

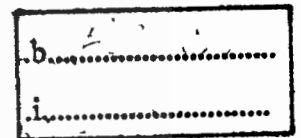
CHROMIUM EVAPORATION FROM STAINLESS STEEL INTERCONNECT IN
SOLID OXIDE FUEL CELLS AND ITS PROTECTION



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หัวข้อวิทยานิพนธ์	การระเหยของโครเมียมจากเหล็กกล้าไร้สนิมที่ใช้เป็นแผ่นกันเซลล์ ในเซลล์เชื้อเพลิงชนิดออกไซด์แข็งและการเคลือบป้องกัน
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บทคัดย่อ

ในสภาวะปฏิบัติการของเซลล์เชื้อเพลิงชนิดออกไซด์แข็ง จะเกิดการระเหยของโครเมียมออกจากแผ่นกันเซลล์ที่เป็นวัสดุประเภทเหล็กกล้าไร้สนิม การระเหยของโครเมียมนี้เป็นปัญหาสำคัญที่นอกจากจะทำให้ส่วนประกอบอื่นๆของเซลล์เชื้อเพลิงเกิดการเสื่อมสภาพแล้ว ยังทำให้ประสิทธิภาพและอายุการใช้งานของเซลล์เชื้อเพลิงต่ำลงอีกด้วย ในงานวิจัยนี้ทำการศึกษาการระเหยของโครเมียมจากเหล็กกล้าไร้สนิมเกรด AISI 441 เปรียบเทียบกับชิ้นงาน AISI 441 ที่มีการเคลือบป้องกันการระเหยด้วยสารเคลือบอีก 2 ชนิด นั่นคือ 1). การเคลือบป้องกันด้วย Manganese cobalt spinel (MnCo_2O_4 : Mn-Co spinel) ที่เคลือบผิวด้วยวิธีทางไฟฟ้า (Electroplating) และ 2). การเคลือบป้องกันด้วย Lanthanum strontium manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$: LSM) ที่เตรียมขึ้นด้วยวิธี Sol-gel จากการทดลองพบว่า การระเหยของโครเมียมจากเหล็กกล้าไร้สนิมเกรด AISI 441 ที่ไม่ได้ทำการเคลือบถูกจำกัดด้วยจลนพลศาสตร์ของปฏิกิริยา ในช่วงอัตราเร็วเชิงเส้นของก๊าซออกซิเจนเป็น 0.8-3.0 cm/s และมีค่าพลังงานกระตุ้นเท่ากับ 24.74 kJ/mol ส่วนการระเหยของโครเมียมออกจากชิ้นงานเคลือบทั้ง 2 ชนิด นอกจากจะไม่ได้ช่วยลดการระเหยของโครเมียมแล้ว กลับพบว่ามี การระเหยของโครเมียมในอัตราที่สูงกว่าของชิ้นงานที่ไม่ได้เคลือบ ซึ่งอาจเป็นไปได้ว่าสารเคลือบที่ใช้ รวมไปถึงวิธีการเคลือบทั้ง 2 ชนิดนั้น ไม่เหมาะสม ในกรณีของการใช้สารเคลือบ Mn-Co spinel ชั้นเคลือบที่ปกคลุมชิ้นงานอาจจะมี ความหนาแน่นและความหนาน้อยเกินไป ส่วนกรณีของ LSM น่าจะเกิดจากวิธีการเคลือบที่ไม่เหมาะสม ซึ่งควรจะมีการปรับปรุงแก้ไขต่อไปในอนาคต เช่น ใช้วิธีการเคลือบ LSM วิธีอื่นที่ทำให้การยึดเกาะระหว่างพื้นผิวของชั้นเคลือบและโลหะเพิ่มขึ้น หรือการเพิ่มความหนาแน่นของชั้นเคลือบทั้ง Mn-Co spinel และ LSM เป็นต้น

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Abstract

Chromium evaporation from metallic interconnect in cathodic condition of solid oxide fuel cells (SOFCs) at high temperatures, is a critical problem leading to not only deterioration of cell materials but also degradation of the cell power and shorter lifetime. This research studied chromium evaporation of two different coating materials and methods that were AISI 441 coated with manganese cobalt spinel (MnCo_2O_4 : Mn-Co spinel) by electroplating method and AISI 441 coated with lanthanum strontium manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$: LSM) derived by sol-gel method comparing with uncoated AISI 441. The results showed that chromium evaporation from uncoated AISI 441 was limited by kinetics of reaction in linear velocity range of 0.8-3.0 cm/s and its activation energy was 24.74 kJ/mol. It was incredibly that both coating samples could not suppress chromium release from materials. On the contrary, chromium evaporation rates from both samples were higher than that of uncoated sample. This might be described by the reason that both coating samples did not suit for interconnect application owing to too loose and thin Mn-Co spinel coated and not appropriate coating method of LSM sol-gel. Therefore, dense Mn-Co spinel and LSM sol-gel coatings by more suitable methods to increase adhesion and density of coatings should be further studied.

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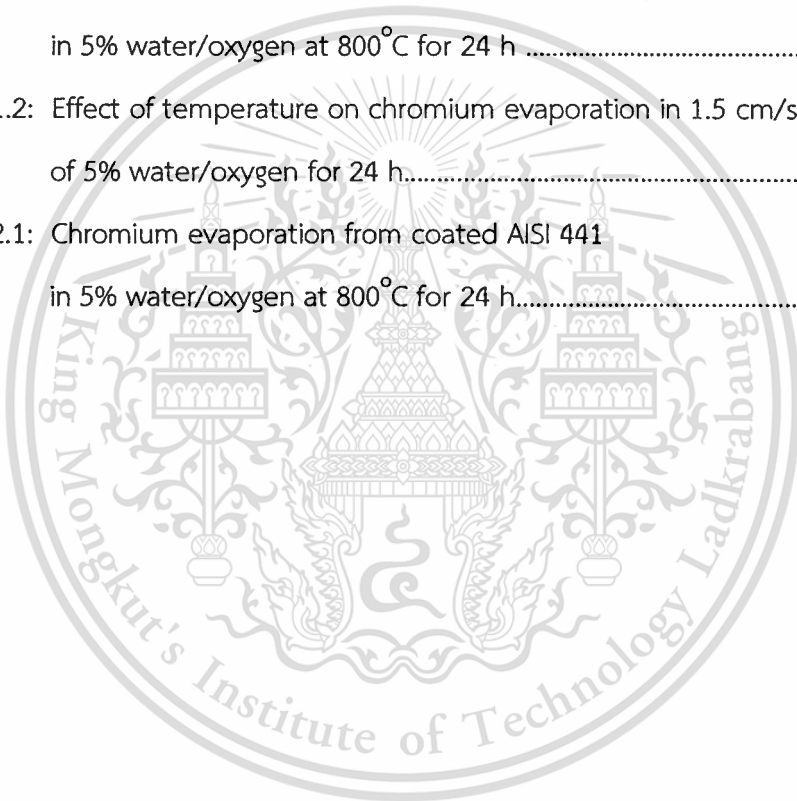
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Chapter 1

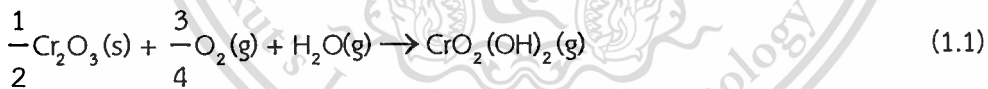
Introduction

1.1 Background

At present, the major energy sources that human are used for living are petroleum and natural gas. Unfortunately, these energy sources are not only the cause of environmental problems, i.e. greenhouse effect, but also running out. The researchers attempt to find clean renewable and sustainable energy instead of petroleum and natural gas. Hydrogen energy is one of the interesting ways tried to use by converting its energy to electrical energy. The convertor is called fuel cell especially solid oxide fuel cells (SOFCs) that are the most efficient fuel cell [1].

The electrolyte of SOFCs is ceramics material, so the operating temperature is necessary high for ionic conductivity. In addition, expensive platinum catalyst is negligible [2].

The important problem of SOFCs is degradation of metallic, chromium-containing alloys, interconnect. When these alloys are in the cathodic condition, chromium oxide passive film was evaporated to gas state [3, 4]. Predominant reaction that occurred in humidified oxidizing atmosphere is [5-7]



The aim of this research is to study the phenomenon of chromium evaporation from commercial grade stainless steel, AISI 441, simulated the cathodic condition in SOFCs. In this work, the effects of linear velocity of wet oxygen stream and operating temperature on chromium evaporation are observed. From the experiment, we can find the activation energy of reaction. Thereafter, the experiment is tested again in the same manner for protective coatings on AISI 441.

1.2 The research scopes

Chromium evaporation is studied in simulated cathodic condition in SOFCs. The samples tested are uncoated AISI 441, AISI 441 coated with manganese cobalt spinel (Mn-Co; MnCo_2O_4) by electroplating method and AISI 441 coated with lanthanum strontium manganite (LSM; $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$) derived by sol-gel method. The compositions of AISI 441 are shown in Table 1.1. The scopes of this research are as follow.

- 1). Determine effect of wet oxygen flow rate (5%water/oxygen) on chromium evaporation.
- 2). Investigate effect of operating temperature on chromium evaporation and find its activation energy.
- 3). Find the appropriated condition i.e. suitable coating time, electrical current and calcinated period for electroplating coating of Mn-Co.
- 5). Prepare LSM sol-gel and coat on AISI 441 by dipped coating method.
- 8). Study chromium evaporation from coated samples and compare with uncoated sample.

Table 1.1 Compositions of AISI 441.

Element	Cr	C	Mn	Si	Al	Nb	Ti	Mo	Fe
Wt. %	17.83	0.01	0.24	0.60	0.006	0.55	0.13	0.01	Balance

Chapter 2

Theory

2.1 Fuel cells (FCs) [8]

Fuel cell is an electrochemical device converting chemical energy to electrical energy. Fuel cell composes of electrodes, that are anode (negative electrode) and cathode (positive electrode), and electrolyte where is between two electrodes. Figure 2.1 shows the schematic of a fuel cell.

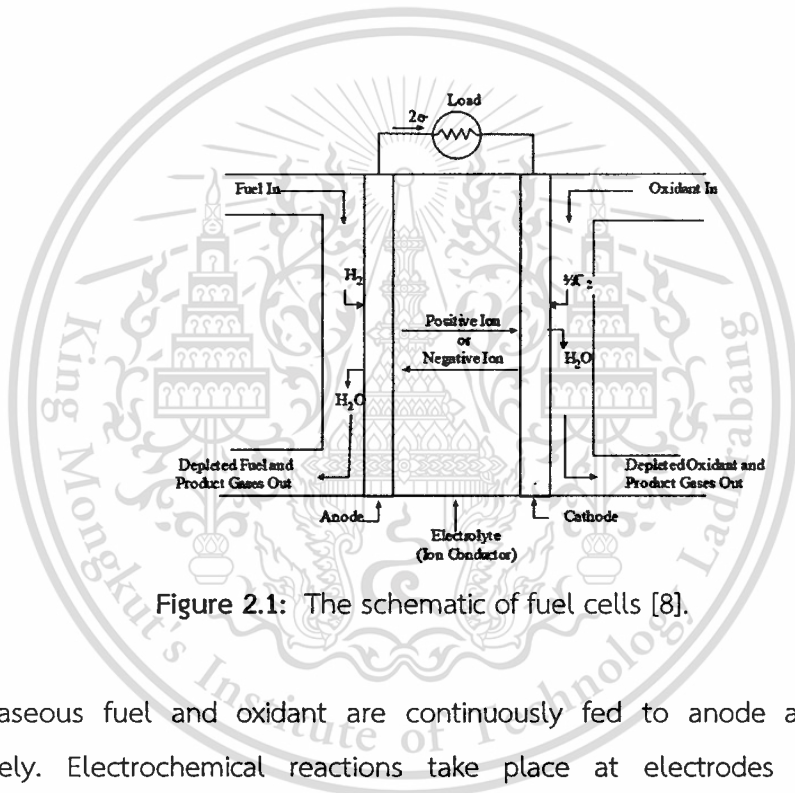
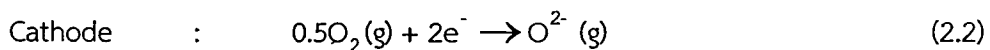
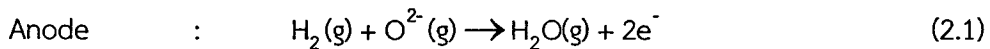


Figure 2.1: The schematic of fuel cells [8].

Gaseous fuel and oxidant are continuously fed to anode and cathode respectively. Electrochemical reactions take place at electrodes to produce electricity. The reactions are shown as follows [9].



2.1.1 Classification of fuel cells [1, 8, 10]

Fuel cells are classified to 6 types that are

1). Polymer electrolyte membrane fuel cells (PEMFCs)

PEMFCs use an ion exchange membrane as an electrolyte, for example, fluorinated sulfonic acid polymer or other similar polymers that are able to conduct protons. The fuel fed to anode side is hydrogen. The operating condition is usually less than 120°C , so the expensive electrocatalyst is required.

2). Direct methanol fuel cells (DEFCs)

DEFCs are similar to PEMFCs i.e. use polymer as an electrolyte. However, DEFCs use liquid methanol as a fuel instead of hydrogen.

3). Alkaline fuel cells (AFCs)

Potassium hydroxide (KOH) is an electrolyte for this fuel cell. The concentration of KOH is 85% for operating temperature 250°C or 35-50% KOH for operating temperature 120°C .

4). Phosphoric acid fuel cells (PAFCs)

Concentrated phosphoric acid is used as an electrolyte for this fuel cell at operating temperature $150\text{--}220^{\circ}\text{C}$. Disadvantage points of PAFCs are poor ionic conductivity and CO poisoning reaction with catalyst platinum at anode may occur.

5). Molten carbonate fuel cells (MCFCs)

The electrolyte in this fuel cell is usually a combination of alkali carbonates, which is retained in a ceramic matrix of LiAlO_2 . The fuel cell operates at $600\text{--}700^{\circ}\text{C}$ where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction.

6). Solid oxide fuel cells (SOFCs)

Ceramic is used as an electrolyte. Thus, high temperature operating condition is required for excellent ionic conductivity.

2.2 Solid oxide fuel cells (SOFCs) [11]

SOFCs have been mainly developed because of their exceptional potential that can produce electricity reaching up to 65% efficiency. Furthermore, hydrogen, methane and carbon dioxide from several sources can be used as fuel gases.

2.2.1 Principle of SOFCs

The principle of SOFCs is shown in Figure 2.2. Oxygen gas fed to cathode is reduced to oxide ion and diffuses through solid oxide electrolyte to anode side for reacting with fuel fed to anode. Electrons are produced from this reaction and move to cathode side while electrical power is generated.

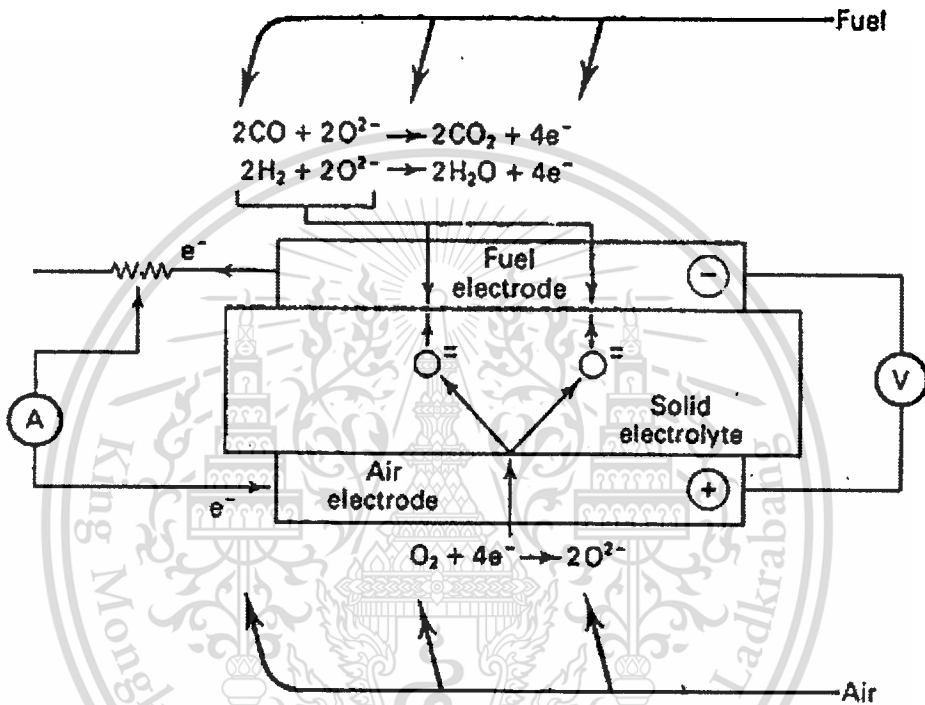


Figure 2.2: The principle of SOFCs [11].

2.2.2 Classification of SOFCs

SOFCs are classified to 2 types that are tubular SOFCs and plate or planar SOFCs.

1). Tubular SOFCs [12]

The components are assembled in the form of a hollow tube, with the cell constructed in layers around a tubular cathode; air flows through the inside of the tube and fuel flows around the exterior as shown in Figure 2.3. The disadvantages of this type are not only the complicated construction but also high investment costs.

2). Planar SOFCs [13]

Planar SOFCs had been developing from tubular SOFCs by increasing operating area while decreasing cell size in order to produce higher current density than tubular SOFCs. Planar SOFC is more efficient than tubular SOFC because it has higher current path per unit area, moreover, the construction of planar SOFCs is less complicated than that of tubular SOFCs, so planar SOFCs are cheaper than another one.

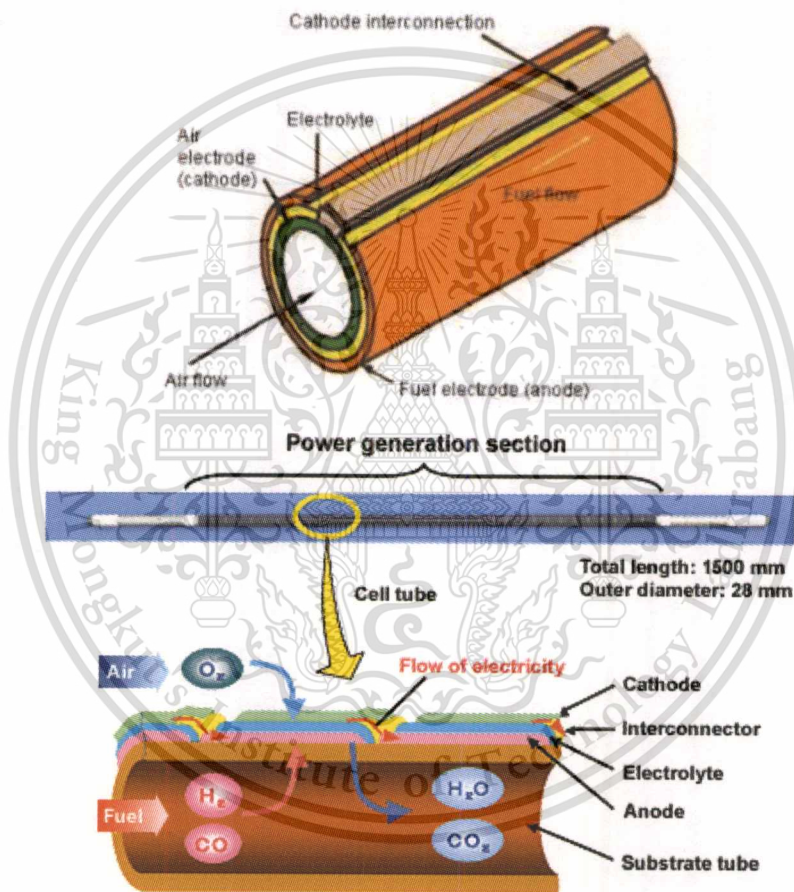


Figure 2.3: Tubular solid oxide fuel cell [12, 14].

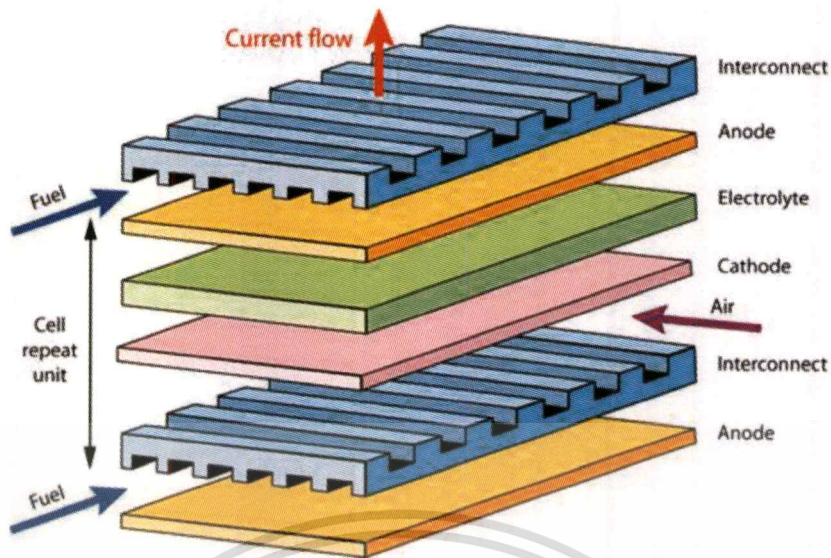


Figure 2.4: Planar solid oxide fuel cell [13].

2.3 Interconnect

In SOFCs, the combination of anode, electrolyte and cathode called single cell. In planar SOFCs, many single cells are connected in series with interconnect which is responsible as follows.

- 1). Conduct the electricity produced from each single cell to an external circuit.
- 2). Separate fuel flow of one cell and oxidant flow of another cell.

The materials that are suitable for using as interconnects should have properties as follows [2, 15].

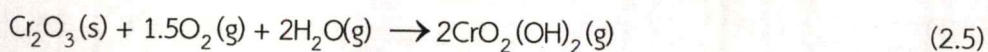
- 1). Stable at high temperature.
- 2). High temperature oxidation resistance in both anodic and cathodic atmospheres.
- 3). Excellent electrical conductivity with preferably nearly 100% electronic conduction.
- 4). Thermal expansion match with other parts of SOFCs.
- 5). Low permeability for hydrogen and oxygen to minimize the direct combination reaction.
- 6). Chemical compatibility with the materials its contact.
- 7). No reaction or inter diffusion between interconnect and its adjacent components, specifically anode and cathode.
- 8). Easy to fabricate.
- 9). Adequate high temperature strength and creep resistance.

The traditional material used as interconnect in SOFCs is costly ceramic material because operating temperature is as high as 1000°C. Furthermore, the construction of ceramic interconnect is complicated leading to high investment cost. Nowadays, when intermediate temperature SOFCs operated in the range of 600-800°C have been developed metallic interconnect can be used. The advantages of metallic interconnect are not only higher electrical conductivity while operating temperature is lower but also easier to construct than that of ceramic interconnect.

Ferritic stainless steels are the interesting candidate used as metallic interconnects because of its cost, strength, high melting point (not melt at operating condition of 600-800°C), high electrical conductivity, thermal expansion match with other cell parts and high oxidation and corrosion resistance [16]. The oxidation resistance occurs from chromium in materials. If the materials have more than 12% chromium contents, chromium will react with oxygen gas in air to form chromia scale (Cr_2O_3) that is protective film [4]. Chromia scale will cover the steel and prohibit oxygen to react with other components, so the rust cannot form. Unfortunately, at high temperature like SOFCs' condition, chromia scale evaporation occurs destroying passive film and, therefore, reducing SOFC lifetime.

2.4 Chromium evaporation

Chromium in stainless steel forming as chromium oxide passive film that covers on surface of the alloy can evaporate under high temperature condition of dried or humidified air or oxygen. The main evaporation reactions occur as follows [17].



Equations (2.3) - (2.5) show that many phase of chromium can evaporate to gas state depending on operating temperature, partial pressure of oxygen and humidity, as Figures 2.5 – 2.7 [18].

In Figure 2.5, effect of temperature on the formation of chromium gaseous species is carried out in dry air at partial pressure of oxygen is 2.13×10^{-4} Pa. The figure shows that chromium evaporation rate of every species are increasing while operating temperature is higher. The main chromium volatile species in dry air is CrO_3 at all temperature range.

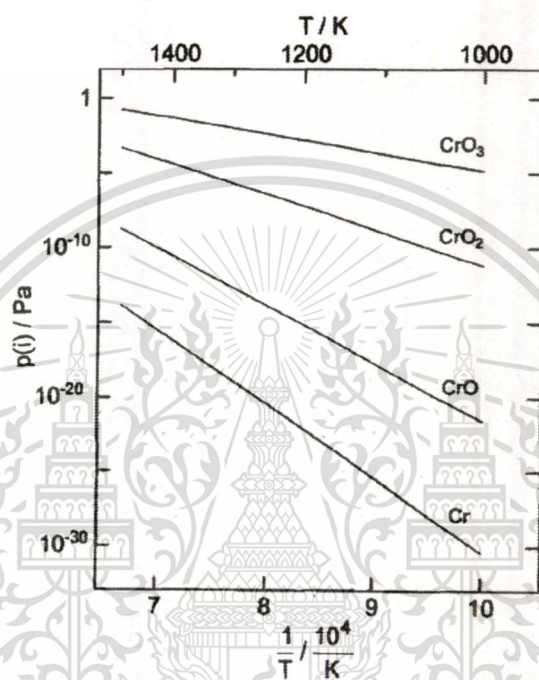


Figure 2.5: Effect of temperature on the formation of chromium gaseous species on chromia scale in dry air at partial pressure of oxygen is 2.13×10^{-4} Pa [18].

Figure 2.6 shows effect of partial pressure of water on the formation of chromium gaseous species on chromium oxide surface in humid air at partial pressure of oxygen is 2.13×10^{-4} Pa. At low partial pressure of water, lower than 100 Pa, the main chromium volatile species is CrO_3 like the main chromium volatile species in dry air. At higher partial pressure of water than 100 Pa, the main chromium volatile species become $\text{CrO}_2(\text{OH})_2$.

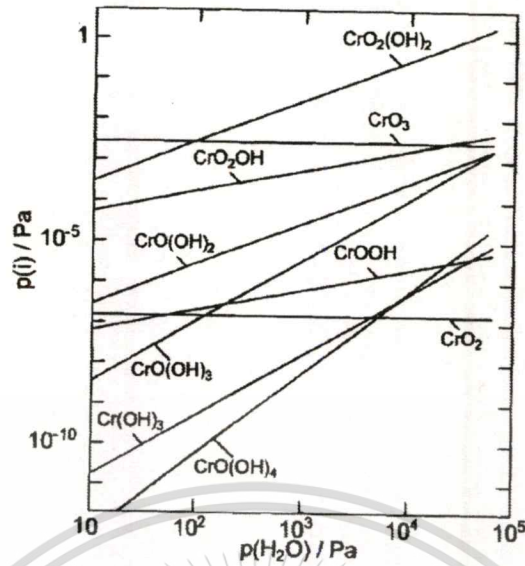


Figure 2.6: Effect of partial pressure of water on the formation of chromium gaseous species on chromia scale in humid air at partial pressure of oxygen is 2.13×10^{-4} Pa [18].

In Figures 2.5 - 2.7, we can observe that the most chromium gaseous species found in dry air and humid air are CrO_3 and $\text{CrO}_2(\text{OH})_2$ respectively. In addition, if operating temperature and/or moisture content are increasing, all species of chromium gaseous evaporated also increase.

Figure 2.7 shows the experiment that determines the partial pressure of chromium gaseous species evaporated from chromia scale comparing with that evaporated from chromium-containing ceramics like lanthanum chromite and lanthanum strontium chromite. The results show that the most chromium gaseous species is still $\text{CrO}_2(\text{OH})_2$ on every surface but evaporation rates are different. The minimum chromium evaporation occurs on lanthanum strontium chromite surface that is lower than evaporation on lanthanum chromite and chromia scale respectively. From this figure, we can summarize that chromium evaporation on ceramics interconnect is lower than metallic interconnect.

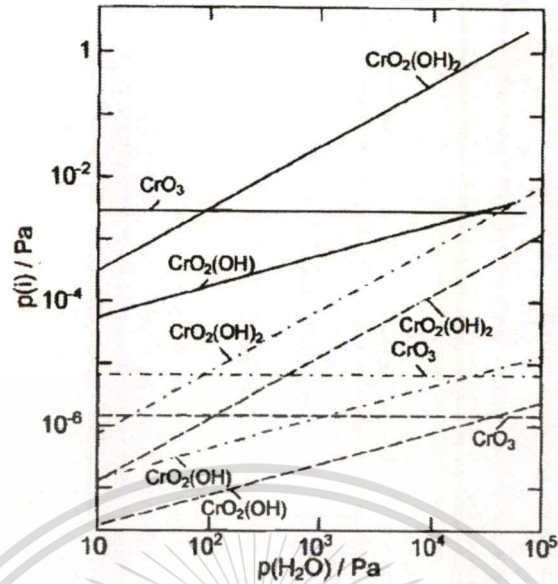


Figure 2.7: Effect of partial pressure of water on the formation of chromium gaseous species on

- (———) Chromia scale
- (- - - -) Lanthanum chromite (LaCrO_3) and
- (- . - . -) Lanthanum strontium chromite ($\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$)

In humid air that has partial pressure of oxygen is 2.13×10^{-4} at 1223 K [18].

2.5 Chromium evaporation protective coating

As mentioned above, chromium evaporation from ceramics interconnect is lower than metallic interconnect but ceramics interconnect is more expensive and has lower electrical conductivity. Thus, research and development of metallic interconnect have been proceeding for reducing chromium evaporation. The researchers found that protective coatings on metallic interconnect could reduce chromium evaporation. At present, many researchers study both coating materials and coating methods. However, the best coating material and method are not indicated. Coating properties are disclosed as following [2, 19].

- 1). Ability to reduce chromium evaporation.
- 2). High electrical conductivity or low area specific resistance (ASR).
- 3). Thermal expansion match with others cell part.

- 4). Chemical interaction with metallic interconnect and electrode can ignore.
- 5). Low interface resistance.

2.6 Coating method

This thesis studied chromium evaporation of AISI 441 coated by electrodeposition (electroplating) and chemical solution deposition (sol-gel).

2.6.1 Electrodeposition (electroplating) [20]

Electrodeposition is the application of metallic coatings to metallic or other conductive surfaces by electrochemical process. The schematic of electroplating method is shown in Figure 2.8

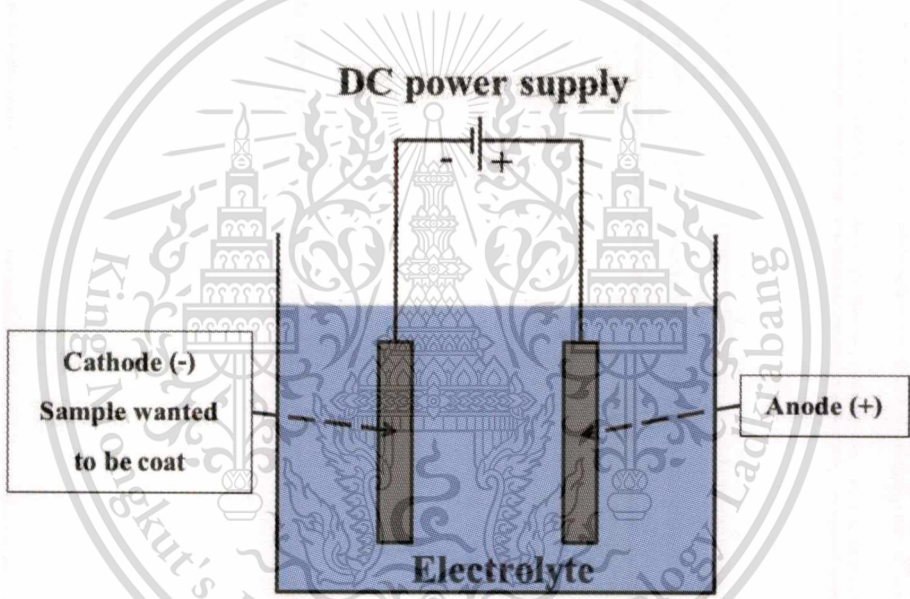
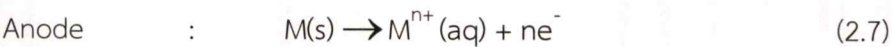


Figure 2.8: The schematic of electroplating method

The sample wanted to coat is put in cathode side while electrical conductive material is used as an anode in electrolysis cell. Both electrodes are dipped into electrolyte solution. The reactions are shown as following equations [21].



Every plating solution contains ingredients which serve one or more of the following functions.

- 1). To provide a source of coating metal.
- 2). To form complex with ions of the depositing metal.
- 3). To provide electrical conductivity.
- 4). To stabilize solution e.g. against hydrolysis reaction.
- 5). To act as pH buffer.
- 6). To modify or regulate the physical formation of the deposit.
- 7). To aid in dissolving the anode.
- 8). To modify other properties, either of the solution or the deposit.

2.6.2 Chemical solution deposition (sol-gel) [22, 23]

Sol-gel is the application used for fabricating a homogeneous inorganic networking polymer. Colloidal suspensions that are non-bonding precursors called “sol” are integrated and form a network in a continuous liquid phase called “gel”. The starting precursors usually form metals surrounded by reactive ligands. Then during stirring, the starting mixture is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Gel is slowly formed while removal solvent is processed. This transformation specifies shaping and sizing of gel particles. The sample wanted to coat is dipped into the obtained gel and then put into an oven to evaporate the solvent and put into a furnace to calcine. After calcination, the crystal structure of coating material is obtained.

Chapter 3

Literatures review

In 1974, lanthanum chromite has been used as a ceramics interconnect in solid oxide fuel cells (SOFCs) because operating temperatures of SOFCs were above 1000°C . At lower operating temperature around $700\text{--}850^{\circ}\text{C}$, electrical conductivity of this material becomes lower while electrical conductivity of metallic alloys are still high. Thus, other chromium-based alloys have also been tested [19]. However, chromium evaporation from chromium-containing alloys is an obstacle for applying as an interconnect in practice. The phenomenon of chromium evaporation from both chromium oxide pellets and chromium-containing alloys have been studied and the way out to decrease chromium release or protect the alloys has been also researched [2, 6, 7, 18, 24-33].

Caplan et al. [26] studied the phenomenon of chromium oxide evaporation from chromium oxide pellets by heating them at $1000\text{--}1200^{\circ}\text{C}$ in various atmospheres and found that oxidation of chromium oxide led to chromium evaporation. Chromium evaporation occurred in oxygen, more in wet oxygen, but none in argon or wet argon.

Hilpert et al. [18] modeled thermodynamics data by ChemSage computer program and realized the formation of chromium gaseous species in various conditions. The results show, as in Figures 2.5-2.7 in Chapter 2, that CrO_3 and $\text{CrO}_2(\text{OH})_2$ were the most species found in dry air and humid air respectively. Increasing operating temperature and/or moisture content led to the increase of all chromium evaporation gaseous species contents. Moreover, chromium evaporation on chromia scale, lanthanum chromite and lanthanum strontium chromite surface led to the difference of chromium evaporation rates. The minimum evaporation rate occurred on lanthanum strontium chromite surface in comparison with chromium evaporation on lanthanum chromite and chromia scale respectively.

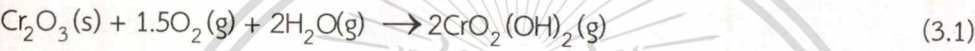
Tedmon [32] modeled equation to explain oxidation behavior of chromium and iron-chromium alloy. He found that oxidation of these samples involved with 2 processes: the first one was the solid state diffusion of ionic species, with parabolic kinetics, and produced chromium oxide or chromia scale (Cr_2O_3) with limiting

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thickness. The second one was the oxidation of chromium oxide to volatile species with linear kinetics. The chromia scale thickness could be appraised by parabolic rate constant and surface-reaction rate constant.

Yamauchi et al. [7] studied chromium evaporation from chromium oxide compacted in nitrogen-oxygen-water, nitrogen-water and nitrogen-oxygen. The rate of mass loss in nitrogen-oxygen-water was found to be one order of magnitude higher than the rates in nitrogen-water and nitrogen-oxygen atmospheres. This could be explained that the deterioration of chromia oxide scale occurred in water-oxygen mixture. Evaporation of chromium oxide was probably based on the following reaction.



Gindorf et al. [6] tested chromium evaporation from chromium oxide powder in different flow rate of 10% humid air at 1223 K. Figure 3.1 shows the result of their experiment.

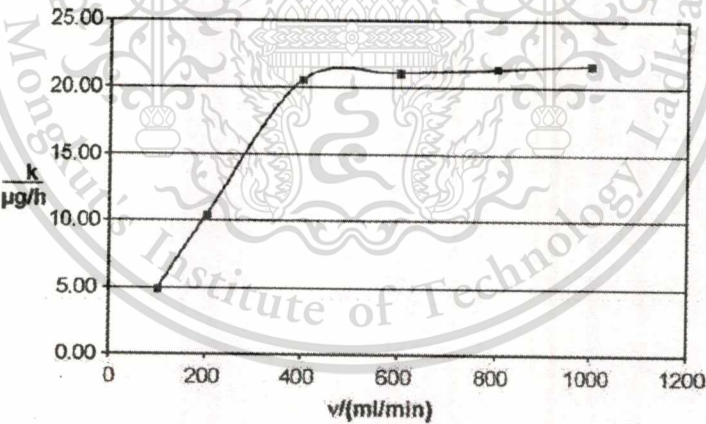
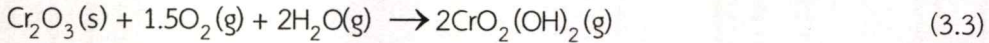


Figure 3.1: Chromium evaporation rate of chromium oxide scale in humid air, $P(\text{H}_2\text{O})=0.1$ bar at 1223 K for different flow rate [6].

They observed that the effect of humid air flow rate on chromium evaporation rate was separated into 2 sections: (1) higher chromium evaporation rate with increasing gas flow rate and (2) constant chromium evaporation rate when gas flow rates were above 400 ml/min. Additionally, they presented the thermodynamic

computation using data bases of IVTANTHERMO and Ebbinghaus and found that evaporation reactions should be as follows.



Comparing experimental result with computational result, they found that $\text{CrO}_3(\text{g})$ and $\text{CrO}_2(\text{OH})_2(\text{g})$ were major vapor species at low and high humidity respectively.

Asteman et al. [24, 25] studied effect of water vapor and temperature on chromium evaporation from 304L steel. The result showed that chromium evaporation rate depended on temperature and concentration of water vapor. At high temperatures, flow rate and humidity could early induce breakaway corrosion. Furthermore, the loss of chromium tended to convert the protective chromia-rich oxide scale initially formed into a non-protective, iron-rich oxide.

Opila et al. [29] reported the influence of partial pressure of water and oxygen on chromium evaporation corresponding with Equation (3.3). It was found that partial pressure of chromium gaseous species depended on $P(\text{H}_2\text{O})^n$ and $P(\text{O}_2)^m$ where that power law exponents were $n=0.96$ and $m=0.77$.

Stanislawski et al. [31] investigated chromium evaporation from chromium-based alloys that were ducrolloy, nickel-based alloys, cobalt-based alloy and iron-based alloys i.e. austenitic and ferritic stainless steels. Firstly, they studied chromium evaporation rate from ducrolloy in 1.88% humid air at 800°C . The result shows in Figure 3.2.

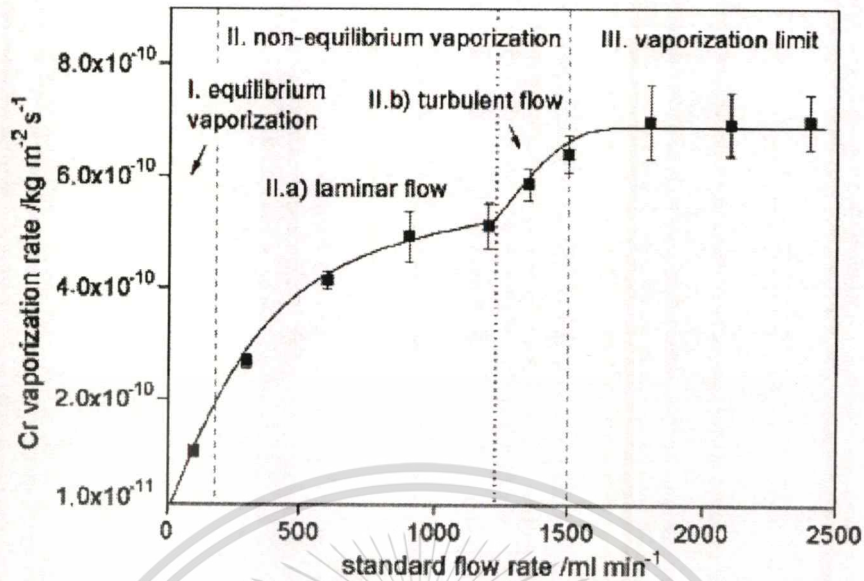


Figure 3.2: Effect of air flow rate on chromium evaporation rate from ducrolloy in 1.88% humid air at 300 °C [31].

From Figure 3.2, Stanislawski et al. observed that the phenomenon of chromium evaporation was divided into three zones. Zone I was the region where air flow rates was lower than 130 ml/min. This zone was an equilibrium state between chromia scale formation and evaporation of chromium gaseous. At Zone II, gas flow rates were in the range of 130-1500 ml/min, in this zone, non-equilibrium evaporation took place. They explained that the diffusion of chromium gaseous species in air was not high enough to maintain equilibrium. In this period, chromia scale deposited on the alloy surface. The last zone, Zone III, where gas flow rate was higher than 1500 ml/min, chromium evaporation was limited by kinetics. The maximum chromium evaporation rate was reached in this period. After that, they studied chromium evaporation from other steels. They summarized that the different contents of manganese, titanium, aluminum, silicon and tungsten in alloys led to different types of outer oxide scales i.e. $(\text{Cr,Fe})_3\text{O}_4$, $(\text{Cr,Mn})_3\text{O}_4$, Al_2O_3 , TiO_2 and Co_3O_4 . The difference of outer oxide scales led to difference of chromium evaporation rates such as, chromium evaporation from $(\text{Cr,Mn})_3\text{O}_4$ scale was lower than that of chromia scale from ducrolloy for about 61-75% under the same condition. The lowest chromium evaporation rates were detected from Al_2O_3 and Co_3O_4 scales. However, alumina-forming alloys had low electrical conductivity while Co-based alloys had

high electrical conductivity. Furthermore, the result showed that chromium evaporation from Co_3O_4 was lower than that of chromia scale for about 90%. Therefore, Co_3O_4 coatings were an interesting possibility for solving chromium evaporation from interconnect.

As mentioned above, chromium evaporation is a major problem lowering lifetime of interconnect in cathodic condition, especially, in atmosphere of air or oxygen containing-water vapor, the most volatile species is chromium acid (H_2CrO_4) which transported with the oxidant gas through cathode to cathode/electrolyte interface and competes with oxygen to electrochemically react and blocks interface with chromium (III) called "chromium-poisoning". Chromium poisoning leads to decomposition of cathode perovskite material and spinel formed. Another problem is the formation of oxide scale leading to higher electrical resistance. Hence, the researchers have been studying protective coatings for prohibiting chromium release from chromium-containing alloys. Their thermal expansions, electrical conductivities, area specific resistance (ASR), oxidation rates and morphologies were indicated for appropriating coating materials by various coating methods [19].

Stanislowski et al. [30] investigated more suitable sputtered coatings between ceramic perovskites (LSM and LSC) and metallic coatings on crofer 22 APU. The results showed that perovskite coatings could moderately reduce chromium evaporation from crofer 22 APU while metallic coatings (cobalt: Co, copper: Cu and nickel: Ni) could reduce about 3 orders of magnitude (more than 99% reduction) comparing with uncoated crofer 22 APU in 1.88% water/air at 800°C for 1000 h. Therefore, Co, Ni and Cu were identified as promising and cheap coating materials for metallic interconnects.

Kurokawa et al. [27] attempted to suppress chromium release from metallic interconnects. Uncoated and several coated 430 stainless steels, by spraying and dipped coating, were examined in their research. Figure 3.3 shows the chromium transport rate at 1073 K in humid air ($P(\text{H}_2\text{O}) = 1.0 \times 10^{-4}$ Pa) for 24 h. This figure indicated that coated 430SS could reduce chromium transport rate more than 1 order of magnitude, brought the chromium release rate with acceptable limits and could also reduce possible deleterious effects on cell performance.

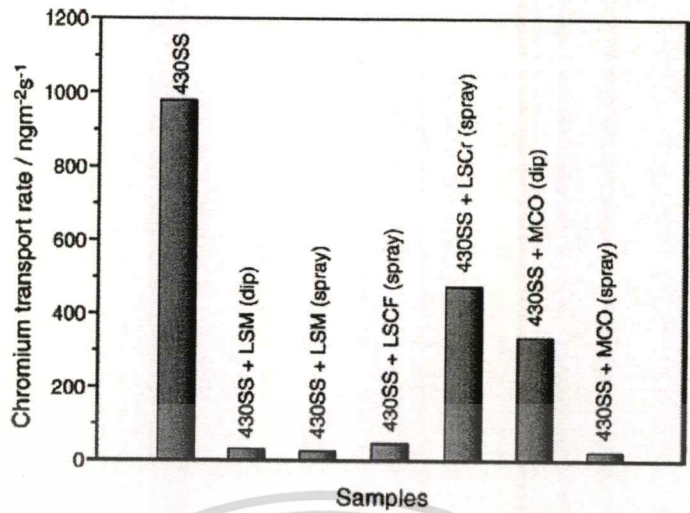


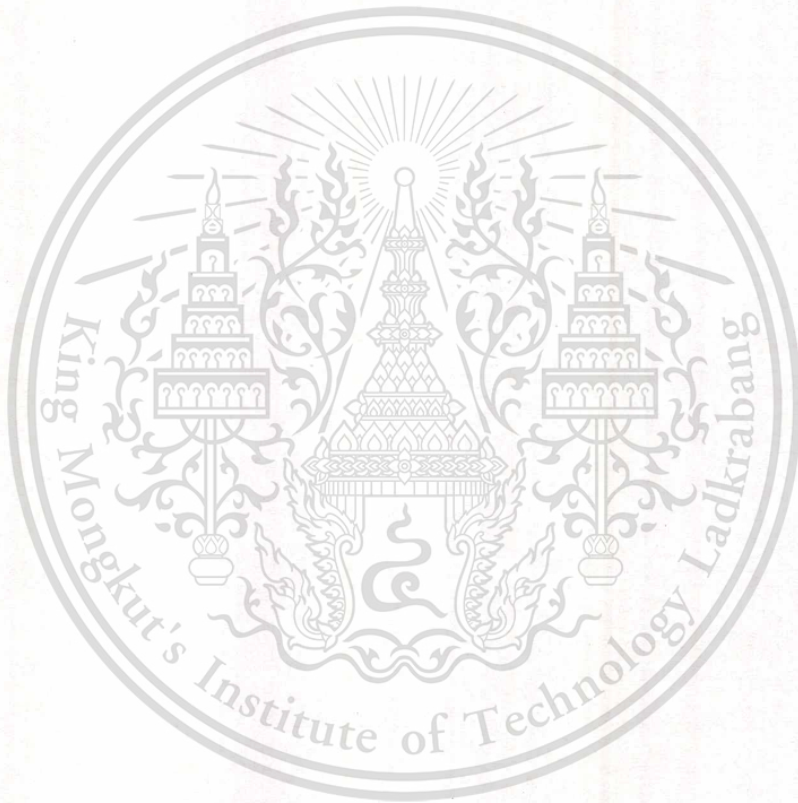
Figure 3.3: Chromium transport rate of uncoated and coated at 1073 K in humid air, $P(H_2O) = 1.0 \times 10^{-4}$ Pa for 24 h [27].

Lee et al. [28] determined electrical properties and oxidation resistances of crofer 22 APU coated with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) and $La_{0.7}Sr_{0.3}MnO_3$ (LSM). They summarized that LSCF was a good candidate coating material for metallic interconnect application. XRD results showed that the oxide layer composed of cobalt iron spinel ($CoFe_2O_4$) in the sample, after oxidized at 800°C for 200 h. They described that reactive element coating made the LSFC change from loose to compact phase structures leading to greatly improving high temperature oxidation resistance of the sample, evidence from SEM results after oxidation. Furthermore, in long term, electrical resistance and ASR of LSCF were lower than LSM.

Wu et al. [33] electroplated cobalt and manganese cobalt spinel (Mn-Co spinel) on SUS 430 and one cell test of uncoated, Co coated and Mn-Co coated were studied. The cell power degradation rate of uncoated, Co coated and Mn-Co coated were 33% for 320 h, 5% and 9% for 1000 h respectively. However, thin Co coating (about 2 μm) allowed fast scale growth while thicker Co coating had thermal expansion mismatch with SUS 430 substrate occurred. On the contrary, higher degradation rate of Mn-Co coating not only prohibited scale growth but also reduced thermal expansion mismatch.

Chen et al. [2] tested electrical conductivity of Mn-Co spinel, manganese chromium spinel (Mn-Cr spinel) and chromium-added in manganese cobalt spinel (Mn-Co-Cr spinel) in different ratios. Mn-Co spinel had the highest electrical

conductivity comparing with other coatings and chromium oxide scale. Addition of chromium in coating led to decreasing electrical conductivity by directly variation. 430SS was coated with dense Mn-Co spinel. ASR, thermal expansion and weight gain were measured. The results showed that dense Mn-Co spinel could significantly reduce chromia sub-scale formation, reduce thermal expansion mismatch and increase electronic conductivity of the scale while ASR could be predicted as approximately $0.5 \Omega \text{ cm}^2$, after 50,000 h at 850°C in air.



Chapter 4

Experimental

4.1 Process overview and experimental setup

Figure 4.1 shows the experimental setup. Oxygen gas was flowed through 3-ways valve that was connected with a flow meter and 2 humidifiers, respectively. The humidifiers were used for adjusting humidity percentage of oxygen stream into ca. 5%. Then wet-oxygen was flowed through quartz column installed inside the furnace. The sample was hung inside the furnace while wet-oxygen gas was flowed through the sample. At the outlet of column, gas was flowed through the condenser where chromium gaseous compounds were condensed into a solution. The outlet gas from the condenser was passed through the water-containing Erlenmeyer flask in order to make sure that all remained chromium compounds in gas stream were condensed into a liquid phase. After experiment, quartz column was cleaned with 0.1 M hydrochloric acid and samples were taken from condenser, Erlenmeyer flask and hydrochloric acid used to clean the quartz column. Samples were analyzed in order to find chromium contents by ICP (inductively coupled plasma).

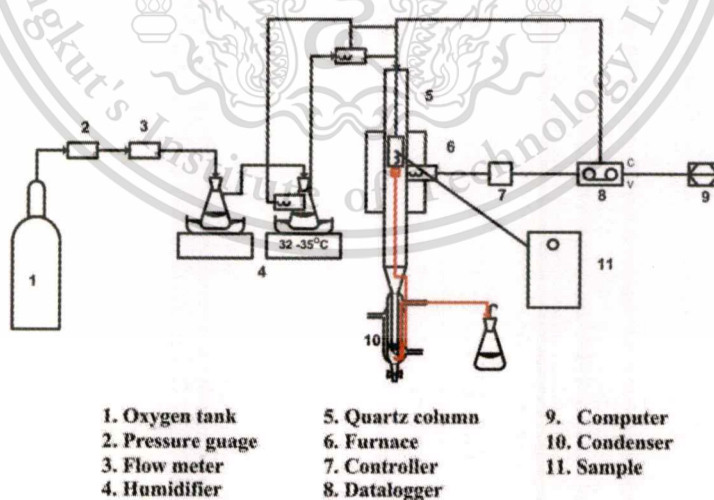


Figure 4.1: Experimental setup

4.2 Types of sample

The experiment was divided into 2 parts:

- 1). Chromium evaporation of uncoated AISI 441 stainless steel
- 2). Chromium evaporation of AISI 441 stainless steel coated with
 - 2.1) manganese-cobalt spinel (Mn-Co ; MnCo_2O_4)
 - 2.2) strontium-doped lanthanum manganite (LSM; $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$)

In summary, the samples used in this research have 3 types that are uncoated AISI 441, AISI 441 coated with Mn-Co spinel and AISI 441 coated with LSM. The sample size is $15 \times 25 \times 1 \text{ mm}^3$. For uncoated samples, all specimens were abraded with 240, 600 and 1200 grit sandpapers. Before the experiments, every sample was cleaned with ethanol in ultrasonic bath for 15 min.

4.3 Uncoated AISI 441

4.3.1 Effect of flow rate on chromium evaporation

The linear velocity was varied in the range of 0.8-3.0 cm/s at constant operating temperature of 800°C . After experiment, quartz column was cleaned with 0.1 M hydrochloric acid and samples were taken from condenser, Erlenmeyer flask and hydrochloric acid used to clean the quartz column. Samples were analyzed in order to find chromium contents by ICP.

4.3.2 Effect of temperature on chromium evaporation

The operating temperature was varied from 650 - 900°C using a constant linear velocity in kinetics limit region (the region where chromium evaporation rate was independent on wet-oxygen flow rate). After experiment, quartz column was cleaned with 0.1 M hydrochloric acid and samples were taken from condenser, Erlenmeyer flask and hydrochloric acid used to clean the quartz column. Samples were analyzed in order to find chromium contents by ICP.

4.4 AISI 441 coated with manganese-cobalt spinel by electroplating method

4.4.1 Electrolyte solution preparation [33]

The electrolyte was prepared from 0.1 M cobalt sulfate, 0.5 M manganese sulfate, 0.7 M sodium gluconate, 1.0 M boric acid and 1.0 M ammonium sulfate. All chemicals supplied by Ajax finechem pty Ltd.

The preparation of 1 L electrolyte solution was started from added 61.830 g boric acid and 152.705 g sodium gluconate into distilled water. Mixed solution was stirred by a magnetic stirrer until completely dissolved. Then, 28.110 g cobalt sulfate was added with continue agitation for 30 min and kept standing for 24 h. After that, 84.505 g manganese sulfate and 13.213 g ammonium sulfate were added together with agitation. The pH of solution was measured and adjusted to 3.0 with ammonium sulfate or 20 %vol sulfuric acid [34]. The schematic of electrolyte preparation is shown in Figure 4.2

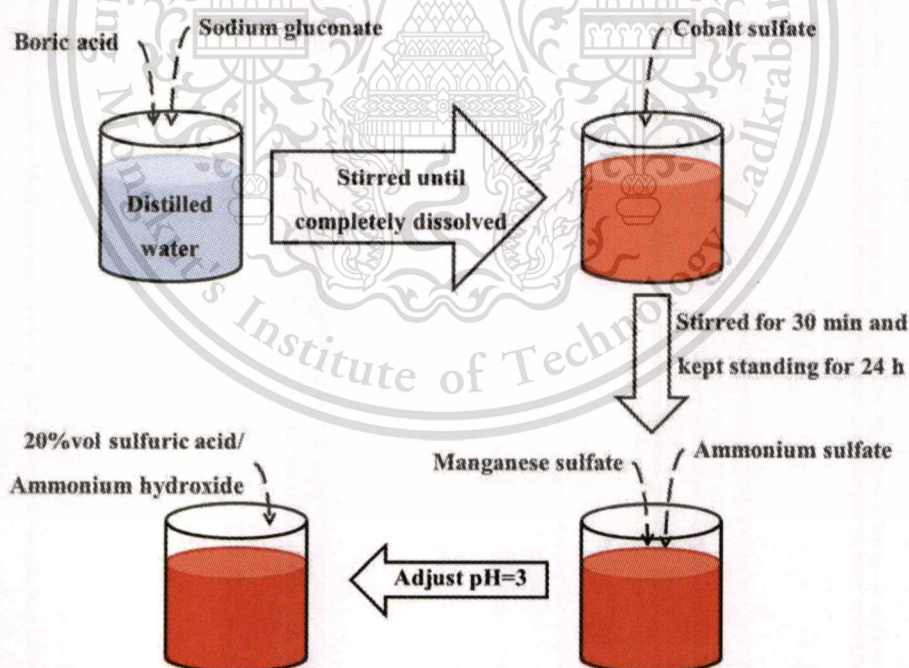


Figure 4.2: Electrolyte preparation

4.4.2 Electroplating coating on AISI 441

For appropriating coating, we varied parameters as follows.

- 1). Sample preparation: after polishing AISI 441 with sandpaper
 - 1.1) sample was not pickled with 25%vol hydrochloric acid
 - 1.2) sample was pickled with 25%vol hydrochloric acid

Then, samples were cleaned with ethanol in ultrasonic bath for 15 min.

- 2). Anode size

- 2.1) Similar size to cathode: $15 \times 25 \times 1 \text{ mm}^3$

- 2.2) Bigger than cathode: $30 \times 40 \times 1 \text{ mm}^3$

- 3). Shape of the container

- 3.1) Cylindrical

- 3.2) Square box

- 4). Electrical current was varied in the range of 0.2-1.5 A

- 5). Consumption time was varied in the range of 1-120 min.

- 6). Calcination time for 2 and 4 h at 800°C . Oxide spinel was formed in this step.

The experimental setup followed as in Figure 2.8

4.5 AISI 441 coated with LSM derived by sol-gel method

4.5.1 Gel preparation

LSM was prepared from lanthanum nitrate hexahydrate, strontium nitrate, manganese nitrate tetrahydrate, citric acid (CA) and ethylene glycol (EG) in molar ratio of stoichiometric metal compound : CA : EG was 1 : 1.2 : 7.2 [35, 36].

7.457 g lanthanum nitrate hexahydrate, 0.905 g strontium nitrate, 5.409 g manganese nitrate tetrahydrate and 4.990 g CA were dissolved together in distilled water. Then, 11.750 ml EG was added into the solution with magnetic stirrer agitation and heated at 80°C until the colorless solution became yellow called gel. Then, gel was prepared for XRD analysis or coated on AISI 441. Figure 4.3 shows the schematic of LSM sol-gel preparation.

4.5.2 Preparation for XRD analysis

Solvent in gel was evaporated at 120°C for 12 h and calcined at 800°C for 4 h. Grinded sample was analyzed by XRD which 2θ was in the range of 20° - 80° and scanning rate was $2^{\circ}/\text{min}$.

4.5.3 Coating gel on AISI 441

The gels were coated in three different procedures.

Procedure 1: AISI 441 was put into the gel.

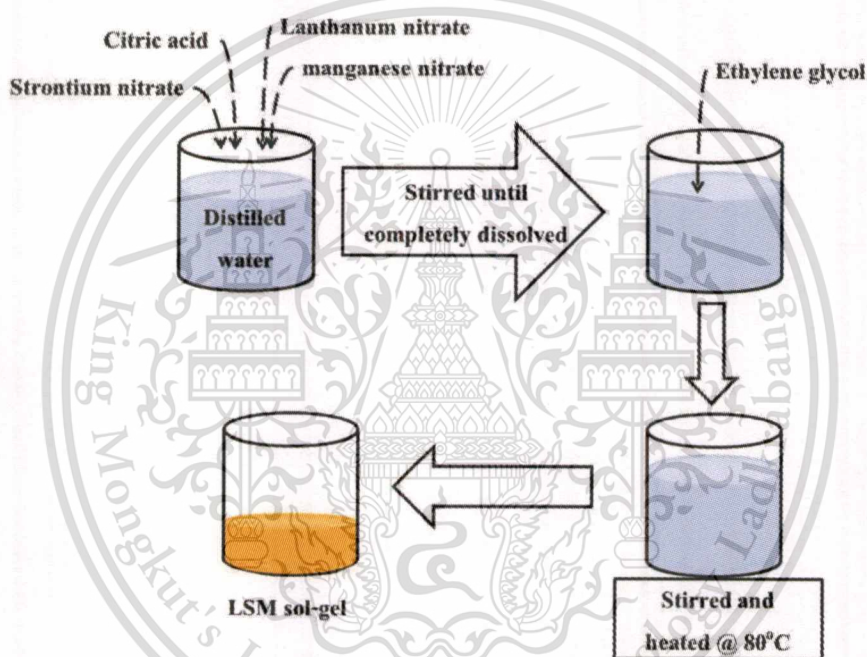


Figure 4.3: LSM sol-gel preparation



Figure 4.4: AISI 441 was put into gel (Procedure 1).

AISI 441 was put into gel and evaporated at 120°C for 1 h. Then, calcined at 800°C for 2 h. Chromium evaporation test was begun if gel covered steel surface.

Procedure 2: AISI 441 was dipped in the gel.

After steel was dipped into gel, it was evaporated at 120°C for 5 min. This step was repeated several times in order to obtain the film on the steel surface. Then, calcined at 800°C for 2 h. Chromium evaporation test was begun if gel covered steel surface. Figure 4.5 shows the schematic of this procedure.

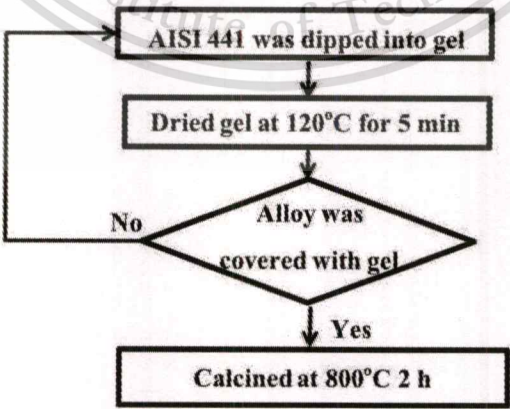


Figure 4.5: AISI 441 coated with LSM sol-gel by coating Procedure 2.

Procedure 3: AISI 441 was dipped and prefired.

This method is similar to Procedure 2. In repeating step, AISI 441 was dipped into gel, evaporated at 120°C for 5 min and prefired at 600°C for 10 min until obtained the film on steel surface. Then, calcined at 800°C for 2 h was achieved and chromium evaporation tested from coated steel if gel covered steel surface. Figure 4.6 shows the schematic of this procedure.

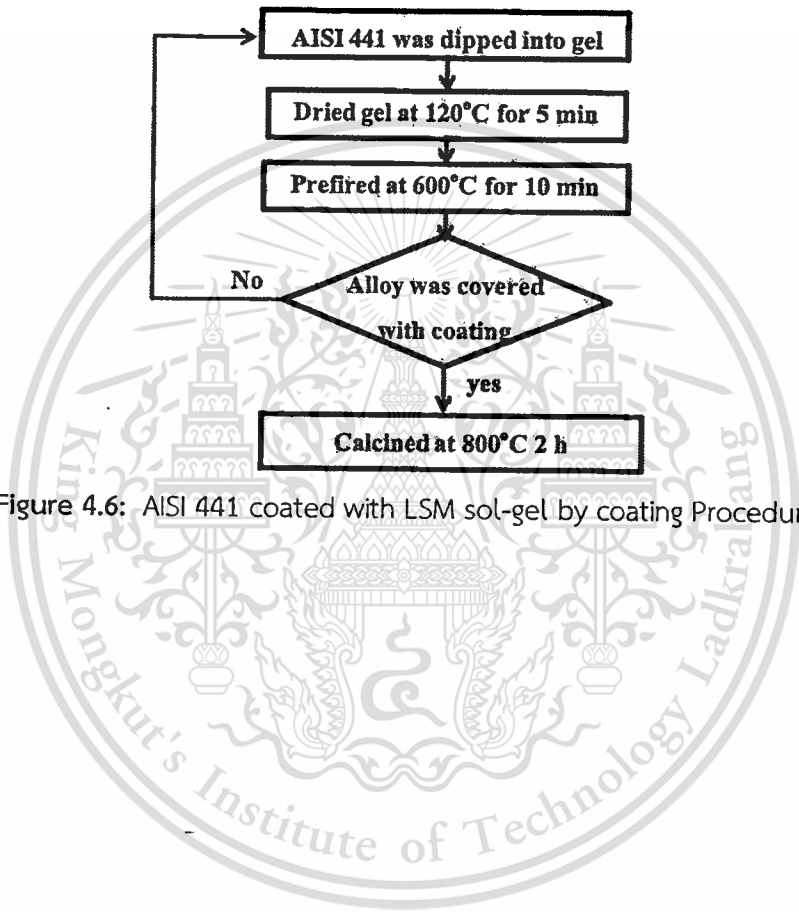


Figure 4.6: AISI 441 coated with LSM sol-gel by coating Procedure 3.

Chapter 5

Results and discussion

5.1 Uncoated AISI 441

5.1.1 Effect of flow rate on chromium evaporation

The effect of flow rate on chromium evaporation at 800°C is shown in Figure 5.1. For AISI 441, it seems that the chromium evaporation content was not dependent on the linear velocity over the whole range of 0.8-3.0 cm/s. This implies that the chromium evaporation was limited by kinetics of reaction that meant the rate of chromium evaporation reaction was less than diffusion rate of chromium gaseous species from the alloy surface. On the contrary for AISI 430, chromium evaporation content increased with increasing linear velocity of wet oxygen over the observed range. This indicates that AISI 430 was limited by mass transport of chromium gaseous species in the linear velocity range of 0.5-3.0 cm/s [37].

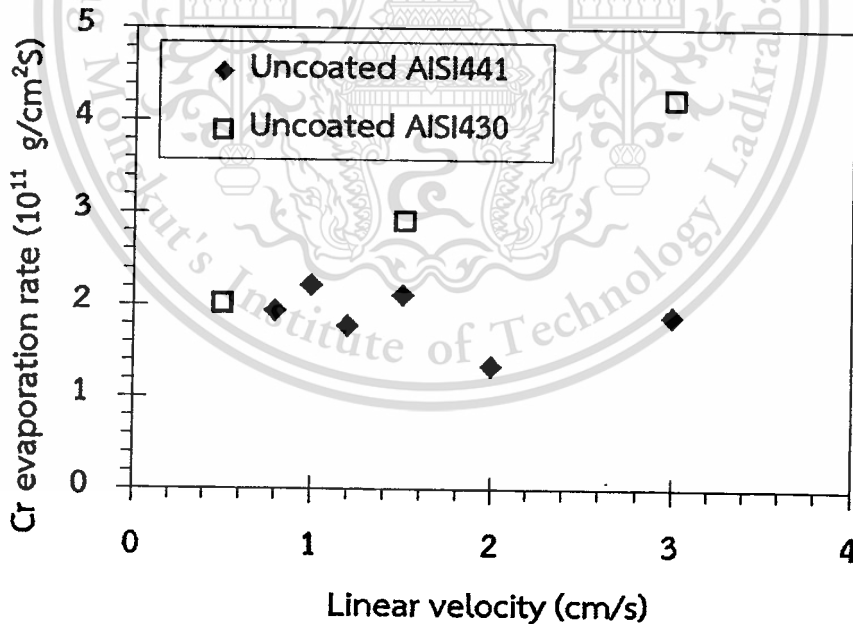


Figure 5.1: Effect of flow rate on chromium evaporation rate from AISI 441 (18% chromium and 0.01% carbon) and AISI 430 (16.30% chromium and 0.04% carbon [2]) in 5%water/oxygen gas stream at 800°C for 24 h [37].

Furthermore, we can observe that chromium evaporation from AISI 441 was lower than AISI 430 under almost experimental conditions particularly at high linear velocity. This might occur from higher chromium contents and lower carbon contents in AISI 441 when compared with AISI 430 [4]. Thus, oxidation resistance of AISI 441 was probably higher than that of AISI 430.

5.1.2 Effect of temperature on chromium evaporation

The effect of temperature on chromium evaporation was determined in the temperature range of 650-900°C and linear velocity was constant at 1.5 cm/s that was in the kinetics limit region. Figure 5.2 shows the results of experiment. We can observe that increasing temperature led to higher chromium evaporation rate. The Arrhenius plot of chromium evaporation reaction from AISI 441 surface is shown in Figure 5.3. The activation energy was calculated to be about 24.74 kJ/mol.

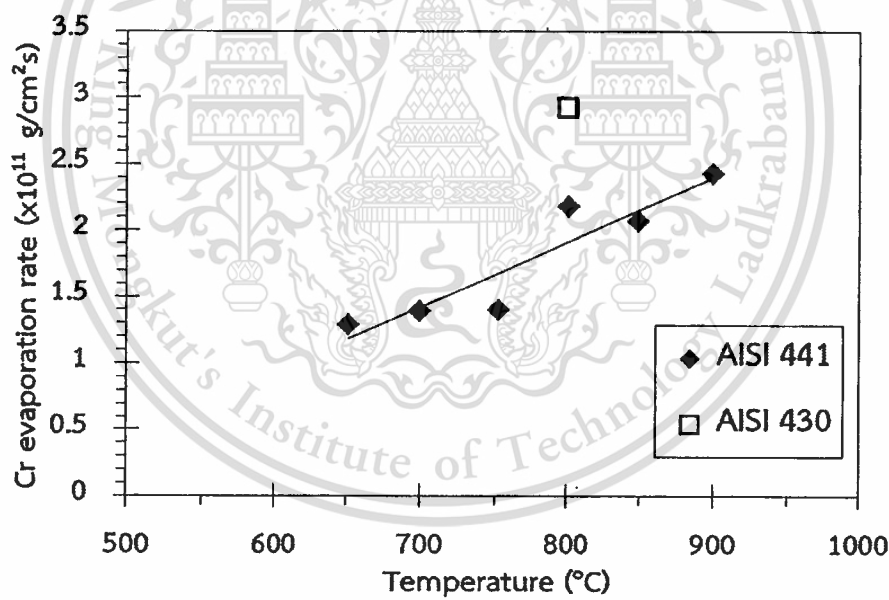


Figure 5.2: Effect of temperature on chromium evaporation from AISI 441 and AISI 430 [37] in 5% water/oxygen gas streams at linear velocity 1.5 cm/s for 24 h.

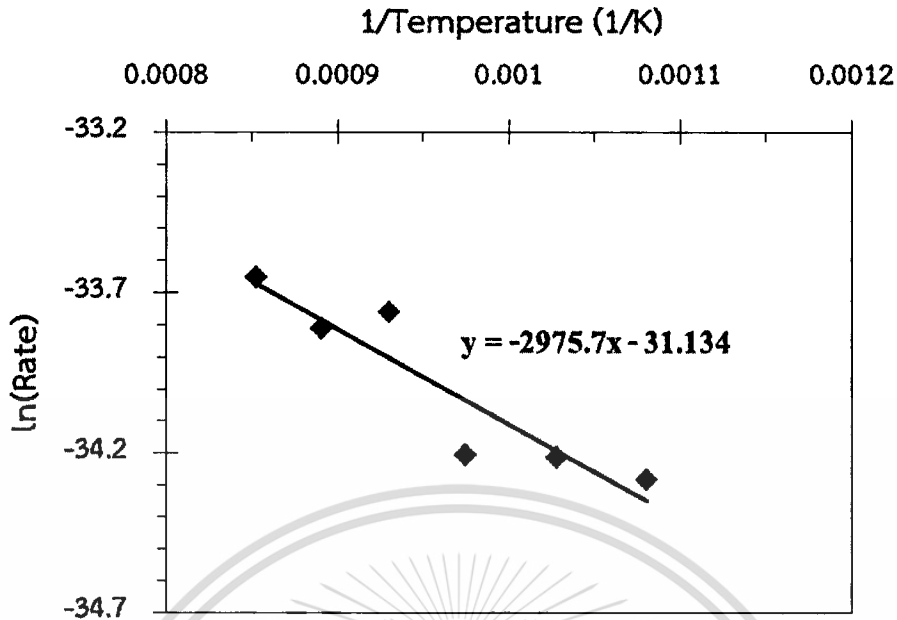


Figure 5.3: Arrhenius plot of chromium evaporation rate.

Figure 5.4 shows the partial pressure of chromium gaseous species, $\text{CrO}_2(\text{OH})_2$, from the experimental comparing with the calculations using thermodynamic data of Opila et al. [29] and Stanisłowski et al. [31] at various operating temperatures. The results show that the partial pressure measured in the experimental was lower than that of calculations from thermodynamic data about two orders of magnitude.

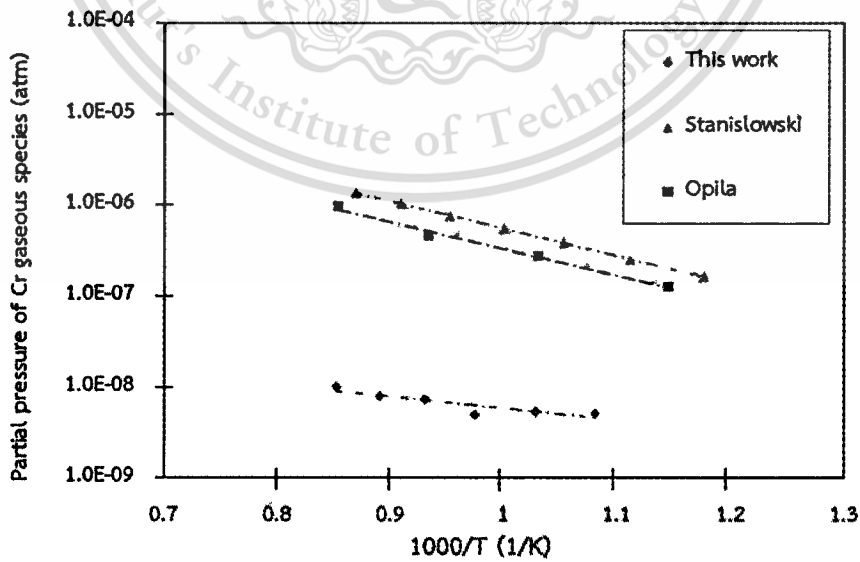


Figure 5.4: Comparison of partial pressure of chromium gaseous species from the experimental and calculation [29, 31].

5.1.3 Observation of surface by SEM and EDS

Figure 5.5 shows SEM and EDS results of uncoated AISI 441 before and after evaporation. After evaporation, the appearance of surface changed when compared with uncoated sample before evaporation. We can observe some fractures on the surface of sample after evaporation as in Figure 5.5b. Furthermore, EDS results of both samples were different. After evaporation, iron detected became lower while chromium, manganese and titanium became higher. This should be because manganese, titanium and chromium in alloy diffused to surface during oxidation reaction and reacted with oxygen in atmosphere. Manganese-chromium spinel (Mn-Cr ; $(\text{Mn,Cr})_3\text{O}_4$) and titanium oxide (TiO_2) probably formed and dispersed in chromia scale [31, 38].

Comparison of SEM and EDS results between uncoated AISI 441 and uncoated AISI 430 after oxidation in 1.5 cm/s of 5% water/oxygen gas stream at 800°C for 24 h are shown in Figure 5.6. From this figure, it can be observed that the grains of scale on AISI 441 were sintered while those of AISI 430 looked separate resulting in more surface area of scale than that of AISI 441. The more surface area, the more possibility that oxygen and water react with chromium scale is. This should be one of the explanations why the chromium evaporation rate of AISI 430 was higher than that of AISI 441.

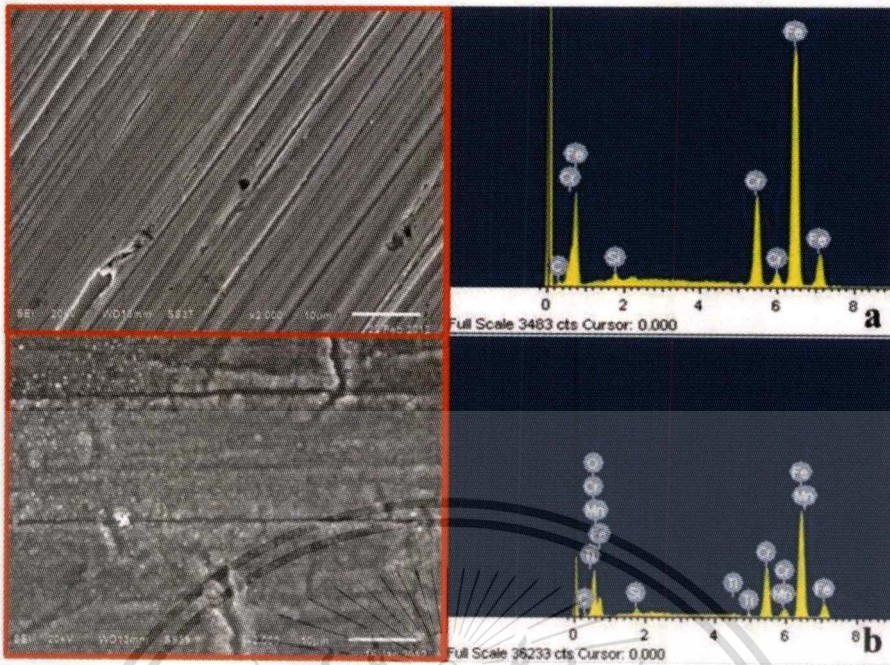


Figure 5.5: SEM and EDS results of a) uncoated AISI 441 before evaporation b) uncoated AISI 441 after evaporation in 1.5 cm/s of 5% water/oxygen at 800°C for 24 h.

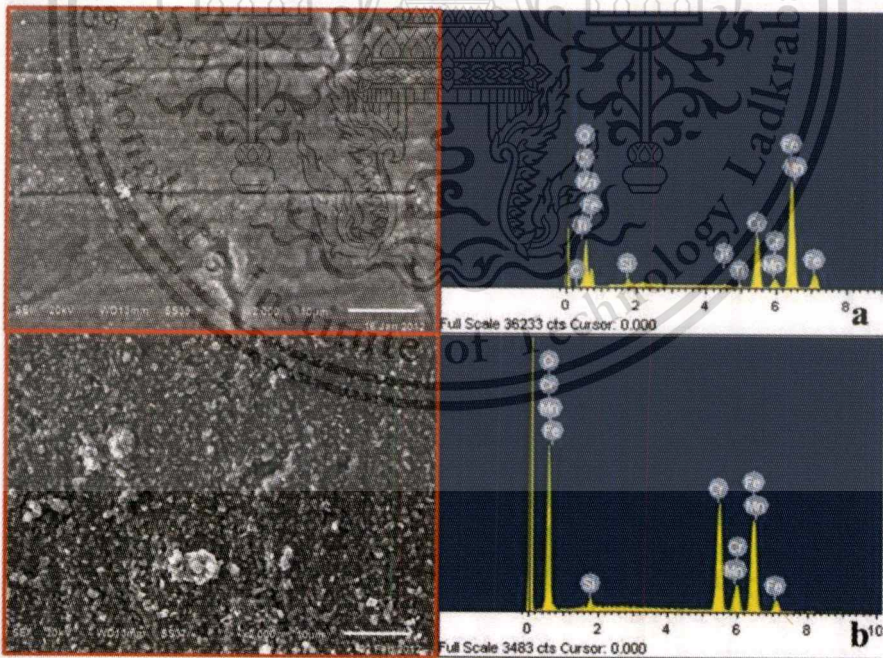


Figure 5.6: SEM and EDS results of that samples after evaporation in 1.5 cm/s 5% water/oxygen stream at 800°C for 24 h a) uncoated AISI 441 b) uncoated AISI 430 [37].

Chapter 6

Conclusions

This thesis studied the phenomenon of chromium evaporation from commercial grade stainless steel AISI 441 comparing with other two samples e.g. AISI 441 coated with Mn-Co spinel by electroplating method and AISI 441 coated with LSM derived by sol-gel method. The experiments were achieved in 5% water/oxygen for 24 h. The influences of gas stream flow rate and operating temperature on chromium evaporation were investigated. From all results, we can summarize as follows.

- 1). Chromium evaporation from uncoated AISI 441 was limited by kinetics of reaction within linear velocity range of 0.8-3.0 cm/s that meant it was independent with gas stream flow rate.
- 2). Higher operating temperature led to increasing chromium evaporation rate and the activation energy of reaction was 24.74 kJ/mol.
- 3). Inappropriate coating materials and methods may lead to higher chromium release than uncoated sample.
- 4). Loose and thin coatings, like Mn-Co spinel, led to breakaway oxidation, so higher chromium releases were detected.
- 5). Dipped coating was not suitable method for coating sol-gel on metallic interconnect as a result of poor adhesion of coatings, spallation, and chromia scale formed during coating process.

6.1 Suggestions

The suggestions for further study of coating metallic interconnect are as follows.

- 1). Morphologies of all samples should be analyzed.
- 2) The roughness of the alloy surfaces prepared by different procedures such as the surface polished by different sandpaper grades with and without pickling should be observed in order to investigate the effect of the surface roughness on the quality of coating and find the suitable surface for each coating method.

5.2 AISI 441 coated with Mn-Co spinel by electroplating method

5.2.1 Appropriate condition of coating

After polished with sandpaper, AISI 441 was coated with Mn-Co by electroplating method. The sample preparation procedure, anode size and shape of container were adjusted. Electrical currents and coating times were also varied.

Firstly, simple coating method like Figure 2.8 was used for our experiment. Electrical current and coating time were varied. However, surface burnt that can be observed as rough surface occurred, as in Figure 5.7.

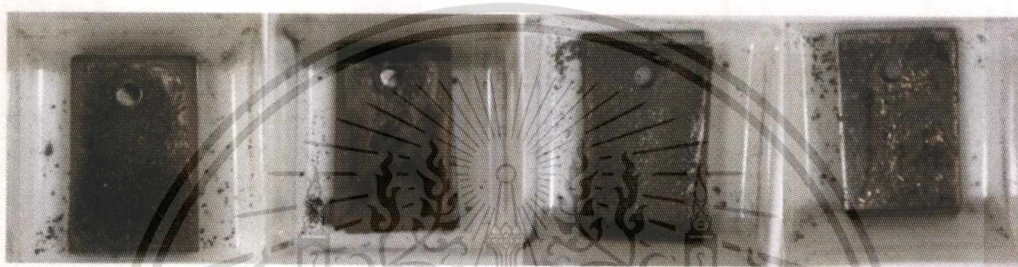


Figure 5.7: surface burnt.

After increasing the anode size to be $30 \times 40 \times 1 \text{ mm}^3$ and reducing consumption times, surface burnt reduced but the appearances still were not absolutely smooth. Meanwhile, when changing the shape of electrolyte container from cylindrical to square box but not increasing anode size and reducing coating time, the burnt reduced as in Figure 5.8. This means that surface burnt occurred because current density was too high and because of a result of non-symmetric charge distribution [39].

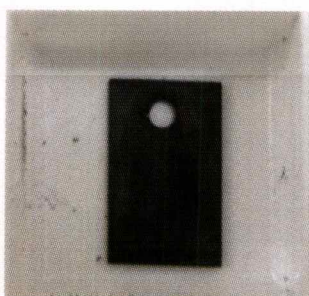


Figure 5.8: AISI 441 coated with Mn-Co after changing container shape.

Figure 5.9 represents good charge distribution. The square box container was used as in Figure 5.10. The distance between the edges of container to electrodes and the distance between electrodes must be balanced in order to make charge distribution symmetry.



Figure 5.9: Charge distribution during cathodic codeposition [40].

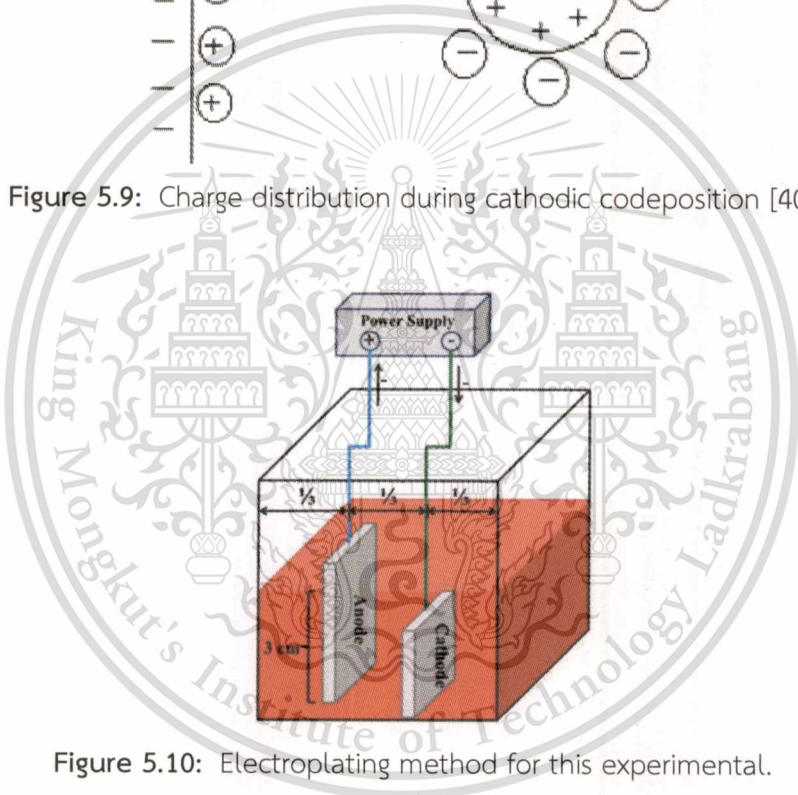


Figure 5.10: Electroplating method for this experimental.

After changing the container from cylindrical to square box, the coated appearance was smoother. However, coating material did not adhered on alloy surface when investigated by SEM. Figure 5.11 shows SEM and EDS results of this sample.

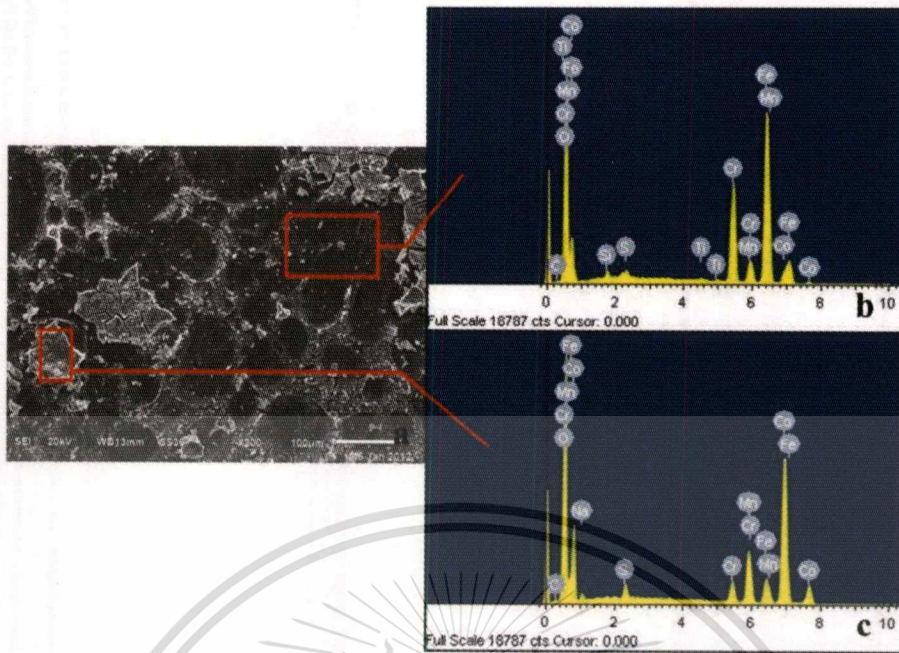


Figure 5.11: a) SEM result of AISI 441 coated with Mn-Co spinel with electrical current 1.5 A for 5 min and calcined for 2 h b) and c) EDS results of background area and swell area respectively.

Figure 5.11 shows the SEM and EDS results of AISI 441 that was polished and cleaned with ethanol in ultrasonic bath for 15 min before coated with Mn-Co spinel. From SEM image, Figure 5.11a, we can observe the two different areas that were swell area (light gray) and background (dark gray). Meanwhile, Figures 5.11b and 5.11c show the EDS analysis of swell area and background area respectively. The swell area was the coating layer covering on the steel while the coating layer was not found in background area.

Finally, the effect of pickling sample was observed. In this experiment, sample pickled with 25%vol hydrochloric acid for 3 min was observed. Pickled and non-pickled samples were cleaned with ethanol in ultrasonic bath for 15 min. The experiment shows that the coating results from both samples were different. Pickled sample had better adhesion of coating material than non- pickled sample. This might describe that tarnish with acid led to the change of surface condition, as in Figure 5.12, and better adhesion of surface was provided [41].

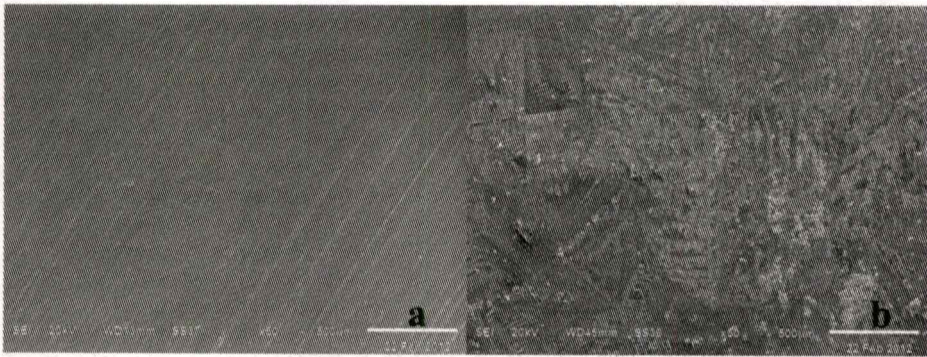


Figure 5.12: SEM results of uncoated AISI 441 a) non- pickled and b) pickled with 25%vol hydrochloric acid for 3 min.

Then, the effect of calcination time was observed. AISI 441 coated with Mn-Co by above method and calcined for 2 h and 4 h were analyzed by XRD. Figures 5.13 and 5.14 show the XRD patterns of these coated samples.

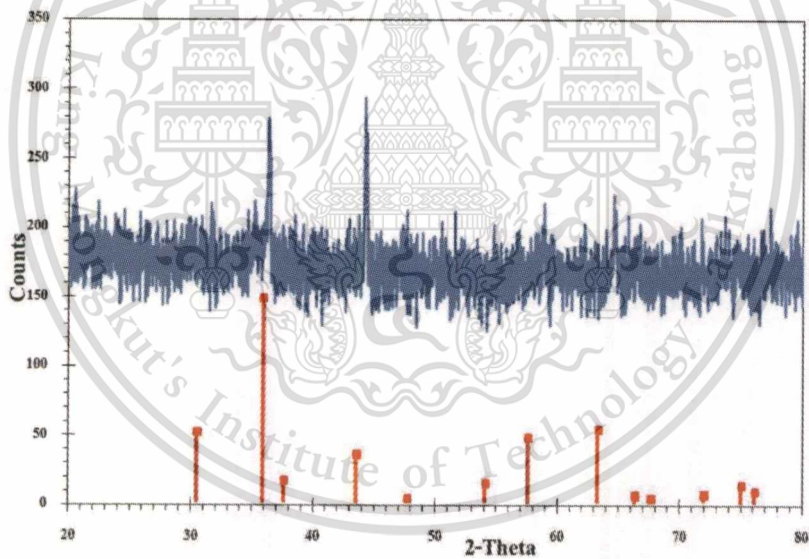


Figure 5.13: XRD pattern of AISI 441 coated with Mn-Co by electroplating method and calcined at 800°C for 2 h.

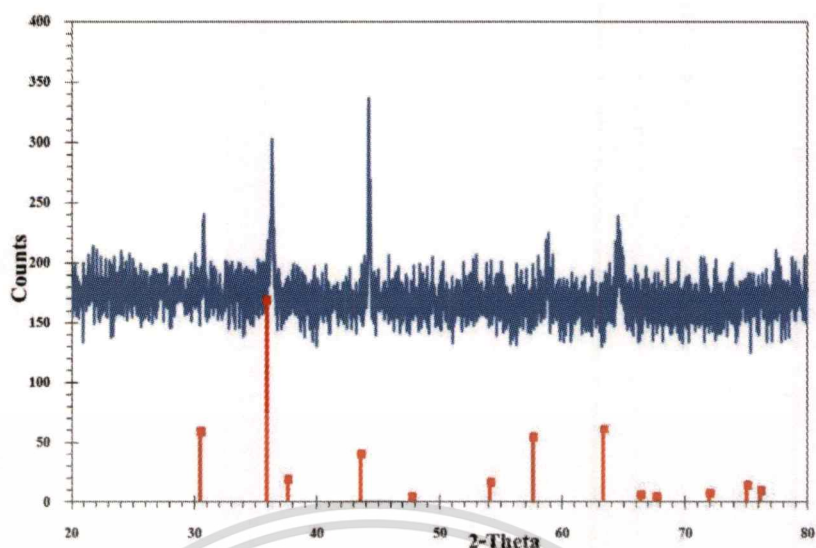


Figure 5.14: XRD pattern of AISI 441 coated with Mn-Co by electroplating method and calcined at 800°C for 4 h.

From Figures 5.13 and 5.14, we can observe that both samples were covered with Mn-Co but crystalline structures were different. Longer calcination time led to more crystalline structure. Hence, after electroplating, coated sample was calcined for 4 h before testing chromium evaporation.

Finally, pickled AISI 441 was coated in square box container. Cathode size used was $15 \times 25 \times 1 \text{ mm}^3$ of AISI 441 while $30 \times 40 \times 1 \text{ mm}^3$ of AISI 430 was used as anode. The best result exposed when electrical current adjusted was 0.2 A for 6 min and calcined at 800°C for 4 h. The SEM image and EDS result of the sample prepared in this condition are shown in Figure 5.15. We can see well-covered coating layer on the alloy surface. EDS result confirmed that the layer we saw from SEM was Mn-Co coating. However, the coating layer was thinner than 4-5 μm noticed from chromium and iron that were detected. This condition was used to coat AISI 441. Then, coated samples were tested chromium evaporation.

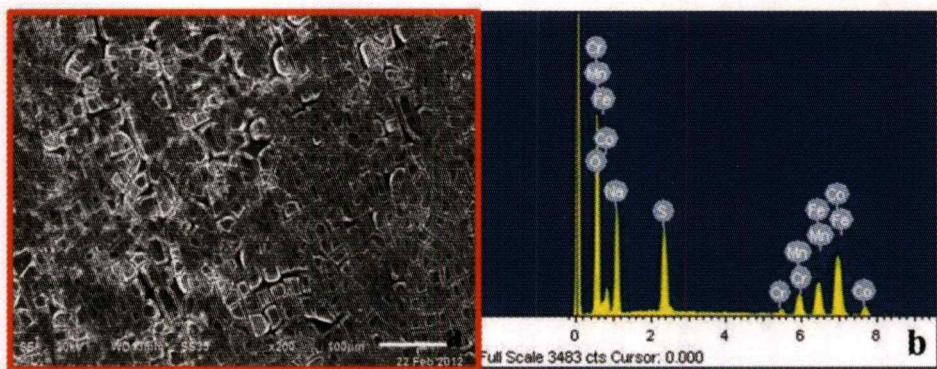


Figure 5.15: a) and b) SEM and EDS results of pickled AISI 441 coated with Mn-Co spinel respectively.

5.2.2 Chromium evaporation test

Chromium evaporation rate from AISI 441 coated with Mn-Co spinel in 1.5 cm/s of 5% water/oxygen stream at 800 °C for 24 h compared with uncoated AISI 441 is shown in Figure 5.16. The results showed that chromium evaporated from AISI 441 coated with Mn-Co spinel was higher than that from uncoated AISI 441.

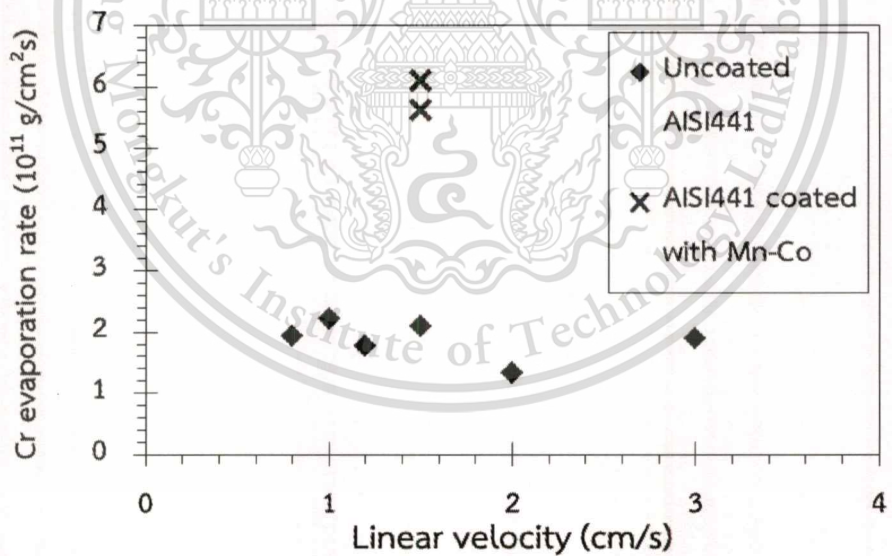


Figure 5.16: Effect of flow rate on chromium evaporation rate from AISI 441 and AISI 430 in 5% water/oxygen gas streams at 800 °C for 24 h.

SEM results of AISI 441 coated with Mn-Co after evaporation are shown in Figure 5.17. We can see that the coating after evaporation spalled out and cracked. EDS results of spalled area and unspalled area are shown in Figure 5.18. Figure 5.18b

shows EDS result of spalled area, in this area coating components, manganese and cobalt, were not detected while high chromium content was detected. On unspalled area, not only coating layer was still detected but high chromium content was also detected. This can be described that chromium could diffuse from alloy through chromia scale, reacted with oxygen and dispersed in coating layer in the form of non-protective $(\text{Mn,Cr})_3\text{O}_4$ spinel [31, 38].

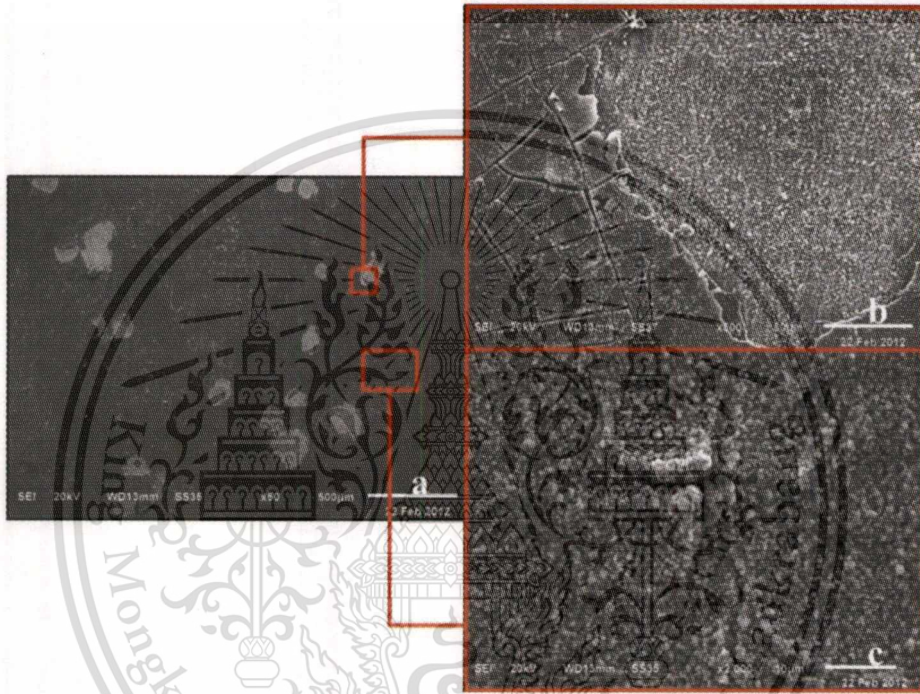


Figure 5.17: SEM results of AISI 441 coated with Mn-Co after evaporation a). overall b). spalled and cracked area c). unspalled area.

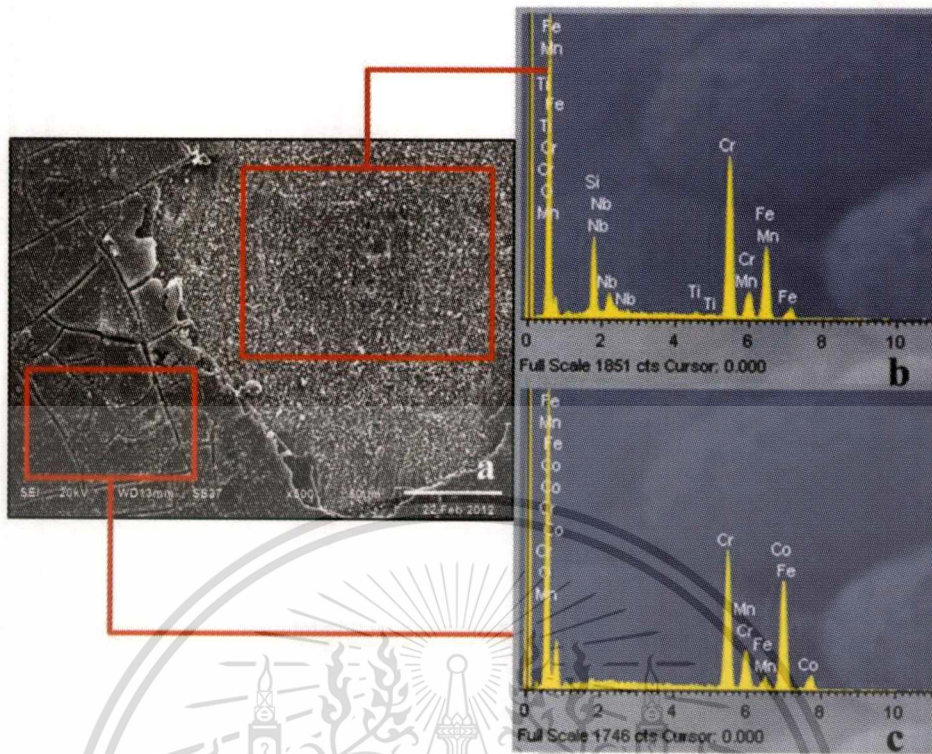


Figure 5.18: a). SEM and EDS results of AISI 441 coated with Mn-Co after oxidation b). spalled area c). not spalled area.

Increasing chromium evaporation from coated AISI 441 surface comparing with uncoated samples possibly occurred because of non-dense spinel microstructure as a consequence of a large amount of cation vacancies in former. cation vacancies and chromium upwardly diffused while oxygen inwardly diffused leading to the growth of the chromia scale. Therefore, breakaway oxidation might occur during oxidation process when chromia scale was too thick. This can be explained by the coating being able to change the stress distribution in the grown oxide scale. Alternatively, Mn- and Co-cations in the spinel phase had excellent mobility, so these species diffused outwardly towards the oxide surface, reacted with oxygen and formed as non-protective $(\text{Mn,Cr})_3\text{O}_4$ [38]. These assumptions can be shown via Figures 5.19 and 5.20.

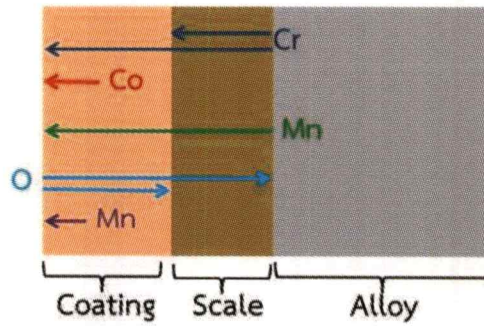


Figure 5.19: Diffusions of coating, metals and oxygen

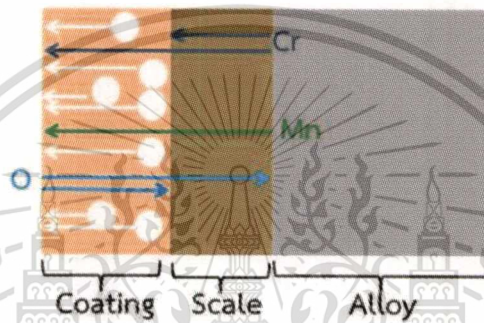


Figure 5.20: Diffusions of metals, oxygen and cation vacancies due to non-dense coating.

5.3 AISI 441 coated with LSM derived by sol-gel method

Apart from Mn-Co spinel coating by electroplating method, LSM coating by sol-gel method was investigated.

5.3.1 XRD result

The composition of grinded sample powders of LSM after calcined were analyzed by XRD. The result of analysis is shown in figure 5.21.

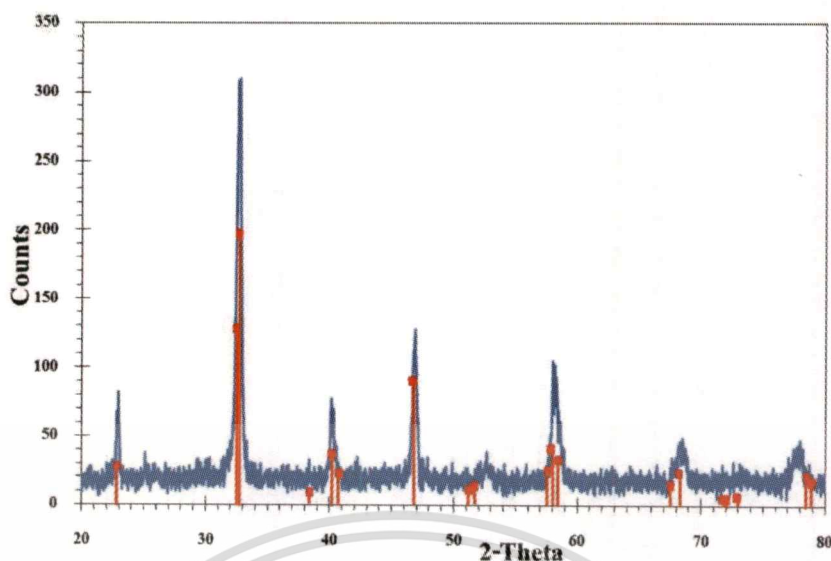


Figure 5.21: XRD pattern of AISI 441 coated with LSM sol-gel derived by sol-gel method.

Blue line in this figure represents sample line from XRD and red lines are the peaks of standard LSM. We can observe that the peaks of sample are at the same angles with standard LSM that means this sample powder are LSM.

5.3.2 Coating results

In this section, three different coating procedures were tried: AISI 441 was putted into the gel (Procedure 1), AISI 441 was dipped into the gel (Procedure 2) and AISI 441 was dipped into gel and prefired (Procedure 3).

AISI 441 coated with LSM by three different procedures are shown in Figure 5.22. We can observe that LSM coatings with first and second procedures in Figure 5.22a and 5.22b were not adhered on AISI 441 surfaces, so these coating ways did not appropriate to use for LSM sol-gel coating. Figure 5.22c shows AISI 441 coated with LSM by dipped into gel and prefired (Procedure 3). The gel adhered on steel surface but it still spalled out.

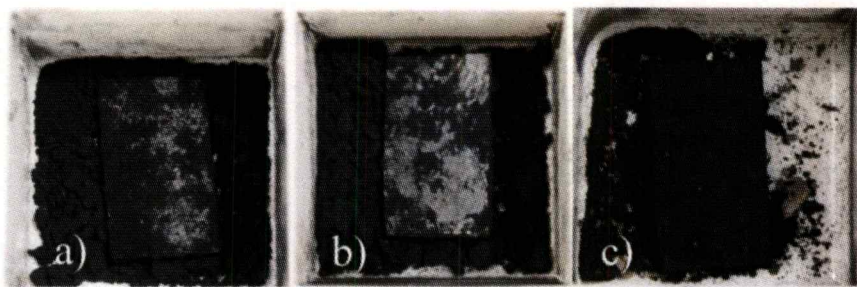


Figure 5.22: AISI 441 coated with LSM by a). put into gel (Procedure 1) b). dipped into gel (Procedure 2) c). dipped into gel and pre-fired (Procedure 3).

5.3.3 Chromium evaporation test

The evaporation test of LSM-coated sample prepared by Procedure 3 was performed in 2 cm/s of 5% water/oxygen stream at 800°C for 24 h. The result was compared with those of uncoated AISI 441 and AISI 441 coated with Mn-Co spinel as shown in Figure 5.23.

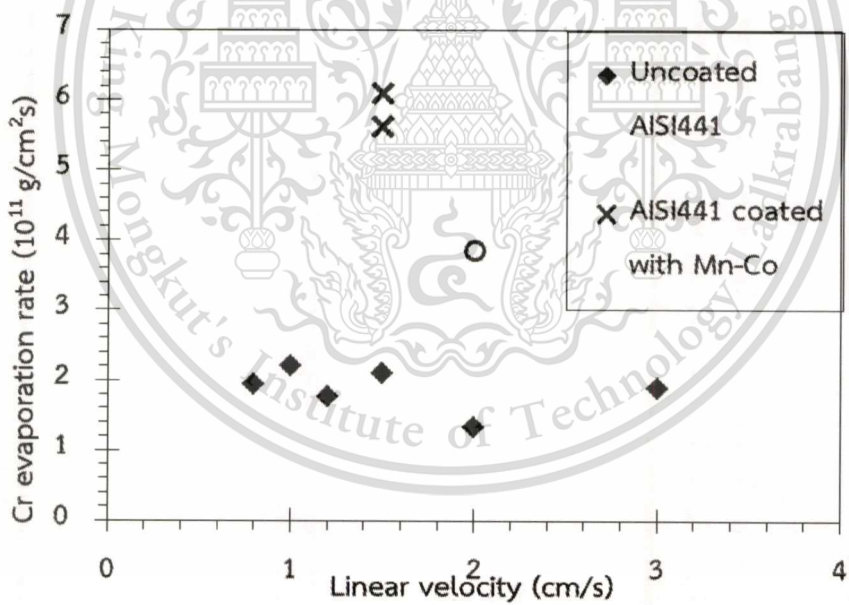


Figure 5.23: Chromium evaporation rate from AISI 441 coated with LSM compared with uncoated AISI 441 and AISI 441 coated with Mn-Co spinel.

Evaporation results showed that chromium evaporation rate of AISI 441 coated with LSM was higher than that of uncoated AISI 441 but still lower than AISI 441 coated with Mn-Co spinel. SEM and EDS results of this sample are shown in

Figure 5.24. Fine particles of outer layer were detected but this layer did not smooth. In addition, from EDS result, not only coating material was detected on the outer layer scale but also chromium. We suppose that increasing chromium evaporation comparing with uncoated samples might occur from coating step that dipped and prefired at 600°C for several times. At this temperature, chromia scale can form on the areas that were not covered with LSM. When evaporation was begun, chromium evaporation occurred promptly. This hypothesis can be described by Figure 5.25. The other possible explanation is that during prefired and calcined processes, LSM was not formed on outer surface. Chromium may diffuse during prefired and calcined processes. Then, chromium-containing coating materials such as LSCM or LSC probably formed. This phenomenon can be explained by Figure 5.26.

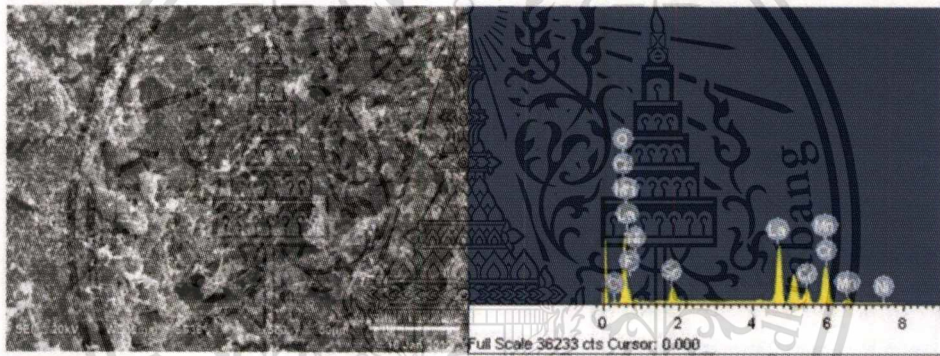


Figure 5.24: SEM and EDS results of AISI 441 coated with LSM sol-gel after evaporation in 1.5 cm/s of 5%water/oxygen stream at 800°C for 24 h.



Figure 5.25: Chromia scale occurred during coating process. Yellow blocks and brown blocks refer to LSM and chromia scale respectively.

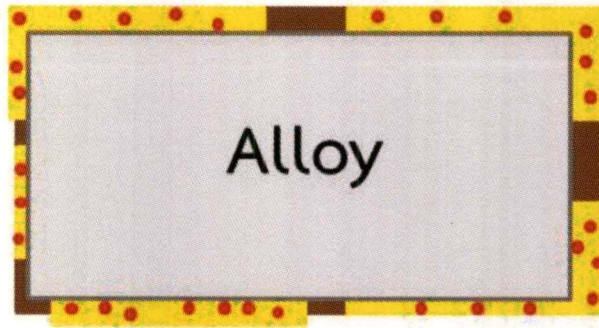


Figure 5.26: Other forms of outer surface produced during coating process. Yellow blocks, brown blocks and red spots refer to LSM, chromia scale and others coating forms respectively.

In summary, the least chromium evaporation occurred from uncoated AISI 441 surface. This can be explained that suitable coating procedures and conditions have not still developed in this research. More research and development of these coating materials are necessary for applying i.e. if we want to use LSM sol-gel as coating, we have to find more appropriate coating way or find the way to increase surface adhesion of stainless steel and coating material. Concurrently, densification of Mn-Co spinel should be promoted either by coating with other methods or finding the solution that can increase coatings density without spallation after electroplating process.

- 3). For Mn-Co coating, the effect of coating thickness on the ability to prohibit chromium evaporation should be studied. Furthermore, the processes after coating to make the coating layer denser should be performed. Thick and dense coating probably suppresses the oxidation and evaporation reaction.
- 4). For LSM sol-gel, other coating methods should be found for reducing the spallation of coating and increasing the adhesive between the alloy surface and the coating layer. Chromium scale must not occur during the process.



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Appendices

Appendix A

Experimental condition

Appendix A-1: Calibration curve of flow meter

Appendix A-2: Calculation for adjusting humidity in gas stream



Appendix A-1: Calibration curve of flow meter

Table A-1.1: Calibration of flow meter in the flow rate range of 20-200 mL/min.

Setting flow rate at flow meter (mL/min)	Results			
	Volume (mL)	Time (s)	True flow rate (mL/min)	Average true flow rate (mL/min)
20	1	6.7	8.96	10.140
	1	5.3	11.32	
50	10	18.6	32.26	34.311
	2	3.3	36.36	
100	10	6.3	95.24	91.737
	10	6.6	90.91	
	10	6.8	88.24	
150	10	4.1	146.34	139.837
	10	4.2	142.86	
	10	4.5	133.33	
200	10	3.1	193.55	193.550
	10	3.1	193.55	

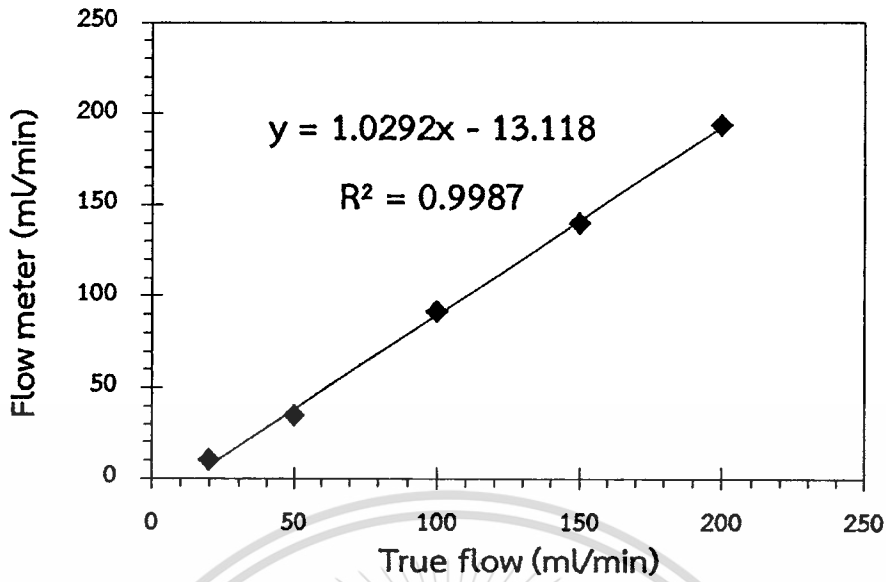


Figure A-1.1: Calibration curve of flow meter in the flow rate range of 20-200mL/min.

From Figure A-1.1, the calibration equation in the range of 20-200 mL/min is as follow.

$$F_{\text{flow}} = 1.0292F_{\text{true}} - 13.118 \quad (\text{A-1.1})$$

Table A-1.2: Calibration of flow meter in the flow rate range of 0.2-2 l/min.

Setting flow rate at flow meter (l/min)	Results					
	Volume (ml)	Time (s)	True flow rate (ml/min)	Average true flow rate (ml/min)	True flow rate (l/min)	Average true flow rate (l/min)
0.2	10	3.7	162.16	156.08	0.162	0.156
	10	3.9	153.85		0.154	
	10	4.3	139.53		0.140	
	10	4	150.00		0.150	
0.6	10	5.3	113.21	112.16	0.113	0.112
	10	5.8	103.45		0.103	
	10	5.4	111.11		0.111	
1	10	1	600.00	615.79	0.600	0.616
	20	1.9	631.58		0.632	
	20	1.9	631.58		0.632	
1.5	30	1.5	1200.00	1162.50	1.200	1.162
	30	1.5	1200		1.200	
	30	1.6	1125.00		1.125	
2	37	1.2	1850.00	1696.43	1.850	1.696
	37	1.5	1480.00		1.480	
	36	1.4	1542.857143		1.543	

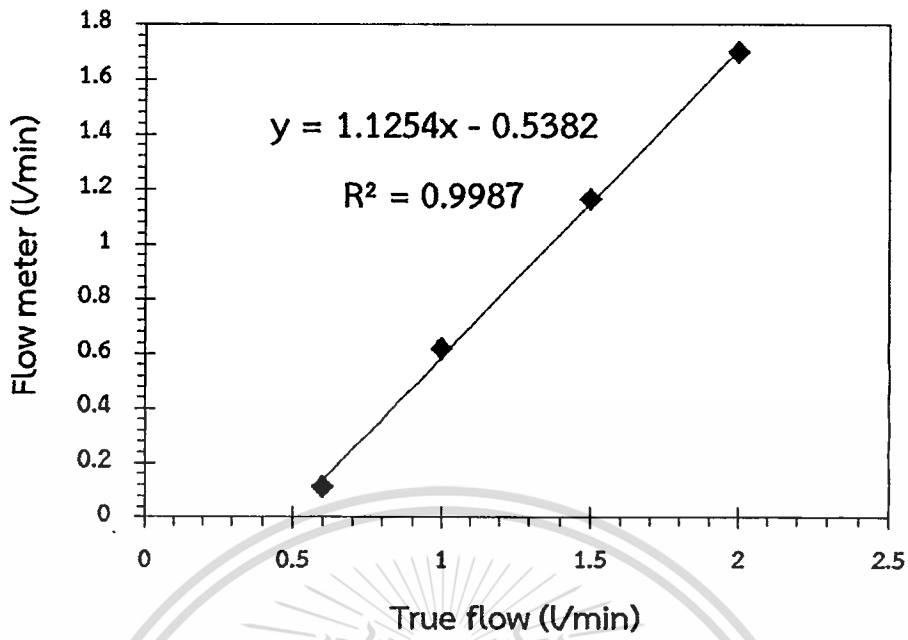


Figure A-1 2: Calibration curve of flow meter in the flow rate range of 0.2-2 l/min.

From Figure A-1.1, the calibration equation in the range of 20-200 ml/min is as follow.

$$F_{\text{flow}} = 1.1254 F_{\text{true}} - 0.5382 \tag{A-1.2}$$

Appendix A-2: Calculation for adjusting humidity in gas stream

Expected water vapor percentage = 5%

Pressure = 1 atm = 101.325 kPa

$$\begin{aligned}\therefore \text{Water vapor pressure} &= 0.05 \times 101.325 \\ &= 5.066 \text{ kPa}\end{aligned}$$

From Antoine equation [42]:

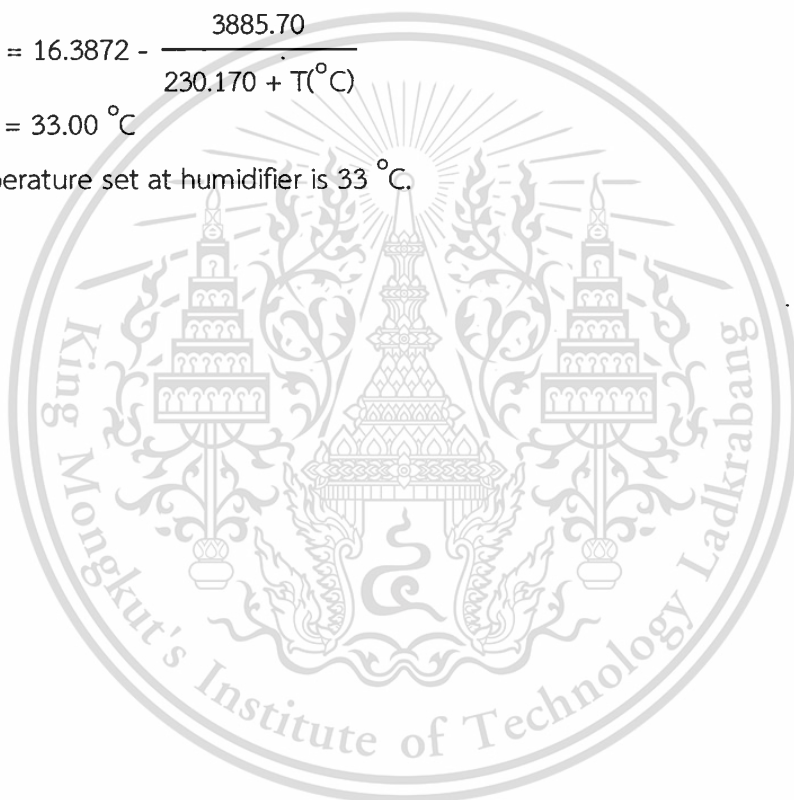
$$\ln P \text{ (kPa)} = A - \frac{B}{C + T(^{\circ}\text{C})}$$

For water: A = 16.3872, B = 3885.70 and C = 230.170

$$\ln(5.066) = 16.3872 - \frac{3885.70}{230.170 + T(^{\circ}\text{C})}$$

$$T = 33.00^{\circ}\text{C}$$

$\therefore$ Temperature set at humidifier is 33°C .



Appendix B

Mn-Co electroplating coating condition

Table B.1: Mn-Co electroplating coating

Condition (C.)	Shape of container		Anode size (mm ³)		Sample preparation		Electrical current (A)	Time (min)	Surface burnt	Remark
	Cylindrical	Square box	15×25×1	30×40×1	Picking	Non-picking				
1	O		O		O		1.5	120	O	
2	O		O		O		1.5	60	O	
3	O		O		O		1.5	15	O	
4	O		O		O		1.5	10	O	
5	O		O		O		1.2	120	O	
6	O		O		O		1.2	15	O	
7	O		O		O		1.2	5	O	
8	O		O		O		1.0	120	O	
9	O		O		O		1.0	60	O	
10	O		O		O		1.0	5	O	
11	O		O		O		0.5	10	O	
12	O		O		O		0.5	5	O	
13	O		O		O		0.5	3	O	
14	O			O	O		1.5	120	O	

Notice: "O" refer to "yes or used" and "X" refer to "no"

Table E.1: Mn-Co electroplating coating (Cont.)

Condition (C.)	Shape of container		Anode size (mm ²)		Sample preparation		Electrical current (A)	Time (min)	Surface burnt	Remark
	Cylindrical	Square box	15×25×1	30×40×1	Picking	Non-picking				
15	○			○	○		1.5	60	○	
16	○			○	○		1.2	60	○	
17	○			○	○		1.0	120	○	
18	○			○	○		0.5	15	○	
19	○			○	○		0.5	5	○	Little burnt
20	○			○	○		0.8	3	○	
21	○			○	○		0.5	3	○	Better than C.20
22	○			○	○		0.3	3	○	worse than C.21
23	○			○	○		1.0	3	○	Smooth 1 side
24	○			○	○		0.5	2	○	
25	○			○	○		1.0	1	○	
26	○			○	○		1.0	2	○	Smooth 1 side

Notice: "O" refer to "yes or used" and "X" refer to "no"

Table B.1: Mn-Co electroplating coating (Cont.)

Condition (C.)	Shape of container		Anode size (mm ²)		Sample preparation		Electrical current (A)	Time (min)	Surface burnt	Remark
	Cylindrical	Square box	15×25×1	30×40×1	Picking	Non-picking				
27	○			○	○		1.5	2	○	
28	○			○	○		1.0	1	○	
29	○			○	○		1.0	1.30	○	Smooth 1 side
30	○			○	○		1.0	1.10	○	
31	○			○	○		1.0	1.20	○	
32	○			○	○		1.0	2	○	
33	○			○	○		1.0	5	○	
34	○			○	○		1.5	2	○	
35	○			○	○		1.5	5	○	Little burnt
36	○			○	○		1.5	4	○	Smooth 1 side
37	○			○	○		1.5	7	○	Worse than C.37

Notice: "○" refers to "yes or used" and "X" refers to "no"

Table B.1: Mn-Co electrolyzing coating (Cont.)

Condition (C.)	Shape of container		Anode size (mm ²)		Sample preparation		Electrical current (A)	Time (min)	Surface burnt	Remark
	Cylindrical	Square box	15×25×1	30×40×1	Picking	Non-picking				
38	○			○	○		1.5	3	○	Smooth 1 side
39	○			○	○		1.0	2	○	
40	○			○	○		1.0	1	○	
41		○		○	○		1.5	5	×	Nearly smooth
42		○		○	○		1.5	1	×	
43		○		○	○		1.5	2	○	Smooth 1 side
44		○		○	○		1.5	5	×	
45		○		○	○		1.5	5	×	
46		○		○	○		1.5	5	×	
47		○		○	○		1.5	5	×	
48		○		○		○	0.8	15	○	
49		○		○		○	0.8	5	○	

Notice: "○" refer to "yes or used" and "×" refer to "no"

Table B.1: Mn-Co electroplating coating (Cont.)

Condition (C.)	Shape of container		Anode size (mm ²)		Sample preparation		Electrical current (A)	Time (min)	Surface burnt	Remark
	Cylindrical	Square box	15×25×1	30×40×1	Picking	Non-picking				
50		○		○		○	0.5	12	○	
51		○		○		○	0.5	5	○	
52		○		○		○	0.2	15	×	Nearly smooth
53		○		○		○	0.2	12	×	Nearly smooth
54		○		○		○	0.2	5	×	Nearly smooth
55		○		○		○	0.2	8	×	Nearly smooth
56		○		○		○	0.2	7	×	Nearly smooth
57		○		○		○	0.2	6	×	The best
58		○		○		○	0.2	4	×	Nearly smooth
59		○		○		○	0.2	3	×	Nearly smooth

Notice: "○" refer to "yes or used" and "×" refer to "no"

Table B.1: Mn-Co electroplating coating (Cont.)

Condition (C.)	Shape of container		Anode size (mm ³)		Sample preparation		Electrical current (A)	Time (mins)	Surface burnt	Remark
	Cylindrical	Square box	15 X 25 X 1	30 X 40 X 1	Pickling	Non-pickling				
60		○		○		○	0.2	2	X	Nearly smooth
61		○		○		○	0.2	1	X	Nearly smooth

Notice: "○" refer to "yes or used" and "X" refer to "no"

Appendix C

Chromium evaporation

Appendix C-1: Chromium evaporation from uncoated AISI 441

Appendix C-2: Chromium evaporation from coated AISI 441



Appendix C-1: Chromium evaporation from uncoated AISI 441

Table C-1.1: Effect of gas stream flow rate on chromium evaporation in 5% water/oxygen at 800°C for 24 h.

Batch	Linear velocity (cm/s)	Sample area (mm ²)	Cr release (μg)	Cr evaporation rate (10 ¹¹ gcm ⁻² s ⁻¹)
1	0.8	746.5012	12.474	1.934
2	1	775.5243	14.802	2.209
3	1.2	759.74	11.622	1.770
4	1.5	719.023	13.052	2.101
5	2	762.3414	8.772	1.332
6	3	759.1434	12.34	1.881

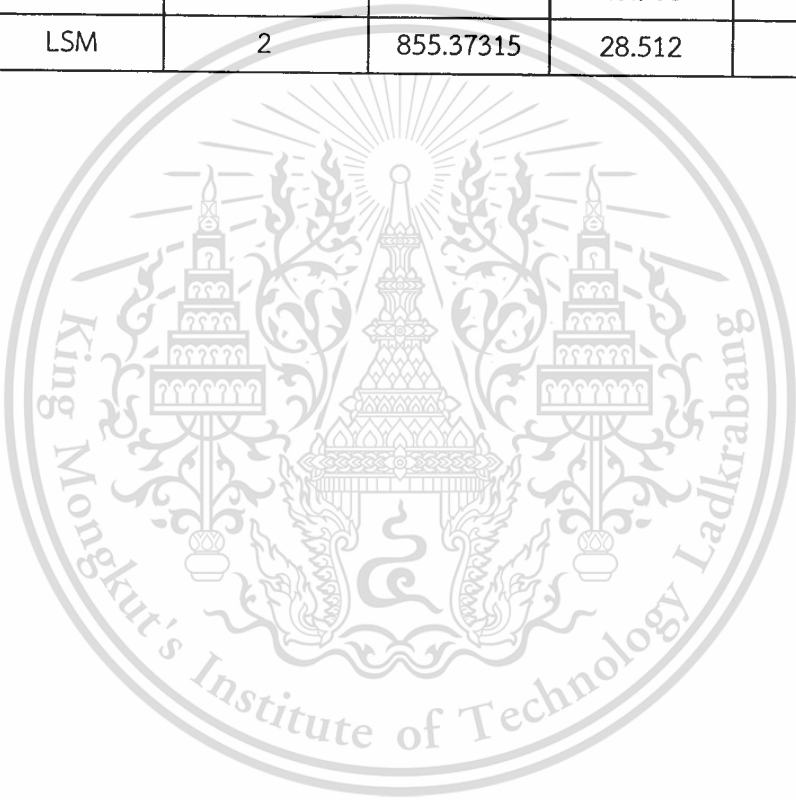
Table C-1.2: Effect of temperature on chromium evaporation in 1.5 cm/s of 5% water/oxygen for 24 h.

Batch	Temperature (°C)	Sample area (mm ²)	Cr release (μg)	Cr evaporation rate (10 ¹¹ gcm ⁻² s ⁻¹)	Partial pressure of Cr gaseous species (10 ⁹ atm)
7	651.98	814.1624	9.0615	1.288	5.199
8	699.485	798.9292	9.564	1.386	5.488
9	752.73	730.5054	8.79	1.393	5.044
10	801.51	694.24835	13.052	2.176	7.489
11	849.62	777.0144	13.864	2.065	7.955
12	899.595	843.6972	17.655	2.422	10.131

Appendix C-2: Chromium evaporation from coated AISI 441

Table C-2.1: Chromium evaporation from coated AISI 441 in 5% water/oxygen at 800°C for 24 h.

Batch	Coating materials	Linear velocity (cm/s)	Sample area (mm ²)	Cr release (µg)	Cr evaporation rate (10 ¹¹ gcm ⁻² s ⁻¹)
13	Mn-Co	1.5	906.1925	43.997	5.619
14	Mn-Co	1.5	871.8732	45.908	6.094
15	LSM	2	855.37315	28.512	3.858



Appendix D

The example of chromium evaporation calculation

Appendix D-1: Chromium evaporation rate

Appendix D-2: Partial pressure of chromium gaseous species



Appendix D-1: Chromium evaporation rate

Calculation of Batch 1:

Linear velocity = 0.8 cm/s

Sample surface area = 746.5012 mm²

Chromium release = 12.474 µg

$$\frac{\text{Chromium release}}{\text{Area}} = \frac{12.474 \times 10^{-6} \text{ g}}{746.5012 \text{ mm}^2} \times \frac{100 \text{ mm}^2}{1 \text{ cm}^2}$$

$$= 1.671 \times 10^{-6} \text{ g/cm}^2$$

$$\text{Chromium evaporation rate} = \frac{\text{Chromium release}}{\text{Area} \times \text{Time}}$$

$$= \frac{1.671 \times 10^{-6} \text{ g/cm}^2}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}}$$

$$\therefore \text{Chromium evaporation rate} = 1.934 \times 10^{-11} \frac{\text{g}}{\text{cm}^2 \text{ s}}$$

Appendix D-2: Partial pressure of chromium gaseous species

Calculation of Batch 7:

Operating temperature = 651.98 °C

Sample surface area = 814.1624 mm²

Chromium release = 9.0615 µg

Linear velocity = 1.5 cm/s

Opila et al. represent the calculation of partial pressure of chromium gaseous species

$$\begin{aligned} \text{Molar rate } (n_{\text{Cr}}) &= \frac{\text{Chromium release}}{\text{Molecular weight} \times \text{Time}} \\ &= \frac{9.0615 \times 10^{-6} \text{ g}}{51.996 \text{ g/mol} \times (24 \times 3600) \text{ s}} \\ &= 2.017 \times 10^{-12} \text{ mol/s} \end{aligned}$$

Assumptions: Ideal gas and constant pressure at 1 atm

$$P(\text{Cr-O-H}) = \frac{n_{\text{Cr}}RT}{V}$$

when $P(\text{Cr-O-H})$ is partial pressure of chromium gaseous species (atm)

n_{Cr} is molar rate (mol/s)

R is gas constant = 82.057 (atm·cm³·mol⁻¹·K⁻¹)

T is absolute temperature (K)

V is gas flow rate (ml/s)

$$\begin{aligned} P(\text{Cr-O-H}) &= \frac{2.017 \times 10^{-12} \times 82.057 \times (651.98 + 273.15)}{1.5 \times \pi \times 2.5^2} \\ &= 5.199 \times 10^{-9} \text{ atm} \end{aligned}$$

Appendix E

Publications

Appendix E-1: The 5th Thailand Metallurgy Conference

Appendix E-2: The manuscript sent for publication in “Oxidation of Metals” via
The 8th Symposium on High-Temperature Corrosion and
Protection of Materials 2012 (HTCPM 2012)



Appendix E-1: The 5th Thailand Metallurgy Conference

The 5th Thailand Metallurgy Conference (TMETC-5)

การระเหยของโครเมียมจากเหล็กกล้าไร้สนิม ซึ่งใช้เป็นแผ่นกั้นเซลล์ในเซลล์เชื้อเพลิง
ชนิดออกไซด์แข็ง

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สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง กรุงเทพฯ

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บทคัดย่อ

เซลล์เชื้อเพลิงชนิดออกไซด์แข็ง (Solid oxide fuel cells, SOFCs) เป็นอุปกรณ์ชนิดหนึ่งที่สามารถเปลี่ยนพลังงานไฮโดรเจนซึ่งเป็นพลังงานยั่งยืนไปเป็นพลังงานในรูปอื่น เพื่อใช้แทนเชื้อเพลิงฟอสซิลที่กำลังจะหมดไป แต่ปัญหาอย่างหนึ่งที่เกิดกับเซลล์เชื้อเพลิงชนิดนี้คือ จะต้องปฏิบัติการที่อุณหภูมิสูง และที่สภาวะนี้เองทำให้เหล็กกล้าไร้สนิม (Stainless steels) ซึ่งนิยมนำมาใช้เป็นแผ่นกั้นเซลล์ (Interconnect) เกิดการระเหยของโครเมียมออกจากเหล็กกล้าไร้สนิม ส่งผลให้มีอายุการใช้งานของเซลล์เชื้อเพลิงชนิดออกไซด์แข็งสั้นลง ในงานวิจัยนี้จะทำการศึกษากการระเหยของโครเมียมออกไซด์จากเหล็กกล้าไร้สนิมเกรด AISI 441 โดยจำลองสภาวะให้เหมือนกับสภาวะที่ขั้วแคโทดในเซลล์เชื้อเพลิงชนิดออกไซด์แข็ง แล้วทำการศึกษากการแพร่ 2 ตัวคือ อัตราการไหลของก๊าซออกซิเจนขึ้นผ่านชั้นงาน และอุณหภูมิ ซึ่งจากการทดลองพบว่า การระเหยของโครเมียมถูกจำกัดด้วยจลนพลศาสตร์ในช่วงอัตราการไหลเชิงเส้นของก๊าซออกซิเจนขึ้นเป็น 0.8 - 3.0 cm/s อัตราการระเหยของโครเมียมมีแนวโน้มเพิ่มขึ้น เมื่ออุณหภูมิเพิ่มขึ้นโดยมีค่าพลังงานกระตุ้น (Activation energy) เป็น 34.07 kJ/mol

คำสำคัญ: การระเหยของโครเมียม, แผ่นกั้นเซลล์, เซลล์เชื้อเพลิงชนิดออกไซด์แข็ง

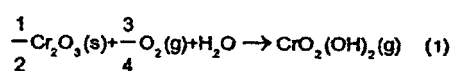
1 ที่มาและความสำคัญ

เป็นที่ทราบกันดีว่า พลังงานหลักที่ใช้ในปัจจุบันมาจากพลังงานจากปิโตรเลียมและถ่านหิน ซึ่งแหล่งพลังงานเหล่านี้กำลังจะหมดไป จึงมีความจำเป็นอย่างยิ่งที่ต้องหาแหล่งพลังงานแหล่งใหม่ที่ยั่งยืน เพื่อใช้ในการดำเนินกิจกรรมต่างๆของมนุษย์ หนึ่งในพลังงานที่ยั่งยืนที่ได้รับความสนใจคือ พลังงานจากไฮโดรเจน โดยวิธีการหนึ่งในการนำพลังงานจากไฮโดรเจนไปใช้คือการนำมาเป็นเชื้อเพลิงสำหรับเซลล์เชื้อเพลิง โดยเฉพาะเซลล์เชื้อเพลิงชนิดออกไซด์ออกไซด์แข็งซึ่งกำลังได้รับความสนใจ เนื่องจากเซลล์เชื้อเพลิงชนิดนี้มีประสิทธิภาพในการผลิตกระแสไฟฟ้าได้สูง นอกจากนี้ยังไม่ก่อให้เกิดมลพิษต่อสิ่งแวดล้อมอีกด้วย [1]

เนื่องจากอิเล็กโทรไลต์ (Electrolyte) ที่นิยมใช้ในเซลล์เชื้อเพลิงชนิดนี้คือ Yttria-stabilized zirconia (YSZ) ซึ่งเป็นวัสดุประเภทเซรามิกส์ ดังนั้นอุณหภูมิ

ในการปฏิบัติการจึงค่อนข้างสูง (ประมาณ 800-1000 °C) เพื่อให้สามารถนำประจุได้ดี และไม่จำเป็นต้องใช้โลหะราคาแพง ดังเช่นแพลทินัมเป็นตัวเร่งปฏิกิริยา [2]

ปัญหาสำคัญอย่างหนึ่งที่พบในเซลล์เชื้อเพลิงชนิดออกไซด์แข็ง คือการเสื่อมสภาพของแผ่นกั้นเซลล์ ซึ่งมักทำจากวัสดุประเภทเหล็กกล้าไร้สนิม เนื่องจากเมื่อเหล็กกล้าไร้สนิมอยู่ในบรรยากาศของแคโทด จะเกิดการระเหยของโครเมียมออกไซด์ (Cr_2O_3) ซึ่งทำหน้าที่เป็น Passive film ปกคลุมอัลลอยอยู่ [3,4] ทำให้ประสิทธิภาพการทำงานและอายุการใช้งานของเซลล์เชื้อเพลิงชนิดออกไซด์แข็งลดลง ปฏิกิริยาหลักที่นำมาซึ่งการระเหยของโครเมียม แสดงดังปฏิกิริยาต่อไปนี้ [5]



วิจิตรา วงศ์พร้อมรัตน์ และคณะ

ในงานวิจัยนี้จะทำการศึกษากลไกการระเหยของโครเมียมจากเหล็กกล้าไร้สนิมเกรด AISI 441 ซึ่งมีองค์ประกอบดังตารางที่ 1 [6] โดยจำลองสภาวะของแผ่นกันแซลล์ให้เหมือนกับด้านแคโทดในเซลล์เชื้อเพลิง

2 การทดลอง

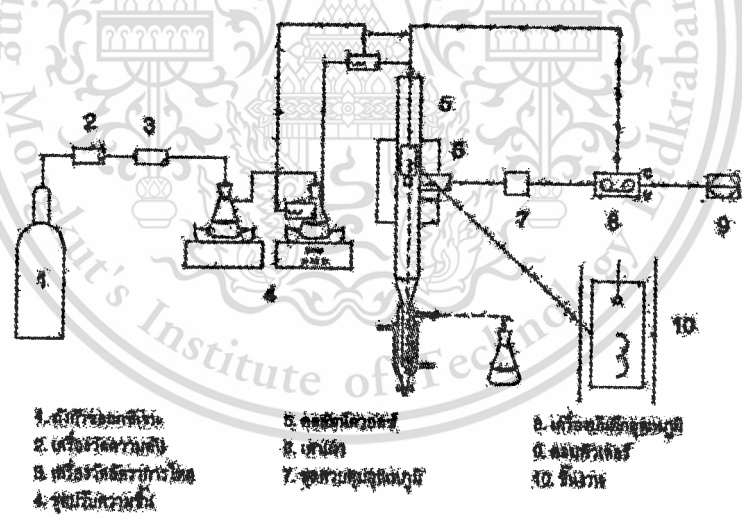
2.1 อุปกรณ์การทดลอง

ชุดอุปกรณ์การทดลองแสดงดังรูปที่ 1 จากภาพก๊าซออกซิเจนจะไหลผ่านวาล์ว 3 ทาง ซึ่งต่อเข้ากับเครื่องวัดอัตราการไหล (Flow meter) หลังจากนั้นจะไหลเข้าสู่ชุดปรับความชื้น 2 ตัว ซึ่งจะปรับให้ก๊าซออกซิเจนมีความชื้นประมาณ 5% ก่อนที่จะไหลเข้าคอลัมน์ควอตซ์ที่ติดตั้งภายในเตาเผา โดยในการทดลองจะทำการแขวนชิ้นงานเหล็กกล้าไร้สนิมเกรด AISI 441 ขนาด 25 × 15 × 1 mm³ ในแนวตั้ง ขณะ

ทำการทดลองก๊าซออกซิเจนขึ้นจะไหลผ่านชิ้นงานออกทางด้านล่างของคอลัมน์ควอตซ์ ที่ทางออกของคอลัมน์ควอตซ์ ก๊าซจะไหลผ่านเครื่องควบแน่น (Condenser) เพื่อให้สารประกอบโครเมียมที่ระเหยออกมาควบแน่นเป็นสารละลาย ส่วนก๊าซที่ออกจากเครื่องควบแน่นแล้วจะผ่านสายยางซึ่งต่อเข้ากับขวดรูปชมพู่ที่มีน้ำบรรจุอยู่อีกครั้ง เพื่อให้แน่ใจว่าสารประกอบโครเมียมที่เหลือในกระแสก๊าซละลายเป็นของเหลวทั้งหมด หลังจากเสร็จสิ้นการทดลอง ทำการล้างคอลัมน์ควอตซ์ด้วยกรดไฮโดรคลอริกความเข้มข้น 0.1 M จากนั้นเก็บตัวอย่างจากเครื่องควบแน่น ขวดรูปชมพู่และน้ำล้างควอตซ์แล้วนำไปวิเคราะห์ปริมาณโครเมียมด้วยเครื่อง ICP (Inductively coupled plasma)

ตารางที่ 1 องค์ประกอบของ AISI 441 [6]

Element	Fe	Cr	C	Mn	P	S	Si	Cb	Ti
Wt. %	80.864	18.000	0.012	0.300	0.023	0.001	0.350	0.450	0.170



รูปที่ 1: แผนภาพการทดลอง

2.2 การศึกษาผลของอัตราการไหลของก๊าซออกซิเจน

ทำการทดลองโดยการปรับเปลี่ยนค่าอัตราการไหลเชิงเส้น (Linear velocity) ของก๊าซออกซิเจนในเตาเผา เป็น 0.8 1.0 1.2 1.5 2.0 และ 3.0 cm/s และตั้งค่าอุณหภูมิในเตาเผาเป็น 800°C ทำการทดลองที่อุณหภูมิดังกล่าวนาน 24 h หลังจากที่ได้ลดอุณหภูมิลงจนถึงอุณหภูมิห้องแล้วให้ทำการเก็บตัวอย่าง ล้างควอตซ์แล้วนำตัวอย่างไปวิเคราะห์ด้วยเครื่อง ICP

2.3 การศึกษาผลของอุณหภูมิ

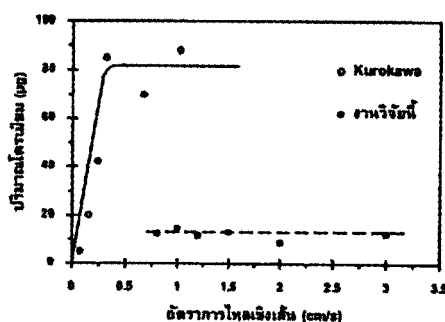
ทำการทดลองโดยตั้งค่าอัตราการไหลของก๊าซออกซิเจนให้คงที่ในช่วงที่การระเหยถูกจำกัดด้วยจลนพลศาสตร์ (Kinetics limit) แล้วทำการปรับเปลี่ยนอุณหภูมิการทดลองเป็น 700 750 800 850 และ 900°C นาน 24 h หลังจากเสร็จสิ้นการทดลองให้เก็บตัวอย่าง ล้างควอตซ์และส่งตัวอย่างวิเคราะห์ด้วยเครื่อง ICP เช่นเดียวกับการทดลองในข้อ 2.1

3 ผลการทดลอง

3.1 การระเหยของโครเมียมเมื่อทำการปรับเปลี่ยนค่าอัตราการไหลเชิงเส้น

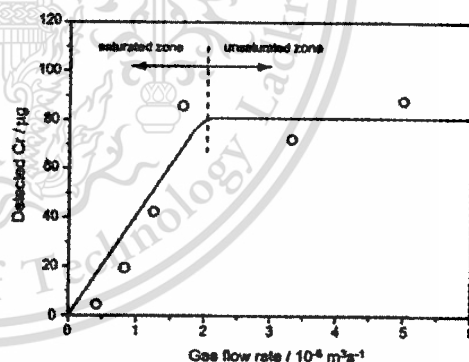
ผลการทดลองการระเหยของโครเมียมที่อุณหภูมิ 800°C เมื่อทำการปรับเปลี่ยนค่าอัตราการไหลเชิงเส้น แสดงดังรูปที่ 2 จากรูปจะเห็นว่า การระเหยของโครเมียมในช่วงอัตราการไหลเชิงเส้นที่ทำการทดลองมีแนวโน้มคงที่ ซึ่งแสดงว่าการระเหยของโครเมียม ณ อัตราการไหลเชิงเส้นดังกล่าวถูกจำกัดด้วยจลนพลศาสตร์ (Kinetics limit) นั่นหมายความว่า อัตราการเกิดปฏิกิริยาการระเหยของโครเมียมจะเกิดช้ากว่าการแพร่ของสารประกอบโครเมียมในสภาวะก๊าซ ($\text{CrO}_2(\text{OH})_2$) ออกจากพื้นผิววัสดุ ปริมาณการระเหยของโครเมียมจึงไม่ขึ้นกับอัตราการไหลของก๊าซออกซิเจน

Hidetoto Kurokawa และคณะ [7] ได้ทำการทดลองในลักษณะเดียวกันนี้กับเหล็กกล้าไร้สนิมเกรด SS 430 ซึ่งมีปริมาณโครเมียม 16.3% โดยมวล ที่อุณหภูมิ 900°C นาน 48 h ปริมาณความชื้น 10% ได้ผลการทดลองดังรูปที่ 3 ซึ่ง Kurokawa และคณะ พบว่ากราฟความสัมพันธ์ระหว่างปริมาณโครเมียมที่ระเหยออกจากชิ้นงานกับอัตราการไหลของก๊าซออกซิเจนถูกแบ่งเป็น 2 ช่วง ได้แก่ ช่วงที่มีอัตราการไหลของก๊าซออกซิเจนต่ำกว่า 2 cm³/s หรือคิดเป็นอัตราการไหล



รูปที่ 2: ผลของอัตราการไหลของก๊าซออกซิเจน ปริมาณความชื้น 5% ต่อการระเหยของโครเมียม ที่อุณหภูมิ 800°C นาน 24 h เปรียบเทียบกับผลการทดลองของ Kurokawa และคณะ ที่อุณหภูมิ 900°C นาน 48 h ปริมาณความชื้น 10%

เชิงเส้นเท่ากับ 0.4 cm/s ในช่วงนี้การระเหยของโครเมียมจะเพิ่มขึ้น เมื่ออัตราการไหลของก๊าซออกซิเจนเพิ่มขึ้น ซึ่งหมายความว่า การระเหยของโครเมียมถูกจำกัดด้วยการแพร่ของสารประกอบโครเมียมในสภาวะก๊าซ และส่วนที่ 2 คือช่วงที่อัตราการไหลของก๊าซออกซิเจนสูงกว่า 2 cm³/s ในช่วงนี้การระเหยของโครเมียมไม่ขึ้นกับอัตราการไหลของก๊าซออกซิเจน แสดงว่าการระเหยของโครเมียมถูกจำกัดด้วยจลนพลศาสตร์

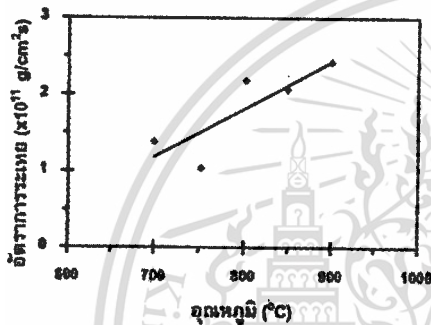


รูปที่ 3: การระเหยของโครเมียมของ SS 430 เมื่อทำการปรับเปลี่ยนอัตราการไหลของก๊าซที่อุณหภูมิ 900°C นาน 48 h ปริมาณความชื้น 10% [7]

เมื่อเปรียบเทียบผลการทดลองในงานวิจัยนี้กับงานวิจัยของ Kurokawa และคณะ จะเห็นว่าสำหรับอัตราการไหลเชิงเส้นตั้งแต่ 0.8 – 3.0 cm/s การระเหยของโครเมียมถูกจำกัดด้วยจลนพลศาสตร์เช่นเดียวกัน ซึ่งแสดงว่า องค์ประกอบที่แตกต่างกันของเหล็กกล้าไร้สนิมไม่ได้ส่งผลต่อพฤติกรรมของการระเหยของโครเมียมในช่วงอัตราการไหลเชิงเส้นดังกล่าว

3.2 การระเหยของโครเมียมเมื่อทำการปรับเปลี่ยนอุณหภูมิ

เมื่อทำการทดลองปรับเปลี่ยนอุณหภูมิ โดยให้อัตราการไหลเชิงเส้นเป็น 1.5 cm/s (ช่วงที่การระเหยของโครเมียมถูกจำกัดด้วยจลนพลศาสตร์) ผลการทดลองเป็นไปดังรูปที่ 4

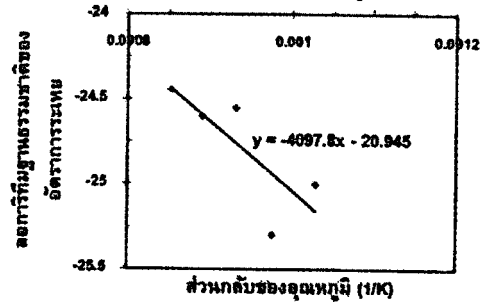


รูปที่ 4: ผลของอุณหภูมิต่ออัตราการระเหยของโครเมียมเมื่อทดลองที่อัตราการไหลเชิงเส้นเป็น 1.5 cm/s นาน 24 h ปริมาณความชื้น 5%

จากรูป จะเห็นว่าอัตราการระเหยของโครเมียมสูงขึ้น เมื่ออุณหภูมิสูงขึ้น และเมื่อเปรียบเทียบปริมาณการระเหยของโครเมียมในงานวิจัยนี้กับงานวิจัยของ Kurokawa และคณะ พบว่า ที่ระยะเวลาปฏิบัติการเท่ากัน ที่อุณหภูมิ 900 °C อัตราการระเหยของโครเมียมในงานวิจัยของ Kurokawa และคณะสูงกว่างานวิจัยนี้ประมาณ 2 เท่า ซึ่งผลดังกล่าวอาจเกิดจากปริมาณความชื้นที่ Kurokawa และคณะใช้ในการทดลองมีค่าสูงกว่าในการทดลองนี้ และ/หรืออัตราการระเหยของโครเมียมออกจากพื้นผิวของ AISI 441 ต่ำกว่าของ SS 430

เมื่อนำผลการทดลองมาพลอตกราฟระหว่างค่าลอการิทึมของอัตราการระเหยของโครเมียมกับส่วน

กลับของอุณหภูมิ จะได้ความสัมพันธ์ดังรูปที่ 5 ซึ่งจาก



รูปที่ 5: ความสัมพันธ์ระหว่างส่วนกลับของอุณหภูมิต่อลอการิทึมฐานธรรมชาติของอัตราการเกิดปฏิกิริยาการ ตามสมการอาร์เรเนียส เมื่อทดลองที่อัตราการไหลเชิงเส้นเป็น 1.5 cm/s นาน 24 h ปริมาณความชื้น 5%

รูปพบว่าค่าพลังงานกระตุ้นในการระเหยของโครเมียมจะมีค่าเท่ากับ 34.07 kJ/mol

4 สรุปผลการทดลอง

การทดลองนี้เป็นการศึกษาการระเหยของโครเมียมออกจากเหล็กกล้าไร้สนิมเกรด AISI 441 โดยจำลองสภาวะการปฏิบัติการให้เหมือนขั้วแคโทด แล้วทำการปรับเปลี่ยนพารามิเตอร์ 2 ตัว คืออัตราการไหลของก๊าซออกซิเจนผ่านชิ้นงานและอุณหภูมิ ซึ่งจากการทดลองพบว่า ในช่วงอัตราการไหลเชิงเส้น 0.8 - 3.0 cm/s การระเหยของโครเมียมถูกจำกัดด้วยจลนพลศาสตร์ของปฏิกิริยา สำหรับผลของอุณหภูมินั้น พบว่าการระเหยของโครเมียมเพิ่มขึ้นเมื่ออุณหภูมิปฏิบัติการสูงขึ้น โดยจากการคำนวณพบว่า การระเหยของโครเมียมมีค่าพลังงานกระตุ้นเท่ากับ 34.07 kJ/mol จากงานวิจัยนี้เป็นการยืนยันว่า มีการระเหยของโครเมียมเกิดขึ้นกับเหล็กกล้าไร้สนิมเกรด AISI 441 เช่นเดียวกับเหล็กกล้าไร้สนิมเกรด SS 430 ดังนั้น ก่อนการนำเหล็กกล้าไร้สนิมไปใช้เป็นแผ่นกันเซลล์ ควรจะมีการนำเหล็กกล้าไร้สนิมไปเคลือบม้องกันการระเหยของโครเมียมก่อน ซึ่งจะต้องมีการศึกษาถึงชนิดของสารเคลือบและวิธีการเคลือบที่เหมาะสมต่อไป

5 กิตติกรรมประกาศ

ขอขอบคุณ คณะวิศวกรรมศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง ที่ให้การสนับสนุนด้านทุนวิจัย และ ขอขอบคุณ ArcelorMittal IMPHY และ SIMaP Laboratory, Grenoble Institute of Technology, Grenoble, ประเทศฝรั่งเศส ที่อนุเคราะห์ชิ้นงานเหล็กกล้าไร้สนิมเกรด AISI 441 ในการทำวิจัย

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Appendix E-2: The manuscript sent for publication in “Oxidation of Metals” via The 8th Symposium on High-Temperature Corrosion and Protection of Materials 2012 (HTCPM 2012)

Publication in the Journal 'Oxidation of Metals' (Peer-reviewed)

Chromium Vaporisation from AISI 441 Stainless Steel Oxidised in Humidified Oxygen

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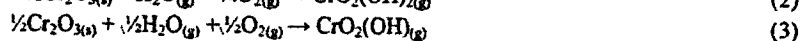
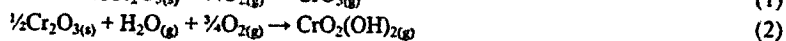
w.wichitra@gmail.com ; harit_th@hotmail.com ; kswalair@kmitl.ac.th ; sco@kmutnb.ac.th

Abstract Chromium vaporisation from chromia-forming alloys when exposed to high temperatures can deteriorate the protective property of oxide scale. This problem affects the lifetime of solid oxide fuel cells and solid oxide electrolyzers using chromia-forming alloys as interconnectors. In this work, AISI 441, a commercial grade stainless steel which chromium vaporisation investigation has not been reported so far, is chosen to study. Chromium vaporisation rates of bare AISI 441 and AISI 430 and AISI 441 and AISI 430 coated with Mn-Co spinel by electroplating method were measured in the atmosphere of 5% H₂O in O₂ over the temperature range of 650 – 900 °C with the linear velocity of the humidified oxygen stream varied in the range of 0.8 – 3 cm/s. For uncoated samples, AISI 441 showed lower chromium vaporisation rate in comparison with AISI 430. Mn-Co spinel coating could reduce the chromium vaporisation rate from AISI 430 surface. However, in contrary, the Mn-Co spinel coating not only could not suppress the chromium vaporisation but also promoted the chromium vaporisation from AISI 441 surface by 2 times.

Keywords: Chromium vaporisation, interconnector, chromia-forming alloy, Mn-Co spinel

INTRODUCTION

The phenomenon of chromium vaporisation from chromium alloys in oxidising conditions at elevated temperatures has been observed by many researchers since before 1960. The research group of Caplan and Cohen¹ was one of the early groups that studied the chromium oxide vaporisation by observing weight loss of Cr₂O₃ pellets exposed in dry and wet oxygen and argon atmospheres at 1000 – 1200 °C for 5 – 100 h. They found that in both dry and wet oxygen the rate of weight loss of Cr₂O₃ increased with increasing temperatures while no weight change occurred under dry and wet argon atmospheres. They also found that the rate of weight loss of Cr₂O₃ exposed in the wet oxygen stream was about two times higher than that in the dry one. Fryburg et al.² investigated the formation of volatile species vaporised from various types of metals and alloys including chromium at the elevated temperature of 1050 °C in oxidising atmospheres containing water vapours. They found that besides the volatile species of CrO₃, under the oxidising atmosphere containing water vapours, CrO₂(OH)₂ was also formed resulting in increasing the rate of chromium evaporation. The most abundant vaporisation reactions taking place in under humidified oxidising atmosphere are as follows^{3,4}:



According to the thermodynamic data, Reaction (2) is a dominant reaction at temperature below 1500°C³⁻⁵.

In the last two decades, chromium vaporisation phenomenon has been more and more concerned since people tried to develop solid oxide fuel cells (SOFCs) to use as electricity generating devices using H₂ as a fuel as well as to use solid oxide electrolyzers as H₂ generators. This is because chromium-forming alloys are one of the most appropriate materials used as interconnectors in planar SOFCs and solid oxide electrolyzers⁶⁻⁹. Many researchers investigated chromium vaporisation of stainless steels such as Crofer 22 APU⁸ specially developed to be an interconnector and typical ferritic stainless steel such as AISI 430⁹ and found that chromium vaporisation rate of those materials were still too high to maintain the lifetime long enough for commercial SOFCs or solid oxide electrolyzers. For this reason, several researchers attempted to improve the properties of interconnector by searching for the appropriate coating materials used to prevent or inhibit chromium vaporisation from the alloys. Perovskites like lanthanum strontium manganese oxide (LSM), lanthanum strontium chromium oxide (LSC) etc. and spinels like manganese cobalt oxide (MnCo₂O₄), cobalt iron oxide (CoFe₂O₄) etc. are promising protective coatings that could significantly reduce chromium vaporisation due to their high electrical conductivity, thermal expansion compatibility with other cell parts, stability in operating condition and ability to inhibit chromium vaporisation from the alloy surface⁹⁻¹³.

The aim of this work is to investigate chromium vaporisation on the surface of AISI 441 stainless steel, the other one of potential commercial-grade ferritic stainless steels used as interconnector¹⁴ comparing with that of AISI 430 stainless steel. Here, the effects of oxygen flow rate and temperature on chromium vaporisation rate were observed. Chromium vaporisation rates were compared with those of AISI 430 and other alloys reported in literature. Furthermore, AISI 441 and AISI 430 were coated with manganese cobalt (Mn-Co) spinel using electroplating method. The chromium vaporisation of coated samples was tested.

EXPERIMENTAL

Chromium Vaporisation Measurement

The studied materials were AISI 430 and AISI 441 stainless steels. Their chemical compositions of AISI 430 and 441 in wt. % are listed in TABLE 1. To measure chromium vaporisation rate, samples were cut into dimensions of 25 × 15 × 1 mm³ for AISI 441 and dimensions of 30 × 20 × 1.4 mm³ for AISI 430. For uncoated samples, the cut samples were polished with sand papers up to 800 grits and cleaned with ethanol.

Chromium vaporisation rates were measured via the experimental apparatus adapted from transpiration method⁵ where O₂ humidified with 5% water vapour was passed through a quartz tube where a sample was placed inside. The temperature inside the tube was controlled by a vertical furnace. The experimental set up is shown in FIGURE 1.

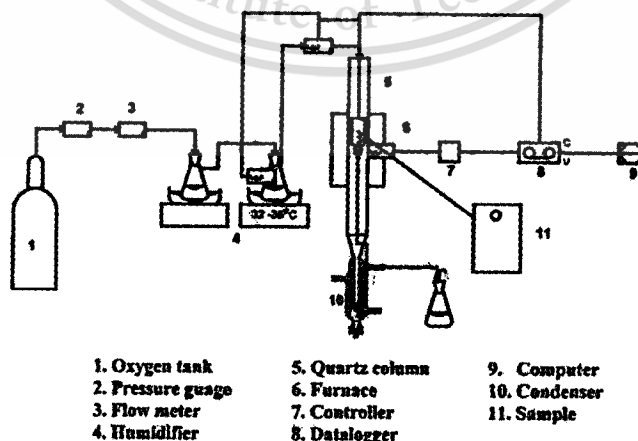


FIGURE 1. Experimental setup.

TABLE 1. The chemical compositions of AISI 430 and AISI 441

Element	Cr	C	Mn	Si	Al	Ti	Nb	Mo	Fe
AISI 430	16.5	0.03	0.4	0.35	N/A	N/A	N/A	N/A	Balance
AISI 441	17.83	0.01	0.24	0.60	0.006	0.13	0.55	0.01	Balance

* Data from ArcelorMittal

Mn-Co Spinel Coating
Electrolyte Solution Preparation¹⁵

The electrolyte was prepared from 0.1 M cobalt sulfate, 0.5 M manganese sulfate, 0.7 M sodium gluconate, 1.0 M boric acid and 1.0 M ammonium sulfate. All chemicals were supplied by Ajax Finechem Pty Ltd. The preparation of electrolyte solution was started from adding boric acid and sodium gluconate into distilled water. Mixed solution was stirred by a magnetic stirrer until completely dissolved. Then, cobalt sulfate was added, stirred for 30 min and kept standing for 24 h. After that, manganese sulfate and ammonium sulfate were added together with agitation. The pH of solution was measured and adjusted to 3.0 using ammonium sulfate or 20 vol.% sulfuric acid.

Sample Coating by Electroplating Method

The alloy samples were cut into the required size and cleaned with ethanol in an ultrasonic bath. Before coating, the samples were pickled in 25% hydrochloric acid for 3 min. The pickled alloy samples were electroplated using the electrolyte solution prepared in Section 2.1 by applying the electrical current of 30 mA/cm² for 10 min. The coated samples were calcined at 800°C for 4 h. The surfaces of coated samples were analysed by scanning electron microscope (SEM) and X-ray diffractometer (XRD).

RESULTS AND DISCUSSION

Uncoated AISI 430 and AISI 441

FIGURE 2 shows the effect of wet oxygen flow rate on chromium vaporisation from uncoated AISI 441 and AISI 430. It can be seen that chromium vaporisation rate of AISI 441 samples was lower than that of AISI 430 at linear velocity higher than 1 cm/s. Furthermore, it seems that within this range of oxygen flow rate the chromium vaporisation rate from AISI 441 surface did not depend on oxygen flow rate which means that chromium vaporisation was limited by kinetics of the reactions. Meanwhile for AISI 430, the chromium vaporisation increased with increasing the oxygen flow rate. This should be because over this range of oxygen flow rate mass transfer rate of Cr volatile species was lower than the rate that reactions occurred thus in this velocity range the reactions were limited by mass transfer of gaseous chromium species.

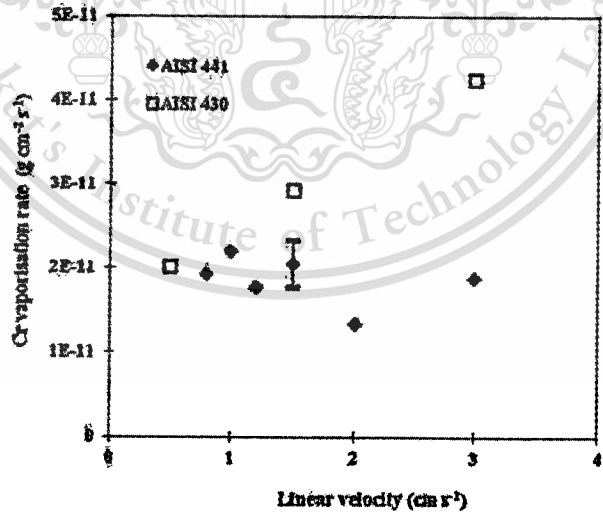


FIGURE 2. Effect of gas flow rate on chromium vaporisation content tested in 5% H₂O in O₂ at 800°C for 24 h

Based on the assumption that Reaction (2) is predominant at 800°C, mass transfer coefficients of Cr volatile species were calculated from gas transport theory¹⁶. The calculated results are shown in TABLE 2.

TABLE 2. Mass transfer coefficients and mass flux of CrO₂(OH)₂ from AISI 430 surface

v (cm s ⁻¹)	Mass transfer coefficient, k_m (cm s ⁻¹)
0.5	0.80
1.0	1.38
1.5	1.95

From the calculated mass transfer coefficients, mass fluxes of chromium volatile species (CrO₂(OH)₂) were calculated using equilibrium constant (K_p) of Opila et al.⁴ and Stanislawski et al.⁶. The calculated results comparing with the experimental results are plotted in FIGURE 3. From FIGURE 3, it can be seen that the measured mass fluxes of CrO₂(OH)₂ are different from the calculated ones by around one order of magnitude and measured mass fluxes of Cr volatile species are closer to the calculated one using K_p of Stanislawski et al. than the one calculated from K_p of Opila et al.

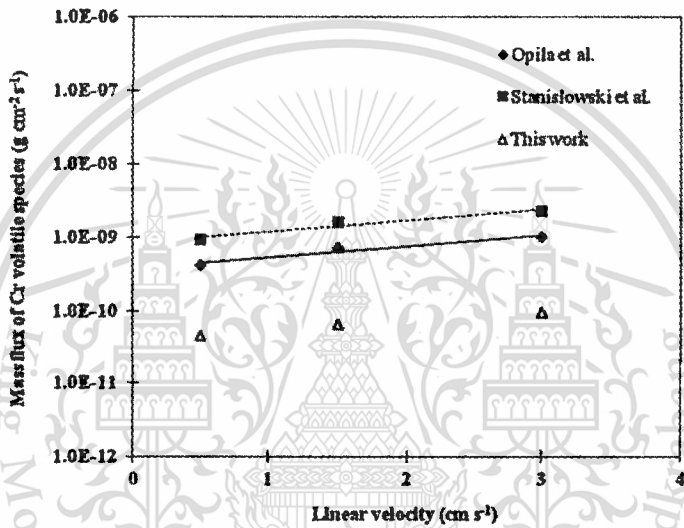


FIGURE 3. Mass fluxes of Cr volatile species as a function of linear velocity of 5% H₂O in O₂ measured from this work, and calculated from equilibrium constant data of Opila et al. and Stanislawski et al. at 800°C.

Chromium release from our AISI 430 and AISI 441 samples and other alloys⁸ are shown in FIGURE 4. Chromium vaporisation from AISI 441 and AISI 430 were tested in 5%water/oxygen at 800°C for 24 h. Other alloys were tested in 1.88% water/oxygen at the same temperature and period of time. From the figure, we can observe that AISI 441 released chromium less than Ducrolloy, AISI 430 and Conicro 5010W but released chromium more than Aluchrom YHf, and Crofer 22APU. However, aluchrom YHf is a ferritic alumina-forming alloy which has too high electrical resistance thus it is not suitable for interconnector application. For Crofer 22APU, although the chromium vaporsiation rate was lower than that of AISI 441, Crofer 22APU is a special alloy developed for using as an interconnector. Hence, in the economic point of view, Crofer 22APU is much more expensive than AISI 441. For this reason, if the effective coating that can significantly inhibit chromium vaporisation from AISI 441 can be developed, this commercial grade chromia-forming alloy should be a good candidate to use as an interconnector material.

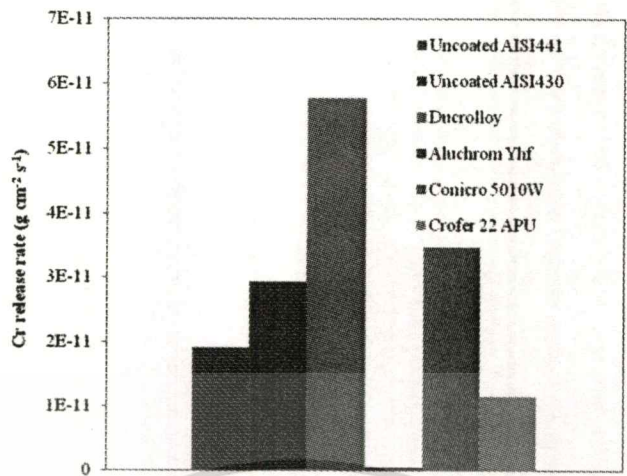


FIGURE 4. Chromium release rates of AISI 441 and AISI 430 measured in 5% H₂O in O₂ at 800°C for 24 h. (from this work) and other alloys tested in 1.88% H₂O in O₂ at 800°C for 24 h⁸.

Effect of operating temperature on chromium vaporisation was carried out at linear velocity was 1.5 cm/s. The results are shown as FIGURE 5.

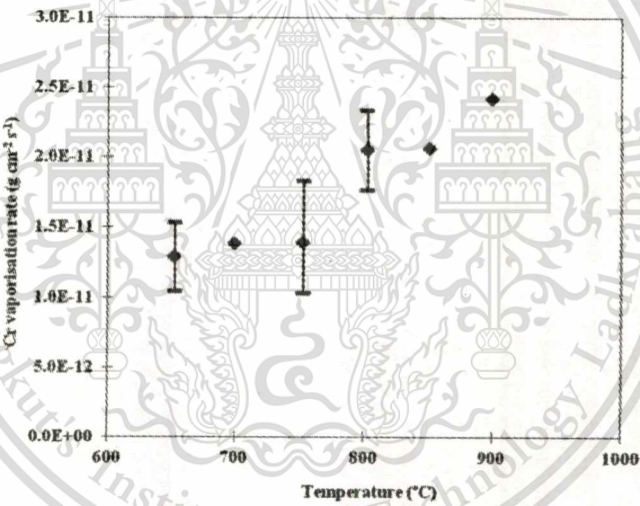


FIGURE 5. Effect of temperature on chromium vaporisation from uncoated AISI 441 and uncoated AISI 430 in 5% H₂O in O₂ at the linear velocity of 1.5 cm/s for 24 h.

As illustrated in FIGURE 5, the chromium vaporisation rate increased with increasing temperature. From this result, Arrhenius plot of chromium vaporisation rate and 1/T was drawn and the observed activation energy was calculated as 24.74 kJ/mol. Since at this linear velocity of gas, the chromium vaporisation rate was limited by the kinetics of chemical reactions, low observed activation energy of overall reactions imply that at this temperature range, the dominant reaction should not be really sensitive to temperature. This result coincides with the thermodynamic data that Reaction (2) should be a dominant reaction in this observed reaction range⁴.

Partial pressure of CrO₂(OH)₂ represented Cr volatile species was calculated using the thermodynamic data reported by Opila et al.⁴ and Stanislawski et al.⁸ at various temperatures and compared with the experimental results from this work. The plot between partial of Cr volatile species and temperature is shown in FIGURE 6. It can be seen that the partial pressure of Cr volatile species measured in this work is about two orders of magnitude lower than those calculated using the thermodynamic data of Opila et al. and Stanislawski et al.

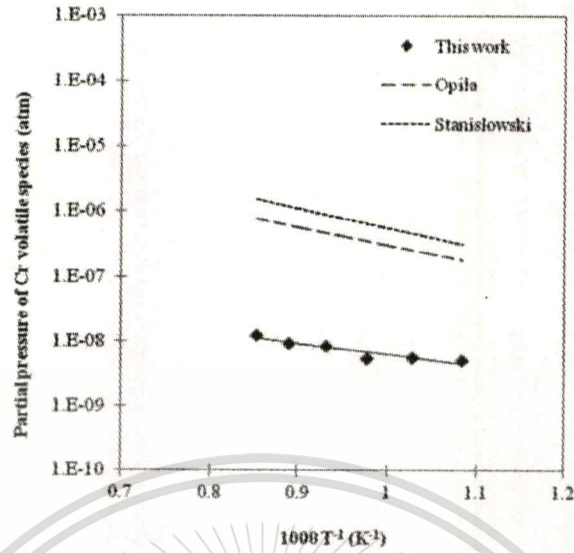


FIGURE 6. Experimental and calculated partial pressure of Cr volatile species in humidified oxygen stream as a function of temperature.

Coated AISI 430 and AISI 441

In the attempt to find a coating material capable for inhibiting the chromium vaporisation, MnCo_2O_4 was chosen to experiment in this work. The electroplating method was applied to coat this Mn-Co spinel on AISI 430 and AISI 441 surfaces. The morphology of the sample surfaces was analysed by SEM. FIGURE 7 shows SEM images of the coated samples.



FIGURE 7. SEM images of the coated surfaces of (a), (b) AISI 430 and (c), (d) AISI 441.

As observed from FIGURE 7, the surfaces of both AISI 430 and AISI 441 were well covered with the coating. Some cracks can be observed on both samples but the coated AISI 441 surface seems to have more

cracks. When observing the SEM images with higher magnification (FIGURES 7(b) and (d)), we can see that in the crack channels were still covered with the coating which means the AISI 430 and AISI 441 surfaces did not reveal. However, the surface of AISI 441 seems more porous. XRD analysis was also performed and the results showed that the Mn-Co spinel was found on the coated sample surfaces.

The chromium vaporisation from the surfaces of AISI 430 and AISI 441 coated with Mn-Co spinel by electroplating method was observed. FIGURE 8 shows the comparison of chromium vaporisation rates of bare and coated AISI 430 and AISI 441 samples.

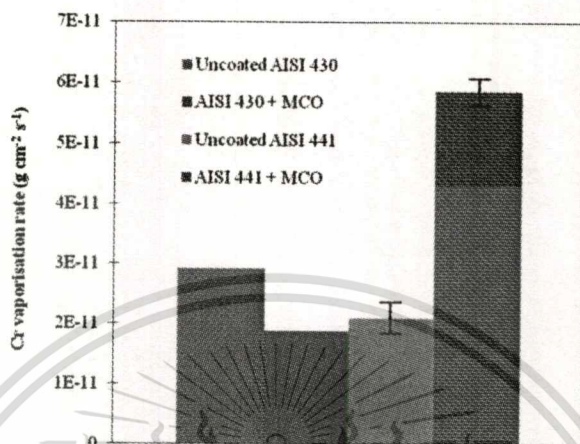


FIGURE 8. Chromium vaporisation rates of bare and MnCo₂O₄ coated AISI 430 and AISI 441 in 5% H₂O in O₂ at 800°C.

As discussed before, it is clear that chromium vaporisation rate from bare AISI 441 surface was lower than that of AISI 430. Consider the results of AISI 430, coated with Mn-Co spinel could reduce chromium vaporisation rate by around 40 %. This result is in agreement the results from literature ⁹. However, in case of AISI 441, the results were contrary. Having Mn-Co spinel coating on top did not only help reduce chromium vaporisation but also promote chromium vaporisation to increase by 2 times. This result seems against the conventional understanding that even if the coating cannot prevent the alloy surface from the chromium vaporisation, it should not make the chromium vaporisation rate increased unless chemical reaction(s) occurred creating substance(s) that can catalyse chromium vaporisation reactions. This assumption needs to be further proved.

CONCLUSIONS

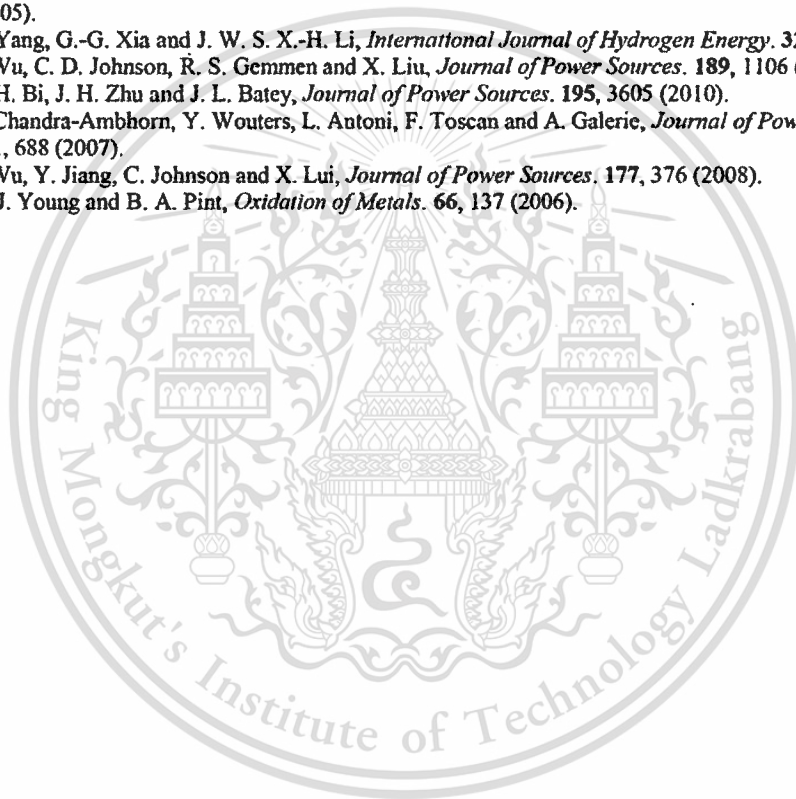
1. Uncoated AISI 441 provided lower chromium vaporisation rate than that of uncoated AISI 430. However, the chromium vaporisation rate of this AISI 441 was still high in comparison with Crofer 22APU.
2. Over observed linear velocity range of 0.8-3.0 cm/s, chromium vaporisation from uncoated AISI 430 surface was limited by mass transfer while chromium vaporisation from uncoated AISI 441 was limited by kinetics of the reactions.
3. For AISI 430, Mn-Co spinel coating could slow down the chromium vaporisation from the alloy surface. However, Mn-Co spinel coating could not only reduce chromium vaporisation but promote higher chromium vaporisation rate from AISI 441 surface.

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