

Materials for use in calcium looping technology for CCS – corrosion processes in high-temperature CO₂

Materiály pro použití v technologii karbonátové smyčky pro CCS – korozní procesy ve vysokoteplotním CO₂

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Carbon Capture and Storage (CCS) technologies are a perspective solution to reduce the amount of CO₂ emissions. One of promising methods is Ca-looping, which is based on carbonation and calcination reactions. During both of these processes, especially calcination, high temperatures (650-950°C) are required. This means high demands on the corrosion resistance of equipment materials. Therefore, we carried out a study to suggest materials with suitable properties for calciner construction, which have to be particularly heat resistant: stainless steels (AISI 304, AISI 316L and AISI 316Ti) and nickel alloys (Inconel 713, Inconel 738, Incoloy 800H). A special device simulating calciner environment was built for this purpose. Chosen materials were tested in temperature 900°C, atmospheric pressure and gaseous environment with composition that can be possible in a calciner. The surfaces of materials were evaluated to determine composition and properties of formed oxide layers. High temperature oxidation was observed on all tested materials and oxide exfoliation occurred on some of tested materials (304, 316L).

INTRODUCTION

Post-combustion calcium looping enables to capture CO₂ from flue gases using the principle of CaO carbonation. The product of carbonation – CaCO₃ is moved to another vessel, where calcination takes place. During the calcination pure CO₂ is captured and CaO regenerated, suitable for another cycle of carbonation. Basic equipment for the calcium looping process consists of two vessels. The first one is carbonator, where CO₂ is captured from flue gas in temperature range 450-750°C. In the second vessel, calciner, temperature above 850°C is required [1,2].

High temperatures together with the environment cause higher demands on the corrosion resistance of equipment materials. Although corrosion in pure CO₂ is

Technologie zachytu a ukládání uhlíku (CCS) jsou perspektivním řešením ke snížení množství emisí CO₂. Jednou ze slibných metod je karbonátová smyčka, která je založena na karbonatačních a kalcinačních reakcích. Oba tyto procesy, zvláště kalcinace, vyžadují vysoké teploty (650-950°C). To znamená vysoké nároky na korozní odolnost materiálů zařízení. Proto jsme provedli studii k návrhu materiálů s vhodnými vlastnostmi pro konstrukci kalcinátoru, které musí být především odolné vůči vysokým teplotám: korozivzdorné oceli (AISI 304, AISI 316L and AISI 316Ti) a slitiny niklu (Inconel 713, Inconel 738, Incoloy 800H). Pro tyto účely bylo postaveno speciální zařízení simulující prostředí kalcinátoru. Vybrané materiály byly testovány za teploty 900°C, atmosférického tlaku a v plynném prostředí se složením, kterého může být dosaženo v kalcinátoru. Povrchy materiálů byly vyhodnoceny z hlediska složení a vlastností vzniklých oxidických vrstev. Byla pozorována vysokoteplotní oxidace a na některých z testovaných materiálů (304, 316L) se objevila exfoliace.

almost insignificant, just a slight amount of water can initiate it [3-5]. Flue gas contains also a wide range of other substances, particularly sulphur and nitrogen oxides and Cl compounds, all of which are soluble in water. In the case of water condensation (e.g. shutdown), they can form strong mineral acids. Also CO₂ is soluble in liquid water where it forms H₂CO₃ to cause acidification as well. The condensate can reach pH 3 and even lower. The corrosion rate in CO₂ containing low concentration of water can reach up to 20 mm/y [3]. During CO₂ capture, some part of the aforementioned substances pass also into the outlet gas as impurities, especially humidity, inert gases (N₂, Ar), oxygen and SO₂. In the case of a carbonate loop, they account for approximately 5 mol% of the outlet gas [6]. Thus, the metal surfaces of the equipment used in CCS technologies can be strongly attacked by corrosion during any technical breaks that

require cooling down of equipment. Therefore, materials with good heat and corrosion resistance, such as stainless steels and nickel superalloys, should be used for the equipment construction. These materials have to be tested to prove their resistance and to suggest the most suitable alloy for CCS equipment construction.

A method for reducing corrosion involves the formation of a protective oxide layer. These layers work as a barrier between material surface and environment. Their properties are dependent on many factors, which are generally defined by the interaction of a metal and a certain environment. A good protective layer has to be enough compact, excessive thick layers are problematic, because exfoliation can appear. F. Rouillard and T. Furukawa show in [7] that steels with 9-12 % Cr oxidize and carburize in CO₂ environment within temperatures above 500°C. Thick duplex oxide layers were formed in 500-600°C CO₂. The outer layer is composed of Fe₂O₃ and Fe₃O₄, the inner part of layer contains mixed Fe-Cr spinel oxide. Grains of the outer oxide layers are considerable bigger. For efficient corrosion protection is important especially small-grained spinel oxide layer.

In the Ca looping environment Cr rich carbides can be formed below the oxide layer (Figure 1), while carburization depth grows with time according to a parabolic law [7-9]. The mechanism of carburization in

CO₂ environment is explained in [8] by diffusion of CO₂ species through pores in an oxide layer while reactions (1) and (2) are in local equilibrium.



Because of oxide forming reactions the oxygen potential tends to a low value on the metal/oxide interface. Therefore, carburisation can occur. These microstructural changes have significant influence on the equipment lifetime, because mechanical properties of material are be changed.

In this study we carried out the first exposure of four stainless steels and three nickel alloys (Table 1) to compare their behaviour in 900°C CO₂. This experiment gives information about possible behaviour of materials in calciner environment.

EXPERIMENT

Materials

Stainless steels and nickel alloys were selected for the exposure because of their heat and corrosion resistivity and availability.

The content of alloying metals is summarized in Table 1. AISI 304, AISI 316L and 316Ti are heat resistant stainless steels with good corrosion properties. The nickel alloys are Inconel 713, Inconel 738. Incoloy 800H is an alloy of iron and nickel used in chemical and power industry for high temperature applications.

The material is assigned simply as a nickel alloy in this paper for briefness. Inconel and Incoloy materials are declared to be very stable at high temperatures and they should resist to carburization. Compare to stainless steels their heat resistance is higher [11]. However, stainless steels are machinable more easily and significantly better affordable.

All the samples were polished to 4000 grit surface finish and degreased ultrasonically and by rinsing with ethanol/acetone. For the exposure they were placed into special ceramic holders.

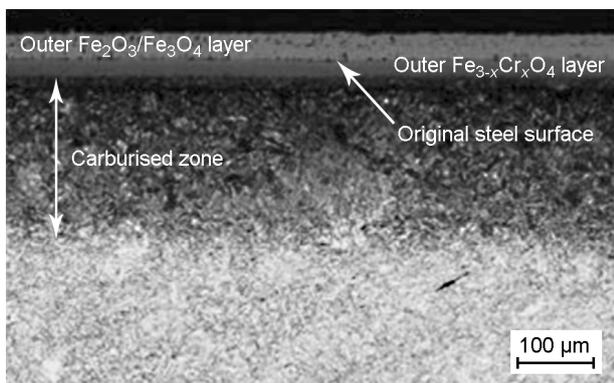


Fig. 1. 12Cr steel cross section after 5000 h exposure in CO₂ at 550°C and 200 bar [7]

Obr. 1. Metalografický výbrus 12Cr oceli po 5000 h expozici v CO₂ za 550°C a 200 bar [7]

Tab. 1. Chemical composition of tested materials (wt.%) [10] / Chemické složení testovaných materiálů (hm.%) [10]

Material	Fe	Cr	Ni	C	Mo	Ti	Al	Mn	Si	Co	W	Ta	S	P
AISI 304	Base	17-19.5	8-10.5	<0,07										
AISI 316Ti	Base	16.5-18.5	10.5-13.5	<0,08	2-2.5	0.4-0.7								
AISI 316L	Base	16.5-18.5	10-12	<0,03	2-2.5			<2	<1				<0,015	<0,045
Inconel 738	<0,35	15.7-16.3	Base	0.15-0.2	1.5-2	3.2-3.7	3.2-3.7			8-9	2.4-2.8	1.5-2		
Inconel 713	<5	11-14	Base	0.02	3.5-5.5	1	5.5-6.5	<1						
Incoloy 800H	>39.5	19-23	30-35	0.05-0.1		0.15-0.6	0.15-0.6							

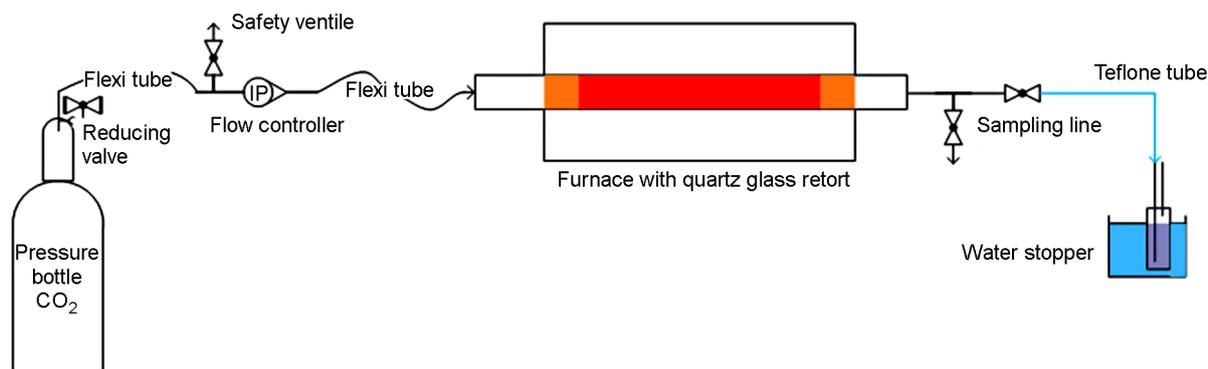


Fig. 2. Experimental device schema
Obr. 2. Schéma experimentálního zařízení

Experimental device

A high-temperature device for corrosion tests was designed and constructed for the Ca looping materials tests (Figure 2). Samples are placed into a tube furnace with retort made of quartz glass, which is fed with CO₂ from a pressure bottle. This type of device is suitable for experiments at high temperatures up to 1000°C and tests in gaseous environment.

Technical carbon dioxide in pressure bottle (purity 99.5 vol.%) was used as working gas. To eliminate adverse effect of ambient air in the system, the quartz glass retort and all tubes were evacuated after placing samples into the furnace and afterwards the system was filled with working gas. Further the system was evacuated and filled with working gas again. The flow of working gas was set by a ball valve and regulated by a small ball valve on a rotameter. The flow of working gas was continuously measured during the experiment by a flow meter.

All the tubes contained in the device are made of stainless steel and flexi tubes are Teflon in core, behind the quartz glass retort was a Teflon tube ended to a water stopper to prevent leaking ambient air to system. The experimental setup was following: the flow of working gas was set to 30 cm³ min⁻¹ directly after settings before experiment. The pressure in the system was reduced to atmospheric pressure by a reducing valve on the bottle with working gas. Warming-up started at 20°C with temperature ramp 5°C per minute to temperature 900°C that was kept for 200 hours. After the experiment was finished, the samples were cooled down within temperature ramp -1°C per minute to final temperature 30°C.

Analyses

The gravimetric data of all samples were evaluated to determine the weight changes of the materials. Further surface analyse was made with scanning electron microscopy (SEM). Microstructures and layers composition were studied using a scanning electron

microscope with electron source tungsten filament (cathode) and energy range 30kV. The elemental microanalysis was made by the method of Energy-dispersive X-ray spectroscopy (EDS).

The top layer of corrosion products created on tested materials was identified by XPS method. Samples were analysed by the XPS with the ESCA Probe P apparatus equipped with Al K α (1486.6 eV) X-ray source with monochromator and a hemispherical analyser. The size of the analysed area is approximately 1 mm². Ar ions of 5 keV energy are used for ion sputtering.

DISCUSSION AND RESULT ANALYSIS

Gravimetry

The gravimetric results (Figure 3) show that all the samples gained a small amount of mass. The most significant mass gain had stainless steels 304 (0.65 g/m² h). This material had excessive thick oxide layer with considerable exfoliation (Figure 4a). Materials 316L, 316Ti and 800H showed exfoliation as well, especially on sides of the samples (Figure 4b). Stainless steel 316Ti has the lowest weight gain (0.09 g/m² h). Both Inconels 738 and 713 had compact oxide layers (Figure

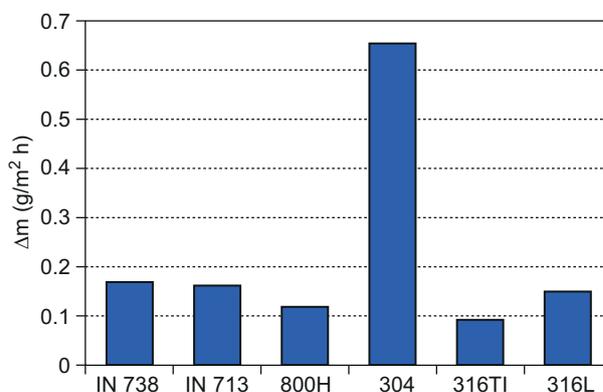


Fig. 3. Gravimetric results
Obr. 3. Výsledky gravimetrie

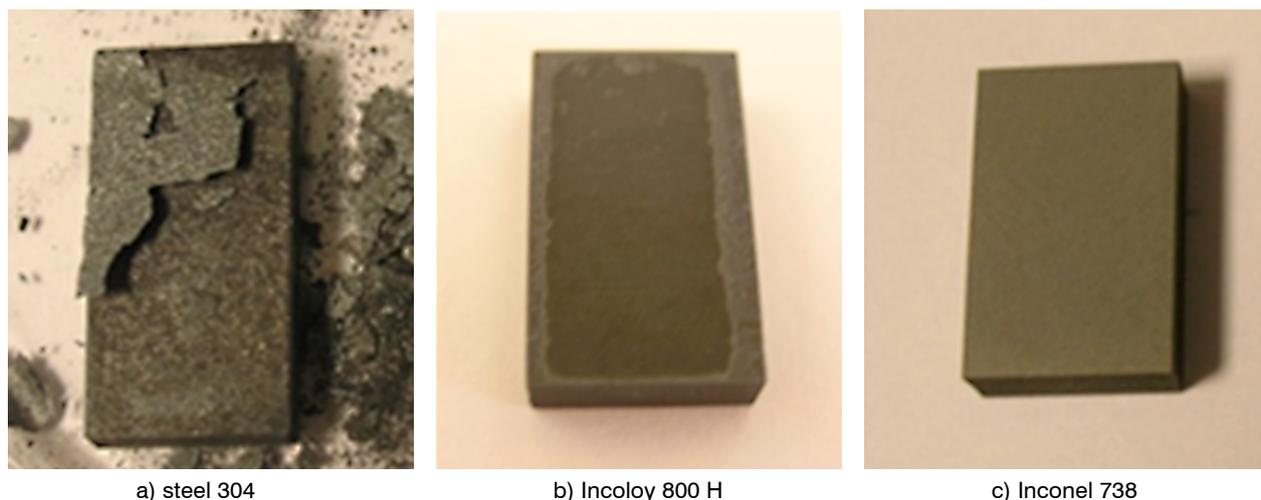


Fig. 4. Materials after 200 h in 900°C CO₂ exposure: a) steel 304; b) Incoloy 800 H, c) Inconel 738
Obr. 4. Materiály po expozici 200 h v 900°C CO₂: a) ocel 304; b) Incoloy 800 H, c) Inconel 738

re 4c). According to these results, we can assume that no corrosion damage of the samples occurred. However, excessive high temperature oxidation was observed certainly on stainless steel 304 and on 316L in lower grade.

SEM-EDS surface analysis

Figures 5-7 show the microstructure of the oxide layers formed on the materials during the exposure in 900°C CO₂ for 200 hours. On the layer of stainless steel 304 is significant exfoliation, the layer is very thick and contains rough grains. EDS analysis showed that the exfoliated parts of layer contained almost only iron oxides, while in the inner layer, which was left on the sample surface, was higher content of Cr, Ni and Mn.

The layers formed on the stainless steels 316L and 316Ti were similar. They both are composed from fine-grained oxide layer on the metal surface and on top of this layer are significant bigger grains of oxides, which are localized regularly. The difference is in the shape of these bigger grains: on 316Ti is the shape cubic, but on the 316L are needle crystals of smaller size. These materials are of very similar composition (Table 1), 316L has slightly lower Ni and C content, but can contain small concentrations of S, P, Mn and Si. Furthermore, several cracks were observed on the oxide layer of 316L. The oxide layer of this material was evaluated as possibly prone to cracking also in [12]. The stainless steel 316Ti is alloyed with 0,4-0,7 % Ti. The oxide layers of both 316 steels contain Fe, Cr, Mn and Ni oxides. In the grains of bigger size were found higher contents of Ni.

All of nickel superalloys formed very fine-grained layers. To see their structures, magnification 1000 times and bigger was used. The most interesting was the layer of Incoloy 800H that was covered with a net-structure of even finer grains (Figure 6b). This layer contained mainly

Cr, Mn and Ti with small amount of Fe, which are usual oxide elements in Ni-Fe alloys [5, 13-15]. Oxide layers of both inconels were formed mainly of Ti and Cr oxides with low amount of Ni. The structures of these layers are even and formed from fine globular oxide particles, that is especially significant on Inconel 713. Particularly the fine-grained structure of the oxides ensures good adhesion of the layer and lower predisposition to cracks of exfoliation appearance.

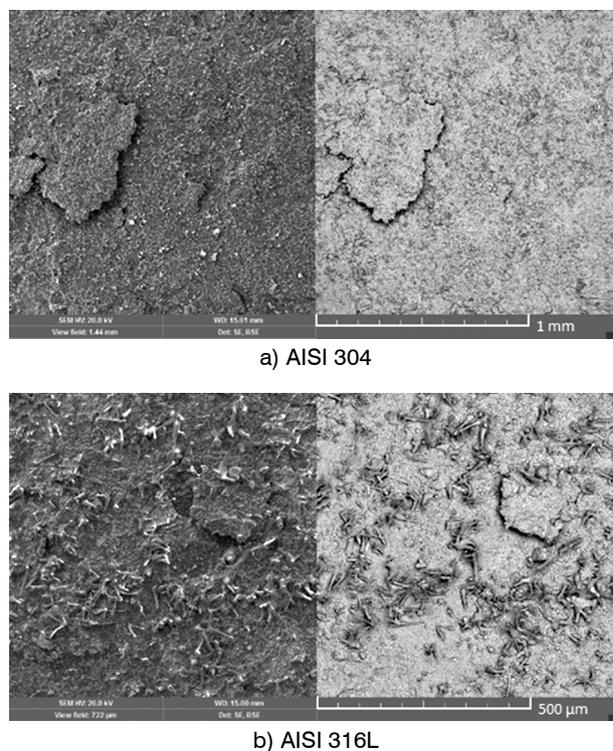
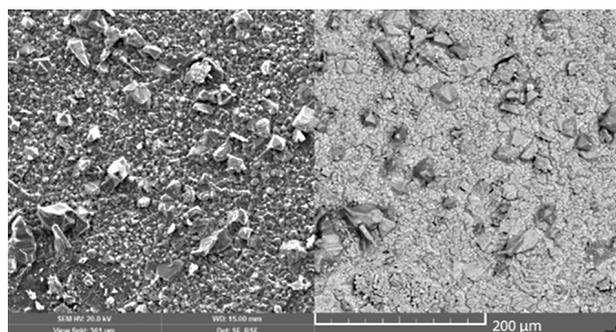
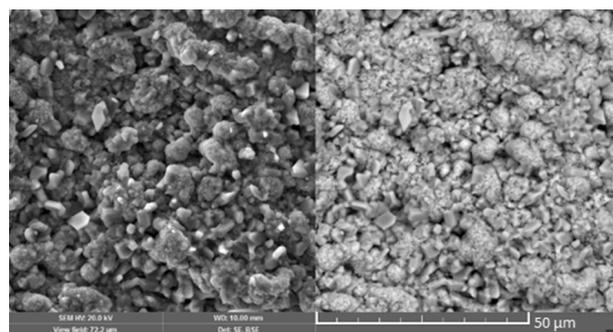


Fig. 5. Microstructures of oxide layers: a) AISI 304, b) AISI 316L

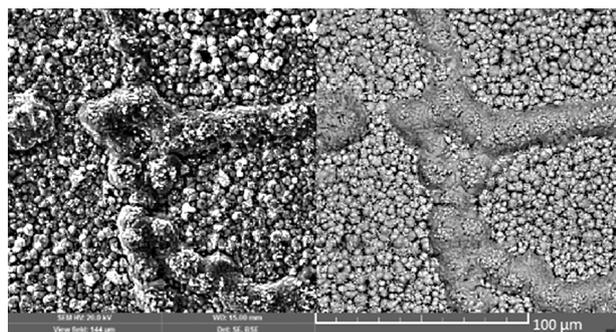
Obr. 5. Mikrostruktury oxidických vrstev



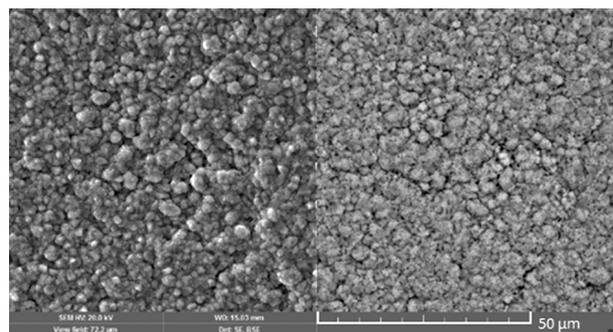
a) AISI 316Ti



a) Inconel 783



b) Incoloy 800H



b) Inconel 713

Fig. 6. Microstructures of oxide layers: a) AISI 316Ti, b) Incoloy 800H

Obr. 6. Mikrostruktury oxidických vrstev

Fig. 7. Microstructures of oxide layers: a) Inconel 783, b) Inconel 713

Obr. 7. Mikrostruktury oxidických vrstev

XPS analysis

On the surface of all samples is present atmospheric contamination C, which can be partially reduced by surface sputtering. Sputtering rate depends on time and on surface structure – sputtering time 10-12 min was chosen for the samples analysed in this study. The basic states of material surface compositions were measured with the

same Ar sputtering time to decrease the influence of the atmospheric C on the content of the other elements. The results are shown in Table 2.

It can be summarized that surface oxidation occurred at all materials in high rate with the obvious migration of following metals: Ti, Cr, Mn, but also Fe. These metals move through material to the surface, where they mostly create oxide layers. Other metals, mainly Ni and Mo are

Tab. 2. Comparison of materials' surface composition before (BS – basic state) and after exposure (exp.) in at.% / Porovnání povrchových složení materiálů před (BS – základní stav) a po expozici (exp.) i at. %

		C	O	Ni	Cr	Mo	Co	Ti	Nb	Fe	Mn
IN1(738)	BS	33.0	7.3	38.7	10.3	1.8	6.9	2.0	–	–	–
	exp.	11.0	59.1	-	2.4	–	–	27.4	–	–	–
IN2(713)	BS	24.7	6.2	55.4	7.2	4.0	–	–	2.5	–	–
	exp.	7.8	58.8	-	18.4	–	–	15.1	–	-	–
304	BS	41.1	2.4	4.6	9.8	–	–	–	–	42.0	–
	exp.	22.2	44.6	4.5	15.9	–	–	–	–	12.4	–
800H	BS	29.3	3.1	22.4	12.3	–	–	–	–	33.1	–
	exp.	7.6	50.2	2.9	12.4	–	–	3.3	–	4.8	18.8
316Ti	BS	30.0	2.0	5.5	12.4	2.6	–	–	–	47.6	–
	exp.	6.4	49.3	2.2	–	–	–	–	–	40.3	1.8
316L	BS	18.4	3.3	7.1	12.1	1.6	–	–	–	57.5	–
	exp.	13.4	59.8	3.6	6.1	0.4	–	–	–	13.8	2.86

in oxide layers present in significantly lower amount compare to the basic metal composition. Ni is less prone to oxidation reactions compared to iron. In the surface of the stainless steel 304 are the most significant peaks of O, Fe, Cr and Ni, which are usual metals present in steel oxide layers. The peaks with the highest intensity in the Inconel 738 spectrum are Cr, Ti and O.

CONCLUSION

To suggest materials behaviour in Ca looping technologies, three stainless steels and three nickel alloys were exposed for 200 hours in 900°C CO₂. This environment is an approximate simulation of ideal calciner conditions. However, the higher content of other substances will be present in real environment, which is the topic of our next research. This experiment was performed as a first test in the device designed for the purpose of testing construction materials for Ca looping equipment.

High temperature oxidation was observed on all tested materials. Furthermore, on the stainless steels 304, 316L, 316Ti and nickel alloy Incoloy 800H appeared different grades of exfoliation caused by excessive thick oxide layers [7]. The exfoliation can lead to equipment damage and regulation devices blocking. Only the samples of Inconel 738 and Inconel 713 had even, coherent layers made of fine-grained oxides with high content of Cr. Therefore, they could be the most promising as the construction materials for the given purpose. However, it is necessary to carry out more tests in different conditions to determine the range of oxide exfoliation of the stainless steels 304, 316L, 316Ti and Incoloy 800H. One of the next goals is to analyse also the carburization of materials tested in this work.

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