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Corrosion studies on coated and bare C-276 material in molten cuprous chloride salt environment

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ABSTRACT

Hydrogen is one of the promising alternative energy carrier candidates and the Copper-Chlorine (Cu-Cl) cycle is a promising thermochemical cycle for hydrogen production, but its commercial viability is yet to be established and several bottlenecks need to be addressed. As Cu-Cl cycle involves high temperature reactions and corrosive chemicals, selection of suitable materials and the potential damage due to corrosion is an important concern for the implementation of technology in commercial scale. Thus, a study on these aspects is essential to realize the entirety of the cycle, including the development of high temperature anti-corrosion equipment materials and the system to evaluate the performance of the materials.

NIGIS * CORCON 2016 * Sept. 18 – 21, 2016 * New Delhi Copyright 2016 by NIGIS. The material presented and the views expressed in this paper are solely those of the author(s) and do not necessarily by NIGIS. This paper represents preliminary investigation of C-276 and corrosion resistant coatings. Different types of coating materials were tested. Diamalloy 4006, YSZ (Yttria-stabilized zirconia) and alumina are the candidate materials selected for corrosion test. The test experiments were carried out on duplicate specimen, with and without coating and generation of corrosion data under static condition in high temperature molten cuprous chloride media at 550°C $\pm 10°$ C for 100 h using quartz reactor system. After the immersion test, visual examination, weight loss analysis, SEM, and EDX were carried out to evaluate the specimens. The study showed severe corrosion of allthe coated specimens.

Keywords: Copper-Chlorine, Thermochemical, high temperature, Corrosion resistant coating

INTRODUCTION

The growing demand for global energy has encouraged the development and utilization of new and efficient renewable energy sources and technologies. Among the variety of sustainable energy pathways recognized, hydrogen has been widely recognized as the most promising fuel and a sustainable energy carrier, which must be produced in a clean method¹. Thermochemical splitting of water utilizing intermediate compounds is a progressing and an environmentally attractive technology for production of hydrogen on large scale. More than 200 thermochemical cycles have been identified and studied since the 1960s for the hydrogen production from water. However, most of the cycles require temperature above 850°C and have low conversion efficiencies². Among the various thermochemical cycles, copper-chlorine (Cu-Cl) cycle is one of the most promising cycle having several advantages compared to the other cycles being investigated involving the highest operating temperature of 550°C The high temperature stages and the corrosive chemicals involved in the Cu-Cl cycle poses challenges including plant design and material selection³. One of the challenging environments for materials to resist corrosion is molten cuprous chloride (CuCl), the product of three reactions. Past literature search shows limited data on the corrosion resistance of materials in molten CuCl. Therefore, the identification of suitable materials and the potential damage due to corrosion is an important concern for the implementation of technology in commercial scale.

University of Ontario Institute of Technology (UOIT)in collaboration with the Univ. Toronto, Canada has identified a number of potential substrate materials⁴. The most appropriate materials for high temperature and corrosive environments reported in literature are ceramics, refractory metals, molybdenum and nickel based alloys, graphite based materials, and Hastelloy C^{4,5}. However, these alloysmay not be able to meet both the high temperature strengthrequirements and high temperature corrosion resistance simultaneously. In order to prevent corrosion, a coating of thermal barrier type has proven the most effective and economical method by enhancing the corrosionresistance at an elevated temperature without destroyingthe mechanical properties of a substrate.UOITand Univ. Toronto identified Ni–Nb–Ti–Zr–Co–Cu, 57Ni–20Zr–3Si–18Ti–2Sn, Ni–Zr–Si–Ti–Sn, Ni–Ta, FeCrMoCBY and Ni₅₇Nb₃₃Zr₅Co₅ as a candidate materials for corrosion resistant coatings [4]. The top coating materials for the thermal barrier are generally composed of CaO, CeO₂, MgO or Y₂O₃ stabilized ZrO₂. Usually Ni-based alloys (e.g. Diamalloy) used for bond coat is applied between a substrate and the top coat to improve the adhesion⁶ and references therein⁷.

Edwin⁸ has evaluated the performance of the two base metals, Ni based super-alloy (Inconel 625) and super austenitic stainless steel (AL6XN) and the metallic (Diamalloy 4006) and ceramic coatings (Alumina and YSZ) exposed to molten CuCl at 500 °C for 100 h. Observations disclose the information that Diamalloy 4006 and YSZ coating provided a better protection than alumina (Al₂O₃.3TiO₂) to the base metal. Later, Azarbayjani⁹ modified the immersion test apparatus and

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evaluated the performance of metallic (Diamalloy 4006 and super hard steel) and ceramic coatings (YSZ) on medium carbon steel. The results suggest that both Diamalloy 4006 and SHS 9172 HVOF coatings seemed to provide better protection to the underlying base metal than YSZ (ZrO_2 18TiO_2 10Y₂O₃). Depending on the study conducted by Edwin and Kaveh, Azhar¹⁰ continued the study to evaluate the coating performance of Super hard steel, Diamalloy 4006, YSZ (ZrO_2 18TiO_2 10Y2O_3) and alumina on medium carbon steel. It infers from the available data that systematic information is missing on the corrosion caused by the molten CuCl and thus more research is required in this area.

Considering above developments, the preliminary investigation of corrosion resistant coatings was initiated. This paper represents Corrosion studies on bare HastelloyC-276 and coated material in molten CuCl salt environment 550°C \pm 10°C for 100 h under static condition and with and without nitrogen atmosphere using quartz reactor system. Diamalloy 4006, Yttria-stabilized zirconia (YSZ), alumina and chromium oxide were selected for the study.

EXPERIMENTAL PROCEDURE

SPECIMEN PREPARATION

Hastelloy C-276 (C-276)having typical composition as shown in Table 1was used as base metal for specimen fabrication. Test specimens were fabricated from rod shaped C-276 available in the local market. The rod shaped specimenswere fabricated using machine cut having dimension of 42 mm x 12 mmwith 180 and 620 grit finishing

The test specimens were clearly marked with distinct identification numbers. The specimens were cleaned with acetone, then xylene followed by acetone and wiped with Whatman filter paper. The specimens were handled carefully with due care to not to leave any finger prints on surface of the specimen. Initial weights and dimensions were recorded prior to experiment.

Table 1: Nominal composition of the Hastelloy C-276 alloy

Element	Ni	Со	Cr	Мо	W	Fe	Si	Mn	Ĉ	P	S	V
Mass %	57.00	2.50	15.50	16.00	4.00	5.50	0.08	1.00	0.010	0.025	0.010	0.35

COATING

The specimens were grit blasted with alumina powder to increase adherence between the bond coat and the substrate. Thespecimens were first sprayed with Diamalloy 4006 bond coat by HVOF and then with ceramic top coat using air plasma spray system. Table 2indicates the details coating materials used in the present study.

Table 2:Characteristics of the coating materials									
Layer	Product	Composition	Process	Thickness (µm)					
Bond coat	Diamalloy 4006	Ni-bal,Cr-20.5,W-10,Mo-	HVOF	100					
		9,Cu-4,B-0.75,C-1,Fe-1							
Top coat	YSZ	Y ₂ O ₃ -8, ZrO ₂ -92	APS	200-300					
	Alumina	Al ₂ O ₃ -99.99	APS	200-300					
	Chromium oxide	Cr ₂ O ₃ -99.98	APS	200-300					
	Yttria	Y ₂ O ₃ -99.99	APS	200-300					

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THERMOGRAVIMETRY ANALYSIS OF MEDIUM

Cuprous chloride (CuCl) salt, AR Grade, 96% purity, supplied by M/s. S. D. Fine Chem. Ltd.was used for study. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) of CuCl was performed with Netzsch STA 449 F3 (Germany). A weight of around 10-12 mg of CuCl was placed in alumina pan and heated in nitrogen atmosphere with 50 ml/min flow from room temperature to 700°C at a heating rate of 10 °C/min.A continuous record of weight loss and heat flow as a function of temperature was obtained (Figure 1).DSC-TGA graph indicates 0.3% weight loss at 100°C, which may be attributed to free moisturecontent.



Figure 1: TGA of CuCl salt

IMMESRION TEST APPARATUS AND PROCEDURE

The methodology for immersion test was developed based on ASTM-G-31-72 standards. The experimental apparatus consists of an quartz reactor (immersion vessel, 2 L capacity) enclosed in furnace with inlet and outlet tubes, a gas feed module comprisinggas cylinder and mass flow controller for nitrogen as well as an scrubber system to control the release of noxious fumes. The test experiments was carried out with coated and uncoated specimens and under static condition in molten CuCl media at $550^{\circ}C\pm10^{\circ}C$ for 100 h using quartz reactor systemwith and without nitrogen purging.

Initially, CuCl was preheated in a vacuum oven at 150 °C for 6 h to ensure removal of any moisture content taking clue from the TGA study. Then, the preheated salt was immediately charged to quartz reactor and sealed by taking necessary precautions to avoid external contamination. The tests were conducted in the quartz reactor assembly as shown in Figure2. The reactor temperature was increased in a programmed manner from room temperature to 550°C with continuous nitrogen purging at 125 SLPH with the help of the user interface console. After attaining 550°C temperature, the specimensattached to the quartz rod were introduced into the reactor and immersed in molten CuCl mass. Nitrogen purging was continued during the experiment at 25 SLPH to maintain oxygen-free environment. The study was continued for 100 h at 550°C under static condition.

After 100 h, the heat supply was cut-off and slowly the specimenswere retrieved from the vessel. The specimenswere immediately washed with EDTA hot solution to remove molten salt followed by washing with water and acetone and dried in the oven at 50-60°C and weighedand dimension measurement was done. In case of extremely adhered products, warm Clark solution was employed for 2-3 minutes to get rid of the corroded product followed by reported water and acetone washings.

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Figure2: Schematic diagram of the quartz reactor assembly

CHARACTERIZATION

Initial and final weight of the exposed specimens was taken to assess corrosion. The microstructure, morphology and chemical composition of the surface and the cross-section of the coatingswere examined by SEM (Scanning electron microscopy, JEOL) equipped with energy dispersive spectrometer (EDS).XRD (X-ray Diffraction, Rigaku) was used to determine hot corrosion products.

CALCULATION OF RESULTS

Corrosion rate was calculated by using following formulae:

Corrosion rate $(mm/y) = 87.6 \times (W / DAT)$

Where,W = weight loss in milligrams, D = metal density in g /cm³ (8.89 g /cm³),A = exposed area of specimen in cm²[($3.14xd \times I$)+ ($0.785xd^2$)], whered: diameter and I: length of immersed specimen,T = time of exposure of the specimen in hours

RESULTS

EXP. 1: Evaluation of Alumina, Yttria and YSZ coating in absence of nitrogen-100 h test

The corrosion test was performed with C-276 specimens (with and without welding) coated with Diamalloy 4006 bond coat followed by alumina, Yttria and YSZtop coatwithout nitrogen purging. Top portion of test specimen near the holewas not coated with base and top coat. The results obtained are shown in Table 3.Figure3 shows the images of specimens before and after reaction. Maximum corrosion was observed on the bottom part of the specimens.

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Sr.	Type of Material	Surface Area, (mm ²)		Weight loss, (%)		Corrosion rate,(mm/y)				
No.		(A)	(B)	(A)	(B)	(A)	(B)			
1.	C-276	1396	1419	18.09	17.36	127.63	120.49			
2.	Alumina	1508	1511	15.46	16.78	101.00	109.36			
3.	Yttria	1609	1617.	12.14	13.02	74.31	79.37			
4.	YSZ	1523	1523	15.08	17.86	97.54	115.58			

(A)Specimen without welded joint and (B) specimen with welded joint



Figure 3:Partially coated specimens in absence of nitrogen (a) Before reaction (b) After reaction without welded joint and (c) After reaction with welded joint

EXP 2: Evaluation of Aluminum oxide, Chromium oxide, YSZ and Chromium titania coating in absence of nitrogen-100 h test

To verify the possibility of corrosion due to penetration, the next experiment was performed with completely coated specimens (without welding) under the similar conditions for 100 h. The base metal was coated with the bond coat of Diamalloy 4006 and top coat of Aluminum oxide, Chromium oxide, YSZ and Chromium titania. Table 4 shows the weight loss and corrosion rate data.Figure4 shows the images of specimens before and after reaction.

Sr. No.	Type of Material	Surface Area,(mm ²)	Weight loss, (%)	Corrosion rate,(mm/y)
1	Aluminum oxide	1555	13.75	87.14
2	Chromium oxide	1540	21.38	136.78
3	YSZ	1523	11.36	73.47
4	Chromium Titania	1553	15.37	97.49

Table 4: Corrosion rate of completely coated specimens in absence of nitrogen

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Figure4:Completely coatedspecimensin absence of nitrogen (a) Before reaction (b) After reaction

EXP 3: Evaluation of Aluminum oxide, Yttria, YSZ and Chromium oxide coating in presence of nitrogen-100 h test

The experiment was then conducted with C-276 specimens (without welding) completely coated with Diamalloy 4006 bond coat followed by Aluminum oxide, Yttria, YSZ and Chromium oxide coating top coat in presence of continuous nitrogen purging at a rate of 125 SLPH. Table5 shows the corrosion rate of completely coated specimens. Figure 5 shows images of completely coated specimens in presence of nitrogen before and after reaction.

Sr. No.	Type of Material	Surface Area, (mm ²)	Weight loss, (%)	Corrosion rate,(mm/y)
1.	Aluminum oxide	1490	14.27	94.39
2.	Yttria	1490	10.29	68.06
3.	YSZ	1490	12.77	84.44
4.	Chromium oxide	1490	6.92	45.75

Table 5: Corrosion rate of completely coated specimensin presence of nitrogen



Figure 5:Completely coated specimens in presence of nitrogen (a) Before & (b) After reaction

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EXP 4: Evaluation of Yttria coating in presence of nitrogen-100 h test

To study the consistency of the coating, four specimens completely coated with Yttria were tested in molten CuCl environment for 100 h in presence of continuous nitrogen purging at a rate of 125 SLPH. The severe attack of CuCl delaminated both of the coating layers of all the specimens as shown in Table 6 and Figure 6

Sr. No.	Type of Material	Surface Area,(mm ²)	Weight loss,(%)	Corrosion rate,(mm/y)
1	Yttria	1492	10.61	24.81
2	Yttria	1492	20.25	47.77
3	Yttria	1492	20.14	46.55
4	Yttria	1492	22.30	51.76

Table 6:	Corrosion	rate of	Yttria	coated	specimen
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Figure 6:CompletelyYttria coated specimens (a) Before testing (b) After testing

CHARACTERIZATION

Figure 7 shows the XRD pattern of the solid corrosion products obtained at the bottom of the quartz reactor apparatus at the end of corrosion test at 550°C for 100 h.The element mapping shows the outer scale mainly composed of Cr_2O_3 , Al_2O_3 , and TiO_2 , and an Al_2O_3 scale formed close to the substrate of the coating material.

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An EDX analysis was performed to confirm the presence of the coating elements. Table 7 shows the elemental composition of the product. Chromium, Nickel, Manganese, Molybdenum, Zirconia, Copper, Iron and Yttrium were all present. Nickel and chromium are the main constituents of the Diamalloy 4006and C-276. Zirconia was present after the layer of Diamalloy 4006 but its particles were diffused in the bond coat.

Element	Cr	Mn	Ni	Cu	Fe	Y	Мо	Zr
Mass %	55.01	12.53	12.39	10.84	3.65	2.59	1.60	1.14

DISCUSSION

The results obtained in various experiments conducted along with the elemental compositions are tabulated in the preceding text. Based on the data it is observed that Corrosion rates are extremely high in presence and absence of oxygen even in Nitrogen atmosphere. This typical corrosion behavior of molten salt could not be interpreted with the available information. It was observed that the coating material is getting peeled offas seen at the end of the test although the integrity of coating application was ensured by following standard set procedures. Initially it was observed that corrosion may be due to moisture, but very little moisture content was observed in TGA analysis. Analysis of corroded products in the vessel indicated the presence of coating products infers that the coating is not getting dissolved in the medium and it appears that in this medium the coating integrity is sacrificed that could be due to severity of CuCl attack. The present data does not lead to conclusive evidence to find the root cause of corrosion behavior of molten CuCl medium. It may beseen that wide variation of results are reported by some other researchers^{4,5,9,10} which indicates the typical corrosion behavior of the medium that needs special attention and further research.

CONCLUSIONS

- Hydrogen generation using Cu-Cl cycle appears lucrative in view of moderate temperature requirement and reasonable high efficiencies of conversion and choice of materials.
- Although several Ni-Cr based materials are known to work in this environment, still there are no fool proof test methods and coatings are reported in the literature for commercial applications.
- Quite expectedly, severe corrosion of materials is seen in CuCl molten slat medium at 550oC as seen in the present testing on C-276.
- Proven thermally sprayed coatings on Hastelloy C-276viz., Yttria, YSZ, Alumina, Chromium Oxide, mixed metal oxides, Titaniaetc., in molten CuCl environmentat 550 °C and for 100 h were found to be not working under present experimental conditions as the coating material peeled off from the base material
- Almost all tested coatings suffered from heavy depletion in presence and absence of nitrogen although moisture content is very low..
- No significant change in the corrosion rate was observed between welded and non-welded test specimens and in presence and in the absence of N2 atmosphere
- Analysis of the corrosion products indicated the presence of coated material that might lead to understanding that coating application also needs to be improved further.
- Currently available data does not give much insight into the typical corrosion behavior of molten CuCl as observed in this typical medium by other researchers and thus further studies need to be continued.

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