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INFLUENCE OF CHROMIUM SALTS ON CORROSION OF INCOLOY 800 H/HT ALLOY IN FLUORIDE EUTECTIC MELT FLINAK

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ABSTRACT

The effect of three chromium salts - potential impurities was analysed with the assumed effect of increasing the corrosion efficiency of eutectic mixture FLINAK on model alloy Incoloy 800 H/HT. The chromium salts additions, namely $CrF_3.3H_2O$, CrF_3 and Cr_2O_3 were used to observe their corrosiveness through dependence on the weight loss of the samples. The SEM observations of the surfaces showed corrosion attack on all samples. The surfaces of the samples, which was exposed to concentrations of 1 mol% and 3 mol% of hydrated CrF_3 appeared to be most damaged in comparison with all other FLINAK mixtures. The SEM-EDS cross-sections showed dealloying of the chromium and enriching of nickel, which is in agreement with general corrosion theory and theory of electrochemical row of standard reduction potentials of the elements. The process of forming corrosion products was demonstrated by WD-XRF complementary analysis of the mixtures after corrosion. The higher chromium and iron content in the mixtures meant a higher weight loss of material. Gravimetric analysis shown strong dependence of weight changes on concentration of added salts. The mass loss of the material with acidic or hydrated salts is several times higher than that with oxides. It is assumed that the main corrosion mechanism involves the formation of gaseous HF, which preferably reacts with the alloying element to form more volatile or, conversely, precipitated corrosion product depending on Gibbs formation enthalpy. In the case of artificial addition of oxides to molten mixture, it will be one of a crucial factor that has to be taken under consideration to suppress the corrosion reaction when it's detected in power plant's corrosion protection system in the future.

KEY WORDS: *high-temperature corrosion, molten salts, fluoride salts, additions, impurities, chromium salts, superalloy, Incoloy, mass loss, gravimetry, SEM-EDS.*

INTRODUCTION

Corrosion is a complex process that involves the electrochemical and biological reactions, geometry and tribological factors as well as mechanical and microstructural properties. Corrosion is an undesirable process and can be prevented by understanding of the corrosion mechanisms. Modeling conditions and materials may be preferred for laboratory testing.

Molten salts reactors are considered as one of the future possible alternatives for green energy. These reactors would have better properties in all respects, e.g. use variety of compositions of molten fuel, wide choice between used materials, amazing safety and economic aspects [1, 2]. For such a great challenge is necessary to use construction materials that withstand high temperatures but also be highly corrosion-resistant with long lifetime.

Incoloy 800 was considered in early-stage developing of molten salts reactors as very good replacement for stainless steels. At that era were developed many other alloys based on nickel, so-called superalloys, e.g. Hastelloys, Monels, Inconels, etc, but Incoloy 800 still remain as good initial-model alloy.

The fluoride mixtures and superalloys will be used in the near future for 4th generation molten salts nuclear reactors and have been studied by various authors from different perspectives [3-5]. In the same way, the eutectic mixture of fluorides LiF, NaF and KF (46.5 – 11.5 - 42 mol%) was developed for transferring huge amount of heat from first loop of nuclear reactors to theirs heat-exchangers. This mixture is well-known on the world's market as FLINAK. FLINAK serve also as very good model high-temperature mixture for corrosion testing [6, 7].

The authors deal with corrosion from a wide variety of interesting perspectives. The literature describes problems with humidity of fluoride salts [8], atmosphere moisture [9], purifying [10], oxide and non-oxide impurities [1, 3, 11], or fission elements [12].

Indeed, much has been published in general about corrosion, but still, adding possible corrosion products as initial impurities at the beginning of corrosion process could led to a new observations and better understanding of corrosion mechanism [1, 3, 7, 11]. This partial work studied influence of selected additives on corrosion of the model alloy INCOLOY 800H/HT in FLINAK. Three chromium additives were selected for observing the effect of possible formation of oxygen and hydrogen compounds and their subsequent effect on further corrosion. The effect of these compounds could result in increased corrosion, at least according to general corrosion theory, but a mechanism is being sought as well as a way to reduce environment's corrosion impact.

MATERIALS AND METHODS

Incoloy 800H/HT alloy (Bibus Metals ag, Switzerland, cold drawled, annealed at 1125 °C, average grain size EN 10204 - 3.1B, composition: 48% Fe / 20% Cr / 30% Ni, other minor elements together less than 2%: Ti, Al, Cu, Mn, Si, C, S) with a diameter of 12 mm was used. The alloy was cut on pieces on laboratory cutting machine IsoMet 5000 (Mitar s.r.o., Slovak Republic). The samples were polished on grinding SiC papers (up to 2000). The samples dimensions were measured by digital micrometer (Bernardo Machinen, Austria, accuracy 0-100/ 0.001 mm). Consequentially, the samples were placed in an ultrasonic cleaner, rinsed with deionized water, dried in acetone, weighed (Pioneer PA214C, OHAUS Corp., USA, readability 0.0001 g) and then transferred to a glove-box for later use.

Used chemicals: CrF_3 (purity: 99%, supplier: Alfa-Aesar), $CrF_3.3H_2O$ (purity: 99.9%, supplier: Alfa-Aesar), Cr_2O_3 (purity: 99.6%, supplier: Alfa-Aesar), LiF (Sigma Aldrich, CAS: 7789-24-4), NaF (Alfa Aesar, CAS: 7681-49-4), KF (Acros chemicals, France) and KHF_2 (Lachema, Czech Republic), all with a purity $\geq$ 99%. Potassium fluoride was dried under vacuum at 200 °C. Eutectic mixture FLINAK (LiF 46.5 – NaF 11.5 – KF 42 mol%) was made in glove-box under high-purity argon atmosphere (purity 99,9999 % Messer Tatragas s.r.o., Slovak Republic) and low oxygen and water content, both kept less than 10 ppm. Every experiment consisted of weighting 25 g of FLINAK and the appropriate addition of chromium salt. All chemicals were added to the FLINAK mixture at concentrations of (0.5 $\rightarrow$ 1 $\rightarrow$ 3 $\rightarrow$ 5) mol%. Each sample was inserted into the mixture and remain completely covered under the mixture.

All groups of testing were performed in laboratory-made water-cooled resistant furnace connected with glove-box. The tests were performed in sintered Al_2O_3 crucibles (Brisk, s.r.o., Czech Republic). The temperature of the furnace was slowly increased by a ramp of 3 °C for minute, because the crucibles of sintered alumina hardly tolerate rapid heating. The temperature was maintained at 650 °C $\pm$ 2 °C with holding-time 8 h at a moment that planned temperature was reached. The samples were spontaneously cooled and after removed from mixture, placed in a boiling 1 molar $Al(NO_3)_3$ aqueous solution to remove fluoride residue. The same cleaning and weighting procedures were performed as at the beginning of the experiment. The value for each mass loss was obtained by averaging the weights of the samples from three separate experiments.

SEM-EDS observations of samples surface were provided on JEOL JSM-6610LV with EDS analyzer OI X-max 80 mm^2, at HV mode, 4.0 nm (30 kV), standardized on Ni, Fe and Cr with INCAEnergy+ software. The XRD analyses with step of 0.26 and in the range of 7-70 Å, cooper (Cu) anode lamp, were done on Panalytical Empyrean and evaluated on HighScore Plus software with COD_2016 reference database. The WD-XRF analyses were done on ARL Advant'X Intellipower 3600 Thermo Scientific with Rh anode in RTG lamp, output 3.6 kW, program UniQuant using standards CAL.222, 223, 227, 230, 240, 242, 250, 274 and 279. The pearls for WD-XRF were made by mixing of 7 g borax (anhydrous Na2B4O7, purity 99.5% metal basis, Alfa Aesar GmbH, Germany, CAS: 1330-43-4) and 1g of chosen mixture in PtAu5 crucible. The mixtures were homogenized on the machine Claisse® M4™ Fluxer on 1000 °C using propane-butane gas (Flaga s.r.o, Slovakia) and spontaneously cooled in pearl form crucible.

RESULTS AND DISCUSSION

The effect of few chemically similar compounds with alloying element, in this case of chromium, was chosen to observe. On the base of composition of alloy Incoloy 800 H/HT, it was possible to take into account chemically stable $CrF_3.3H_2O$ and for comparison, water-free CrF_3. The effect of the mixture 0.4 wt.% CrF_3 + FLINAK was already mentioned here [13] in terms of simple corrosion comparison between Hastelloy-N and stainless steel 316. The findings of the authors were in

good agreement with the findings of other published works. The effect of chemicals similar to the alloy's elements such as Cr, Fe and Ni has been reported in previous work [1].

This work extends it for comparison of bonded water and bonded oxygen content, which are the most common contaminants and cause the greatest complications in chemistry of molten salts. Since oxygen occurs predominantly in its natural form (-II), there was no problem finding a suitable complement to CrF_3, in this case Cr_2O_3. Hydrogen was not used as a hydride, due to the assumed strong influence on the corrosion mechanism act as a strong reducing agent and also for its rapid decomposition at higher temperatures.

Without any obstruction it must be said that the use of all corrosion accelerators led in all cases to a significant increase in the corrosion of the material compared to the loss of corrosion using pure FLINAK mixture (Fig. 1).
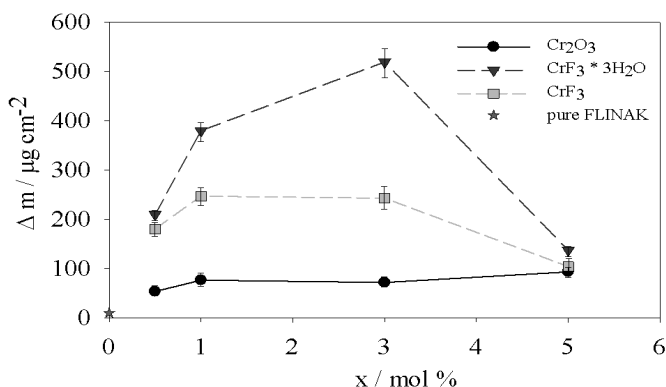

Fig. 1. Dependence of mass loss of Incoloy 800 H/HT on loads of chromium salts into the FLINAK (at 650 °C, 8 hrs holding times).

The samples in the mixtures with hydrated chromium fluoride showed the highest corrosion losses. Additionally, the highest corrosion losses were observed at concentrations of 1 mol% and 3 mol% of $CrF_3.3H_2O$. In all cases a similar type of uniform pitting corrosion was shown, which we chose to show the SEM-EDS analysis of the mixture 3 mol% $CrF_3.3H_2O$ + FLINAK on Fig. 2.
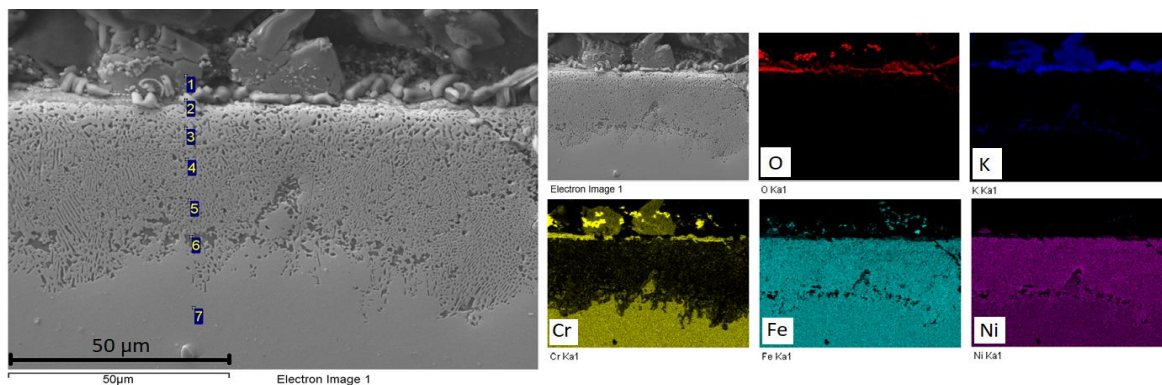

Fig. 2. SEM-EDS scan (left) and elements mapping (right), sample after corrosion with addition 3 mol% of $CrF_3.3H_2O$ into FLINAK.

Also in all cases, analyzes showed selective corrosion which was proven by creation of chromium-depleted zone which became nickel-rich zone. In Fig. 2 element mapping could be observed small amount of chromium oxide, which could be created by reaction of released water with chromium. It should further be investigated whether chromium originally belonged to the alloy or, more probably, came from the added chemical. Paradoxically, the formation of insoluble Cr_2O_3 could explain the weakening of corrosion at a concentration of 5 mol% $CrF_3.3H_2O$. Similar effect with using addition of 5 mol% anhydrous CrF_3 was also observed. The dampening was probably due to pre-saturation of the mixture and significant shift in the internal reactions. The corrosion of the material in FLINAK with the addition of anhydrous CrF_3 and its hydrate was in all cases higher than corrosion with Cr_2O_3.

The critical effect of oxygen on corrosion increase by using chromium oxide in the FLINAK melt has not been demonstrated. To further demonstrate such an effect, a combination with lithium, sodium and potassium oxide could be used in further works. The chromium oxide, in all cases, only slightly increased the mass losses of alloy in comparison with mass loss in pure FLINAK. In all cases, the measurement deviations were very small, so it can be said that all measured values were very similar. In addition, the separation of the colors of the initially homogenous mixture into green and white region was also confirmed by visual observation at all chromium oxide additions. The XRD analysis of mixture with 5 mol% of Cr_2O_3 confirmed that the chromium oxide with traces of lithium and sodium fluorides are located in the green zone (Figure 3 *a*), while only potassium fluoride (KF became hydrated probably during transfer and handling), while lithium and sodium fluoride without chromium oxide were confirmed in the white zone (Figure 3 *b*).
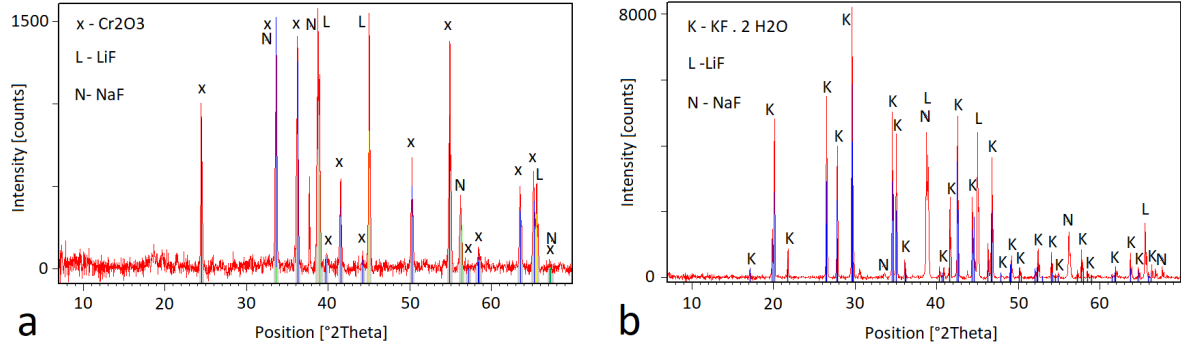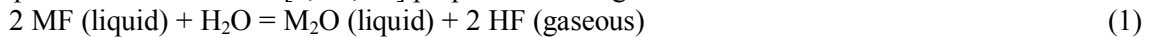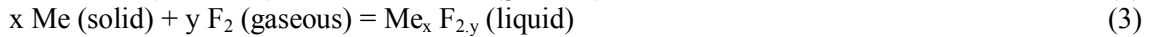

Fig. 3. The XRD post-analysis of the mixture 5 mol% Cr_2O_3 + FLINAK: *a*) the "green" zone and *b*) the "white" zone.

All above-mentioned facts may indirectly lead to the fact that chromium oxide is probably sparingly soluble even in such an aggressive mixture as the molten fluoride mixture and all corrosion of the material is caused only by FLINAK itself. Mentioned facts are also in some correlation with LPR data obtained by these authors [14] who used Cr_2O_3 as sealant. The value of E(corr) of anodized aluminium alloy with Cr_2O_3 was halved with comparison with pure aluminium alloy. This means that the reactivity of Cr_2O_3 is so very low that it could even be used as a protection in aggressive fluoride environments where conventional ceramic materials usually fail.

The chromium fluoride hydrate was proven to be stable up to 200 °C by differential thermal analysis (Derivatograph Q-1500, MOM, Hungary) using air atmosphere and alumina crucibles. Thermogravimetrically was found that above this temperature water is released in a single step. By post XRD analysis after heating on derivatograph was observed amorphous product which may could be CrO_2F_2 according to [15]. This suggests that water, which is likely bound by a chemical bond, may react with the mixture to form acidic potassium fluoride (KF.HF = KHF_2) upon release at higher temperatures. The authors [9, 11, 16] propose following reactions:

$$2\ MF\ (liquid) + H_2O = M_2O\ (liquid) + 2\ HF\ (gaseous) \tag{1}$$
M = K, Na, Li
$$Me + x\ HF\ (dissolved) = MeFx + x/2\ H_2\ (gaseous) \tag{2}$$
$$x\ Me\ (solid) + y\ F_2\ (gaseous) = Me_x\ F_{2.y}\ (liquid) \tag{3}$$
$$MeF_2 + H_2O = MeO + 2\ HF \tag{4}$$
Me = Cr, Ni, Fe, others
$$H_2O\ (gaseous) + 2\ F^- = 2\ HF\ (gaseous) + O^{2-} \tag{5}$$

The metal, which is soluble in fluoride salt and rapidly react with HF yields metal fluoride plus hydrogen [17]. Moisture in salts leads to the formation of HF, which increases further corrosion [18]. From the Fig. 1 is possible to observe that at 5 mol% the corrosion effects on the samples weakens. On the basis of calculated phase diagrams [19] it can be argued that in the case of using a chromium compounds in such the high concentrations could lead even to another corrosion products:
$$CrF_3 + FLINAK = Li_3CrF_3\ /\ Na_3CrF_3\ /\ K_3CrF_6 \tag{6}$$
However, selective corrosion also take place [20]:
$$2\ Cr^{3+} + Cr^0 = 3\ Cr^{2+} + 2\ (e-) \tag{7}$$

And consequently, with taking into consideration of more-negative Gibbs free energy of formation for CrF_2, these authors [21] propose the calculation which was performed for the concurrent dissolution of both elements from the alloy:

$$(1-x)\ Ni\ (alloy) + x\ Cr\ (alloy) + F_2\ (gas) = (1-x)\ NiF_2\ (solid) + x\ CrF_2\ (solid) \qquad (8)$$
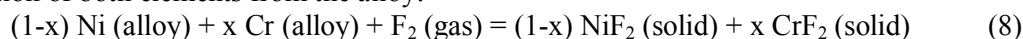
The WD-XRF analyses of the mixtures are summarized in Table 1. The differences in the contents of the elements are indicated by the corresponding color.

Table 1: WD-XRF element analysis of the mixtures after experiments (values are in weight %)

	FLINAK	0 mol% adds	3 mol% Cr_2O_3	3 mol% CrF_3	3 mol% $CrF_3.3H_2O$	5 mol% $CrF_3.3H_2O$
F	7.810	7.500	7.380	6.300	5.230	7.710
Na	61.760	62.590	64.470	67.250	66.280	64.830
K	29.670	28.890	24.170	21.860	19.590	26.040
Al	0.234	0.314	0.484	2.040	1.160	0.361
Si	0.204	0.210	0.228	0.289	0.262	0.223
Ca	0.074	0.218	0.207	0.941	0.413	0.446
Cr	0.000	0.004	0.897	2.720	6.630	5.049
Fe	0.028	0.031	0.040	0.090	0.128	0.089
Ni	0.003	0.000	0.004	0.003	0.011	0.000

In first row are inserted information about analyzed mixtures. That is, the name FLINAK is in fact a pearl formed by mixing 7g of borax and 1g of a mixture, i.e. FLINAK, which was taken from original bottle and served as a reference pearl. The next column are values of the FLINAK mixture after corrosion without any additives, correspond to a point close to zero in Figure 1. The other columns also correspond to their nominal points in Figure 1. The values indicate that Cr_2O_3 is unlikely to be involved in the corrosion process, or very little, thus supporting the above-mentioned findings. Interestingly, with chromium fluoride and also its hydrate, the aluminum, iron and calcium contents are increased. The aluminium is a component of the crucibles and it is well-known information that alumina could react with fluorides. The presence of calcium cannot be deduced, except that it may have been present as a sintering agent in crucibles together with silica and at the same time has a higher affinity to react with impurities in the melt. Higher amount of iron is due to the above-mentioned corrosion reactions (2), (3). The iron fluorides have a more negative Gibbs formation energy and are therefore more willing to react in a fluoride melt than nickel. Thus, the equation (8) also applies to iron rather than nickel. However, from the analysis of 3 mol% $CrF_3.3H_2O$ with corresponding to the highest corrosion losses of the material, it can be deduced that nickel is also involved in the corrosion process. It means that all reactions take place simultaneously but with a preferential tendency towards the content of the corrosive medium and the composition of the alloy and the holding material used.

CONCLUSIONS

The effect of three chromium salts - potential impurities was analysed with the assumed effect of increasing the corrosion efficiency of eutectic mixture FLINAK on model alloy Incoloy 800 H/HT. Salts containing chromium, oxygen, fluorine and water, namely $CrF_3.3H_2O$, CrF_3 and Cr_2O_3 were used to observe their corrosiveness through dependence on the weight loss of the samples.

One of the main ideas of this work was search for corrosion suppressor that could be added into the system to reverse or slow down overall corrosion process and showed important way to the future conversion of soluble products to insoluble products when cleaning coolants in 4th generation nuclear reactors.

It was proven that the mass loss of the material depending on the:
- presence of impurities (acidic, hydrated or alloying-element salts);
- concentration of the additive / impurity used;
- dealloying of chromium from surface layer of the samples;
- all reactions, which take place simultaneously according to a preferential content of the elements in the mixture, the alloy and the holding materialж
- higher weight loss of material resulting to the higher chromium, iron and nickel content in the mixtures after corrosion demonstrated by WD-XRF.

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