheme of the experimental high-temperature device for gaseous environment 1) cylinder with experimental gas mixture 2) pressure relief valve 3) high temperature tube furnace with quartz retort 4) water seal [8]

2. RESULTS

The table with results from XPS spectra (**Table 2**) proves the formation of oxides on the surface of materials during the exposure. The surface oxides are created mainly from Cr and Ni. Carbon monolayer (adventitious

carbon) is usually found on the top layer of the alloy surface. This film is produced during air exposure of the samples and deposited from the residual atmosphere in the vacuum chamber. Example XPS spectrum of exposed sample 625 is shown in **Figure 2**.

SEM in combination with EDS analyses showed oxide layer with a thickness of less than 1 µm for sample 625 (**Figure 3a**) and less than 3 µm for sample 738 with a thin inhomogeneous corrosion layer (**Figure 3b**). On the surface of material 800H, small pits up to a depth of 2 µm were localized (**Figure 4a**) and larger pits up to 8 µm were observed on MoNiCr (**Figure 4b**). Material MoNiCr developed a localized form of corrosion in the crevices. Corrosion products consist mainly of nickel oxides.

Table 2 Result of the composition of the sample surfaces by the XPS method (BS – base state, EXP – exposed state) in atomic percentages.

Alloy		C	O	Cr	Mo	Ni	Ti	Fe	Other
738	BS	33.0	7.3	10.3	1.8	38.7	2.0	-	Co (6.9)
	EXP	5.7	59.6	20.5	0.3	4.2	9.8	-	-
625	BS	27.2	8.1	10.9	6.3	44.9	-	1.3	Nb (1.3)
	EXP	5.7	57.8	33.4	3.1	-	-	-	-
MoNiCr	BS	28.7	4.9	3.8	7.4	51.5	-	3.7	-
	EXP	11.3	37.7	8.2	0.3	42.6	-	-	-
800H	BS	15.1	21.6	14.7	-	20.9	0.1	27.5	-
	EXP	6.8	51.9	32.3	-	1.2	1.6	2.0	Mn (4.2)

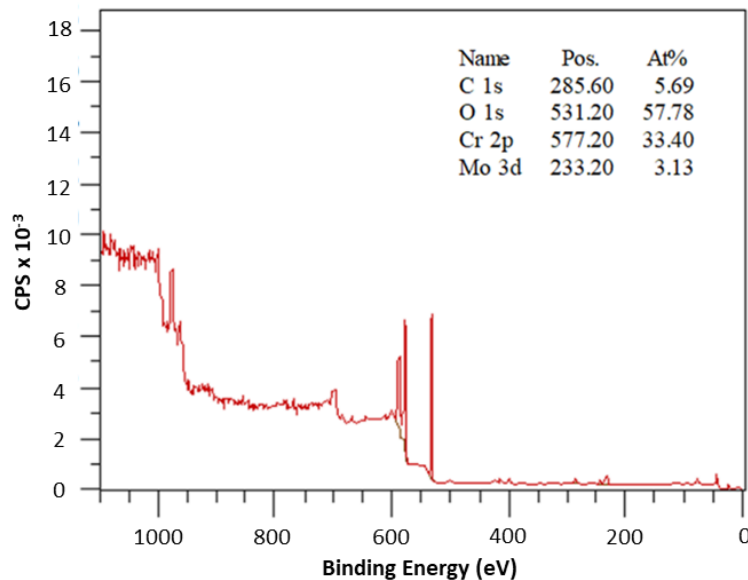


Figure 2 Example XPS spectrum of exposed sample 625(CPS – photoemission intensity in counts per second)

The surface condition of all exposed samples can be seen in the attached SEM photo documentation (**Figure 5**). On the surface of the Inconel 625 sample, no damage is evident from the SEM surface photo-documentation, occasional impurities are visible on the surface (**Figure 5a**), Inconel 738 has a surface covered with a thin layer of corrosion products, the layer is not formed on the entire surface of the sample (**Figure 5b**), the surface of the 800H sample is evenly covered with an oxide layer from the perspective of SEM surface documentation (**Figure 5c**), the MoNiCr sample is affected by local corrosion (**Figure 5d**).

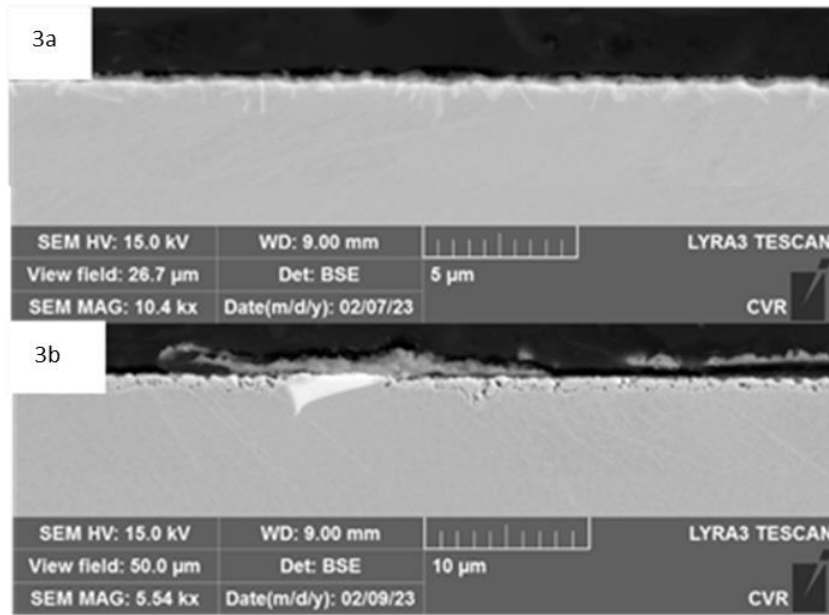


Figure 3 Cross-section of Inconel 625 (3a) and 738 (3b), BSE

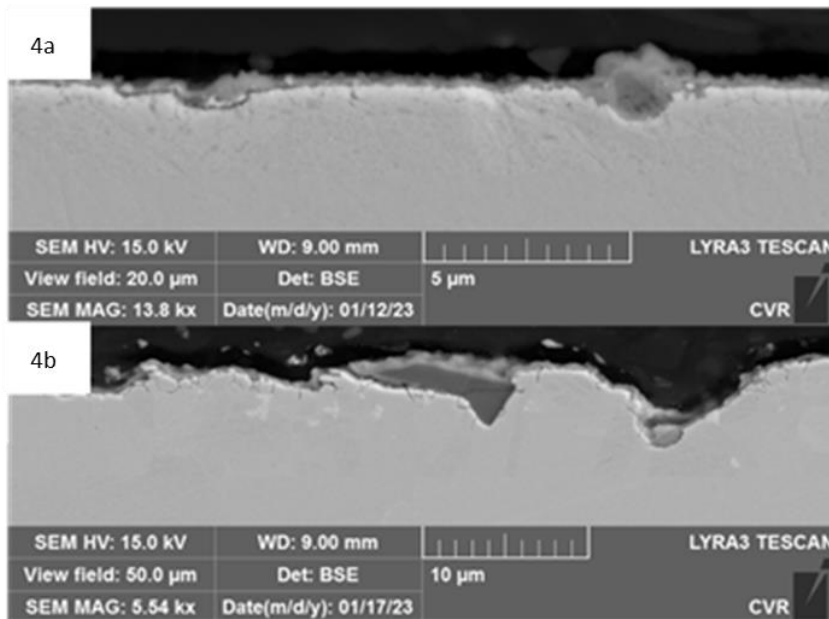


Figure 4 Cross-section of 800H (4a) and MoNiCr (4b), BSE

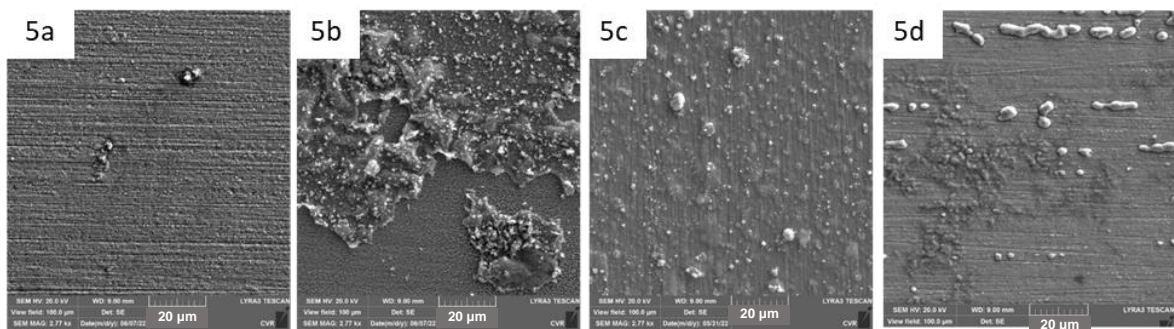


Figure 5 Surface of Inconel 625 (5a), Inconel 738 (5b), 800H (5c), and MoNiCr (5d) after the exposure, SE

3. DISCUSSION

The XPS analyses of the chemical composition of alloys 625 and 738 (**Table 2**) proved the presence of a protective chromium oxide layer, which forms a homogeneous layer and protects the material from high-temperature corrosion and possible pitting corrosion as illustrated in **Figure 3**. However, the impurity content of the flue gas is crucial for pitting corrosion resistance as evidenced by Q. Guo [9], where pitting occurred in the weld area of 625 at lower temperatures (around 200°C) in the presence of H₂S. The effect of impurities will be verified for these two alloys in further exposures.

In contrast to previous Cr-Ni alloys, 800H and MoNiCr alloys contain some iron (more than 39.5 wt.% Fe in 800H), which can complicate the formation of a protective layer during high-temperature oxidation and can lead to breakaway corrosion. Although chromium forms more thermodynamically stable oxides, iron oxides grow faster and create formations with higher iron concentration on the surface. Carbon can pass through the resulting layer, carburization of the base material can occur, and subsequent precipitation of chromium carbides reduces the corrosion resistance of the material. This can lead to pitting corrosion, see **Figure 4**. The ability of the material to form protective layers in a high temperature CO₂ environment is also related to the minimum chromium content, which is reported to be approximately 16 wt% [10,11].

4. CONCLUSION

According to the analyses, a very thin layer of oxides was formed on the surface of the materials after model flue gas exposure. A very thin layer (thickness of about 1 µm) was observed on Inconel 625. A more pronounced inhomogeneous layer was detected (thickness about 3 µm) on the surface of Inconel 738, a thick layer with small pits was observed on 800H, and a localized form of corrosion occurred on MoNiCr.

The nickel-based alloy materials, especially Inconel 625 seems to be more suitable for the model flue gas environment, and their suitability will be verified at 900 °C in further experiments.

ACKNOWLEDGEMENTS

This project TK01030089 was co-financed with the state support of the Technology Agency of the Czech Republic within the Théta Programme

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