TESTING OF CORROSION BEHAVIOR OF NICKEL ALLOYS AT HIGH TEMPERATURES IN MOLTEN SALTS

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Abstract

The use of salt mixtures properties is considered in many future technologies, such as energy storage or medium for nuclear reactors. The key question is to choose a suitable construction material for these devices operating at high temperatures in a corrosive environment. Nickel alloys show high corrosion resistance at high exposure temperatures, and literary sources also describe resistance in the environment of fluoride salts. This work verified the corrosion behavior of two nickel alloys in molten chloride salts. Nickel-based superalloys Hastelloy C22 and MoNiCr were tested in a mixture of chloride salts LiCl - KCl (58.2 - 41.8 wt%). Alloys samples were heated in salt melts for 500 h at 440 °C in an inert atmosphere of argon. After removal, they were analyzed gravimetrically, the composition of the surface layers by the XPS and cross-section of samples using SEM. The gravimetric evaluation showed no significant changes after exposure. This was also confirmed by SEM and XPS results, which demonstrate the formation of very thin layers of nickel and chromium oxides up to 1 μm thick.

Keywords: Nickel alloy, molten chloride salts, corrosion, nuclear reactor

1. INTRODUCTION

The use of nickel alloys is still increasing, mainly due to their high corrosion resistance at high temperatures. The alloys are also resistant to halide salt environments, and therefore the use of nickel alloys is considered in solar power engineering, TES (thermal energy storage), and advanced reactors IV. generation (MSR - Molten Salt Reactor). Fluorides, chlorides, and nitrates are particularly suitable salt mixtures for these technologies. The basic criteria for their selection are thermal stability, low melting point, heat capacity, and other physico-chemical parameters. The most frequently mentioned mixture of fluoride salts in connection with MSR is the binary mixture FLiBe ($LiF-BeF_2$, 67-33 wt%) [1-3]. A mixture of chloride salts LiCl-KCl (58.2-41.8 wt%) was used in this work. Chloride salts are more advantageous mainly due to their low cost, availability, and low melting point. On the other hand, the disadvantage is that chlorides can cause pitting corrosion, which can occur on a surface with a locally damaged passive layer. Chloride corrosion can be reduced by the use of high-alloy steels, by increasing the content of chromium, molybdenum or nickel, and by using high-purity salt mixtures. Impurities such as moisture and oxygen can significantly reduce the corrosion resistance of materials. In general, corrosion in halide salt melts is strongly dependent on impurity concentration, temperature gradient, and activity gradient [3].

2. EXPERIMENT DESCRIPTION

Experimental apparatus was designed and assembled to study the corrosion resistance of materials in salt melt environments (**Figure 1**). The device allows high-temperature exposures (up to about 600 °C) with flowing inert gas argon and operating at a slight overpressure (in this experiment about 0.2 MPa). The main component is a high-temperature tubular autoclave made of AISI 304 stainless steel, with an external ceramic heating system from easytherm.cz s.r.o. and lids sealed with carbon ring seal. In the lid, there is a working gas inlet and outlet and an inlet for a temperature sensor. Inside the autoclave, there is a compartment for test samples. The gas outlet and inlet routes, including valves and sampling points, were constructed from high-temperature and high-pressure stainless-steel connecting components. The inert gas line also included air-water cooling to prevent overheating of components outside the autoclave. At the end of the route, air backflow into the autoclave interior was prevented by a water seal, which also served as a gas flow control device.

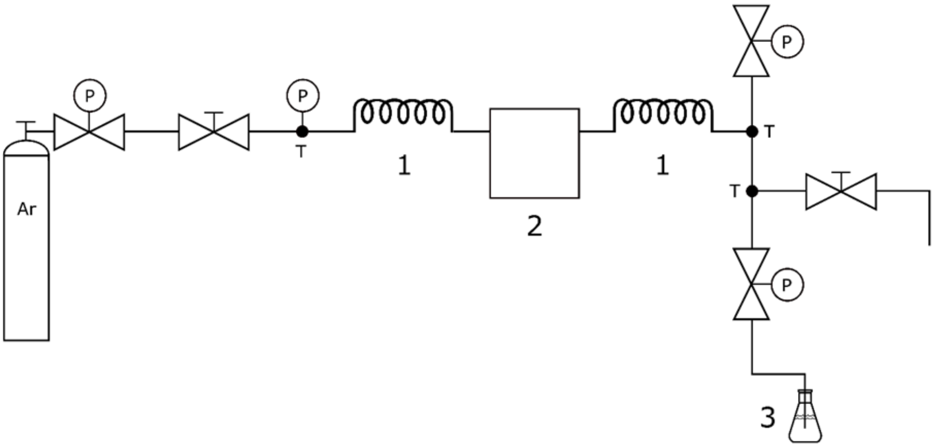

Figure 1 Scheme of experimental device for molten salts environment. 1) air-water cooling 2) high-temperature autoclave with internal sample space 3) water seal. (P) pressure equipment: pressure relief valve/pressure gauge, (T) pipe tee fittings [4]

In the autoclave part of the apparatus, samples of nickel alloys were placed in corundum crucibles with 10 g of the model mixture LiCl - KCl (58.2 - 41.8 wt%). The samples were exposed for 500 hours at a constant temperature of 440 °C and a pressure of 0.2 MPa in an inert flowing atmosphere (argon). Samples of nickel alloys C22 and MoNiCr measuring approximately 10 x 10 x 3 mm were wet-polished with 2500-grit abrasive paper before exposure, degreased in an ultrasonic bath in acetone for 15 min. Next, the samples were accurately measured and weighed for post-exposure gravimetric evaluation of corrosion losses.

The C22 alloy is highly resistant to corrosion, even in solutions containing chlorides. MoNiCr alloy is the trade name of the Czech experimental nickel alloy of the company Skoda JS a.s., which is highly corrosion-resistant in fluoride salt environments and high-temperature applications. The chemical composition of the tested materials is shown in **Table 1**.

Table 1 Composition of tested materials (wt%) [5,6]

Alloy	Cr	Ni	C	Mn	Fe	Si	Mo	Ti	Co	W	V	S	P
C22	20.0-22.5	50.0-63.0	0-0.015	0-0.5	2.0-6.0	0-0.08	12.5-14.5	-	0-2.5	2.5-3.5	0-0.35	0-0.02	0-0.02
MoNiCr	6.0	71.8	0.02	0.09	3.0	0.03	19.0	0.03	-	-	0.01	-	-

The desired experimental temperature was achieved gradually with a temperature ramp of 5 °C per minute, and a constant temperature was maintained inside the autoclave for 500 hours. Inert gas flowed through the interior throughout the exposure of the samples. The cooling of the device was also gradual with a temperature ramp of 1 °C per minute. The reason is the protection of potentially different temperature-expandable oxide layers formed on alloy samples, which could crack due to rapid cooling. The consequence could be the destruction of the layers or their exfoliation, which would affect the subsequent assessment of the condition of the surfaces.

The samples were mechanically removed from the corundum cups after the exposure. Residual salts were removed with distilled water, cleaned with acetone, and placed under vacuum. After that, gravimetry, XPS (X-ray photoelectron spectroscopy) analysis of the sample surface, and SEM (Scanning Electron Microscopy) analysis of the surfaces and cross-sections of the samples were performed.

3. DESCRIPTION OF RESULTS

The gravimetric evaluation did not show relevant weight changes after exposure. According to the surface analysis, the resulting oxide layers were very thin and therefore the mass changes of the samples were outside the detection limits and therefore inconclusive. The weights before and after exposure of each sample are shown in **Table 2.**

Table 2 Weights of alloy samples (m_0 - sample weights before exposure, m_{500} - sample weights after exposure, m_X - weight difference)

Material		**m_0 (g)**	**m_{500} (g)**	**m_X (g)**
C22	**Sample 1**	1.9626	1.9624	0.0002
	Sample 2	2.2179	2.2178	0.0001
MoNiCr	**Sample 1**	3.3975	3.3975	0
	Sample 2	3.2565	3.2564	0.0001

Table 3 Results of the composition of the sample surfaces by the XPS method (GS - ground state, EXP - exposed state) in atomic percentages

Alloy		**Cr**	**Ni**	**C**	**Fe**	**Mo**	**O**	**Co**
C22	**GS**	11.2	39.7	28.9	1.1	12.4	3.8	3.0
	EXP	9.6	33.2	28.1	2.7	7.8	17.3	-
MoNiCr	**GS**	3.8	51.5	28.7	3.7	7.4	4.9	-
	EXP	4.3	40.8	7.5	-	8.9	33.8	-

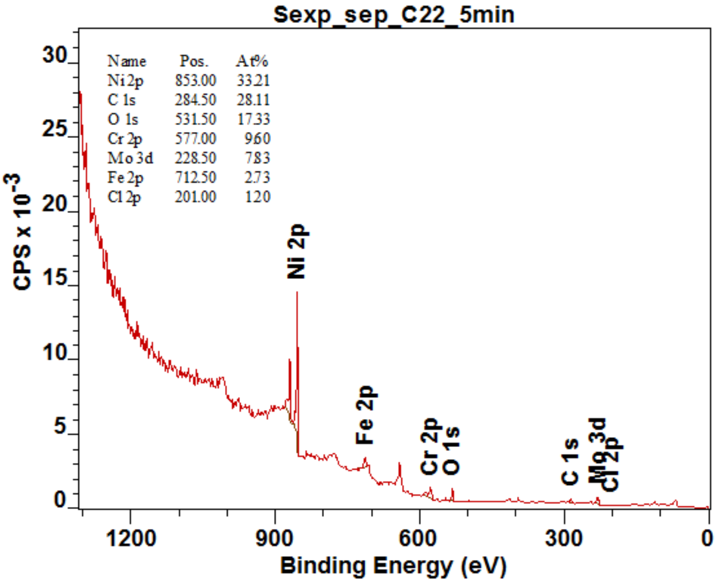

Figure 2 Example XPS spectrum of exposed sample C22 (CPS - photoemission intensity in counts per second)

The samples were analyzed by XPS without and after argon-ion sputtering. The table of results of XPS spectra (**Table 3**) shows the formation of tenuous oxides layers on the surface of exposed materials. After exposition, the surfaces of both materials were mainly composed of NiO oxide and Cr_2O_3. Fe (in the case of the C22 sample) and Mo were also detected. 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 is also deposited from the residual atmosphere in vacuum chambers [7]. Example XPS spectrum of exposed sample C22 is shown in **Figure 2.**

Analysis of the surfaces and cross-sections of the samples was performed using SEM. Analysis showed a very thin layer of damaged material less than 1µm for sample C22 (**Figure 3**) and less than 0.5 µm for sample MoNiCr. In the MoNiCr sample cross-sections, inhomogeneities were found below the surface of the material (at a depth of approximately 0.5 µm), which will be further analysed by EDS analysis (**Figure 4**).

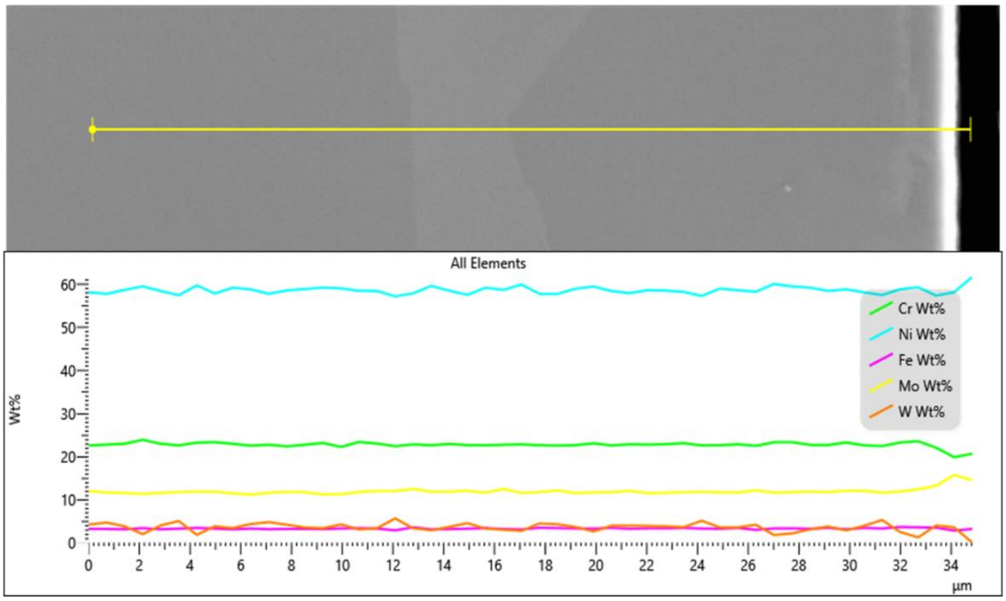

Figure 3 Example SEM line scan of exposed sample C22

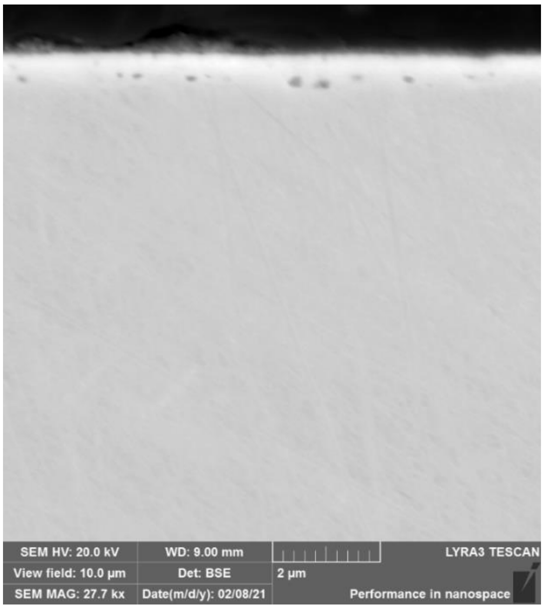

Figure 4 Cross-section of MoNiCr sample after exposure (by SEM)

4. CONCLUSION

As part of the presented work, an experimental device for high-temperature testing of structural materials for technologies using molten salts was designed and constructed. The investigated candidate materials demonstrated high corrosion resistance, very thin homogeneous layers of oxides with a maximum thickness of 1 µm (C22 sample) and 0.5 µm (MoNiCr sample) were formed on their surface.

The basic composition of the surface layers was determined by the XPS method, and the structure of the layers by the SEM method. During the XPS analysis, it was revealed that a more detailed determination of the composition and, above all, of the ratios of individual metal bonds in the surface layers is very complicated due to the overlapping of the individual measured peaks. In the next step, deconvolution of the detailed XPS spectra will be performed to determine the proportion of mixed metal oxides and chlorides, respectively.

From a corrosion point of view in a LiCl-KCl salt environment under an inert gas atmosphere, the tested materials can be suitable construction material, however, it is necessary to verify material behaviour and subsurface damage after extended exposure, its durability in a radiation environment, and a salt environment containing impurities. Above all, the moisture in the salts and the oxygen content in the atmospheres of the salt installations will have a significant influence on the corrosion behaviour of the alloys.

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