High temperature oxidation behaviour of nanostructured cermet coatings in a mixed CO₂ – O₂ environment

M A Farrokhzad and T I Khan
University of Calgary 2500 University Dr. NW, Calgary, Canada
E-mail: mafarrok@ucalgary.ca

Abstract. Nanostructured ceramic-metallic (cermet) coatings composed of nanosized ceramic particles (α-Al₂O₃ and TiO₂) dispersed in a nickel matrix were co-electrodeposited and then oxidized at 500°C, 600°C and 700°C in a mixed gas using a Thermo-gravimetric Analysis (TGA) apparatus. The mixed gas was composed of 15% CO₂, 10% O₂ and 75% N₂. This research investigates the effects of CO₂ and O₂ partial pressures on time-depended oxidation rates for coatings and compared them to the results from atmospheric oxidation under similar temperatures. The increase in partial pressure of oxygen due to the presence of CO₂ at each tested temperature was calculated and correlated to the oxidation rate of the coatings. The results showed that the presence of CO₂ in the system increased the oxidation rate of cermet coatings when compared to atmospheric oxidation at the same temperature. It was also shown that the increase in the oxidation rate is not the result of CO₂ acting as the primary oxidant but as a secondary oxidant which results in an increase of the total partial pressure of oxygen and consequently higher oxidation rates. The WDS and XRD analyses results showed that the presence of nanosized TiO₂ particles in a nickel matrix can improve oxidation behaviour of the coatings by formation of Ni-Ti compounds on oxidizing surface of the coating which was found beneficiary in reducing the oxidation rates for cermet coatings.

1. Introduction
Nanostructured ceramic-metallic (cermet) coatings are engineered materials produced by incorporating nanosized ceramic particles such as Al₂O₃ or TiO₂ particles into a metal matrix such as nickel. The cermet coatings can be produced using several coating techniques among which co-electrodeposition technique is being commonly used in the industry due to relatively simple equipment and low costs [1-2]. As a result of high demand from the oil and gas production industry for using low cost surface protective coating materials, in recent years there has been an increase in the number of applications where cermet coatings were used to improve mechanical properties, corrosion, and high temperature oxidation resistance of alloyed components [3-6]. The In-Situ Combustion (ISC) process for oil production is a newly proposed unconventional method that utilizes extreme heat (generated by burning the lighter hydrocarbon compounds from the reservoir) to reduce the viscosity of heavier bitumen compounds which then allow an easier extraction from oil reservoirs [7-8]. In the ISC process, hot atmospheric air is injected into the oil reservoir as the feed for an underground combustion process. Due to burning of the light hydrocarbons and combustion reactions in the reservoirs, temperatures can reach as high as 500 °C to 700 °C [7, 9].

The presence of hot oxidizing gases creates a severe environment for metal degradation. In the ISC technique, the presence of high temperature gases, mostly C₆H₆ and O₂, at 500°C to 700°C generated in the ignited combustion front gases can lead to the rapid degradation of pipes and tubing used in the...
oil extraction process [11-12]. Steel alloys are used throughout the oil production industries; however, due to the extreme conditions in the ISC environment, the steel products have limited use. On the other hand, due to the huge volume of tubes and pipes needed for bitumen extraction, the use of high temperature corrosion resistant alloys (CRA’s) is uneconomical; therefore, there is a need to develop new types of specialty metal coatings that can withstand the extreme conditions of the ISC. Although electrodeposited nanostructured cermet coatings have shown superior high temperature oxidation resistance in many extreme industrial applications [5], they are not yet fully employed for use as protective coatings in equipment and piping in oil production. As a result, there is a need to develop function specific coatings that can withstand the high temperature oxidation and erosion to which oil production components are subjected to for the ISC process [8]. The analysis of the combustion gases from ISC experiments has shown that CO2 and/or CO gases can be present in the in-situ combustion produced gas. The CO2 gas can be found to a maximum level of 15% of volume, whereas CO has only been found in a trace amount in the produced combustion gas [10]. In the high temperature combustion zone, exothermic combustion reactions between oxygen and some light hydrocarbons (that are a part of bitumen chemical composition) create the heat which allows the heavier hydrocarbons to be separated from the sand. The stoichiometric reaction for the combustion of these light hydrocarbon ingredients can be written as [9]:

\[
CH_{x}O_{y} + \left(1 - \frac{m}{2} + \frac{x}{4} - \frac{y}{2}\right)O_{2} \rightarrow (1 - m)CO_{2} + mCO + \frac{x}{2}H_{2}O
\]  

(Reduct 1)

Note that reaction 1 is only one of the many stoichiometric reactions that can be written for the in-situ combustion process: but the reactants and products chemicals for all of them are the same chemical compounds. Providing a nickel coating layer onto a steel surface can provide improved oxidation and corrosion resistance at low temperatures, however at elevated temperatures, nickel has a tendency to lose its oxidation resistance and the nickel coating softens (due to the grain growth) resulting in degradation of the coating. To improve the high temperature oxidation resistance of nickel coatings, nano-sized oxide particles can be dispersed into the nickel metal matrix [1-4] using the electrodeposition method. Several studies have shown that the presence of even small amounts of the oxide particles in the nickel matrix can lead to a significant improvement in the oxidation resistance and mechanical properties of the coating [13-19]. In theory, the oxidation growth as a function of time can be linear, logarithmic or parabolic equations [20]. The oxidation process in metals involves the growth of the oxide layer through a diffusion process. The mathematics for this diffusion and oxide layer growth rate is per Fick’s first law and can be written as [21]:

\[
\frac{dx}{dt} = -D \frac{\partial C}{\partial x}
\]

Where \(D\) is the diffusion coefficient and \(C\) is the concentration of transferred charged particles. By integration of both sides of the equation, the simple oxidation thickness per function of time is:

\[
x^2 = k't + C_1
\]

Where \(k'\) is a parabolic rate of oxidation constant and \(C_1\) is a general constant value. One theory that has been proven to be more accurate and can be applied to a vast majority of the metals is the Wagner theory of oxidation based on Fick’s diffusion laws. The Wagner theory provides a parabolic rate equation in which the oxide scale growth rate on the metal is controlled by diffusion of charged particles (electrons, cations and ions) crossing the oxide-gas scale [22-24]. Similar to the pure metals, the oxidation kinetics of electrodeposited coating can be described by calculating the growth time constant “\(a\)” from the following equation [25-27]:

\[
\frac{\Delta m}{A} = kt^a + C_2
\]

Where \(\Delta m\) is the oxidation mass change, \(A\) is the surface area, \(k\) is the oxidation rate constant, \((t)\) is the time of oxidation, \((a)\) is the growth time constant and \(C_2\) is another general constant value. This
research examines the thermal stability and high temperature oxidation behaviour of the double-ceramic cermet coatings at 500°C, 600°C and 700°C in mixed gases composed of O₂, CO₂ and N₂ with a chemical composition similar to that experienced in the in-situ combustion process.

2. Experimental procedure

2.1. Materials
This study used two types of nanosized ceramic powders: alumina (α-Al₂O₃) and titania (TiO₂) purchased from M K Impex Corp. Ltd. The purity for α-Al₂O₃ powder was 99.95% (with traces of Na: 300 ppm, Si: 3.5 ppm, Ca: 1.6 ppm, Fe: 0.2 ppm, and Co: 0.8 ppm). The purity for TiO₂ powder was 98% (with traces of Al: 20 ppm, Ca: 75 ppm, Mg: 65 ppm, Nb: 119 ppm, S: 165 ppm and Si: 102 ppm). The average grain size (measured using TEM) for Al₂O₃ was 20 nm and 50 nm for TiO₂. The substrate material was made from a hot-rolled AISI-1018 carbon steel sheet and the specimens for co-electrodeposition were cut in a rectangular shape (length: 15 mm, width: 6 mm and thickness: 1 mm). The mill scale was removed by mechanical cleaning and the surface was prepared to a 600 grit finish. The surfaces were then cleaned in alkaline solutions (E-Kleen 102-ETM and E-Kleen 129-LTM) and finally an acid pickling solution (with 31% HCl) was used to remove any remaining grease or other contaminants.

2.2. Microstructural Characterization
For the grain size analysis of the powders a Tecani F20-200 kV (the Netherlands) transmission electron microscope (TEM) in bright-field (BF) mode was used. A JSM-8200 JEOL micro-probe (Tokyo, Japan) scanning electron microscopy (SEM) in the back-scattered electron mode (BSE) was used for the images of the cross-sections of coatings and oxidized specimens. The element maps were also produced using the wavelength dispersive spectroscopy (WDS) of the same JSM-8200 JEOL micro-probe. A Rigaku Multiflex X-ray diffractometer (Japan) was used for the X-ray diffraction spectroscopy of oxidized specimens.

2.3. Co-electrodeposition of coating
The standard Watt’s bath formula was used for the chemical composition of the electrolyte solution and the concentrations of ceramic particles in the electrolyte solution were obtained from previous research [14, 28-30, 37]. The pH of the electrolyte solutions was 4.0 to 4.2, and the temperature of electrolyte solution was kept between 50 to 55°C. The electrolyte solutions for double-ceramics cermet coatings were also composed of two mixtures of ceramic powders which were called; A1 and B1 coatings. The coatings classification and the compositions of the electrolyte bath solutions are summarized in table 1.

| Coatings | Molar Concentration | Particles in electrolyte [gr/lit] | Stirring Speed [rpm] | Electrolyte Composition |
|----------|---------------------|----------------------------------|----------------------|-------------------------|
| A1       | Al₂O₃: 0.25 M  TiO₂: 0.25 M | Al₂O₃: 25.5  TiO₂: 20 | 350 | Standard Watt’s bath solution: Nickel Sulphate Hexahydrate (1M), Nickel Chloride Hexahydrate (0.2 M), and Boric acid (0.5M), dissolved in distilled water. |
| B1       | Al₂O₃: 0.375 M TiO₂: 0.125 M | Al₂O₃: 38.25  TiO₂: 10 | 380 | |

The anode was made of commercial high purity nickel (99.9%). The coatings were produced using a standard DC setup for electroplating. A current density of 2 A/dm² was applied for 60 minutes for the electrodeposition of the coatings. Scanning electron microscopy (JEOL JXA-8200) was used to
measure the average electrodeposited coating thickness. The produced average thickness was measured to be 40±5 μm.

2.4. TGA Oxidation
For thermo-gravitmetric analysis, a simultaneous symmetrical thermoanalyser (Setaram, TGA 16, KEP technologies, France) was used. The thermo-gravitmetric analysis was conducted at 500°C, 600°C and 700°C on specimens coated with A1 and B1 double-ceramics cermet coatings. The sensitivity level for mass change measurement was 1μg and the maximum allowed weight of specimens was 1 gram. The mixed gas consisted of 15% CO2 and 10% O2 with the remainder being N2. The oxidation time was 86,400 seconds (24 hours) for the 500°C and 600°C tests, and 100,000 seconds (27.7 hours) for the 700°C test.

3. Results and discussion

3.1. Characterization of coatings
The appearance and morphology of the coatings deposited for both A1 and B1 ceramic mixture were, in general, similar and a uniform distribution of Al2O3 and TiO2 particles in the nickel matrix was produced for all the coatings. The cross-section of the A1 cermet coatings produced with a current density of 2 A/dm² is displayed in figure 1(left). The WDS element mapping of the cross-section of the coatings with respect to nickel, aluminum and titanium elements, shown in figure 1 (middle and right images), also indicated a uniform distribution of dispersed particles in the nickel matrix. The total particle volume fractions in the nickel matrix were 11.8 % for A1 coating and 9.2% for B1 coatings.

3.2. Thermo-gravitmetric analysis of coatings
The oxidation “mass change as a function of time” graphs are illustrated in figure 2. The solid lines are the TGA mass change results for A1 and B1 double-ceramic cermet coating specimens oxidized in the mixed CO2-O2 environment. The dotted lines on these plots show the mass change per unit of area of similar coating specimens oxidized in the air. The values for the “oxidation rate constant (δ)” and “growth-rate time constant (α)” for cermet coatings oxidized in atmosphere were calculated in the previous work by the same authors [27].

Figure 1. SEM image of cross-section (left) and WDS compositional analysis (middle) of A1 coating. Element maps (right) showing A1coating surface (A), nickel (B), aluminum (C) and titanium (D)
3.3. Discussion on effect of partial pressure of CO2

Unlike carbon and nitrogen, which do not directly react chemically with nickel, oxygen reacts with nickel as a primary or secondary oxidant and forms nickel oxide. The chemical reaction between oxygen as the primary oxidant and nickel can be written as:

$$2\text{Ni}(s) + \text{O}_2(g) = 2\text{NiO}(s)$$  \hspace{1cm} (Reaction 2)

Meanwhile, carbon from CO$_2$ can act as a secondary oxidant by decomposing into carbon monoxide (CO) and oxygen and then can introduce the additional oxygen into the nickel in which the oxygen first adsorbs and then diffuses into the nickel lattices:

$$\text{Ni}(s) + \text{CO}_2(g) = \text{NiO}(s) + \text{CO}(g)$$  \hspace{1cm} (Reaction 3)

The diffusing oxygen ions eventually react with migrating nickel cations to the surface and form the thickness of the NiO layer or they recompose into the pores inside the NiO layer or coating and form oxygen molecules (Rahmel and Tobolski et al.) [32]. For the voids that exist near the surface, it can be assumed that the amount of pressure inside the voids and the chemical composition of the gas in the pores is the same as the pressure and the chemical composition of the external atmosphere (i.e. atmospheric pressure and chemical composition for this study). However the chemical pressure and the chemical composition of the gas inside of the pores that is further into the bulk of the coating is not the same as the pressure and chemical composition of the external atmosphere. For calculating the pressure and chemical composition of the diffused ions from oxidizing gases into the pores and voids within the bulk of coating material, it should be noted that the partial pressure of reacting oxygen will be at equilibrium with cations ($\text{Ni}^{\text{II}}$) migration towards the oxide layer and as it is defined by activity of $\text{Ni}^{\text{II}}$ when reaction 2 is written by half cell oxidation equation ($2\text{Ni} \rightarrow 2\text{Ni}^{\text{II}} + 2\text{e}^-$):

$$2\text{Ni}^{\text{II}} + 2\text{e}^- + \text{O}_2 \rightarrow 2\text{NiO}$$  \hspace{1cm} (Reaction 4)

$$\Delta G^\circ = -RT \ln \left( \frac{a_{\text{NiO}}^2}{a_{\text{Ni}^{\text{II}}} \times a_{\text{O}_2} \times a_e^2} \right) = -RT \ln \left( \frac{1}{a_{\text{Ni}^{\text{II}}} \times a_{\text{O}_2}} \right)$$  \hspace{1cm} (4)

Where $a_{\text{NiO}}$ and $a_e$ are equal to unity and $a_{\text{O}_2} = p_{\text{O}_2}$ [36]. In fact in an equilibrium condition the activity of the nickel cation ($a_{\text{Ni}^{\text{II}}}$) can also be considered almost equal to unity at the oxide/gas interface (when it is considered as vapour pressure of the condensed element) but in the bulk of the material, its activity corresponds to the amount of oxygen that is diffused into the bulk of the material. Therefore the equilibrium partial pressure of oxygen as a function of nickel activity becomes:
By calculating the Gibbs free energy of nickel oxidation for reaction 2 for the tested temperature, the oxygen partial pressure will be:

$$\Delta G^\circ \approx (2 \times \Delta G^\circ_{NiO} - (2 \times \Delta G^\circ_{Ni} + \Delta G^\circ_{O_2})$$

$$\Delta G^\circ \approx (2 \times \Delta H^\circ_{NiO} - 2 \times T \Delta S^\circ_{NiO}) - (2 \times \Delta H^\circ_{Ni} - 2 \times T \Delta S^\circ_{Ni} + \Delta H^\circ_{O_2} - T \Delta S^\circ_{O_2})$$

$$\Delta G^\circ \approx 2 \times \Delta H^\circ_{NiO} - 2 \times T \Delta S^\circ_{NiO} - 2 \times \Delta H^\circ_{Ni} + 2 \times T \Delta S^\circ_{Ni} - \Delta H^\circ_{O_2} + T \Delta S^\circ_{O_2}$$

Where standard values for $\Delta H^\circ$, $\Delta G^\circ$, $\Delta S^\circ$ are given in table 2:

| Substance | $\Delta H^\circ$ [kJ/mol] | $\Delta G^\circ$ [kJ/mol] | $\Delta S^\circ$ [J/mol.°K] |
|-----------|--------------------------|--------------------------|--------------------------|
| Ni        | 0                        | 0                        | 30                       |
| O₂        | 0                        | 0                        | 205                      |
| NiO       | -244                     | -216                     | 39                       |
| CO        | -111                     | -137                     | 198                      |
| CO₂       | -394                     | -394                     | 214                      |

Therefore the Gibbs free energy at test temperatures and in the pressure for reaction 2 becomes:

$$\Delta G^\circ \approx (2 \times -244000 - 2 \times 39T) - [(0 - 2 \times 30T) + (0 - 205T)]$$

$$\Delta G^\circ \approx -488000 [J/mol] + 187 T [J/mol.°K]$$

The amount of partial pressure of oxygen in the bulk of nickel oxide (as a result of diffusion) can be calculated using equation 5:

$$P_{O_2} = \frac{1}{a^2_{Ni}} \exp \left( \frac{\Delta G^\circ}{RT} \right)$$

Table 3. Partial pressure of oxygen in the bulk of nickel oxide

| Temperature | $\Delta G^\circ$ [J/mol] | $P_{O_2}$ |
|-------------|--------------------------|-----------|
| 500°C (773 °K) | -343499           | 6.13 x 10^{-24} atm |
| 600°C (873 °K) | -324749           | 3.70 x 10^{-20} atm |
| 700°C (973 °K) | -306049           | 3.71 x 10^{-17} atm |

Nickel will not be oxidized below these pressures shown in table 3 (also called the dissociation partial pressure of Ni) at the given temperature. This also means that the oxygen partial pressure in the bulk of the pores will be increased as a function of temperature and consequently the oxidation rate will increase as was observed in these experiments (see figure 2). Meanwhile the oxygen partial pressure inside the pores in the bulk (for a non-cracked oxide layer) is a small fraction of the oxygen partial pressure for the oxidizing environment (the partial pressure of oxygen in air is approximately 0.21 atm.). This is due to the fact that in an oxidizing surface, the transfer of oxygen from the high oxygen side (the external atmosphere) to a low oxygen side (pores) is a low rate mass transfer process [22, 36]. The diffusion of oxygen in the bulk is assumed to be from adsorption of oxygen molecules at the gas-metal interface followed by a chain of “formation-decomposition-reformation” process where the oxide dissociates and releases oxygen which then migrates inward to low energy sites such as pores or voids around the deposited $\alpha$-Al$_2$O$_3$ or TiO$_2$ particles [22]. Sheasby et al. described that since CO and CO$_2$ do not react with nickel, the nature of their diffusion is mass transportation through a short-circuit path such as high-angle grain boundaries [34]. From reaction 3 we can calculate the O$_2$ partial pressure associated with the secondary oxidant (CO$_2$):
\[ \text{Ni}(s) + \text{CO}_2(g) = \text{NiO}(s) + \text{CO}(g) \]
\[ \Delta G^\circ \approx (\Delta G^\circ_{\text{NiO}} + \Delta G^\circ_{\text{CO}}) - (\Delta G^\circ_{\text{Ni}} + \Delta G^\circ_{\text{CO}_2}) \]
\[ \Delta G^\circ \approx [(\Delta H^\circ_{\text{NiO}} - T\Delta S^\circ_{\text{NiO}}) + (\Delta H^\circ_{\text{CO}} - T\Delta S^\circ_{\text{CO}})] - [(\Delta H^\circ_{\text{Ni}} - T\Delta S^\circ_{\text{Ni}}) + (\Delta H^\circ_{\text{CO}_2} - T\Delta S^\circ_{\text{CO}_2})] \]
\[ \Delta G^\circ \approx -244000 - 39T - 111000 - 198T + 30T + 394000 + 214T \]
\[ \Delta G^\circ \approx 39000 \text{[J/mol]} + 7T \text{[J/mol.°K]} \]

Although CO and CO\(_2\) do not react with nickel, they can act as the secondary oxidant and release oxygen to react with Ni. The activity of nickel (\(a_{\text{Ni}}\)) is about the unity, therefore the calculated ratio between the partial pressures for the CO/CO\(_2\) system are:

\[ \frac{p_{\text{CO}}}{p_{\text{CO}_2}} = a_{\text{Ni}} \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \] (6)

**Table 4. Partial pressure for CO/CO\(_2\) system**

| Temperature \(\text{[°K]}\) | \(\Delta G^\circ\) \[\text{J/mol}\] | \(\frac{p_{\text{CO}}}{p_{\text{CO}_2}}\) |
|-----------------------------|----------------|-----------------|
| 500°C (773 °K) | 44411 | 9.97 x 10\(^{-4}\) |
| 600°C (873 °K) | 45111 | 1.99 x 10\(^{-3}\) |
| 700°C (973 °K) | 45811 | 3.47 x 10\(^{-3}\) |

Table 4 shows that only small amounts of oxygen released from the conversion of CO\(_2\) to CO (reaction 3) become available as the secondary oxidant and the majority of CO\(_2\) remains inactive in the system. The oxygen partial pressure associated with the secondary oxidant at each temperature can be calculated by considering the redox reaction between CO to CO\(_2\):

\[ \text{CO}_2(g) = \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \] (Reaction 5)

\[ \Delta G^\circ \approx (\Delta G^\circ_{\text{CO}} + \frac{1}{2}\Delta G^\circ_{\text{CO}_2}) - (\Delta G^\circ_{\text{CO}_2}) \approx 282000 \text{[J/mol]} - 87 T \text{[J/mol.°K]} \]

The partial pressure associated with reaction 5 can be written as:

\[ p_{\text{O}_2} = \left(\frac{p_{\text{CO}}}{p_{\text{CO}_2}}\right)^2 \exp\left(-\frac{2\Delta G^\circ}{RT}\right) \] (7)

Therefore the partial pressure of oxygen as the secondary oxidant for each test temperature becomes:

**Table 5. Partial pressure of oxygen as the secondary oxidant**

| Temperature \(\text{[°K]}\) | \(\Delta G^\circ\) \[\text{J/mol}\] | \(p_{\text{O}_2}\) |
|-----------------------------|----------------|----------------|
| 500°C (773 °K) | 214749 | 9.52 x 10\(^{-24}\) atm |
| 600°C (873 °K) | 206049 | 5.55 x 10\(^{-20}\) atm |
| 700°C (973 °K) | 197349 | 5.37 x 10\(^{-17}\) atm |

A comparison between the primary and secondary oxidant O\(_2\) partial pressure is provided in table 6:
Table 6. A comparison for partial pressure for primary and secondary oxidants

| Temperature       | Primary O2 Oxidant Partial Pressure (2Ni + O2 = 2NiO) | Secondary O2 Oxidant Partial Pressure (Ni + CO₂ = NiO + CO) | Secondary to Primary Partial Pressure Ratio |
|-------------------|------------------------------------------------------|-------------------------------------------------------------|---------------------------------------------|
| 500°C (773 °K)    | 6.13 x 10^{-24}                                      | 9.52 x 10^{-24}                                             | 1.55                                        |
| 600°C (873 °K)    | 3.70 x 10^{-20}                                      | 5.55 x 10^{-20}                                             | 1.50                                        |
| 700°C (973 °K)    | 3.71 x 10^{-17}                                      | 5.37 x 10^{-17}                                             | 1.45                                        |

From tables 5 and 6 and by comparing the oxygen partial pressure between the primary and the secondary oxidants, it can be concluded that in the presence of a CO/CO₂ oxidizing system, the O₂ partial pressure in the voids and pores in the bulk of the coating material will be greater as compared to a system, which consists of only oxygen. This also means that a slightly higher oxidation rate for a CO₂/CO gas system is expected as compared to an atmospheric system.

3.4. Discussion on effect of partial pressure of O₂

Since reactions 2 and 3 are both thermodynamically possible for the tested temperature in these experiment, the standard state Gibbs free energy (ΔG°) exchanged between the reactants and products should be negative and that means that the equilibrium partial pressure of O₂ is:

$$p_{O_2} = \exp\left(\frac{\Delta G^o}{RT}\right)$$

(8)

Where T is the temperature, $$p_{O2}$$ is the equilibrium partial pressure of the reaction (or as secondary oxidant, the partial pressure of oxygen from dissolution of CO₂: CO₂ → CO + ½O₂). Changes in partial pressure of oxygen can affect the oxidation rate constant (k) of most metals including nickel according to [22, 36]:

$$k' \propto (p_{O_2})^{\frac{1}{4}}$$

(9)

The value for n is unique to each metal and it can be found by analyzing the oxidation reaction with respect to exchange of ions, cations and electrons in oxidation process when they are written in Kröger nomenclature formulation [36]. The growth of the oxide layer in a cation deficient NiO occurs at the gas-oxide layer interface. When the exchange of ions, cations and electrons in oxidation of Ni is written in Kröger formulation, it becomes:

$$O_2 + 2Ni = 2NiO + 2V''_Ni + 4 \cdot \cdot$$

(Reaction 6)

Where the left side of the reaction is reactants and the right side is the products, $$V''_Ni$$ is the doubly charged cation vacancy (2 for Ni) and $$\cdot \cdot$$ is the number of electron holes (4 for Ni). The thermodynamic equilibrium for the exchange of reactants and products at gas-oxide interface when considering the activity of compounds can be written as:

$$K = \frac{[NiO]^2 \times [C_{V''_Ni}]^2 \times [C_h]^4}{[O_2] \times [Ni]^2} = \frac{1 \times [C_{V''_Ni}]^2 \times [C_h]^4}{p_{O_2} \times 1} = \frac{[C_{V''_Ni}]^2 \times [C_h]^4}{p_{O_2}}$$

(10)

Where [NiO], [$$C_{V''_Ni}$$] and [$$C_h$$] are the concentration (activity) of products and [O₂] and [Ni] are the concentration (activity) of the reactants. The activity of oxygen corresponds to the partial pressure of the reactive oxygen. Similarly, the activity of solids (Ni and NiO) is equal to unity. The equation 10 becomes:

$$p_{O_2} \propto [C_{V''_Ni}]^2 \times [C_h]^4$$

(11)
Since for every two cation vacancies in Ni there are four electron holes \((V'^{\prime\prime}_{Ni} = 2 \cdot \hat{h})\) then:

\[
p_{O_2} \propto \left[ C_{V'^{\prime\prime}_{Ni}} \right]^2 \times \left[ C_{V'^{\prime}_{Ni}} \right]^4 \propto \left[ C_{V'^{\prime}_{Ni}} \right]^6
\]

or

\[
C_{V'^{\prime\prime}_{Ni}} \propto (P_{O_2})^{1/6}
\]

Another possibility for reaction 6 is when an electron hole is associated with one cation vacancy or:

\[
\frac{1}{2}O_2 = O + V'^{\prime}_{Ni} + \hat{h}
\]  

(Relation 7)

And hence equation 13 becomes:

\[
C_{V'^{\prime}_{Ni}} \propto (P_{O_2})^{1/4}
\]

Recent research has confirmed that both types of defects from reactions 6 and 7 are possible [22]. For an oxidation reaction to progress, the outward flux of Ni cations \((J_{Ni^+})\) should equal inward migration of oxygen cation (or vacancies in Ni), \((J_{O^-} = J_{Ni^+})\) but in the opposition direction, hence Fick’s first law (equation 1) becomes:

\[
\frac{dx}{dt} = k'J_{Ni^+} = -k'J_{Ni^+} = -k'x D_{Ni^+} \left( C^\prime_{V'^{\prime}_{Ni}} - C^\prime_{V'^{\prime}_{Ni}} \right)
\]

Where \(D_{Ni^+}\) is the diffusivity coefficient of cation migration, \(C^\prime_{V'^{\prime}_{Ni}}\) is the vacancy concentration at the metal-oxide (Ni-NiO) interface and \(C^\prime_{V'^{\prime}_{Ni}}\) is vacancy concentration in oxide-gas (NiO-O2), therefore equations 13 and 14 respectively become:

\[
\frac{dx}{dt} = -k'x D_{Ni^+} \left( p^{1/6} O_2(NiO-O2) \right) - \left( p^{1/6} O_2(Ni-NiO) \right)
\]

or

\[
k' \propto \left( p^{1/6} O_2(NiO-O2) \right) - \left( p^{1/6} O_2(Ni-NiO) \right)
\]

\[
\frac{dx}{dt} = -k'x D_{Ni^+} \left( p^{1/4} O_2(NiO-O2) \right) - \left( p^{1/4} O_2(Ni-NiO) \right)
\]

or

\[
k' \propto \left( p^{1/4} O_2(NiO-O2) \right) - \left( p^{1/4} O_2(Ni-NiO) \right)
\]

Since the oxygen partial pressure at the oxide-gas interface is greater than the partial pressure of diffusing oxygen in oxide-metal interface, therefore we have:

\[
k' \propto p^{1/6} O_2(NiO-O2)
\]

\[
k' \propto p^{1/4} O_2(NiO-O2)
\]

The chemical composition of the oxidizing mixed gas used for this experiment was prepared based on the literature review of chemical composition of produced gas in the in-situ combustion which showed that the maximum volume of CO2 to be 15% and the maximum volume for O2 to be 10%. Since the TGA equipment applies an atmospheric pressure during the oxidation tests, the equivalent partial pressure of CO2 to 15% of the total gas volume creates an oxygen partial pressure equivalent to:

\[
15\% \times 1 \text{ atm} = 0.15 \text{ atm}.
\]

Similarly the partial pressure of oxygen to 10% of the total gas volume is equivalent to:

\[
10\% \times 1 \text{ atm} = 0.1 \text{ atm}.
\]

The combined partial pressure from both CO2 and O2 is greater to 0.25 atm which is greater than the partial pressure of oxygen from dry air in atmospheric conditions (0.21 atm.). Therefore per equations 16 and 17, we should experience an increase in oxidation rate constant \((k')\) close to 3% to 5%. The mass change results in figure 2 showed the correlation between this increases in the oxidation rate constant to the presence of CO2.
3.5. Microanalysis of oxidized coatings
Figure 3 is SEM images of the cross-sections and surfaces of A1 specimens oxidized at 500°C, 600°C and 700°C. In comparison with oxidation in dry atmosphere for the same temperature and oxidation time, these images showed similar microstructural features of the coatings and oxide layers between oxidized specimens in the mixed gas to the oxidized specimens in dry atmospheric condition [27].

![Figure 3. SEM of A1 coatings oxidized in mixed gas (15%CO₂-10%O₂) at: 500°C (left), 600°C (center) and 700°C (right)](image)

3.6. Element maps and XRD analyses of oxidized coatings
Figure 4 represents the element distribution maps for aluminum (Al) and titanium (Ti). These elements maps are based on microprobe WDS area scan analyses from the surfaces of A1 and B1 coatings oxidized in mixed gas (15% CO₂-10% O₂) at 500°C, 600° and 700°C. The element map analyses of non-oxidized coating surfaces were also included for comparison. XRD analyses were conducted on the surfaced of A1 and B1 coatings oxidized in mixed gas at all three temperatures and the graphs and compound analysis results are given in figure 5.

![Figure 4. WDS Aluminum and Titanium maps for A1 oxidized in mixed gas (15%CO₂-10%O₂): non-oxidized (top-left), at 500°C (top-right), at 600°C (bottom-left) and at 700°C (bottom-right)](image)

It should be noted that WDS scanning by JEOL-8200 microprobe was not sensitive enough to detect the presence of carbon; therefore the search for carbides or other carbonic compounds (as a result of oxidation of the coating with CO₂ or CO) was conducted using XRD. Element maps for titanium and aluminum on oxidized B1 coatings in a CO₂ rich mixed gas were similar to the maps from oxidized A1 coatings, therefore only the results for A1 coatings are presented. The aluminum maps showed an
outward migration of Ni cations, thus imposing an obscuring effect on aluminum content as a function of temperature, which was seen previously in atmospheric oxidation of A1 and B1 coatings. The element maps for Ti and Al suggest that the TiO$_2$ particles actively remain on the surface as compared to Al$_2$O$_3$ particles (Fig. 4). Oxidized cermet coatings containing dispersed TiO$_2$ particles showed formation of nickel titanate compounds; NiTiO$_3$ and Ni$_3$TiO$_5$ [38-41]. The formation of Ni-Ti compounds could affect nickel oxidation resistance in two ways; firstly, it can have some alloying effects between the dispersed particles and the Ni matrix. Zeng et al [42] have argued that formation of the NiTiO$_3$ may contribute to the lower oxidation rates for the alloys, especially at temperatures below 750°C. Secondly XRD results of the oxidized surface showed that these nickel titanate can be found in the oxidized surface, suggesting that unlike the Al$_2$O$_3$ particles where upward migration of Ni did not form any Ni-Al compounds and the migrating Ni cations may have bypassed the dispersed Al$_2$O$_3$ particles, for TiO$_2$ particles, the Ni-Ti compounds can affect the number of migrating Ni to the surface. Therefore for coatings with dispersed TiO$_2$, the migration of Ni cations does not leave the upper part of the coating empty of dispersed particles. Literature review shows that nickel titanate NiTiO$_3$ can be formed in the presence of NiO and TiO$_2$ at around 600°C [39-40]. However Ni$_3$TiO$_5$ is a meta-stable phase that can be found in stable phase at a higher temperature [38, 40-41]. The XRD analyses also confirmed that when the temperature was increased, the frequency of finding these compounds in the oxide layer also increased, which is an indicator of an increase in the quantity of the compounds in the oxide layer. Carbon has an extremely low solubility in the non-molten form of nickel and therefore the carburization of Ni coatings and formation of C-Ni compounds (carbides) does not occur at the temperatures used in this project. The absence of C-Ni carbides or graphite in pure or reacted forms in the oxide layer formed on the coating surfaces was later confirmed with XRD analysis results. Due to the low solubility of C in Ni at low temperatures, the practical data for Ni-C solids is nonexistent, however Singleton and Nash et al [35] have constructed a Ni-C phase diagram using computer models and also based on some measured values from other literatures and have concluded that Ni-C at below eutectic can only exist in metastable form (Ni-Ni$_3$C). The XRD analysis in this research did not detect this metastable form Ni-C system. Additionally, nitrate or nitride compounds of nickel (i.e. nickel (II) nitrate: Ni(NO$_3$)$_2$ ) were not found in XRD analysis, therefore it was concluded that the nitrogen (N$_2$) in the mixed gas does not react with nickel for the temperatures used in this research.

**Figure 5.** XRD analyses for A1 coatings oxidized in mixed gas at: 500, 600 and 700°C
4. Conclusion
The TGA experiment was designed to study the effect of oxidation of the double-ceramic oxides cermet coatings in a gaseous environment containing CO₂ and O₂. Based on the results, it was showed that the presence of CO₂ in the system can increase the oxidation rate compared to oxidation at atmospheric conditions. It was concluded that the increase in the oxidation rate is not the result of carbon-dioxide acting as the primary oxidant but as a secondary oxidant agent. Carbon does not dissolve in nickel at low temperatures (below the eutectic temperature), but CO₂ can act as the secondary oxidant by decomposing into CO and releasing extra oxygen to the surface of the oxidizing coating. It was found that the additional oxygen from the decomposition will increase the total partial pressure of oxygen in the voids which results in higher oxidation rates. The increase in partial pressure due to the presence of CO₂ was calculated and then correlated to the oxidation rate. The results showed that the oxidation behaviour of the coatings in an atmosphere of CO₂ was similar to that observed under atmospheric conditions. The titanium element maps showed a relative stability and presence of titanium on the surfaced of oxidized coatings which is believed to be caused by formation of Ni-Ti compounds (Ni₃TiO₅ and NiTiO₃) which was also confirmed by XRD analyses.

5. Acknowledgements
The authors would like to thank the department of Mechanical and Manufacturing Engineering of the University of Calgary, Alberta, Canada, Natural Science and Engineering Research Council of Canada (NSERC), and Statoil Canada Ltd. for their financial support.

6. References
[1] Sautter F K 1963 J. Electrochem. Soc.110, Issue 6, 557–560
[2] Gupta P K, Tiwari A N, and Agrawal B K 1989 Trans. Japan Instit. Met. 23 320–327
[3] Saha R K, Haq I U, Khan T I and Glenesk L B 2010 Key Eng. Mat. 442 187–194
[4] Saha R K, Khan T I and Glenesk L B and Haq I U 2009 Ceram. Trans. 208 37–44
[5] Chang L M, Liu J H and Zhang R J 2011 Mat. Corrs. 62, Issue 10, 920–925
[6] Kannan K R, Vasntasree V and Hocking M G 1984, Coatings and Surface Treatment for Corrosion and Wear Resistance (New York: Ellis, Horwood) pp 263–275
[7] Moore R G, Laureshen C, Belgrave J M, Ursenbach M, Mehta S A 1995 Fuel 74 1169–1175
[8] Roche P 2009 In-Situ Combustion, New Technology Magazine (September 2009)
[9] Mamora D D 1993, Kinetics of In-Situ Combustion, PhD Thesis, (Stanford University)
[10] Xu H 2001, In-Situ Upgrading of Heavy Oil, M. Sc. Thesis, (University of Calgary)
[11] Brooks S, Ferguson J M, Meadowcroft D B and Stevens C G 1978, Materials and Coatings to Resist High Temperature Corrosion (London: Applied Science Publishers) pp. 121–138
[12] Brigham W E, Castanier L 1998, Reservoir Engineering, Chapter 16, (The National Energy Technology Laboratory -NETL)
[13] Ciubotariu A C, Benea L, Varsanyi M L, Dragan V 2008 Electrochim. Acta 53 4557
[14] Saha R K and Khan T I 2010, Surf. Coat. Tech. 205 890–895
[15] Gül H, Kilic F, Aslan S, Alp A, Akbulut H 2009 Wear 267 976–990
[16] Erb U 1995, Nanostruture Mater. 6 533–538
[17] Bockris J O M and Razumney G A 1967, Fundamental Aspects of Electrocrystallization
[18] Walsh F C. and Herron M E 1991, *Jour. Physic, D: Appl. Phys.* 24 217–225
[19] Qu N S, Chan K C, Zhu D 2004 *Scripta Mater.* 50 1131–1134
[20] Ernest Birchenall C 1982, *High Temperature Corrosion – NACE 6* 3–7
[21] Wahab M A 2005 *Solid State Physics* (Oxford: Alphas Science International) Chapter 6
[22] N. Birks N, Meier G H, Pettit F S 2006, *Introduction to the High-Temperature Oxidization,* 2nd Edition, (Cambridge: Cambridge University Press)
[23] Davis J R 1999 *Heat-Resistant Materials*, (Ohio: ASM International) p.36
[24] Gesmundo F and Viani F 1981 *J. Electrochem. Soc.* 128, Issue 2, 470–479
[25] Susan D F and Marder A R 2002 *Oxid. Met.* 57 131–158
[26] Susan D F and Marder A R 2002 *Oxid. Met.* 57 159–180
[27] Farrokhzad M A , Khan T I 2012 *Key Eng. Mater.*510-511 32–42
[28] Gabe D R 1978 *Principle of Metal Surface Treatment and Protection* 28 (Oxford: Pergamon)
[29] Kim M J, Kim J S, Kim D J, Kim H P 2009 *Met. Mater. Int.* 15, No. 5, 789–795
[30] Kuo S L , Chen Y C, Ger M D and Hwu W H 2004 *Mater.Chem. Phys.* 86 5–10
[31] Rahmel A and Tobolski J, Werkst. U 1965 *Korr* 15 662
[32] West J M 1980 *Basic Corrosion and Oxidation* (Chichester: Ellis Horwood Ltd.)
[33] Sheasby J, Boggs W E and Turkdogan E T 1985, *Mater. Sci.*18 127
[34] Singleton M and Nash P 1989 *Bulletin of Alloy Phase Diagrams*- The C-Ni (Carbon-Nickel) System- 10, No.2
[35] Bradford S A 2001 *ASM Handbooks- Corrosion* 13 (Ohio: ASM International) pp. 62–76
[36] Feng Q, Li T, Teng H, Zhang X , Zhang Y, Liu Ch, Jin J, 2008 *Surf. Coat. Tech.*202 4137–44
[37] Laqua W, Schmalzried H 1982 *NACE 6*, 110–114
[38] Lopes K P et al 2009 *J. Alloys Compd.* 468 327–332
[39] QIU Ai-tao et al 2011, *Trans. of Nonferrous Met. Soc. China* 21 1808–1816
[40] Taylor D J, Fleig P F, Schwab S T and Page R A 1999 *Surf. Coat. Tech.* 465, pp.120–121
[41] Zeng C L, Li M C, Liu G Q, and Wu W T 2002, *Oxid. Met.* 58, Nos. 1/2, pp.171–184