

**Comparative Study on High Temperature Oxidation
of Cobalt-Based Alloy and AISI 316 Stainless Steel**

Pratchaya Lertprasert



**A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, Faculty of Engineering,
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2018**

การศึกษาเปรียบเทียบการเกิดออกซิเดชันที่อุณหภูมิสูง
ของโลหะผสมที่มีโคบอลต์เป็นองค์ประกอบหลักและเหล็กกล้าไร้สนิมเกรด 316

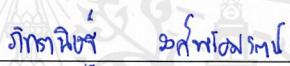


ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
วิศวกรรมศาสตรบัณฑิต สาขาวิชาวิศวกรรมปิโตรเคมี
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
ปีการศึกษา 2561

Title	Comparative Study on High Temperature Oxidation of Cobalt-Based Alloy and AISI 316 Stainless Steel
By	Mr. Pratchaya Lertprasert
Field of Study	Petrochemical Engineering
Advisor	Dr. Patthranit Wongpromrat
Co-Advisor	Dr. Phacharaphon Tunthawiroon

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

Thesis Committee


Chairman
(Dr. Patthranit Wongpromrat)
Committee
(Asst. Prof. Dr. Nuttapol Lerkkasemsan)
Committee
(Dr. Natthanon Phaiboonsilpa)

Title Comparative Study on High Temperature Oxidation of
Cobalt-Based Alloy and AISI 316 Stainless Steel

By Mr. Pratchaya Lertprasert

Advisor Dr. Patthranit Wongpromrat

Co-Advisor Dr. Phacharaphon Tunthawiroon

Field of Study Petrochemical Engineering

Affiliation Department of Chemical Engineering, Faculty of Engineering

Abstract

At the present, there are many metals used for high temperature section of chemical and petrochemical processes. Some metals have low investment cost but maintenance costs increase with time since it must be operated at high temperatures. Stainless steels that are used as tubes or heating coils release chromium that causes shorter service lifetime which may reduce profit and production capacity. The objective of this research is to study the oxidation of AISI 316 stainless steel and cobalt-based alloy (CoCrMo) in oxygen gas, having linear velocity of 3.0 cm/s at 1,000°C for the duration times range of 0-48 hours. The weight gains of the specimens were recorded and interpreted to the oxidation kinetics. From the results, the oxidation rate equations of AISI 316 stainless steel and CoCrMo alloy in oxygen gas at 1,000°C are $m^{0.5644} = 1.6187 \times 10^{-2} \cdot t$ and $m^{2.8546} = 6.6384 \times 10^{-6} \cdot t$, respectively. When m is weight gain per specimen surface area (mg/mm²) and t is oxidation time (h). The morphologies and compositions of the oxidized surface were examined by scanning electronic microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

Keywords: AISI 316 stainless steel, CoCrMo alloy, Oxidation, SEM, EDS

เรื่อง	การศึกษาเปรียบเทียบการเกิดออกซิเดชันที่อุณหภูมิสูงของโลหะผสมที่มีโคบอลต์เป็นองค์ประกอบหลักและเหล็กกล้าไร้สนิมเกรด 316
โดย	นายปรัชญา เลิศประเสริฐ
อาจารย์ที่ปรึกษา	ดร. ภัทรานิษฐ์ วงศ์พร้อมรัตน์
อาจารย์ที่ปรึกษาร่วม	ดร. พชรพล ตันทวิรุฬห์
สาขาวิชา	วิศวกรรมปิโตรเคมี
สังกัด	ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

บทคัดย่อ

ในปัจจุบันมีโลหะหลายชนิดที่ใช้เป็นวัสดุสำหรับหน่วยปฏิบัติการที่มีอุณหภูมิสูงของอุตสาหกรรมเคมีและปิโตรเคมี โลหะที่ถูกเลือกใช้บางชนิดมีราคาต้นทุนต่ำ แต่เมื่อเวลาผ่านไปค่าบำรุงรักษามีค่าสูงขึ้นในทุกๆปีตามอายุการใช้งานเพราะต้องปฏิบัติการที่มีอุณหภูมิสูง ที่สภาวะนี้เหล็กกล้าไร้สนิมซึ่งนิยมนำมาใช้เป็นท่อหรือหน่วยนำความร้อนจะเกิดการระเหยของโครเมียมทำให้อายุการใช้งานสั้นลง ซึ่งอาจจะทำให้ขาดทุนหรือความสามารถในการผลิตลดลง งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการเกิดออกซิเดชันของโลหะผสมโคบอลต์และเหล็กกล้าไร้สนิมเกรด 316 ในสภาวะที่มีอัตราการไหลของแก๊สออกซิเจนเท่ากับ 3 เซนติเมตร/วินาที ที่อุณหภูมิ 1,000 °C ในช่วงเวลา 0-48 ชั่วโมง บันทึกจลนพลศาสตร์ของการออกซิเดชันโดยใช้การวัดน้ำหนักที่เปลี่ยนแปลงไปของตัวอย่างก่อนและหลังการทดลองในแต่ละช่วงเวลา พบว่าสมการการเกิดปฏิกิริยาออกซิเดชันของเหล็กกล้าไร้สนิมเกรด 316 และโลหะผสมโคบอลต์มีค่าเป็น $m^{0.5644} = 1.6187 \times 10^{-2} \cdot t$ และ $m^{2.8546} = 6.6384 \times 10^{-6} \cdot t$ ตามลำดับ จากนั้นศึกษาลักษณะพื้นฐานวิทยาและองค์ประกอบของออกไซด์ที่เกิดขึ้นหลังจากทำการทดลองโดยใช้เครื่อง Scanning electronic microscopy (SEM) และ Energy dispersive x-ray spectroscopy (EDS).

คำสำคัญ: เหล็กกล้าไร้สนิม, โลหะผสมโคบอลต์, พื้นฐานวิทยา

Acknowledgements

I would like to express my deep appreciation and gratitude to my advisor, Dr. Patthranit Wongpromrat, Department of Chemical Engineering, King Mongkut's Institute of Technology Ladkrabang for her guidance, suggestions and assistance in this project. Without her supervision and constructive assistance, this project would not have been in its present shape.

I would like to acknowledge lecturers of Chemical Engineering Department, King Mongkut's Institute of Technology Ladkrabang, for knowledge, instructions and their kindness.

Besides my advisor, I would like to thank Dr. Phacharaphon Tunthawiroon, Department of Industrial Engineering, King Mongkut's Institute of Technology Ladkrabang for him guidance and for supplying the sample of this project.

I would like to thank Chemical Engineering Department, King Mongkut's Institute of Technology Ladkrabang for supporting research equipments.

Finally, my achievement would never be possible unless there is heartly support from my family. The deepest and sincere gratitude goes to my grandmother and grandfather for their endless love, encouragement and understanding throughout the entire period of my study.

Table of Contents

	Page
Abstract	I-II
Acknowledgements	III
Table of Contents	IV-V
List of Figures	VI
List of Tables	VII
Nomenclature	VIII
Chapter I. Introduction	1
1.1 Background	1
1.2 Objectives	2
1.3 Scope of work	2
1.4 Expected output	2
Chapter II. Theory and Literature Review	3
2.1 Mechanism of metal-oxygen reaction	3
2.2 Super alloy	4-6
2.3 Cobalt Based Alloy	6
2.4 Stainless Steel	7
2.5 Austenitic Stainless Steel	8-9
2.6 Effect of alloying elements in Austenitic Stainless Steel	9-10
2.7 Kinetics of oxidation	10-12
2.8 Characterisation techniques	12-13
2.8.1 SEM	12
2.8.2 EDS	13
2.9 Literature Review	13-15
Chapter III. Experimental	16
3.1 Experimental setup	16
3.2 Preparing samples	17
3.3 Experimental conditions	17
3.4 Characterisation of materials	17-18
Chapter IV. Results and Discussion	19
4.1 Kinetics of oxidation	19-21
4.1.1 AISI 316 Stainless Steel	19-20
4.1.2 CoCrMo Alloy	20-21
4.2 Observation of surface by SEM and EDS	22-24
Chapter V. Conclusion	25
5.1 Suggestion	25

	Page
References	26
Appendices	27
Appendix A	28-31
Appendix B	32
Appendix C	33
Bibliography	34



List of Figures

	Page
Figure 2.1: The steps of metal-oxygen reaction.	3
Figure 2.2: Processing methods used to generate various portions of a jet turbine engine.	4
Figure 2.3: Single-Crystal Super alloys, nominal compositions (wt%). Adapted from Erikson, 1996.	5
Figure 2.4: Classification of super alloy.	6
Figure 2.5: Isothermal section of Fe-Cr-Ni diagram at 750°C.	8
Figure 2.6: Common kinetic laws for the rate of growth of oxide layer	10
Figure 2.7: Schematic of main components of SEM.	12
Figure 2.8: Oxide surface appearance of the samples after 100, 300, and 1,000 h of oxidation; right: SEM micrograph at spallation border for the sample after 1000 h of oxidation.	13
Figure 2.9: Schematic of oxidation stage of AISI 340 alloy in air.	14
Figure 2.10: Mass gain curves obtained during isothermal cobalt based Phynox oxidation between 800 and 1,100°C in air.	14
Figure 2.11: SEM cross section shown morphologies on the cobalt-based alloy (phynox) after 24 h oxidation in air at 900°C and 1,000°C.	15
Figure 3.1: Experimental Setup.	16
Figure 3.2: Chart of experiment work.	18
Figure 4.1: Oxidation curve of AISI 316 stainless steel oxidized with-linear velocity oxygen gas 3 cm/s 1,000°C.	19
Figure 4.2: Double logarithm plot oxidation curve of AISI 316 stainless steel oxidized with linear velocity oxygen gas 3 cm/s 1,000°C.	20
Figure 4.3: Oxidation curve of CoCrMo Alloy oxidized with linear velocity-oxygen gas 3 cm/s 1,000°C.	20
Figure 4.4: Double logarithm plot oxidation curve of CoCrMo Alloy oxidized with linear velocity oxygen gas 3 cm/s 1,000°C.	21
Figure 4.5: Samples after oxidation from experiments (left: AISI 316 stainless steel; right: CoCrMo alloy).	22
Figure 4.6: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s oxygen gas at 1,000°C for 12 h.	23
Figure 4.7: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s oxygen gas at 1,000°C for 24 h.	23
Figure 4.8: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s oxygen gas at 1,000°C for 36 h.	23
Figure 4.9: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s oxygen gas at 1,000°C for 12 h.	24
Figure 4.10: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s oxygen gas at 1,000°C for 24 h.	24
Figure 4.11: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s oxygen gas at 1,000°C for 36 h.	24
Figure A-1.1: Calibration curve of flow meter in the flow rate of 0.2-2 l/min.	30
Figure A-2.1: Calibration curve of temperature in furnace .	31

List of Tables

Page

Table 2.1:	Composition range of five different stainless steel group.	7
Table 3.1:	Composition of CoCrMo.	17
Table 3.2:	Composition of AISI 316 Stainless Steel.	17
Table A-1.1:	Calibration of flow meter in the flow rat range of 0.2-2 l/min.	29
Table A-2.1:	Calibration of temperature in furnace.	31
Table B-1:	Weight gain measurement of AISI 316 stainless steel in oxygen gas.	32
Table B-2:	Weight gain measurement of CoCrMo alloy in oxygen gas.	32



NOMENCLATURE

AISI	American Iron and Steel Institute
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive X-Ray Spectroscopy
CoCrMo	Cobalt Chromium Molybdenum



CHAPTER I

INTRODUCTION

1.1 Background

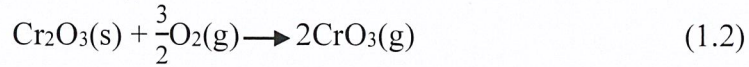
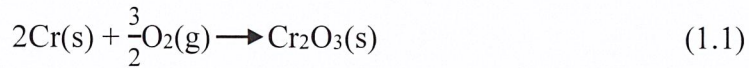
At present, many chemical and petrochemical processes are operated at high temperature to achieve reasonable production rates or, as in cracking furnaces, to promote endothermic reactions. Cracking (or pyrolysis) furnaces are used to produce olefins such as ethylene and propylene, which are subsequently used to make the commodity materials, i.e. polyethylene and polypropylene. The hydrocarbon stream mixture is heated by passing through a tube. The tube units (or coils) are expected to survive for 5 years or more whilst operating at temperatures up to 1,100°C. The materials used for cracking furnace tubes are centrifugal cast heat resisting steel or austenitic alloys containing high chromium level. Process economics are enhanced by higher operating temperatures, creating a demand for improved heat-resistant alloys.

The technical domains in which high temperature corrosion is of importance can be categorized into 5 headings: thermal machines (internal combustion engines or gas turbines), used for surface, marine and air transportation or for energy conversion (steam or gas turbines), including their inlet and outlet devices; chemical industry, i.e. organic chemistry (steam cracking, catalytic cracking, chlorination, etc.) inorganic chemistry or metallurgical industry (roasting, thermal and thermomechanical treatments, etc.); incineration of industrial waste; electric heating devices (electrical resistances, furnace walls, etc.); nuclear engineering.

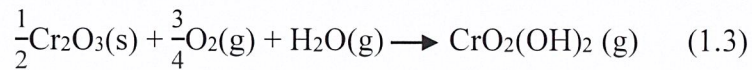
Cobalt-based alloys have been used for several years in the manufacturing of various components such as blades or combustion chambers in gas turbines (both the industrial type and aero-engines). These are operated at high temperatures ranging up to 1,200°C. Therefore, the corrosion resistant coupled with high temperature resistant material for gas turbine application is needed. However, the main disadvantage of cobalt-based alloy is its expensive cost when compared with stainless steel.

Austenitic stainless steels can be found in a wide range of applications, such as super-heaters, re-heater tubes, and boilers components which are subjected to thermal fluctuations under normal operation conditions; therefore, protection against degradation caused by high temperatures in vigorous environment is necessary. This protection can be achieved the formation of a protective scale of Cr_2O_3 which slows down the degradation of the metals.

The important problem of the processes that is operated at high temperatures is the degradation of alloys. When alloys are operated at high temperatures, Chromium in the alloys would react with O_2 and forms chromium oxide or chromia scale (Cr_2O_3) covering the surface. This is protective layer preventing the direct contact of O_2 and the alloy components. Thus, the rust cannot be formed. A situation arises with chromium which undergoes two oxidation reaction that occur in dry oxygen are:



On the other hand, the predominant reaction that occurs in humidified oxidizing atmosphere is:



However, no research related the oxidation at high temperatures of CoCrMo alloy and AISI 316 stainless steel. Thus, in this study, oxidation of CoCrMo alloy and AISI 316 stainless steel with different times are investigated.

1.2 Objectives

1.2.1 To study the oxidation kinetics using weight gain measurement of CoCrMo alloy and AISI 316 stainless steel.

1.2.2 To examine the oxide morphologies using SEM and EDS.

1.3 Scopes of Work

1.3.1 Investigate oxidation behaviors and oxide morphologies on CoCrMo alloy and AISI 316 stainless steel after high temperature oxidation in oxygen gas linear velocity of 3.0 cm/s at 1,000°C for the duration times range of 0-48 hours.

1.4 Expected Output

1.4.1 The oxidation kinetics, SEM and EDS of CoCrMo alloy and AISI 316 stainless steel.

CHAPTER II THEORY AND LITERATURE REVIEW

2.1 Mechanism of metal-oxygen reaction

The reaction of a metal with O_2 to form one mole of its oxide can be shown as equation 2.1. Where M is the reacting metal and M_xO_y is the oxide.

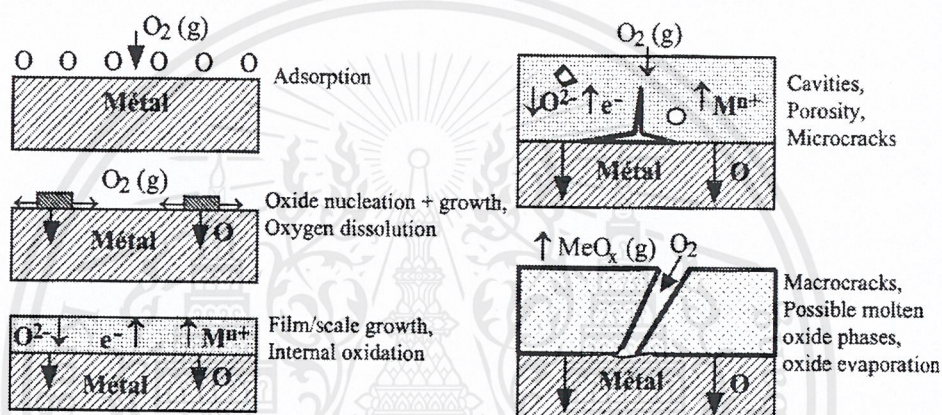


Figure 2.1: Schematic of main phenomena occurring during metal oxidation[1].

Figure 2.1 show main phenomena occurring during metal oxidation. When metal is exposed to an oxidant (e.g. O_2), it is adsorbed on the surface of the metal. Oxide nuclei forms and grows as a film, completely covering the metal surface. This film acts as a diffusion barrier separating the metal and oxidant. The reaction could proceed whenever the electrons can diffuse through the oxide layer and reach the surface where the reaction with oxygen atoms occurs. On the other hand, oxygen ions and/or metal ions diffuse through the layer and the reaction is then proceeded. Cavities and microcracks could develop inside the scale during its growth as a result of stress generation in the scale, so cracking and spallation could be formed.

2.2 Super alloy[2]

Super alloy is an alloy that exhibits excellent mechanical strength and creep resistance at high temperatures. Super alloys are metallic materials for service at high temperatures, in hot zone of gas turbine, jet engines, etc.

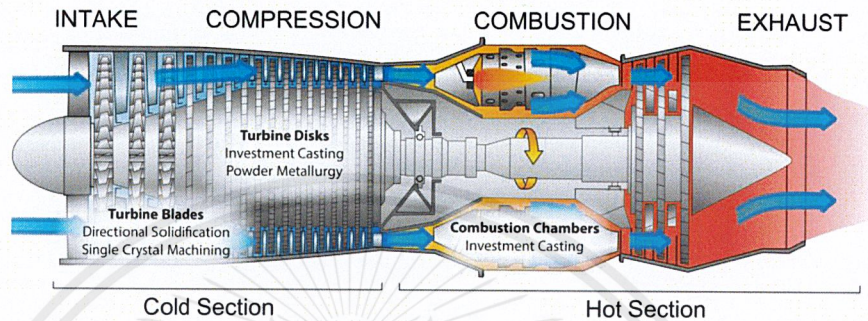


Figure 2.2: Processing methods used to generate various portions of a jet turbine engine.

Super alloys develop high temperature strength through Solid Solution Strengthening (SSS) that is a type of alloying that can be used to improve the strength of the metals. The technique works by adding atoms of one element (alloying element) to the crystalline lattice of another element (the base metal). So, that make super alloys have any properties such as high temperature creep resistance (1,050-1,200°C), good fatigue life, high corrosion resistance and good surface stability.

2.2.1 Classification of super alloy

Super alloys are often classified into generations and until today there were 5 generations (The 6th generation is in the form of project at National Institute of Material Science in Japan NIMS). The 1st generation super alloys contain a relatively huge amount of chromium in the comparison with other generations. The 2nd and the 3rd generations contain about 3 wt% and 6 wt% of rhenium which is a very expensive addition which leads to an improvement in creep strength and fatigue resistance respectively. The excellent creep behavior at high temperatures (about 1,100°C) is attributed with the recent generation of super alloys.[2], [3]

	Cr	Co	Mo	W	Ta	V	Nb	Al	Ti	Hf	Re
1st Generation											
PWA1480	10	5	0	4	12			5	1.5	0	
Rene N4	9	8	2	6	4		0.5	3.7	4.2	0	
SRR99	8	5	0	10	3			5.5	2.2	0	
RR2000	10	15	3	0	0	1		5.5	4	0	
AM1	8	6	2	6	9			5.2	1.2	0	
AM3	8	6	2	5	4			6	2	0	
CMSX2	8	5	0.6	8	6			5.6	1	0	
CMSX3	8	5	0.6	8	6			5.6	1	0.1	
CMSX6	10	5	3	0	2			4.8	4.7	0.1	
AF56	12	8	2	4	5			3.4	4.2	0	
2nd Generation											
CMSX4	7	9	0.6	6	7			5.6	1	0.1	3
PWA1484	5	10	2	6	9			5.6	0	0.1	3
SC180	5	10	2	5	9			5.2	1	0.1	3
MC2	8	5	2	8	6			5	1.5	0	0
Rene N5	7	8	2	5	7			6.2	0	0.2	3
3rd Generation											
CMSX10	2	3	0.4	5	8			5.7	0.2	0.03	6
Rene N6	4.2	12.5	1.4	6	7.2		0.1	5.75	0	0.15	5.4
TMS75	3	12	2	6	6			6	0	0.1	5
TMS113	2.89	11.93	1.99	5.96	5.96			6.56	0	0.1	5.96
	Cr	Co	Mo	W	Ta	V	Nb	Al	Ti	Hf	Re

Figure 2.3: Single-crystal super alloys, nominal compositions (wt%).
Adapted from Erikson, 1996. [4]

2.2.1.1 Nickel-based super alloys

Nickel-based super alloys can be either Solid Solution Strengthening or precipitating hardening. Solid Solution Strengthened alloys such as Hastelloy are used only in applications which require very modest strength. Most Nickel-based alloy contain 10-20% Cr, up to 8% Al and Ti, 5-10% Co, and small amounts of B, Zr and C.

2.2.1.2 Iron-based super alloys

Iron-based super alloys are characterized by high temperature as well as room temperature strength. Apart from this, it has good resistance to creep, oxidation, corrosion and wear.

2.2.1.3 Cobalt-based super alloys

Cobalt-based super alloys have their origin in the stellite alloys. Cobalt alloys have higher melting points than nickel alloys. Cobalt alloys show superior thermal fatigue resistance and weldability over nickel alloys.

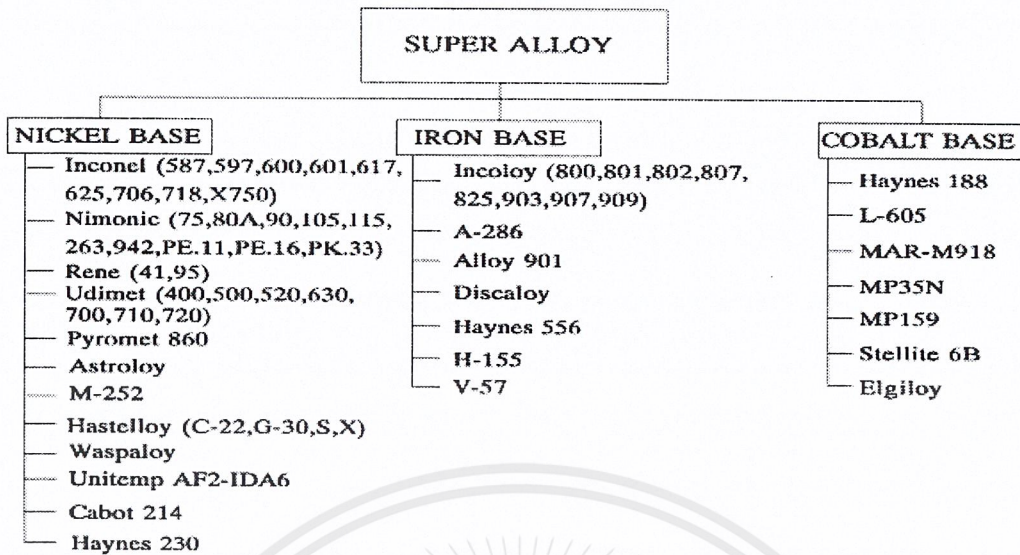


Figure 2.4: Classifications of super alloys [3]

2.3 Cobalt-based alloys [5]

Cobalt-based materials are alloyed with chromium, nickel, and tungsten. Due to the high cost of these alloys, they are used where severe conditions prevail and require high temperature strength and hardness, excellent wear, galling, corrosion, and/or erosion resistance.

Cobalt alloys have good magnetic properties, corrosion resistance, wear resistance, and high temperature strength. Cobalt (Co) alloys have been used since 1907 when Elwood Haynes obtained the first patents on cobalt–chromium compositions.

Historically, many of the commercial cobalt-base alloys are derived from the cobalt–chromium–tungsten (Co-Cr-W) and cobalt–chromium–molybdenum ternaries (Co-Cr-Mo). These properties arise from the crystallographic nature of cobalt, the solid-solution-strengthening effects of Cr, W, and Mo, the formation of metal carbides, and the corrosion resistance imparted by Cr.

Many properties of the alloy originate from the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and molybdenum, the formation of extremely hard carbides and the corrosion resistance imparted by chromium. Due to its excellent resistance to degradation in the oral environment, the first medical use of cobalt-base alloys was in the cast of dental implants. Various in vitro and in vivo tests have shown that the alloys are biocompatible and suitable for use as surgical implants. Today, the use of cobalt alloys for surgical applications is mainly related to orthopedic prostheses for the knee, shoulder and hip as well as to fracture fixation devices. [6]

2.4 Stainless steel [7]

Stainless steel is a generic term for alloy steels containing at least 11 wt% of chromium. At this level chromium can form a coherent, adherent and regenerating layer of chromium oxide (Cr_2O_3) on the steel surface when exposed to oxygen. The Cr_2O_3 film is protective to air and water, protecting the steel from corrosion. Stainless steels can be divided into 5 groups where each group involves various grades with defined standard composition ranges. The 5 groups of stainless steels are ferritic, austenitic, duplex, martensitic and precipitating hardening(PH) stainless steels characterizing with their crystallographic microstructure. Table 2.1 gives a summary of the nominal composition range of five groups with their characteristics.

Stainless Steels	C (Wt%)	Cr (Wt%)	Ni (Wt%)	Mo (Wt%)	Other (Wt%)
Martensitic	0.03-2.20	10.5-18.0	0-7.0	0-4.0	Mn, Si, V, N, Cu
Ferritic	<0.25	10.5-30.0	0-4.5	0-4.5	Mn, Si, N, Ti/Nb, Al
Duplex	<0.05	18.0-30.0	1.0-8.0	1.0-5.0	Mn, Si, N, Cu, W
Austenitic	<0.08	16.0-30.0	8.0-35.0	0-7.0	N, Nb, Ti, Cu
Precipitation Hardening	<0.20	10.0-17.0	4.3-26.0	0-5.0	Mn, Si, Al, Ti, Nb, V, Cu, W

Table 2.1: Composition range of 5 different stainless steel group

Chromium and nickel, the most important alloying elements in stainless steels, are powerful ferrite and austenite stabilizers respectively. So they are considered as the references to categorize the effect of other alloying elements; those promoting ferrite are classified under chromium as ferrite stabilizers and the austenite stabilizer elements are classified under nickel.

2.5 Austenitic stainless steel[8]

Austenitic stainless steels contain 16-28 wt% chromium and sufficient amount of austenite stabilizer elements such as nickel, manganese and carbon in order to maintain austenitic microstructure at room temperature. Nickel is the basic substitution element used to stabilize austenite, so the austenitic stainless steels are usually considered as Fe-Cr-Ni ternary alloys. Figure 2.5 shows an isothermal section of the ternary Fe-Cr-Ni equilibrium diagram at 750 °C. The positions of 2 well-known austenitic grades, 18Cr-12Ni and 20Cr-25Ni, are marked in the diagram.

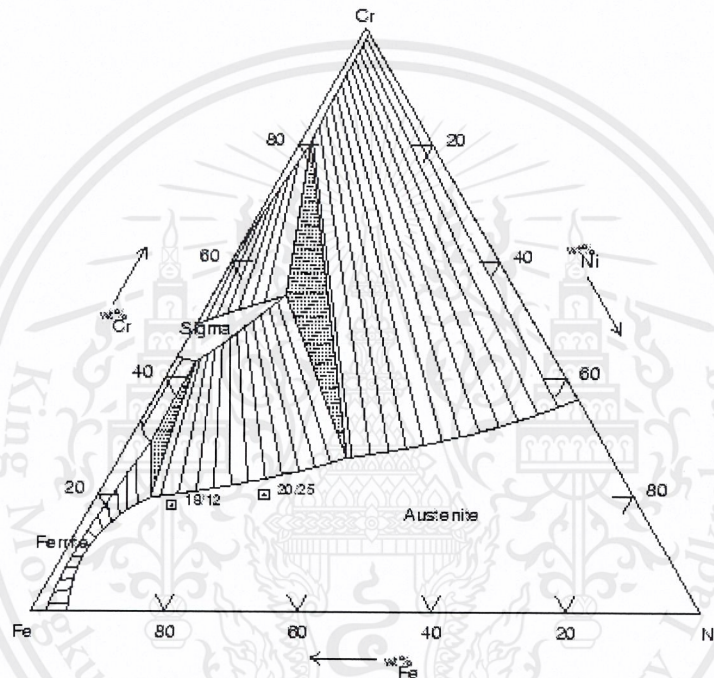


Figure 2.5: Isothermal section of Fe-Cr-Ni diagram at 750°C[8].

Other alloying elements either interstitial like C and N, or substitution such as Mn, Mo, Si, Ti, Nb, W, V, Cu, Al, etc. may also be added to give the desired properties. The effect of important alloying elements will be discussed later.

Austenitic stainless steels have many advantages from a metallurgical point of view.

- Their austenitic (FCC, face-centered cubic) structure is very tough and ductile down to absolute zero.
- Austenitic stainless steel also do not lose their strength at elevated temperatures as rapidly as ferritic (BCC, body-centered cubic) iron-based alloys.

- Austenitic stainless steel can be made soft enough (i.e., with a yield strength about 200 MPa) to be easily formed by the same tools that work with carbon steel, but they can also be made incredibly strong by cold-work, up to yield strengths of over 2000 MPa.

Austenitic stainless steels have many disadvantages from a metallurgical point of view.

- Austenitic stainless steels are less resistant to cyclic oxidation than ferritic grades because of their greater thermal expansion coefficients which tend to cause the spallation of protective oxide coating.
- The fatigue endurance limit is only about 30% of the tensile strength. This, combined with their high thermal expansion coefficients, makes them especially susceptible to thermal fatigue.

2.6 Effect of alloying elements in austenitic stainless steel[9]

2.6.1 Chromium:

Chromium is the most important alloying element in stainless steels because the stainless character occurs when chromium is over a minimum level (~11 wt%). The higher chromium content leads to the denser and stronger oxide passive film. However, too much chromium (e.g. over 25%) may promote formation of intermetallic sigma phase and cause embrittlement. Chromium is a strong ferrite stabilizer, so a combination of austenite stabilizer elements (Ni, Mn, N, C, etc.) is always required to maintain the austenitic microstructure. In creep resistant alloys chromium takes part in the precipitation of different second phases as both main constituent element (e.g. in $M_{23}C_6$ and sigma phase) and substituent one (e.g. in G phase)[9].

2.6.2 Nickel:

Nickel is an austenite stabilizer and increases the toughness, ductility, weld ability and general corrosion resistance of stainless steels, especially against pitting corrosion. Nickel usually dissolves in carbides as partial substitution of chromium; whereas it is a major constituent in some other types of precipitates, like G phase.

2.6.3 Carbon:

Carbon atoms occupy the interstitial sites within the FCC structure of austenitic stainless steels providing a solid solution strengthening effect. On a percentage basis carbon is the strongest austenite stabilizer element but its use is limited due to low solubility in austenite and also sensitization.

2.6.4 Manganese:

Manganese is an austenite former and used as a replacement of nickel; however, the alloy exhibits less corrosion resistance. It increases the nitrogen solubility in austenite without forming nitrides and also contributes with nitrogen strengthening effect[10]. Manganese addition has some disadvantages i.e. its weakening effect on the passive film and also increasing the risk of pitting corrosion at manganese sulfide inclusion sites.

2.6.5 Silicon:

Silicon, which is a ferrite stabilizer, improves the oxidation resistance of the stainless steel by forming a dense silicon oxide sub-layer on the surface. It is an effective element where sulfuric and nitric acids are presented in the environment.

2.6.6 Molybdenum:

Molybdenum is a strong ferrite former. It enhances the general corrosion resistance of stainless steels, especially against pitting corrosion. Molybdenum improves creep strength by solid solution hardening and facilitating carbide precipitation[8].

2.7 Kinetics of Oxidation[11]

The kinetics of oxidation process must be considered along with the thermodynamics when assessing the suitability of a material for high temperature use. The rate of oxidation of alloy can be described by 3 kinetic equations as linear, parabolic and logarithmic, as shown in Figure 2.6.

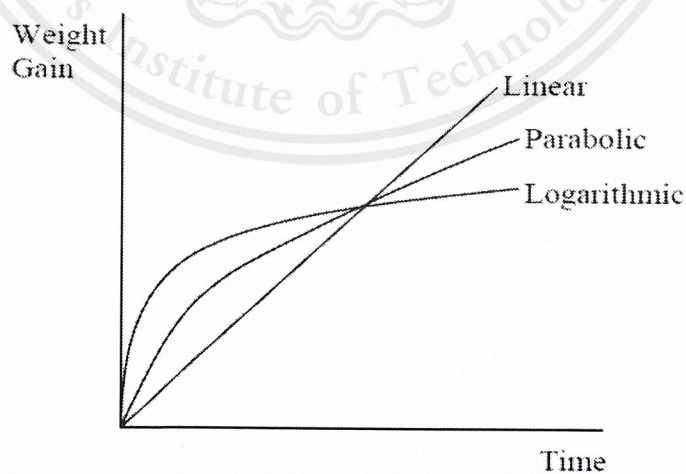


Figure 2.6: Common kinetic models for the rate of growth of oxide layer.

Reaction rates and corresponding rate equations for the oxidation of metals are function of a number of factors such as temperature, oxygen partial pressure, oxidation time, surface preparation, and pretreatment of the metal.

2.7.1 Linear rate equation

The rate of linear oxidation is constant with time following Equation 2.2,

$$W = k_t \cdot t \quad (2.2)$$

Where W is weight gain per specimen surface area (mg/mm^2), t is time (h), and k_t is the linear rate constant ($\text{mg}\cdot\text{mm}^{-2}\cdot\text{h}^{-1}$). Linear oxidation is characteristic of metals for which a porous or cracked scale is formed so that the scale does not represent a diffusion barrier between the two reactants.

2.7.2 Parabolic rate equation

Parabolic rate law is given in Equation 2.3,

$$W^2 = k_p \cdot t \quad (2.3)$$

The square of weight gain per specimen surface area W^2 (mg/mm^2)², is proportional to time t (h), and k_p is the parabolic rate constant ($\text{mg}\cdot\text{mm}^{-2}\cdot\text{h}^{1/2}$)². During oxidation growth, the rate of oxidation is limited by solid-state diffusional transport of the reactants or electrons through the scale, and as the scale grows in thickness the distance for diffusion increases, such that the reaction rate decreases with time.

2.7.3 Logarithmic rate equation

When metals are oxidized under certain conditions, typically at low temperatures of up to about 400°C. It is initially quite rapid and then drops off to low or negligible rate. Such behavior has been described by logarithmic functions such as in Equation 2.4 and Equation 2.5.

$$x = k_1 \log(t + t_0) + A \quad (\text{Direct logarithm}) \quad (2.4)$$

$$\frac{1}{x} = B - k_{il} \log t \quad (\text{Inverse logarithm}) \quad (2.5)$$

Where A and B are constants, k_1 and k_{il} are the rate constants, t is the oxidation time and X is the thickness of the scale or weight gain per surface unit area, etc.

In some cases it may be found that the oxidation is initially parabolic and then the reaction becomes linear. This situation may happen if the metal surface is not protected by a layer of scale, in which case one of the steps in the oxidation process, rather than the rate of solid state diffusion, will control the rate of oxidation. This situation may also occur if a protective scale spalls off or cracks, if a porous scale develops. This combination between parabolic and linear oxidation is called para linear oxidation.

2.8 Characterisation and techniques

2.8.1 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture) and crystalline structure.

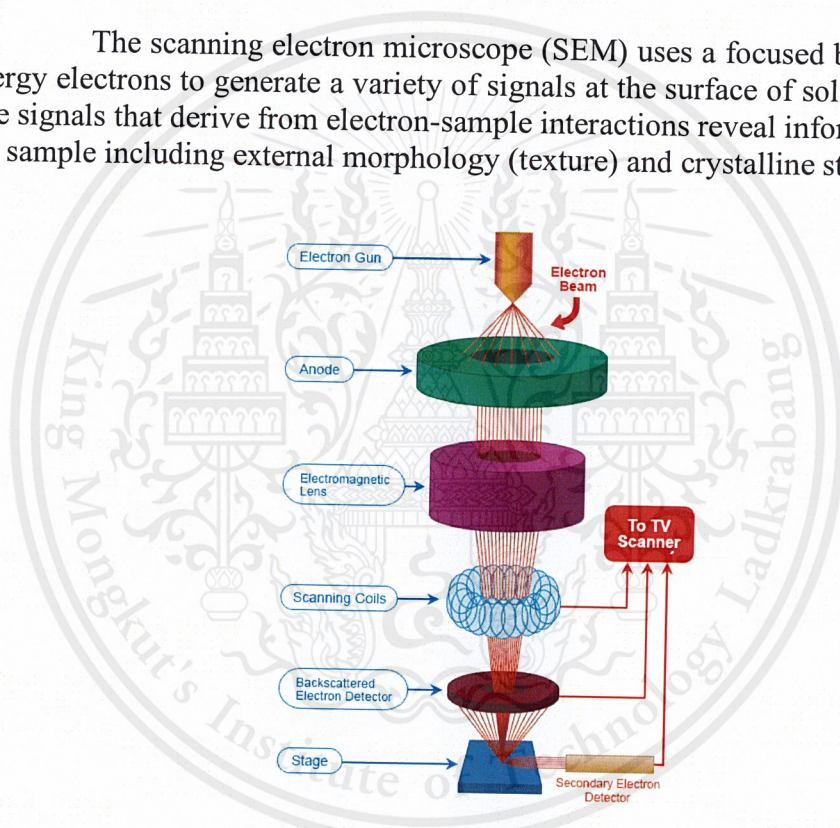


Figure 2.7: Schematic of main components of SEM.

In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays variations. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS) and crystalline structure.

2.8.2 Energy dispersive x-ray spectroscopy (EDS)

EDS is an additional tool installed beside SEM. The objective of EDS is to analyse the chemical composition of the materials. The emitted X-ray photon enters to the detector where the results are interpreted in terms of the spectrum. EDS can be used to determine chemical elements presented in the sample.

2.9 Literature Review

Abdolvahid et al[12] studied oxidation behaviors of 3 types of stainless steels, namely AISI 321, AISI 316 and AISI 409. They found that oxide layers were formed on all stainless steel surfaces, and their masses and thicknesses increased with oxidation time. Among them, AISI 409 ferritic stainless steel revealed higher oxidation rate more than AISI 321 and AISI 316 austenitic stainless steel. The presence of cracks was evident in oxide layers of austenitic stainless steels, which can be related to their low thermal shock resistivity. On contrary, due to the lower coefficient of thermal expansion in ferritic stainless steel no significant crack was observed.

Nezakat et al[13] studied about the oxidation of stainless steel 316L and 310S in air environment. They found that difference in their chemical components was believed to be responsible for their different oxidation resistances. The major difference in the chemical composition of the alloys is in the nickel and chromium contents.



Figure 2.8: Oxide surface appearance of the samples after 100, 300, and 1000 h of oxidation; right: SEM micrograph at spallation border for the sample after 1000 h of oxidation[13]

The main cause of oxide spallation is due to the stresses induced by a temperature drop. This drop in temperature can be due to fast cooling of the alloy after oxidation or thermal cycling of the alloy in service. Since no thermal cycling was involved in the experiment, the former cause led to the spallation of the oxide scale.

Li Ning[14] studied the oxidation behavior of AISI 430 alloy in air that was the simulation of the interconnector working environment in the planar solid oxide fuel cells (SOFCs). He described the oxidation steps in air which consist of 3 steps.

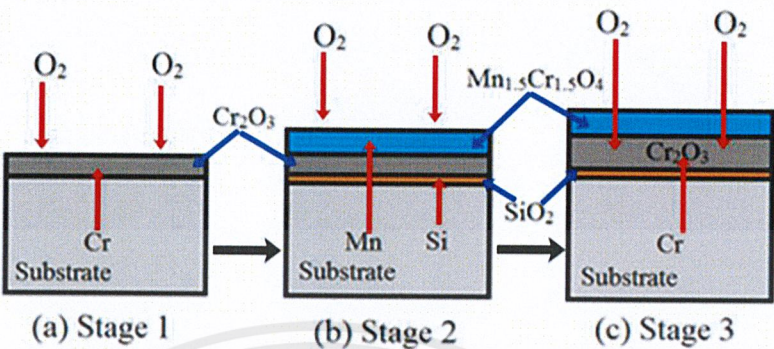


Figure 2.9: Schematic of oxidation stage of AISI 430 Alloy in air.

The oxidation was followed by 3 steps. At the step 1, the oxidation is mainly controlled by the diffusion of Cr^{3+} because of selective oxidation, and a thin protective Cr_2O_3 oxide layer is formed rapidly. After that at step 2, the oxidation is mainly controlled by the diffusion of Mn^{3+} which results in the formation of an outer spinel layer ($\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$), this occurs as the Mn^{3+} diffuses faster than Cr^{3+} . After that at step 3, the percentage composition of Mn and Si in the alloy are small, the oxidation is controlled by the diffusion of Cr^{3+} again. At this step, the oxygen transports through the spinel layer to the chromia layer and the Cr ions diffuse to the chromia layer; both of them react with each other, which make the Cr_2O_3 layer thicker.

Buscail et al.[15]oxidized cobalt-based phynox alloy in the temperature range of 800-1,000°C. The kinetic behavior follow the parabolic laws under isothermal conditions.

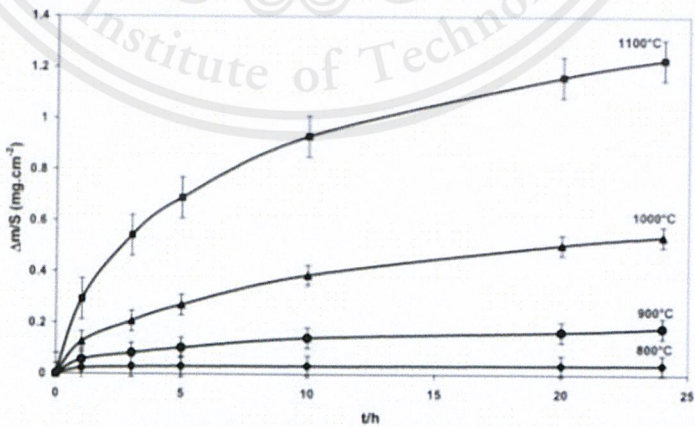


Figure 2.10: Mass gain curves obtained during isothermal oxidation of cobalt-based Phynox between 800 and 1,100°C in air.

From Figure 2.11 [15] they found that after 24 h oxidation at 900°C, the scale present on the surface is mainly composed of two spinel phase CoCr_2O_4 and $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$. Cr_2O_3 oxide is also detected on the surface. After 13 thermal cycles at 1,100°C, the scale is composed of CoCr_2O_4 and CoMoO_4 . Cr_2O_3 is also detected on the surface.

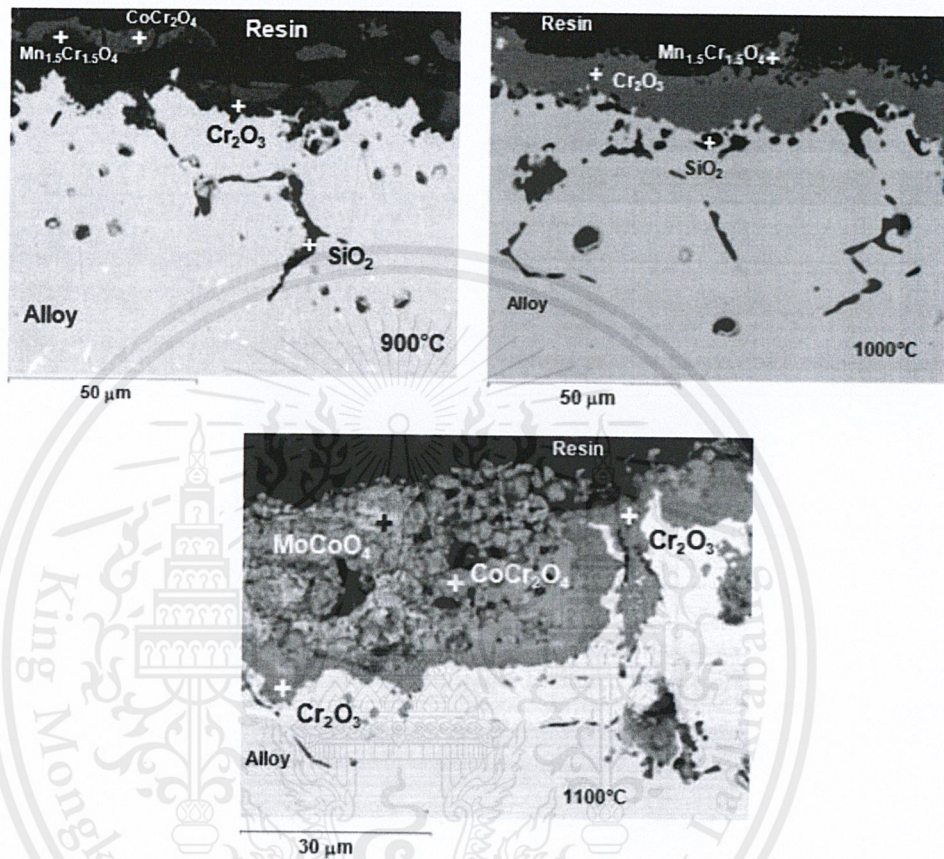


Figure 2.11: SEM cross section shown morphologies on the cobalt-based alloy (phynox) after 24 h oxidation in air at 900°C and 1,000°C. After 13 thermal cycles at 1,100°C[15].

CHAPTER III RESEARCH METHODOLOGY

3.1 Experimental setup

The experimental setup is shown in Figure 3.1. Oxygen gas flowed passing the regulator valve and flow meter. Quartz column installed inside the furnace. The sample was hung inside the column while dry-oxygen gas flowed through the sample. At the outlet of column, gas flowed through the condenser for condensed gaseous compounds into 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. Before and after the experiments, samples were weighed and weight gain of each sample was calculated in order to find oxidation kinetics and analyze surface morphologies by SEM analysis.

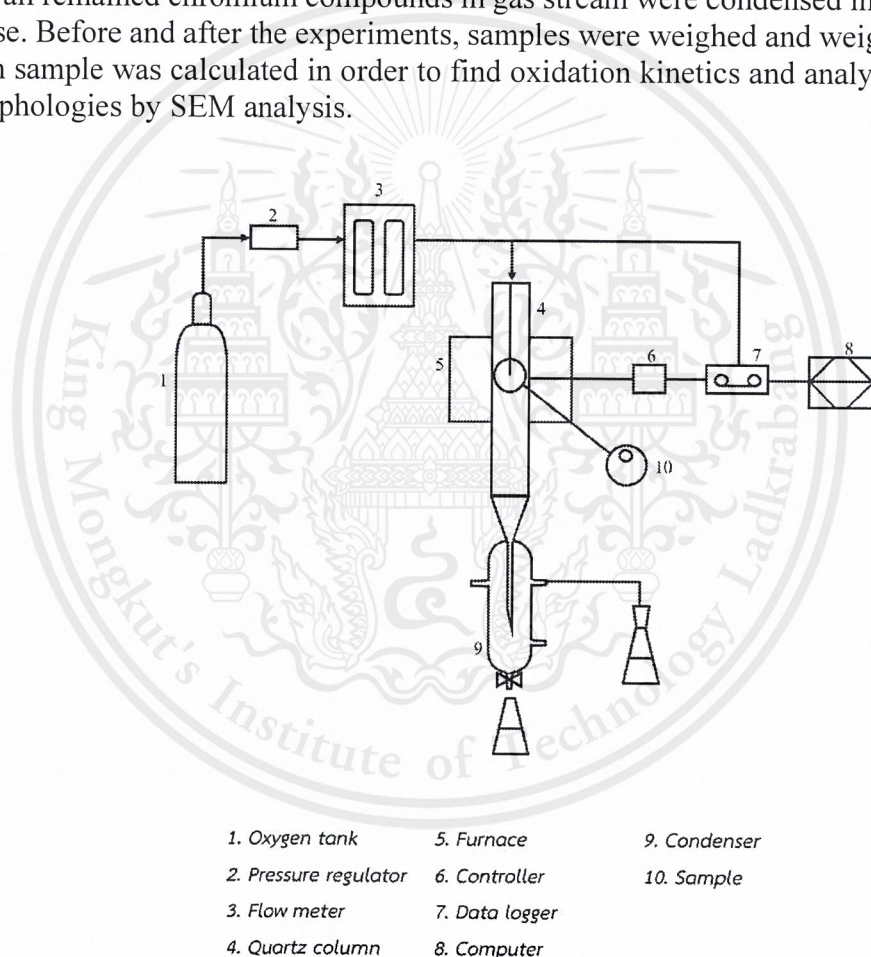


Figure 3.1: Experimental setup

3.2 Preparing samples

The studied specimens were CoCrMo alloy and AISI 316 stainless steel. Their chemical compositions are listed in Table 3.1 and Table 3.2, respectively. Before the experiments, every sample are weighted and cleaned with ethanol in ultrasonic bath for 15 minutes.

Table 3.1 Compositions of CoCrMo.

Element	Cr	Mo	C	Si	Mn	Co
Wt. %	26.7	5.90	0.04	0.61	0.45	Bal.

Table 3.2 Compositions of AISI 316 stainless steel. (Given by supplier)

Element	Cr	Mo	C	Si	Mn	Ni	Cu	Fe
Wt. %	17.94	2.84	0.05	0.61	1.84	11.05	0.26	Bal.

3.3 Experimental conditions

The time of oxidation was varied in the range of 0-48 h at constant operating temperature 1,000°C with oxygen gas linear velocity of 3.0 cm/s.

3.4 Characterisation of materials

After experiment, every sample were taken from quartz column to measure weight gain. After that, the morphologies and chemical compositions on the surface were analyzed by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

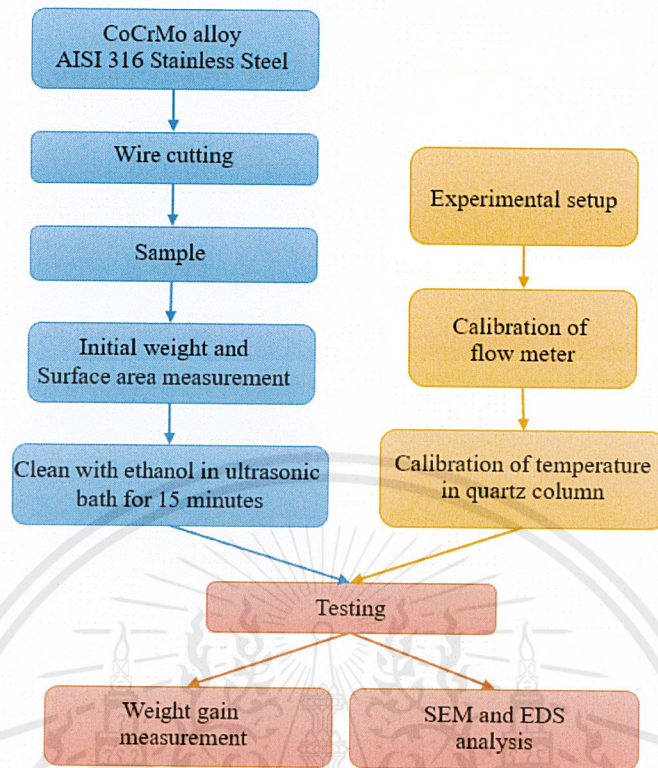


Figure 3.2: Procedures of experimental work

Figure 3.2 shows the procedures of experimental work. CoCrMo alloy and AISI 316 stainless steel were designed to cut by wire cutting machine. After that, every sample was weighted and measured surface area and then cleaned with ethanol in ultrasonic bath for 15 min. In experimental setup, flow meter was calibrated and the volumetric flow rate of oxygen gas was converted to gas linear velocity. Also, the temperature in quartz column is calibrated in order to control the temperature at the position of the samples. When preparation and experimental set up were completed, experimental could start with each set of oxidation times. After the experiments, every sample was measured weight gain and analyzed by SEM and EDS.

CHAPTER IV RESULTS AND DISCUSSION

4.1 Kinetics of Oxidation

4.1.1 AISI 316 Stainless Steel

The oxidation of AISI 316 stainless steel was determined in the oxidation time range of 0-96 h and linear velocity and temperature were constant at 3.0 cm/s and 1,000°C, respectively. Figure 4.1 shows the oxidation results of experiment. We can observe that the weight gain increases slowly at initial oxidation period and increase rapidly when the oxidation time was increased.

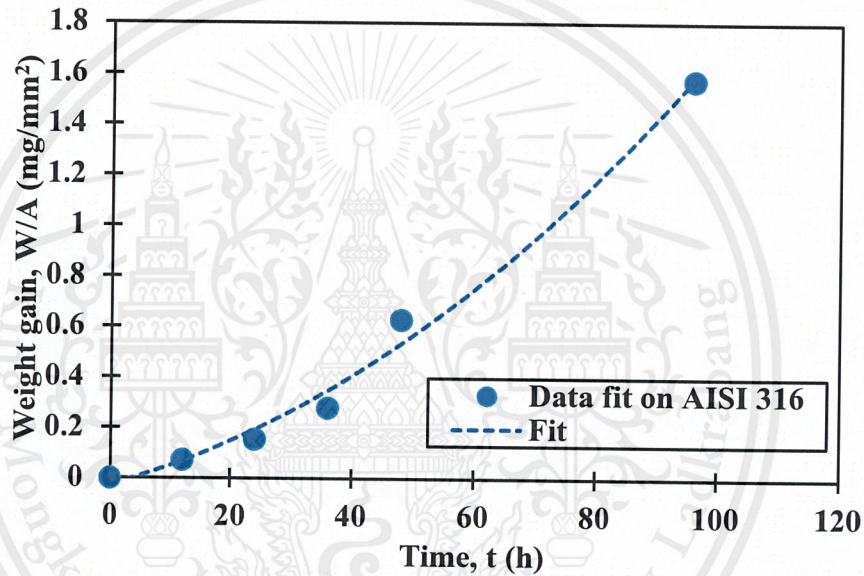


Figure 4.1: Oxidation curve of AISI 316 stainless steel oxidized with linear velocity oxygen gas of 3.0 cm/s at 1,000°C.

In order to find the oxidation rate equation, it can be described by Equation 4.1.

$$m^n = k \cdot t \quad (4.1)$$

where

m = weight gain per surface unit
 k = oxidation rate constant
 t = oxidation time
 n = order of oxidation equation

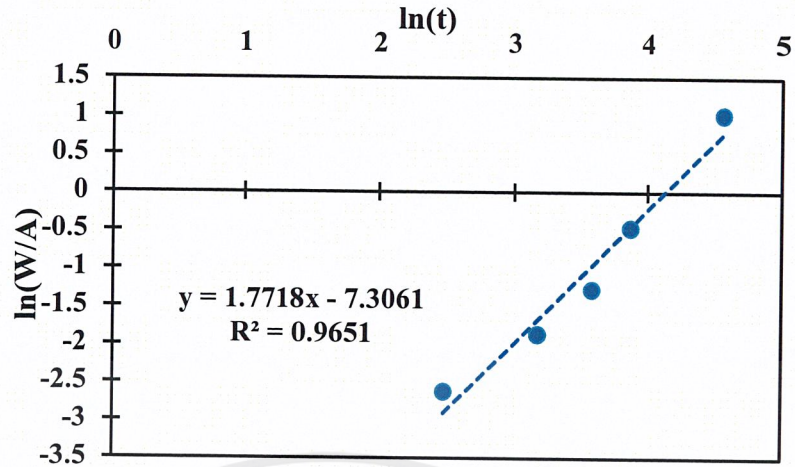


Figure 4.2: Double logarithm plot oxidation curve of AISI 316 stainless steel oxidized with linear velocity oxygen gas of 3.0 cm/s at 1,000°C.

The best fit is at $n = 0.5644$ and $k = 1.6187 \times 10^{-2} (\text{mg} \cdot \text{mm}^{-2} \cdot \text{h}^{-1})^{0.5644}$.

4.1.2 CoCrMo Alloy

The oxidation of CoCrMo alloy was determined in the oxidation time range of 0-36 h and linear velocity and temperature were constant at 3.0 cm/s and 1,000°C, respectively. Figure 4.2 shows the oxidation results of experiment. We can observe that the weight gain increases rapidly at initial and slowly when the increase oxidation time. The weight gains are shown in Figure 4.3 as expected for Equation 2.3 in Chapter 2, which describe the parabolic rate law.

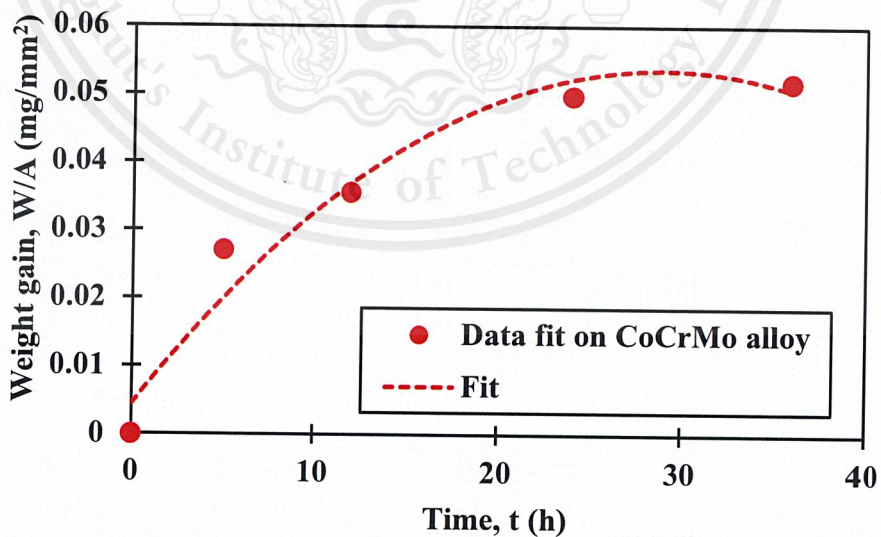


Figure 4.3: Oxidation curve of CoCrMo alloy oxidized with linear velocity oxygen gas of 3.0 cm/s at 1,000°C.

In order to find the oxidation rate equation, it can be described by Equation 4.1.

$$m^n = k \cdot t \quad (4.1)$$

where

m	= weight gain per surface unit
k	= oxidation rate constant
t	= oxidation time
n	= order of oxidation equation

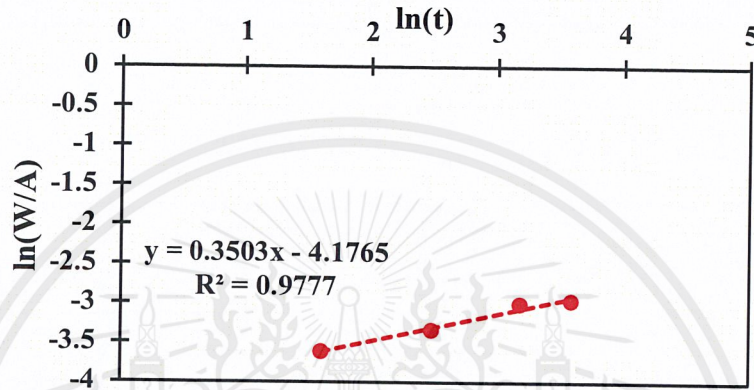


Figure 4.4: Double logarithm plot oxidation curve of CoCrMo alloy oxidized with linear velocity oxygen gas of 3.0 cm/s at 1,000°C.

The best fit is at $n = 2.8546$ and $k = 6.6384 \times 10^{-6} (\text{mg} \cdot \text{mm}^{-2} \cdot \text{h}^{-1})^{2.8546}$.

Thus, the oxidation rate equation of AISI 316 Stainless Steel is;

$$m^{0.5644} = 1.6187 \times 10^{-2} \cdot t \quad (4.2)$$

Thus, the oxidation rate equation of CoCrMo alloy is;

$$m^{2.8546} = 6.6384 \times 10^{-6} \cdot t \quad (4.3)$$

From the results, CoCrMo alloy shows higher oxidation than AISI 316 stainless steel for the oxygen gas at temperature of 1,000°C.

The weight change is directly related with the corrosion, the more weight changes, the greater corrosion will be. Hence experimental work indicated that the CoCrMo alloy has better corrosion resistance than AISI 316 austenitic stainless steel in oxygen gas environment. One must kept in mind that this experiment was performed only for short heating time at 1,000°C.

From figure 4.1 and 4.3 one can easily predict that the oxide grows on CoCrMo specimens follow the parabolic rate law whereas the oxide layer grows on AISI 316 stainless steel can be seen as parabolic at the initial stage. When the scale thickness reaches to critical thickness, the scale has high cracking rate and become non-protective. This process is called “breakaway oxidation”.

4.2 Observations of surface by SEM and EDS

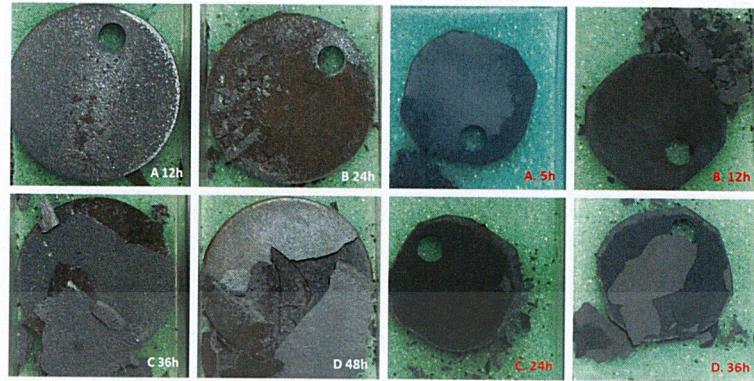


Figure 4.5: Samples after oxidation from experiments with linear velocity oxygen gas of 3 cm/s at 1,000°C for the duration times range of 0-48 h. (left: AISI 316 stainless steel; right: CoCrMo alloy).

From Figure 4.5, it can be seen that every sample were spalled due to stress in the scale-alloy system results from differential thermal contraction of metal and oxide on cooling. The result of scale spallation is that oxidizing gas is able to easily access to depleted alloy surface, which may not be able to reform the protective oxide.

Figures 4.6 - 4.8 show SEM and EDS results of AISI 316 stainless steel after oxidation for 12, 24 and 36 h, respectively. We can observe the grain on surface and the size of grain was when the oxidation time increased. Furthermore, EDS result of 3 samples shows iron, chromium, manganese, nickel and oxygen were detected on the surface of oxide scales. It can be predicted that the scale is mainly composed of 4 phases Fe_3O_4 , FeCr_2O_4 , $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$ and Cr_2O_3 .

Figures 4.9 – 4.11 show SEM and EDS results of CoCrMo alloy after oxidation for 12, 24 and 36 h, respectively. We can observe the grain scale egg-shape in the surface of CoCrMo oxidized for 12 h more obviously than other samples. Furthermore, EDS result of 3 samples shows cobalt, chromium, molybdenum and oxygen were detected on the surface of oxide scales. It can be predicted that the scale is mainly composed of 2 spinel phases (CoCr_2O_4 and $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$) and Cr_2O_3 .

Comparison of SEM and EDS results between AISI 316 stainless steel and CoCrMo alloy after oxidation in 3.0 cm/s of oxygen gas stream at 1,000°C for 12, 24 and 36 h, it can be observed that grain scale on CoCrMo alloy looked like a sphere and in different oxidation time it was hard to distinguish the growth of grain scale. Grain scale of AISI 316 stainless steel was quite larger when oxidation time increased. Considering 12 h and 36 h of oxidation time, we observed that in 36 h of oxidation time have a sharp of scale more than 12 h.

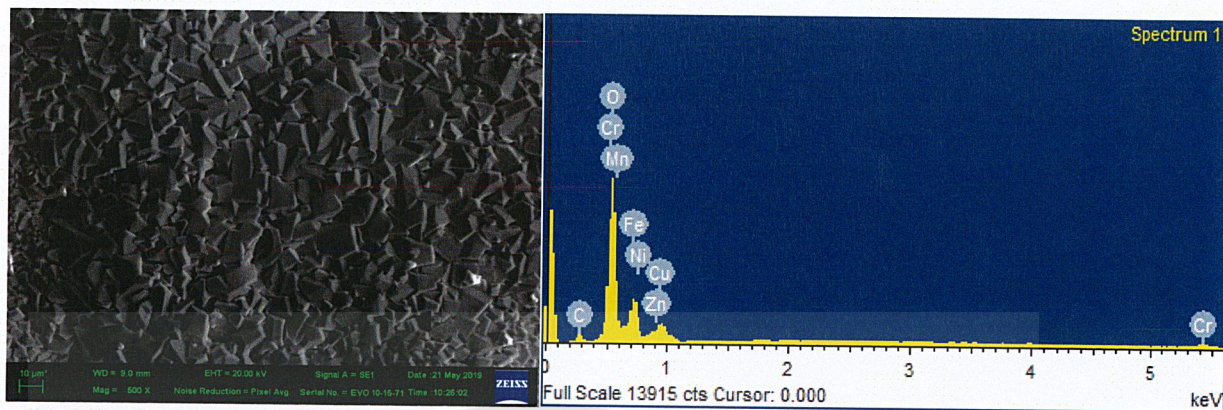


Figure 4.6: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s of oxygen gas at 1,000°C for 12 h.

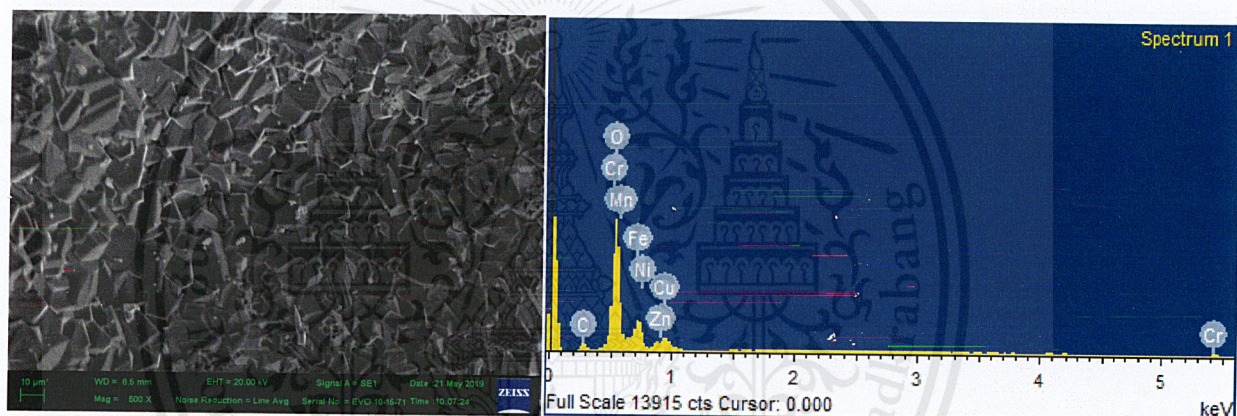


Figure 4.7: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s of oxygen gas at 1,000°C for 24 h.

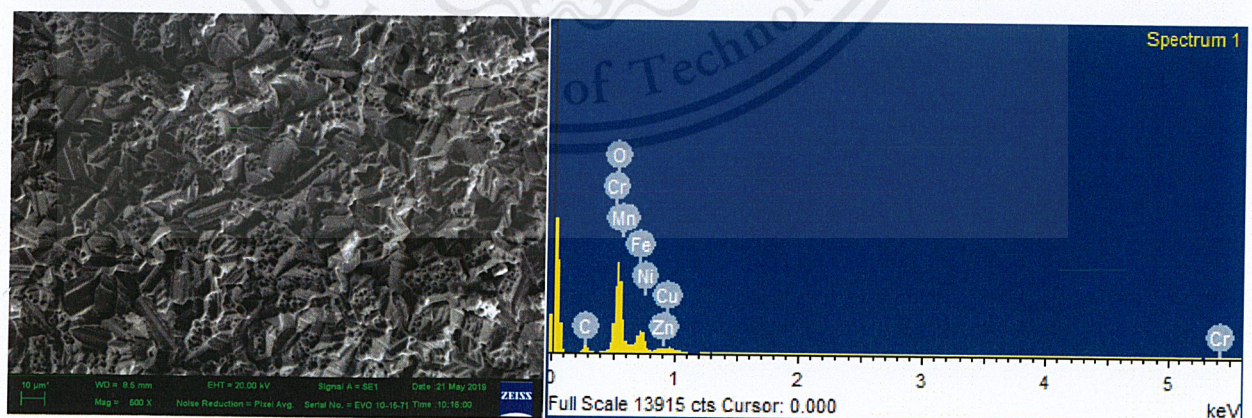


Figure 4.8: SEM and EDS results of AISI 316 stainless steel after tested in 3.0 cm/s of oxygen gas at 1,000°C for 36 h.

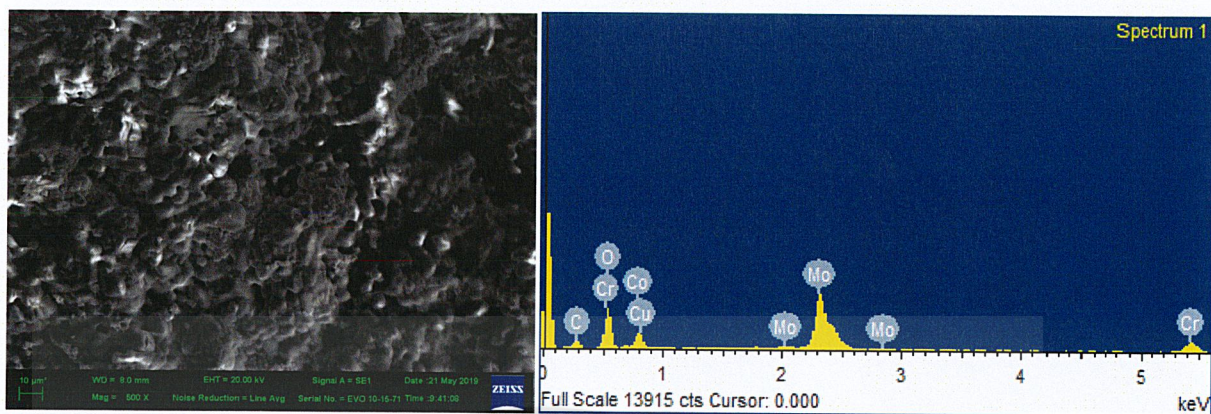


Figure 4.9: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s of oxygen gas at 1,000°C for 12 h.

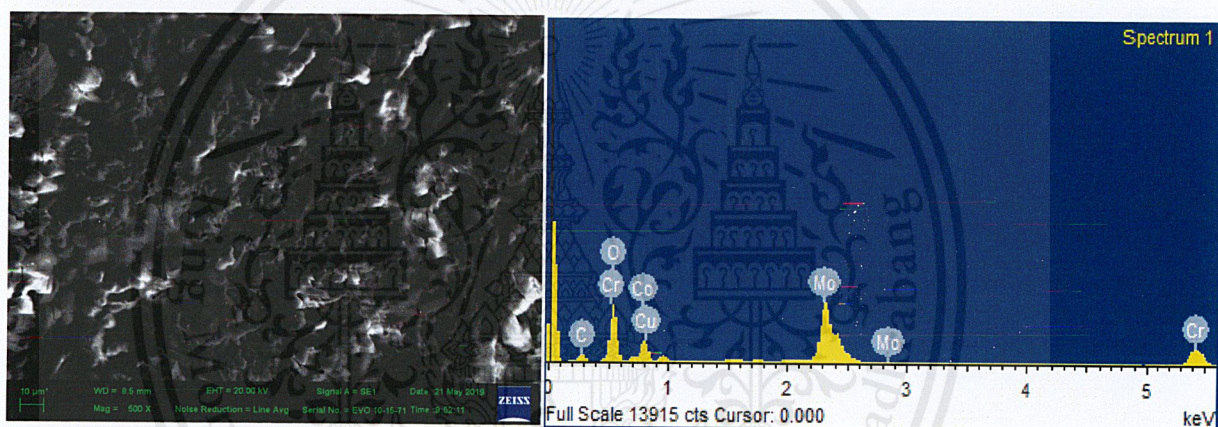


Figure 4.10: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s of oxygen gas at 1,000°C for 24 h.

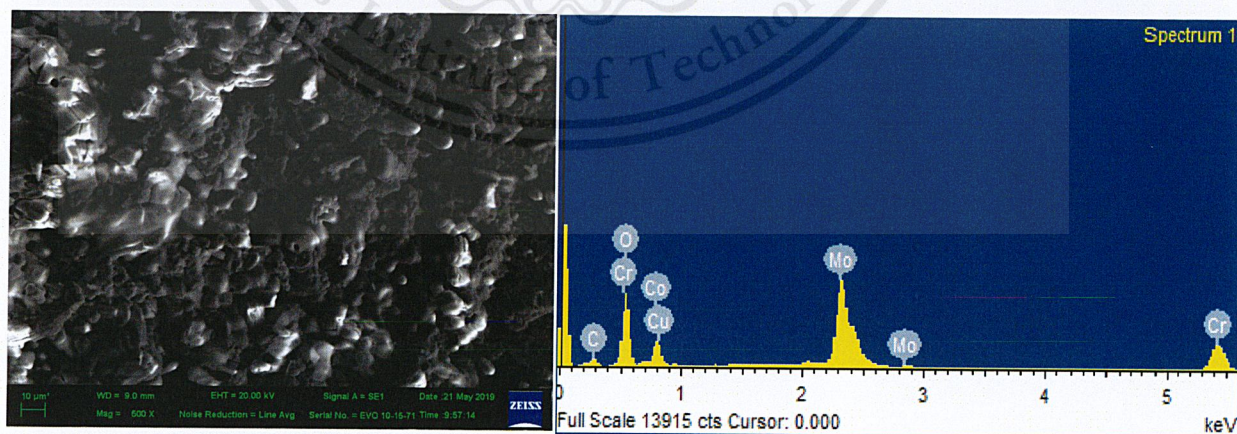


Figure 4.11: SEM and EDS results of CoCrMo alloy after tested in 3.0 cm/s of oxygen gas at 1,000°C for 36 h.

CHAPTER V CONCLUSION

The thesis studied the oxidation of AISI 316 stainless steel and CoCrMo alloy. The experiments were achieved in 3.0 cm/s of oxygen gas linear velocity at 1,000°C for 0-48 h. From all results, we can summarize as follows.

1. CoCrMo alloy showed better oxidation resistance which was comparable to that of AISI 316 stainless steel in oxygen gas environment because weight change is directly related with the corrosion, the more weight changes, the greater corrosion will be.
2. Grain size on surface of both AISI 316 stainless steel and CoCrMo alloy are larger when oxidation time increase.
3. SEM results showed different grain shape between CoCrMo alloy and AISI 316 stainless steel. Chemical composition would be detected on the scale on the surface. For CoCrMo alloy, EDS results showed chemical compositions consist of cobalt, chromium, molybdenum and oxygen. For AISI 316 stainless steel, EDS results showed chemical compositions consist of iron, chromium, manganese, nickel and oxygen.

5.1 Suggestions

The suggestions for further study of AISI 316 stainless steel and CoCrMo alloy are as follows.

1. Chromium and cobalt evaporation of all samples should be demonstrated.
2. FE-SEM analyses of cross section microstructure of samples to observe oxide growth layer.
3. The influences of gas stream flow rate and operating temperature should be investigated.

References

- [1] and J. F. P. Sarrazin, A. Galerie, *Mechanism of high temperature corrosion : A kinetic approach*. Trans Tech Publ., Stafa - Zuerich, 2008.
- [2] D. Klarstrom and P. Crook, *Cobalt Alloys : Alloying and Thermomechanical Processing* §, no. February 2016. Elsevier Ltd., 2017.
- [3] I. A. Choudhury, "Machinability of nickel-base super alloys : a general review," vol. 77, pp. 278–284, 1998.
- [4] "CM-186-LC-ALLOY-SINGLE-CRYSTAL-TURBINE-VANES-ASME-Tubo-Expo-1998.pdf." .
- [5] M. Knezevic, J. S. Carpenter, M. L. Lovato, and R. J. McCabe, "ScienceDirect Deformation behavior of the cobalt-based superalloy Haynes 25 : Experimental characterization and crystal plasticity modeling," *Acta Mater.*, vol. 63, pp. 162–168, 2014.
- [6] Marti A, "Cobalt-base alloys used in bone surgery.," *Injury*.
- [7] M.F. Mcguire, *Stainless Steels For Design Engineers*. 2018.
- [8] T. Sourmail, "Simultaneous Precipitation Reactions In Creep Resistant Austenitic Stainless Steels," 2001.
- [9] I. M. B. D. Peckner, *Handbook Of Stainless Steels*. 1977.
- [10] T. Sourmail, "Precipitation In Creep Resistant Austenitic Stainless Steels," 2001.
- [11] J. P. Schaffer, *The Science And Design Of Engineering Materials*. Boston: Web McGrawHill, 1999.
- [12] A. Movahedi-rad, "Oxidation behavior of AISI 321 , AISI 316 , and AISI 409 stainless steels : Kinetic , thermodynamic , and diffusion studies," 2016.
- [13] M. Nezakat, H. Akhiani, and J. Szpunar, "Oxidation Behavior of Austenitic Stainless Steel 316L and 310S in Air and Supercritical Water," vol. 2, no. April 2016, pp. 1–8, 2017.
- [14] N. Li, "Study the oxidation behavior and residual stresses of AISI 430 alloy in air with water vapor To cite this version : HAL Id : tel-01325234 L ' U NIVERSITE P ARIS -S ACLAY PRÉPARÉE À L ' UNIVERSITE PARIS-SUD Par," 2016.
- [15] H. Buscail, F. Riffard, C. Issartel, and S. Perrier, "Oxidation mechanism of cobalt based alloy at high temperatures (800 – 1100 u C)," vol. 47, no. 6, pp. 404–411, 2012.



Appendix A

Experimental Condition

Appendix A-1: Calibration curve of flow meter

Appendix A-2: Calibration curve of temperature in furnace



Appendix A-1: Calibration curve of flow meter

Table A-1.1: Calibration of flow meter in the flow rat range of 0.2-2 l/min

Settling flow rate at flow meter (l/min)	results			
	Volume (ml)	Time (s)	True flow rate (l/min)	Average true flow rate (l/min)
0.2	10	5.16	0.12	0.12
	10	4.80	0.13	
	10	5.30	0.11	
0.4	10	2.61	0.23	0.22
	10	3.10	0.19	
	10	2.52	0.24	
0.6	10	1.20	0.50	0.43
	10	1.60	0.38	
	10	1.43	0.42	
0.8	10	1.03	0.58	0.71
	20	1.19	0.50	
	20	0.57	1.05	
1.0	20	0.70	0.86	0.71
	20	1.88	0.64	
	20	1.92	0.63	
1.2	20	1.45	0.83	0.81
	20	1.70	0.71	
	20	1.36	0.88	
1.4	20	1.41	0.85	0.92
	20	1.26	0.95	
	20	1.25	0.96	
1.6	20	1.07	1.12	1.09
	20	1.21	0.99	
	20	1.04	1.15	
1.8	30	1.45	1.24	1.32
	20	0.92	1.30	
	30	1.27	1.42	
2.0	30	1.36	1.32	1.50
	30	1.17	1.54	
	30	1.10	1.64	

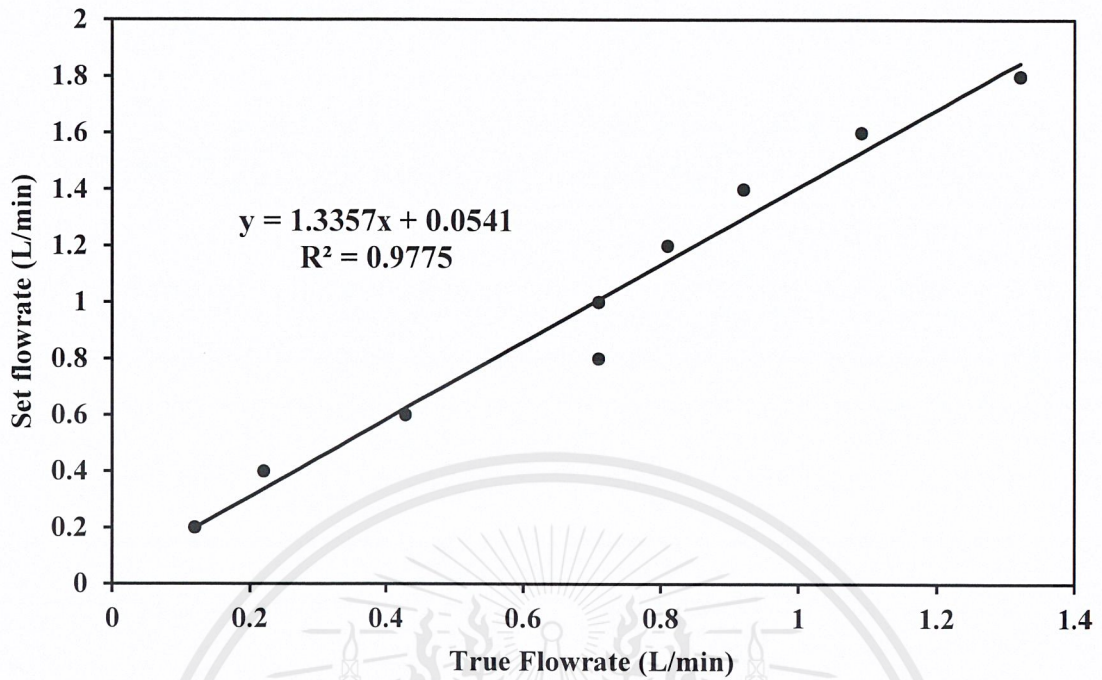


Figure A-1.1: Calibration curve of flow meter in the flow rate range of 0.2-2 l/min

From Figure A-1.1, the calibration equation in the range of 0.2-2 l/min as follow;

$$F_{\text{flow}} = 1.3357 F_{\text{true}} + 0.0541 \quad (\text{A-1.1})$$

Appendix A-2: Calibration curve of temperature in furnace

Table A-2.1: Calibration of temperature in furnace.

Setting Temperature (°C)	Temperatures from thermocouple (°C)			Average Temperature of Thermocouple (°C)
	1	2	3	
500	617	625	622	621.3
600	725	718	722	721.6
700	820	819	818	819.0
800	935	940	937	937.3
900	1025	1018	1014	1019.0
1000	1103	1102	1098	1101.0

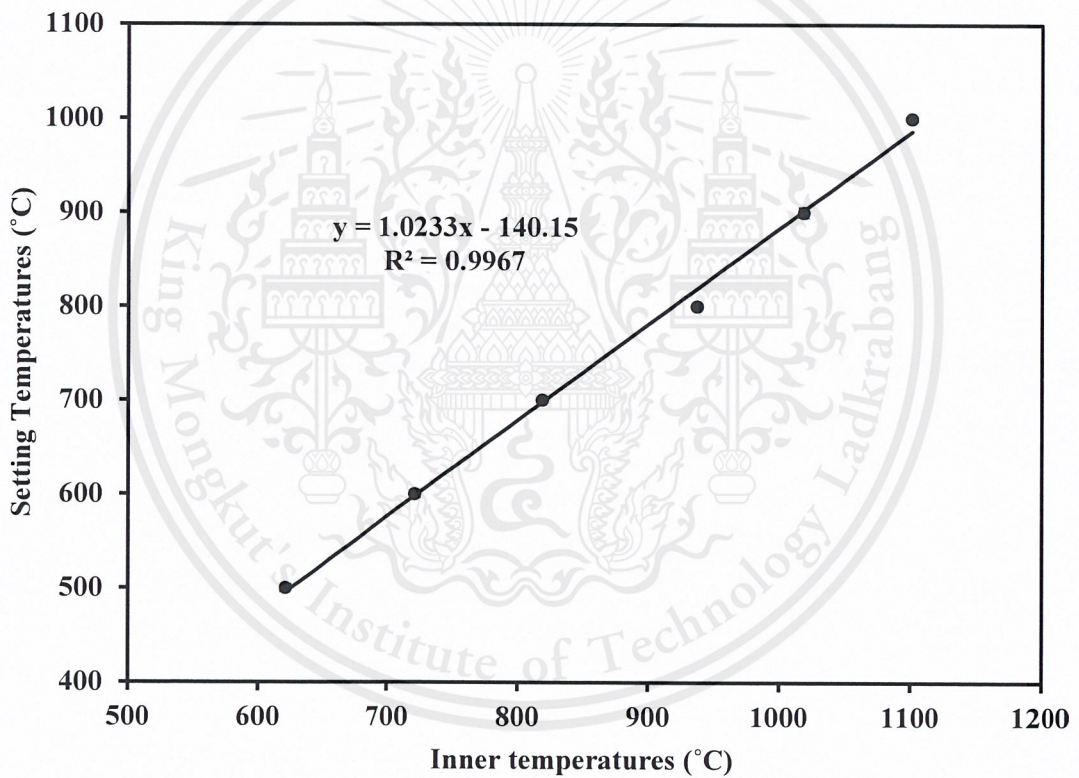


Figure A-2.1: Calibration curve of temperature in furnace

From Figure A-2.1, the calibration equation of temperatures in furnace as follow;

$$T_{\text{setting}} = 1.0233 T_{\text{furnace}} - 140.15 \quad (\text{A-2.1})$$

Appendix B: Experimental Results from Experiments

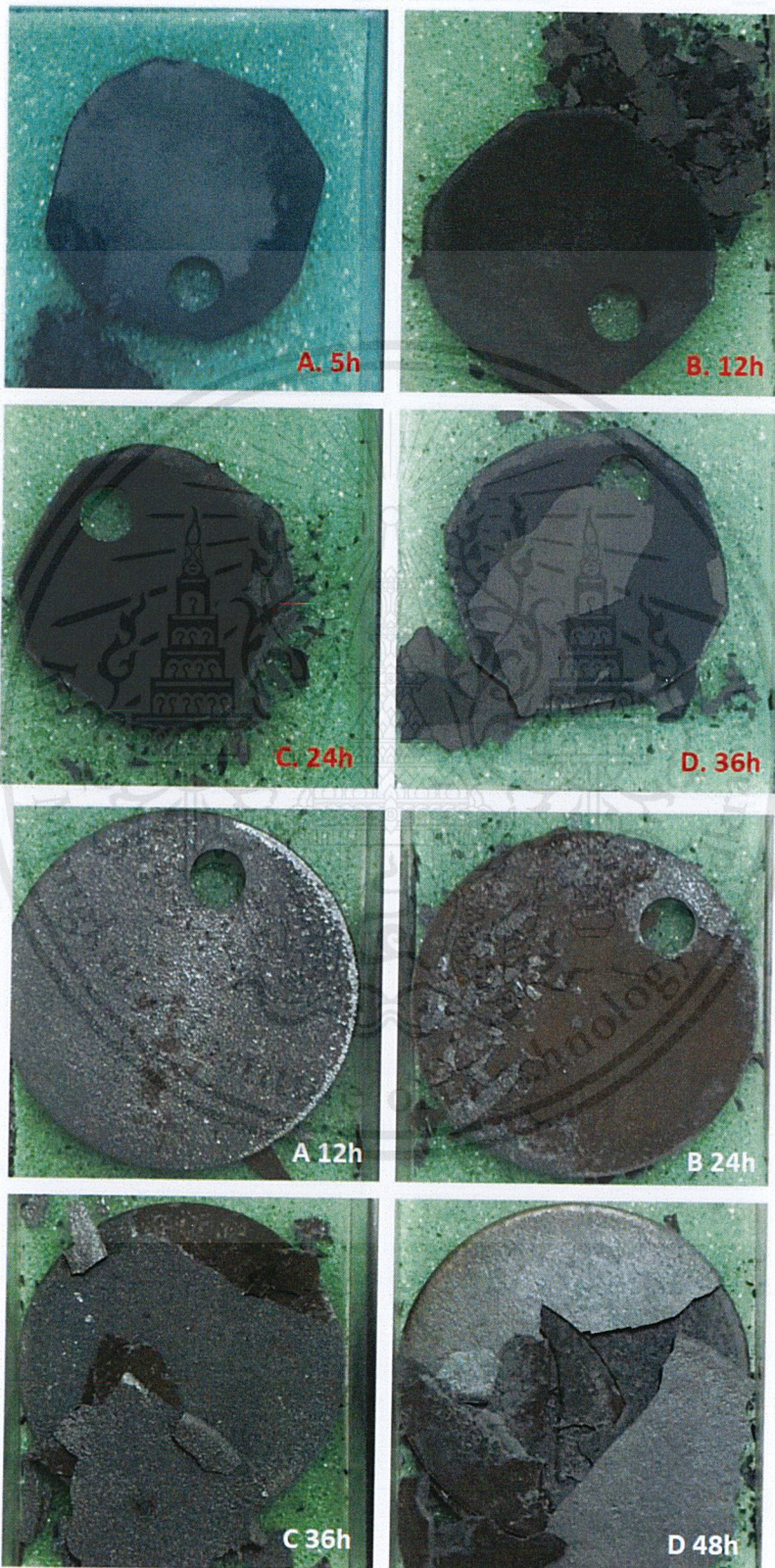
Table B-1: Weight gain measurement of AISI 316 stainless steel in linear velocity oxygen gas of 3.0 cm/s at 1,000°C for the duration times range of 0-96 h.

Time (h)	Initial Weight (mg)	After test weight (mg)	Weight gain, W (mg)	Surface area, A (mm ²)	W/A (mg/mm ²)
0	0	0	0	0	0
12	12.1344	12.2629	0.1285	1,768.9033	0.0726
24	12.1127	12.3878	0.2751	1,773.1385	0.1551
36	12.1138	12.6108	0.4970	1,776.5461	0.2798
48	12.1217	13.2375	1.1158	1,775.8176	0.6283
96	12.1318	14.9118	2.7800	1,766.7876	1.5735

Table B-2: Weight gain measurement of CoCrMo alloy in linear velocity oxygen gas of 3.0 cm/s at 1,000°C for the duration times range of 0-36 h.

Time (h)	Initial Weight (mg)	After test weight (mg)	Weight gain, W (mg)	Surface area, A (mm ²)	W/A (mg/mm ²)
0	0	0	0	0	0
5	5.5816	5.6093	0.0277	1,023.4537	0.0271
12	5.5973	5.6340	0.0367	1,031.9849	0.0356
24	5.5971	5.6480	0.0509	1,022.6448	0.0498
36	5.6001	5.6557	0.0546	1,052.7761	0.0519

Appendix C: Samples after oxidation from Experiments with linear velocity oxygen gas of 3 cm/s at 1,000°C for the duration times range of 0-48 h. (Red: CoCrMo, White: AISI 316 Stainless Steel)



BIBLIOGRAPHY

Name: Mr. Pratchaya Lertprasert
Date of Birth (DD/MM/YY): 17/08/96
Address: 599/110 Pailin Villa, Phosri Road, Markkhaeng Sub-District, Muang Udonthani District, Udonthani 41000
E-mail: eaw.pratchaya@gmail.com
Academic Background:

2009 – 2014	Udonpittayanukoon School, Udonthani
2015 – present	Degree of Bachelor of Engineering (Petrochemical Engineering), Department of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok

Working Experience:

June – July 2018	Student trainee at Thaipolyacrylic Company Limited Nakhon Pathom
------------------	---