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Corrosion tests of various alloys in fluorides of lithium, sodium and potassium (FLiNaK) medium for molten salt reactors in the temperature range of 550-750ºC using electrochemical techniques

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Hydrogen (H_2) is an alternative to petroleum based environment polluting transport fuel. High temperature process heat in the range of 500-1000°C is needed for (H_2) production by water splitting. This heat can be generated in molten salt nuclear reactors. Compatibility of materials is a bottle neck problem in this process. Corrosion behaviours of different alloys have been evaluated in fluoride eutectic FLiNaK in the temperature range of 550-750°C under static and dynamic conditions. Electrochemical polarization and impedance techniques have been used to estimate corrosion rate. The results show that the corrosion process is controlled by activation and in some cases by formation of passive layer. In static mode, the corrosion rates followed the order: Inconel 625 > Inconel 617 > Inconel 600 > Incoloy 800 > Ni 220 > Hastelloy N > Incoloy 800 HT. In dynamic mode, Haselloy N and Incoloy 800 show better corrosion resistance in comparison to other alloys.

Keywords: FLiNaK, Fluorides, Molten salt, Alloys, Corrosion

There are no standard commercially available high-performance heat transfer fluids beyond 600°C. High pressures associated with water and gaseous coolants (such as helium) at elevated temperatures impose limiting design conditions for the materials in most energy systems. Molten fluoride salts have been proposed for use as primary reactor coolants media for transfer of high temperature process heat from nuclear reactors to hydrogen production facilities[1]. These salts are characterized by high thermal conductivities, high specific heats, low viscosities, low vapour pressures and high boiling points. Materials corrosion has however been recognized as an issue in molten fluoride salts. In the studies performed by National Aeronautic and Space Administration (NASA), it was concluded that the tendency for common alloying constituents to corrode in molten fluoride salts increased in the following order: Ni, Co, Fe, Cr, and Al, with Al being the most prone to dissolution. In Fe–Ni–Cr based alloys, the primary constituent that is most prone to dissolution is Cr[2-4]. With fluoride salts, the rate of corrosion is higher due to carbon content of the alloys because of the formation of Cr-carbide phase at the grain boundaries[4,5]. Olson *et al.*[6] performed corrosion studies in molten fluoride salts and found that the Ni-plated Incoloy-800 H showed a remarkable corrosion resistance as compared to the un-plated Incoloy-800H. Graydon *et al.*[7] carried out corrosion testing of Inconel-600 with the FLiNaK at 700°C and observed that the specimen coupon had an affected depth of approximately 250 micron for the 90 days test. A test facility has been constructed to study the in-situ corrosion behaviour of various alloys in the molten salt environment using the eutectic mixture of fluorides of lithium, sodium and potassium (FLiNaK). As melting points of each individual salt component are too high for coolant applications, the mixing of LiF, NaF and KF into ternary systems reduces the melting point to more practical levels. For in-situ corrosion measurements, electrochemical technique (Tafel Plot) was used. This test facility will also serve as a tool for development of instrumentation and provide handling experience of fluoride salts. Further, corrosion testing in FLiNaK environment has to be performed at high temperature under inert environment. The paper deals with the facility installed and the results obtained on the corrosion study.

India is embarking on construction of high temperature reactors for utilisation of Thorium for power production and hydrogen generation. India has 319,000 tons of thorium reserves which is 12.2% of world's Thorium resources and is the fourth largest country in this regard[8,9]. Thorium (Th) is a potential substitute energy source for fissile uranium isotopes. In molten salt reactors, fluoride eutectics (FLiNaK) containing $^{233}UF_4$ and $^{232}ThF_4$ can be used as coolant and fuel. FLiNaK is one of the well suited eutectic[10]. Pure fluoride salts are, on an average, electrochemically neutral but system transients and fluctuations generate fluorine atoms which are most electronegative and react aggressively with almost all materials[11]. Due to aggressive nature of molten salts at high temperature, material corrosion and salt purity are major problems in the operation of molten salt reactors. Ni based super alloys are known to be highly corrosion resistant[12] for use with molten salt medium, Hatealloy N used by ORNL in MSRE underwent fretting corrosion under neutron irradiation[13]. Hence, complete corrosion tests/analysis of the materials are essential prior to their use in the actual reactor. In this paper, a corrosion test facility developed at RED, BARC, for selecting suitable materials for future Indian 600 MWth innovative high temperature rector programme and the corrosion aspects of a few nickel based compatible alloys are described, presented and discussed in detail.

Experimental Section

Test Facility

The test facility consisted of two cylindrical vessels called melt tank and main vessel. Both the vessels were made of Inconel-625. The mixture of salts were initially melted in the melt tank and then transferred to main vessel, which was connected to melt tank with a pipe line (transfer line). Argon gas pressure was used for transferring the molten salt from the melt tank to main vessel or vice versa. Both melt tank and main vessels were provided with the band heaters to melt the salts and to maintain the desired temperature. Trace heating was also provided to pipe line between the two vessels. The main vessel was provided with the magnetic impeller for stirring the molten salt for dynamic corrosion study. The level of molten salt in both the vessels was measured by using conductivity probes (each vessel having two numbers). Temperature measurement in the vessels was carried out using Inconel sheathed ungrounded thermocouples. In order to maintain inert atmosphere of the molten salt in both the vessels, high purity argon gas is purged and vented to atmosphere through a water scrubber. Figure 1 shows the picture and schematic of the test facility. The design parameters are given in Table 1. In addition, the main vessel had provisions/ ports for accommodating the Working electrode, Reference electrode and Counter electrodes for making in-situ electrochemical corrosion measurements.

Chemicals

All chemicals were of AR grade and used as such. LiF, NaF and KF were taken in 46.5, 11.5 and 42.0 mole per cent ratio and were thoroughly mixed to form a homogeneous mixture and sufficient quantity was loaded in the test vessel to get the adequate level of melt so that the electrodes could be immersed in the melt. The mixture was heated gradually from 150°C onward in the inert atmosphere maintained with

Table 1 — Design Parameters of the test facility

S. No.	Parameters	Values
1	FLiNaK salt composition	Eutectic mixture of FLiNaK (46.5%LiF+11.5%NaF+42%KF mol %)
2	Max. heater power	3 kW
3	Design temperature	800°C
4	Operating temperature	750ºC
5	Vessel material	Inconel 625
6	Operating pressure	0.5 kg-f/cm^2
7	Salt inventory	5 kg

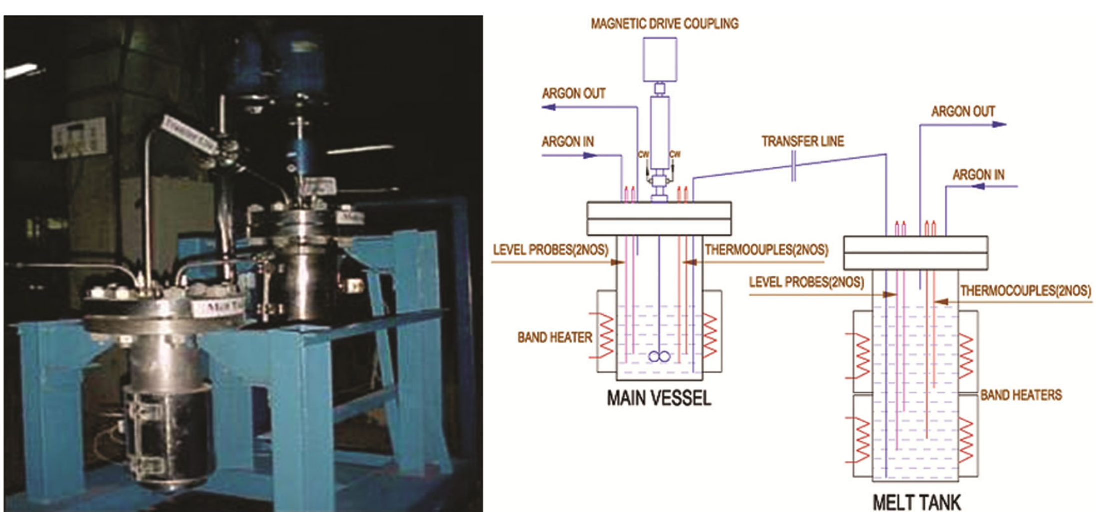

Fig. 1 — Photograph and schematic of molten fluoride salt test facility

Table 2 — Nominal composition (wt%) of alloys studied for corrosion behaviour

Alloy	Cr	Mo	Cu	Al	Ti	Fe	C	Co	Ni	Mn	Si	Nb+Ta
Inconel-625	23.0	10.0	-	0.4	-	5.0	-	1.0	58.0	0.5	-	3.15-4.25
Inconel-617	22.1	9.6	-	1.1	0.4	1.1	0.1	12.4	52.9	0.1	-	-
Inconel - 600	15.5	-	0.5	-	-	8.0	0.15	-	72.0	1.0	-	-
Incoloy-800	17.2	0.05	10.75	0.5	0.57	38.76	0.1	-	26.4	2.83	-	0.02(Nb) 3.4(Zn)
Incoloy- 800HT	18.9	-	11.9	-	0.43	39.2	-	-	26.3	-	-	3.2(Zn)
Hastelloy- N	13.7	10.6	-	-	-	4.8	-	-	50.0	1.6	-	19.4(W)
Ni - 220	-	-	-	-	-	0.1	-	-	99.13	0.23	0.54	-

flowing high purity argon gas to ensure the removal of moisture and air from the salt mixture. The temperature of the vessel was then raised above the eutectic melting point of mixture (445°C). After confirming the desired melt level, the electrochemical measurements were performed.

Electrochemical measurements

In situ Corrosion tests were carried out on different alloys viz. Inconel 625, Inconel 617, Inconel 600, Incoloy 800 Incoloy 800 HT, Hastelloy N, Ni 220 at temperatures 550, 600, 650, 700 and 750°C using electrochemical polarization (Tafel plot) technique is given in Table 2. A Metrohm make potentiostat-galvanostat (PG stat -100) was used both in two and three electrodes mode. Since, the three electrode mode gave very noisy signals; data acquired with two electrode mode was only used in this study. Potential was varied from -0.5 to 0.5 volts in a linear sweep mode (normal staircase step potential: 0.0005 V) with scan rate of 0.001 V/s. Platinum rod of 3 mm diameter was used as reference (coupled with counter) electrode. Test material rod with 2.4 mm diameter was used as working electrode. Corrosion current (I_{Corr}) obtained from the intersection of cathodic and anodic Tafel lines was used for the estimation of corrosion rate. During measurements, vessel (autoclave) was connected to the PG stat ground.

Results and Discussion

AC impedance spectra

For the interpretation of the chemical behaviour of a system by EIS spectra, the whole set of data was fitted with the following equivalent circuit given in the Fig. 2. In this equivalent circuit, R_s is the electrolytic resistance between the reference and the working electrode, C_{dl} is the double layer capacitance of the interface between the electrode and the electrolyte, R_{ct} is the charge transfer resistance of reactions in the electrolyte, C_{ox} and R_{ox}, the capacitance and resistance of the surface film respectively. In our analysis, the

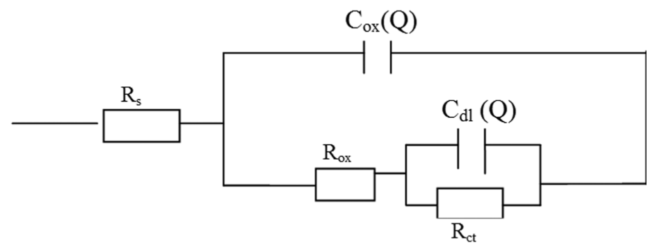

Fig. 2 — Equivalent circuit model

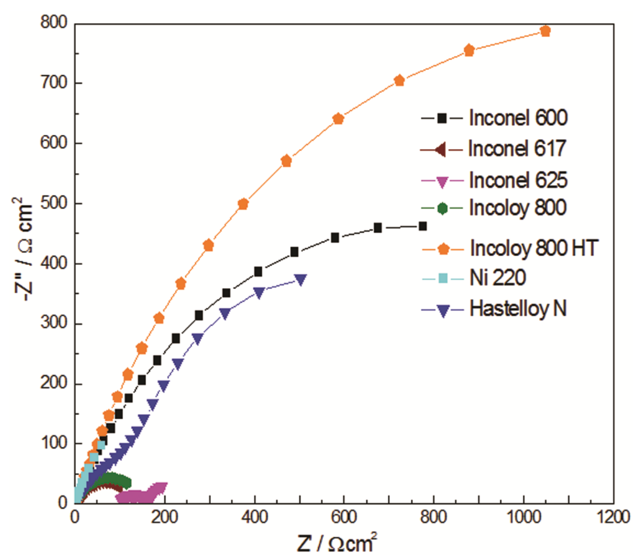

Fig. 3 — Impedance plots for different Structural Materials at 650°C

data fitted well for a CPE (Constant Phase Element,Q) instead of C_{dl} / C_{ox}, a pure capacitance. Figure 3 gives Nyquist plots for Inconel 600, 617, 625, Incoloy 800, Incoloy 800 HT Hastelloy N and Ni – 220 at 650 in molten salts.

Ptentiodynamic polarisation

Figure 4 shows the polarization curves obtained for different materials under this study at 650°C in molten salts. These plots clearly show that Corrosion studies in static and dynamic (stirring) mode were performed for the Ni containing alloys. Amongst studied alloys in static mode, the corrosion rates found to increase with increasing temperature.

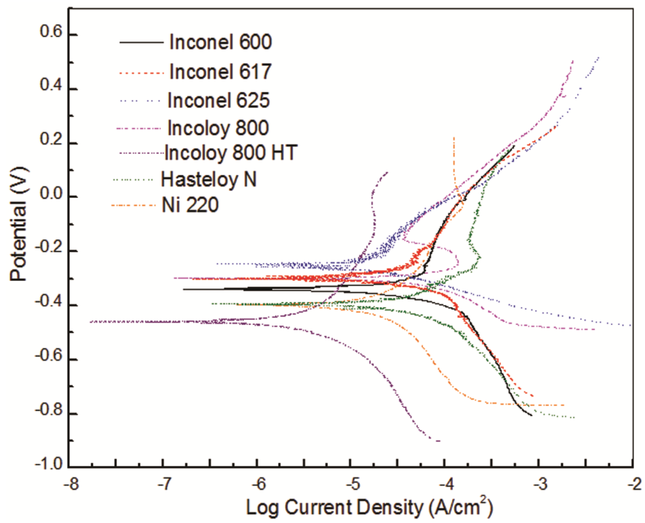

Fig. 4 — Tafel plots for different Structural Materials at 650°C

For hydrogen generation and electrify production with high efficiency, temperatures in the range of 500-1500 are required. Molten salt mixtures are best suited for this, due to low vapour pressure at high temperatures as energy transport medium. Fluorides of lithium, sodium and potassium (FLiNaK) eutectic are one of them studied by NASA. But the material compatibility and salt eutectic purity are major problems faced[14].

AC impedance spectra

The impedance spectra exhibit one single depressed semicircle indicates that the charge transfer takes place at the metal/salt interface. The increasing diameter of the Nyquist semi-circles with time is an indication of increasing corrosion protection. The large diameter of semicircle of Incoloy 800 HT as compared to the other structural material under study indicates the formation of some protective salt layer on the alloying surface. Nyquist plot for Inconel 625 clearly showed two time constants unlike the other alloys. The smallest semicircle observed with Inconel 625 indicated its highest corrosion rate. The presence of a semicircle at higher frequency followd by the emergence of a tail like shape at lower frequency suggests formation of a salt layer and the onset of diffusional effects controlling the overall corrosion process. Thus, for all the materials studied in this work, both charge transfer as well as diffusion of ions through a surface salt layer seems to control the overall reaction, depending on the stability of the surface layer and temperature, to different extents.

Ptentiodynamic polarisation

A substantial reduction of the corrosion current density (I_{corr}) for Hastelloy N and Incoloy 800 HT as

Table 3— Static mode corrosion rates in mpy

Temp °C	Inconel 600	Inconel 617	Inconel 625	Incoloy 800	Incoloy 800 HT	Hastelloy N	Ni 220
550	6.2	10.0	-	17.4	1.79	4.79 (4.40)	0.97
600	12.2	18.2	6.1	30.1	1.5	20.2 (5.75)	2.96
650	25.9	22.7	5.0	31.2	1.45	18.5 (6.87)	1.53
700	25.4	33.9	71.3	45.4	3.2	26.55	-
750	15.8	97.9	127.6	33.2	4.73	29.84	-

compared to Inconel alloys and Incoloy 800. The cathodic current density of Incoloy 800 HT is significantly lower than that of Hastelloy N. This observation suggests the formation of some protective layer on the surface of Incoloy 800 HT. Ni-220, a predominantly Ni-containing alloy with no Cr, showed almost similar behaviuor to that of Hastelloy. Table 3 gives data of corrosion rate measurements carried out in static conditions in the FLiNaK medium in temperature range of 550- 750°C.

In static mode, the corrosion rates were found to increase with increasing temperature. A National Aeronautic and Space Administration (NASA) study[15] determined that the tendency for common alloying constituents to corrode in molten fluoride salts increased in the following order: Ni, Co, Fe, Cr, Al. Whereas addition of refractory metals like Nb, Mo, and W expected to be relatively free from attack and increases the resistivity of the material. At high temperatures corrosion rate increased with increasing the chromium content in the metal alloy. The corrosion products of metals by fluoride melts are soluble in the molten salt; accordingly passivation is precluded and corrosion depends directly on the thermodynamic driving force of the corrosion reactions. The Ni-201 alloy, which is predominantly Ni with minor alloying additions, was resistant to corrosion. The order of corrosion was Inconel 625 > Inconel 617 > Inconel 600 > Incoloy 800 > Hastelloy N > Ni 220 > Incoloy 800 HT. The combination of Zn (3.2%) and Ti (0.43%) present in the Incoloy 800 HT may be responsible for .its resistivity. Presence of Al (0.4%) and Cr (23%) in Inconel 625 may be responsible for its higher corrosion rate.

Corrosion studies were carried out for Inconel 625, Incoloy 800 and Hastelloy N in FLiNaK in the temperature range of 550-750°C and at varying stirring rates (0-400 rpm). This was done to compare the corrosion rates of the above materials under static condition with those at simulated flow conditions in the actual system. Impedance data observed the decreased in the diameter of semicircle with

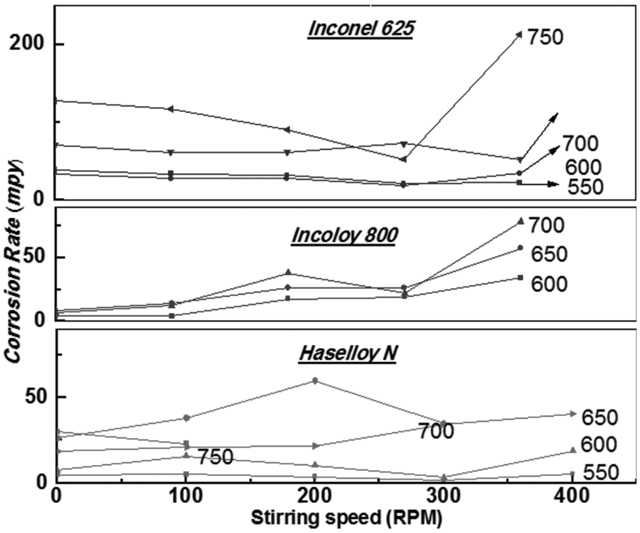

Fig. 5 — Corrosion rates as a function of stirring speed at various temperatures

increasing stirring speed indicating an increase in the corrosion rate. Figure 5 shows the corrosion rate plots for Hastelloy N, Incoloy 800 and Inconel 625 in a dynamic condition with stirring rates ranging from 0-400 rpm.

Conclusion

The corrosion rate followed the order: Inconel 625 > Inconel 617 > Inconel 600 > Incoloy 800 > Ni 220 > Hastelloy N > Incoloy 800 HT. In dynamic mode, Hastelloy N is found to be better than Incoloy 800 HT at 650°C, but at 700°C, Incoloy 800 HT showed more corrosion resistance.

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