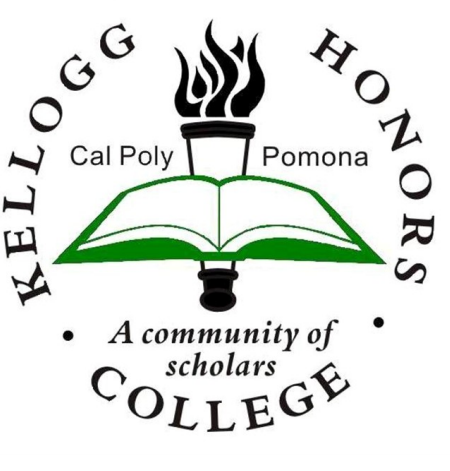


# Hot Corrosion Resistance of Nickel Chromium Alloys for Biomass Applications

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Kellogg Honors College Capstone Project



## 1. Background

The corrosion of metallic alloys at high temperatures is an increasing problem to industry as society turns to alternative methods of generating energy to decrease the dependence of non-renewable energy sources such as coal. One such renewable fuel source is biomass, which typically contains wood, straw, grasses, and other organic materials. Biomass contains high concentrations of alkali metals and chlorine which react to form alkali salts. During the combustion process moisture from the biomass is released and the alkali salts are volatilized to form gaseous species that potentially react with sulfur from the combustion gas. The products of this reaction are potassium chloride and potassium sulfate which condense onto the internal components of the boilers, ultimately resulting in severe corrosion. This form of corrosion, i.e., corrosion occurring under molten salt films, is known as hot corrosion. In the case of biomass applications, the hot corrosion attack occurs in the 500 - 700°C temperature range, and is more specifically known as Type II hot corrosion. This type of corrosion is characterized by a non-uniform pitting attack upon the metal. In order to deter hot corrosion, chromium is used as an alloying element because of its ability to form a protective and adherent oxide scale. In this project, the effect of chromium was studied by subjecting several binary Ni-Cr alloys and a low alloy steel to corrosive attack from a thin salt film of potassium chloride and potassium sulfate at 700°C for various times. The results of this study include microstructural analysis.

## 2. Objective

Observe the corrosion of low alloy steel and nickel-chromium alloys when exposed to Type II hot corrosion in a molten salt mixture of potassium chloride and potassium sulfate.

## 3. Hypothesis

Increasing the amount of chromium in binary nickel chromium alloys will result in improved resistance to hot corrosion attack when compared to low alloy steel.

## 4. Experimental Procedure

Low alloy steel and nickel-chromium containing 5, 7.5, and 10 wt % chromium were utilized in this study. Specimens were machined using (electrical discharge machining), EDM, to obtain the desired dimensions of (1.5cm x 1.5 cm x 0.3 cm). A 600 grit surface finish was achieved using silicon carbide grit paper. Samples were exposed to reagent grade potassium chloride, KCl, and potassium sulfate, K<sub>2</sub>SO<sub>4</sub>. The salt film was obtained by dripping an aqueous supersaturated solution of potassium chloride and potassium sulfate onto one major face of the sample. The sample was then placed onto a hot plate, where the water evaporated, leaving behind a salt coating equivalent to 3—8 mg/cm<sup>2</sup> as depicted in Figure 4-1 and Figure 4-2. The salt coating obtained was a eutectic mixture containing 42.5 mol% K<sub>2</sub>SO<sub>4</sub> with the balance, 57.5 mol % as KCl<sup>1</sup>. Samples were then placed onto alumina crucibles in a horizontal tube furnace at a temperature of 700 °C in stagnant air for varying test times of 1, 25, 49 and 100 hours. Upon test completion, samples were mounted in epoxy and destructive metallographic analysis was performed. Optical microscopy, scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) was used to identify the phases formed during exposure to the corrosive environment.



Figure 4-1: (a) Salt solution applied (b) Water begins to evaporate (c) Resulting tenacious salt film

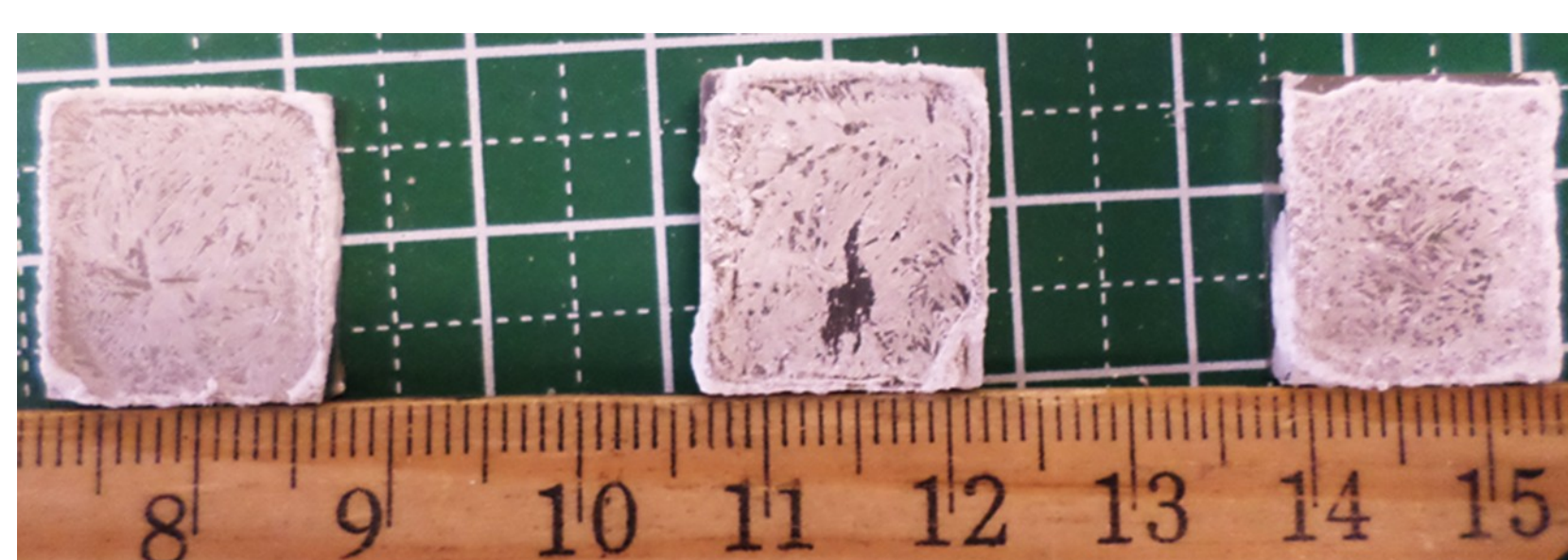


Figure 4-2: Typical salt coating prior to exposure

## 5. Results

### 5a. Selection of Post Test Macrographs After 25 Hour Exposure

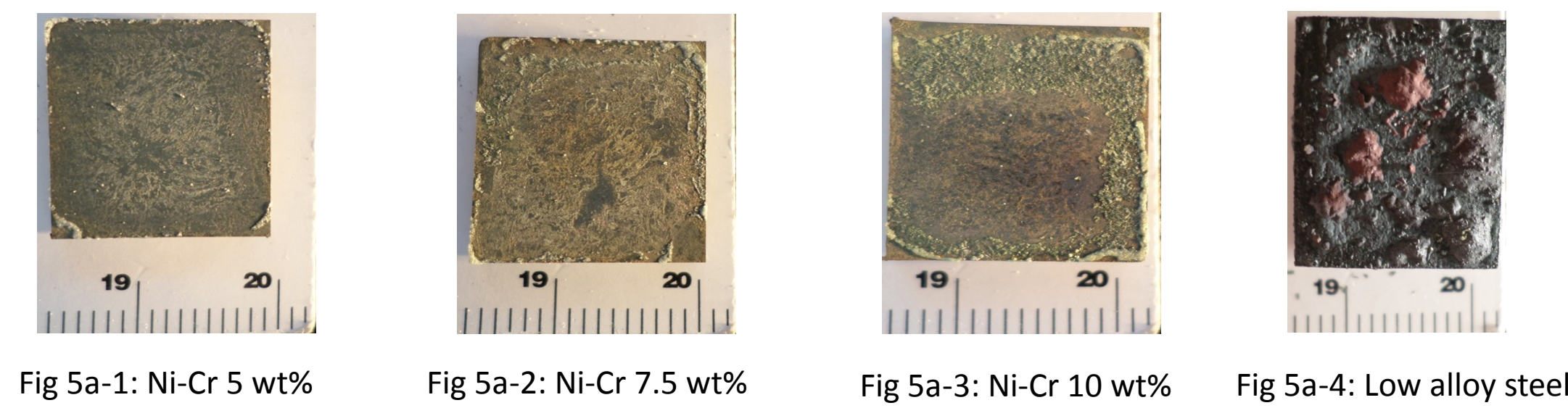


Fig 5a-1: Ni-Cr 5 wt% Fig 5a-2: Ni-Cr 7.5 wt% Fig 5a-3: Ni-Cr 10 wt% Fig 5a-4: Low alloy steel

### 5c. SEM & EDS

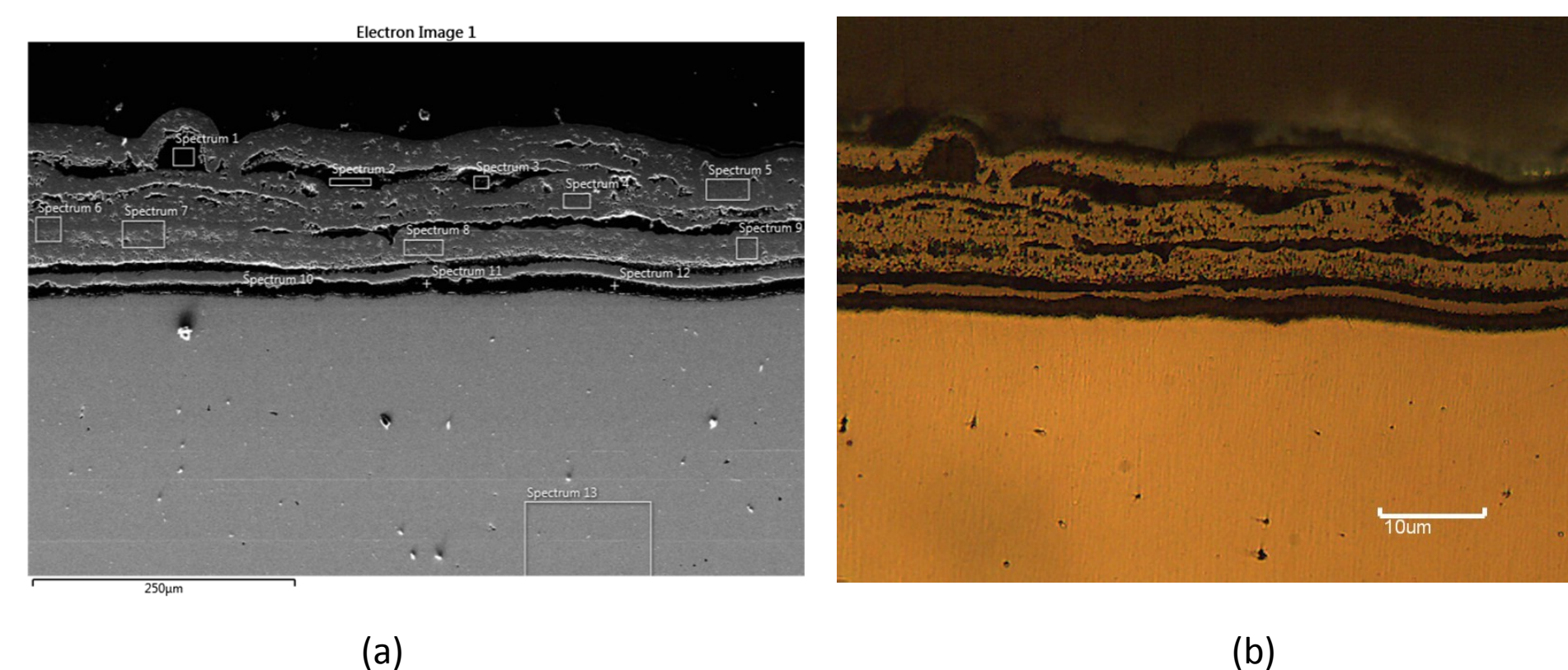
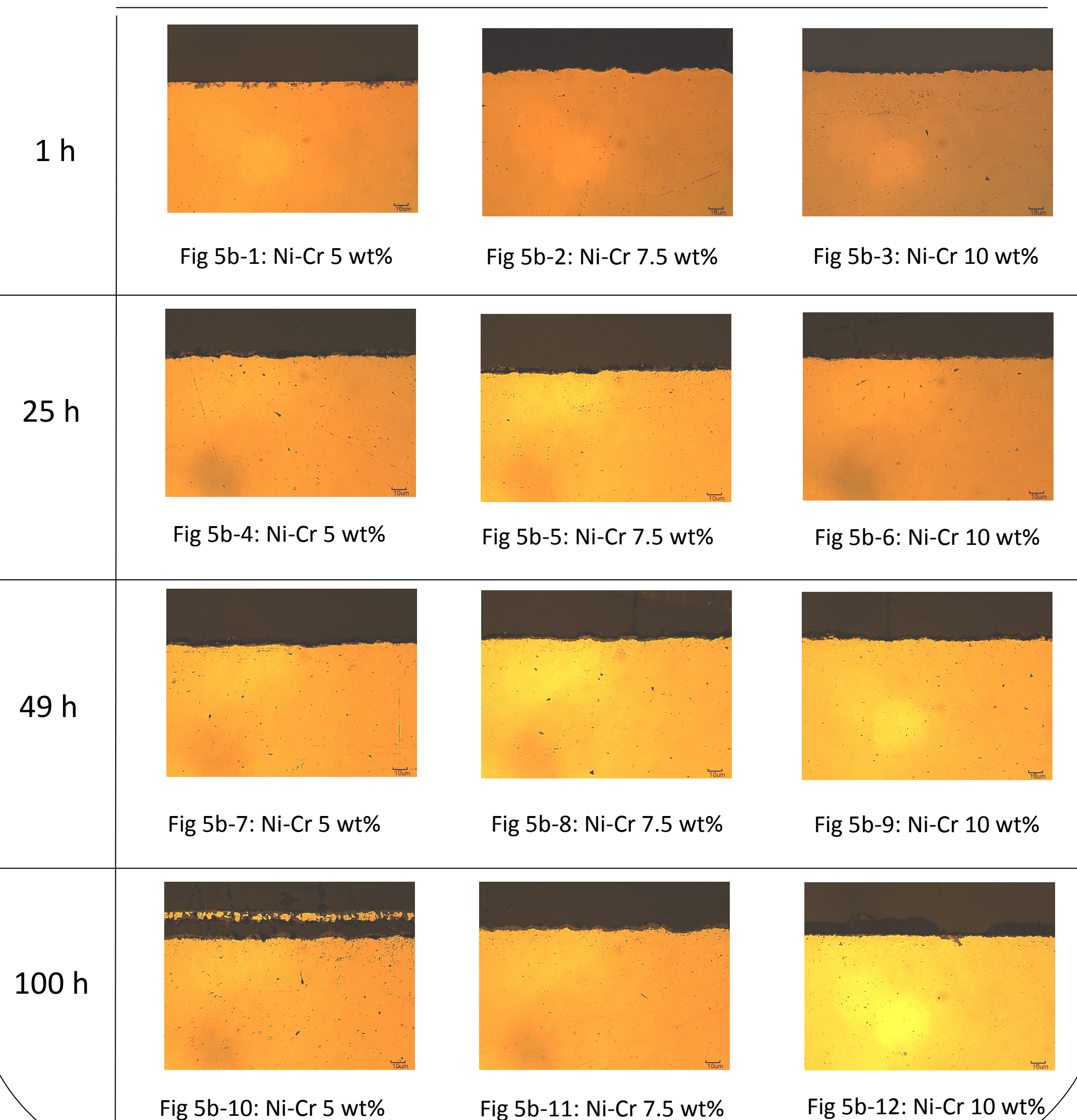


Fig 5c-1: (a) Secondary electron image from the oxidation product formed on the low alloy steel after 25 hours (b) Optical micrograph of low alloy steel after 25 hours

Table 5c-1: Results from EDS analysis measured in weight % corresponding to Figure 5c-1a

Spectrum	O	Fe	Cl	Cr
1	10.83	37.79	51.38	--
2	22.33	74.10	0.29	0.82
3	24.19	62.61	1.00	2.44
4	23.38	69.92	--	5.73
5	22.56	75.70	--	1.20
6	23.03	72.40	--	3.55
7	22.71	74.48	--	2.35
8	23.85	66.11	--	7.90
9	22.77	74.43	--	2.14
10	23.97	66.25	--	6.75
11	26.51	37.45	4.40	28.33
12	24.59	57.07	1.67	8.55
13	22.60	70.08	--	4.10

### 5b. Optical Microscopy



### 5d. XRD Results After 49 Hour Exposure

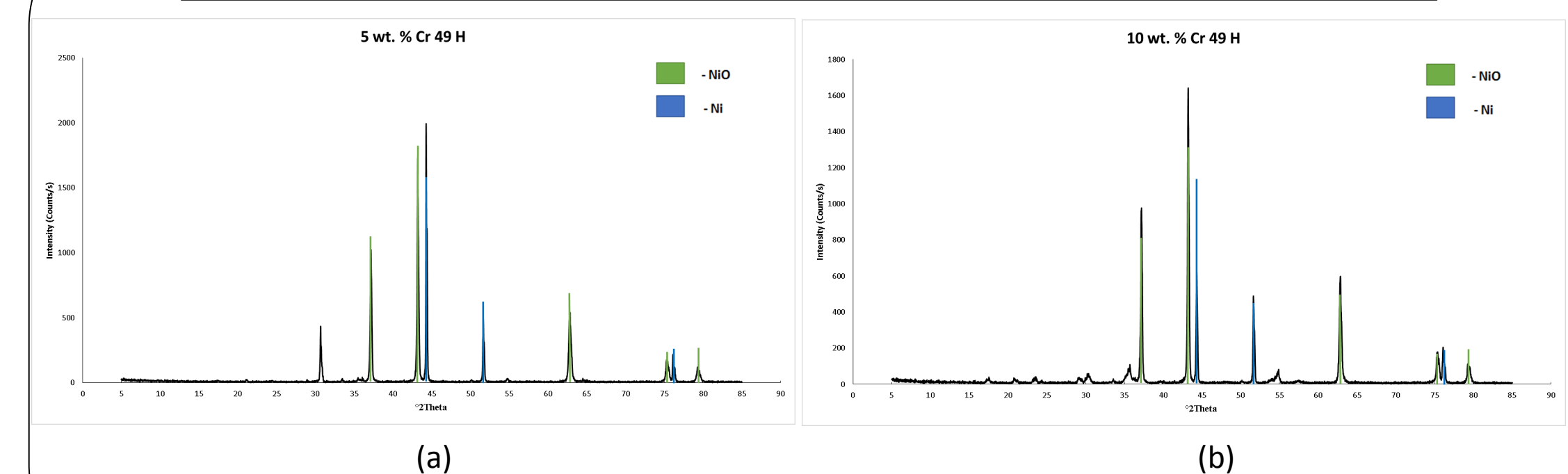
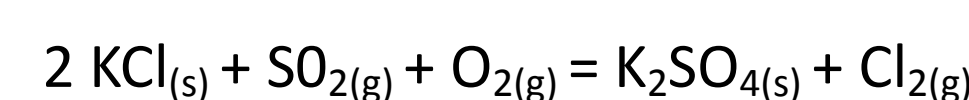


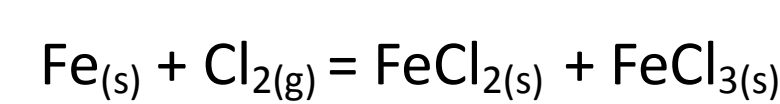
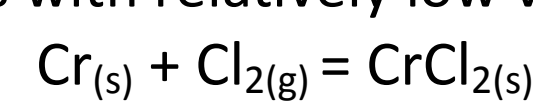
Fig 5d-1: (a) Nickel and nickel oxide phases identified on 5 wt. % Cr (b) Nickel and nickel oxide phases identified on 10 wt. % Cr

## 6. Discussion

Potassium is known to form various low melting eutectics with a wide variety of species leading to increased corrosion when compared to non-eutectic salt mixtures.<sup>1,2</sup> Figure 6-1 depicts the typical regions of corrosion that occur within a biomass boiler. This corrosion is governed by the thermodynamic stability of the salt mixture which is influenced by the partial pressure of oxygen and chlorine in the environment as depicted in Figure 6-2. During the combustion process the volatile potassium chloride reacts with the sulfur dioxide, SO<sub>2</sub> (g) from the atmosphere to form the molten salt as indicated below.



The gaseous chlorine formed then reacts with the metal constituents as shown below to form iron and chromium chlorides with relatively low vapor pressures.<sup>3</sup>



The chlorides of Fe and Cr have relatively low vapor pressures above 300°C and sublimate from the alloy surface to be oxidized by the gaseous atmosphere leading to the formation of a porous non-protective oxide layer as depicted in Figure 6-3.

Optical microscopy from metallographic cross-sections of low alloy steel exposed to this simulated test environment shows a layered and non-protective bulky oxide consistent with the literature.<sup>1,3,5</sup> EDS analysis of the oxide layers confirmed the presence of iron chlorides near the metal-oxide interface and iron oxides near the metal-salt interface. In comparison, nickel-chromium samples showed no appreciable hot corrosion attack under similar test conditions, due to the stability of nickel chlorides that sublimate in temperatures in excess of 850°C from the metal surface. The relative stabilities of the metal chlorides is shown in Figure 6-3 with the temperature range in Figure 6-4.

Optical microscopy of the nickel-chromium displayed a decreasing hot corrosion front as the chromium content increased. Pitting of the surface is evident for longer exposure times, especially for the 5 wt. % sample.

X-ray diffraction of the nickel-chromium samples indicate the presence of nickel oxide for both the 5 and 10 wt. % Cr-Ni samples.

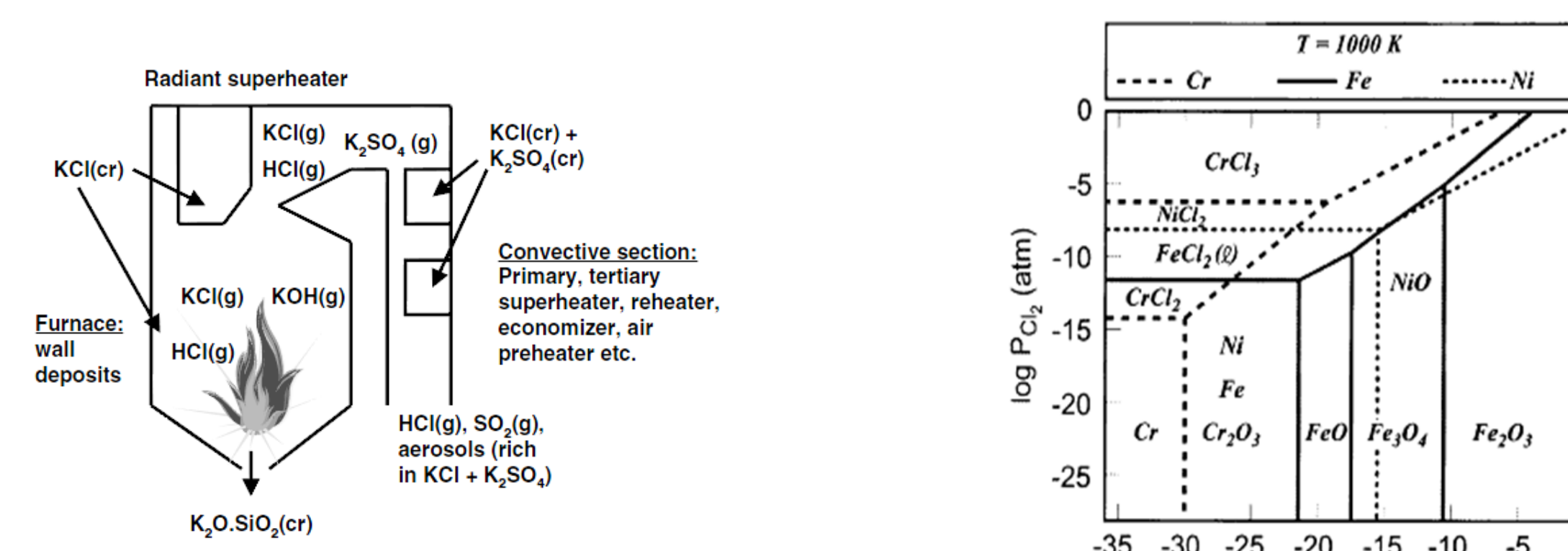


Fig 6-1: Principal pathways of potassium, sulfur and chlorine in a biomass-fired boiler<sup>1</sup>

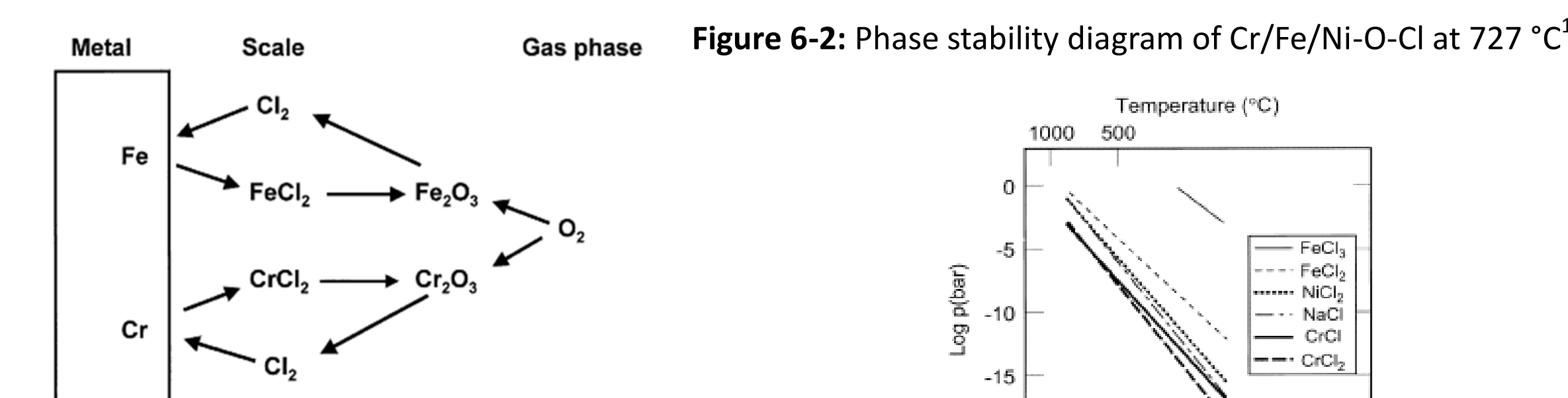


Figure 6-3: Interface reaction of chlorine with base metal<sup>1</sup>

Figure 6-4: Vapor pressure of various chlorides<sup>1</sup>

## 7. Summary and Conclusions

The corrosion behavior of low alloy steel (Fe - 4 wt. % Cr - 0.5 wt. % Mo) and binary nickel-chromium alloys containing 5, 7.5 and 10 wt. % chromium was studied using the salt drip coat test method. The tests were conducted isothermally at 700 °C in stagnant air. After testing, the samples were examined using optical microscopy, scanning electron microscopy, (SEM), coupled with energy dispersive spectroscopy, (EDS), and x-ray diffraction. SEM and EDS analysis confirmed the presence of iron chlorides and iron oxides for the low alloy steel which had the least resistance to hot corrosion under the test conditions forming a layered and porous oxide. XRD identified the presence of nickel oxide in the nickel-chromium samples that displayed superior resistance against the hot corrosion attack under the potassium chloride - potassium sulfate eutectic at 700°C. Optical microscopy revealed pitting attack with increased corrosion at longer testing times for the Ni - 5 wt. % Cr alloy. Increasing amounts of chromium content proved to be beneficial in mitigating against hot corrosion under stagnant air conditions.

Additional testing is recommended using sulfur containing atmospheres to better simulate the flue gas environment generated during biomass firing. Type II hot corrosion typically requires higher partial pressures of SO<sub>2</sub>(g) and longer times for the eutectic to establish a molten alkali salt to lead to further corrosion.

## 8. Acknowledgements

I would like to first acknowledge my faculty advisor Dr. Vilupanur A. Ravi for his guidance, patience and support. I would also like to thank Dr. Juan Carlos Nava for his input and advice. Much appreciation is extended to Armen Kvyran for assistance in SEM/EDS, to Sutinee Sujittosakul for assistance in XRD, and to Norton Thongchua and Kishan Patel for assistance in polishing. Additionally, I would like to thank Charles Gepford for his support. Thanks to Dr. Erin McDevitt (ATI) for creation of the binary nickel-chromium alloys and Tim Hudny (Elite Technologies) for EDM.

## 9. Future Work

A high temperature electrochemical setup will be used to measure corrosion rates in situ in a mixture of SO<sub>2</sub>—SO<sub>3</sub>—O<sub>2</sub> environments. This will allow for better simulation of the gas composition found within biomass boilers. In addition, commercially available alloys such as Hastelloy and Inconels will be tested.

## 10. References

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