HOT CORROSION BEHAVIOUR OF SLURRY ALUMINIDE COATING IN MOLTEN ALKALI SALTS

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by

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DECLARATION

I hereby declared that I have conducted, completed the research work and written the dissertation entitled: “**Hot Corrosion Behaviour of Slurry Aluminide Coating in Molten Alkali Salts**”. I also declared thatit has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVATIONS

CSP	Concentrated Solar Power
TES	Thermal Energy Storage
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
XRF	X-ray fluorescence
XRD	X-ray Diffraction
PV	Photovoltaics
IDZ	Interdiffusion Zone
HTLA	High Temperature Low Activity
LTHA	Low Temperature High Activity
PVD	Physical Vapour Deposition
CVD	Chemical Vapour Deposition

LIST OF SYMBOLS

°	Degree
°C	Degree Celsius
wt.%	Weight Percentage
R	Gas Constant
K	Absolute Temperature
nm	Nanometre
cm^2	Square Centimetre
mm	Millimetre
μm	Micrometre
g	Gram
V	Voltage
θ	Theta
λ	Lamda
gf	Gram Force
K^{-1}	Inverse Kelvin
HV	Vickers Pyramid Number
h	Hours
D_{50}	Mean Particle Size
ΔG	Gibbs Free Energy
ΔH	Enthalpy

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TINGKAH LAKU KAKISAN PANAS BUBURAN ALUMINIDA DALAM LEBURAN GARAM ALKALI

ABSTRAK

Ketahanan bahan adalah penting dalam aplikasi suhu tinggi seperti Penyimpanan Tenaga Terma (PTT) dan Tiub Dandang Pemanas Suhu Tinggi Biojisim. Salah satu cabaran yang akan dihadapi oleh bahan yang digunakan dalam PTT dan Tiub Dandang Pemanas Suhu Tinggi Biojisim adalah sentuhan berterusan dengan garam leburan yang bersifat mengakis pada suhu yang tinggi. Projek ini adalah bertujuan bagi membangunkan salutan aluminida pada substrat keluli tahan karat 304 dengan menggunakan teknik salutan aluminisasi buburan dan untuk menilai kelakuan kakisan salutan aluminida dalam pelbagai komposisi garam leburan. Dalam kajian ini, keluli tahan karat 304 tidak bersalut dan keluli tahan karat 304 bersalut aluminida telah tertakluk kepada ujian kakisan dalam 2 jenis garam leburan (95.5 wt.% KCl + 4.5 wt.% NaCl dan 60 wt.% $NaNO_3$ + 40 wt.% KNO_3) selama 100 jam pada suhu 700°C. Selepas selesai ujian kakisan, ujian penurunan jisim dan kakisan untuk setiap sampel ditentukan. Keluli tahan karat 304 bersalut Al menunjukkan rintangan kakisan yang lebih baik dalam garam leburan 2 dengan pembentukan fasa seperti FeNi, $Al_3Fe_2Ni_9$, dan Al_2O_3 dengan nilai kadar kakisan 0.4334 mm/y. Seterusnya, keluli tahan karat 304 tidak bersalut menunjukkan rintangan kakisan yang paling rendah dalam garam leburan 1 dengan pembentukan fasa seperti FeNi, $Cr_{0.6}Fe_{1.4}NiO_4$, Fe_2NiO_4, dan Fe_2O_3 dengan nilai kadar kakisan 3.4123 mm/y. Oleh itu, salutan aluminida yang dihasilkan dengan menggunakan teknik aluminisasi buburan dapat melindungi lapisan logam substrat daripada serangan kakisan.

HOT CORROSION BEHAVIOUR OF SLURRY ALUMINIDE COATING IN MOLTEN ALKALI SALTS

ABSTRACT

Material durability is important in high-temperature applications such as Thermal Energy Storage (TES) and Biomass Superheater Boiler Tubes. One of the challenges that materials used in TES and Biomass Superheater Boiler Tubes are constant contact with corrosive molten salt at high temperatures. This project aims to develop an aluminide coating on 304 stainless steel substrates by using the slurry aluminizing coating technique and to evaluate the corrosion behaviour of aluminide coating in various molten salt compositions. In this study, the uncoated 304 stainless steel and aluminide-coated 304 stainless steel were subjected to corrosion tests in 2 types of molten salts (95.5 wt.% KCl + 4.5 wt.% NaCl and 60 wt.% $NaNO_3$ + 40 wt.% KNO_3) for 100 h at 700°C. After completion of the corrosion test, the weight loss and corrosion test for each sample were determined. The Al-coated 304 stainless steel shows a better corrosion resistance in molten salts 2 by the formation of FeNi, $Al_3Fe_2Ni_9$, and Al_2O_3 phases with 0.4334 mm/y of corrosion rate value. Next, the raw (uncoated) 304 stainless steel shows the lowest corrosion resistance in molten salt 1 by the formation of FeNi, $Cr_{0.6}Fe_{1.4}NiO_4$, Fe_2NiO_4, and Fe_2O_3 phases with 3.4123 mm/y of corrosion rate value. Thus, the aluminide-coating produced by using the slurry aluminizing technique was able to protect the substrate metal layer from corrosion attack.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Renewable energy is the most cost-effective power source in most parts of the world today. According to the International Renewable Energy Agency (IRENA), renewable energy can provide 90 % of the world's electricity by 2050. In fact, the renewable energy technology prices are currently falling. Between 2010 and 2020, the cost of solar-powered electricity fell by 85 %. Falling prices make renewable energy more appealing all over the world, including in low- and middle-income countries, which will account for most of the additional demand for more electricity power source. Cheap renewable electricity could provide 65 % of the world's total electricity supply by 2030.

Renewable energy contributes for a rising percentage of overall world energy production each year. Solar energy is a renewable energy that uses solar technology to convert sunlight into electrical energy using photovoltaic (PV) panels or mirrors that concentrate solar radiation (Guney, 2016). The Malaysian government is eager to promote solar energy as one of the country's major energy sources (Mekhilef et al., 2012). This energy can be converted into electricity or stored in batteries or in Thermal Energy Storage (TES). Furthermore, biomass energy is also known as renewable energy since it is derived from living or formerly living organism (Sharman et al., 2013). Plants, such as corn and soy, are the most frequent biomass resources utilized for energy. These organisms' energy may be burnt to generate heat or transformed into electricity. In Malaysia, biomass energy is mostly obtained from plantation and agricultural leftovers, particularly waste from wood products, palm oil, forestry and logging, sugarcane, paddy straws, and so on (Van Meijl et al., 2012). Since they are environmentally beneficial, both of these renewable energy sources were used in Malaysia.

Furthermore, even the solar energy is environmentally friendly and more convenient but due to being intermittent energy sources it cannot be utilized to its full potential yet. The sun does not always shine all the time due to unpredictable weather. Thus, if this intermittent energy can be stored, it can be employed even during times which the sources are not actively providing energy. Therefore, to overcome this issue, the Thermal Energy Storage (TES) is introduced in solar energy technology for storing thermal energy by heating or cooling a storage medium, which may then be used for heating, cooling, or power generation later. Thermal Energy Storage main use is to overcome the imbalance between energy generation and energy use (Alva et al., 2018). Among the few essential requirements for an effective Thermal Energy Storage system is a storage material with a high energy density, very good insulation to ensure minimal heat loss, a storage material that is chemically stable as well as a completely reversible process that can be repeated numerous times.

Molten salts are the most often utilized material for high temperature applications in TES. This is because they have a large volumetric heat capacity, a high boiling point, good temperature stability, and low vapour pressure. The molten salt is also employed in thermal storage because it can be heated to temperature of up to 565°C (max: 590°C), allowing high-energy steam to be created at utility standard temperatures of 551°C, resulting in high thermodynamic cycle efficiencies. When heated to a very high temperature, solar molten salts can be very corrosive due to thermodynamics, impurity effects, activity and temperature gradients which can deteriorate the metal surface inside the TES at alarming rate at this condition (Sarbu, 2018). According to Bell et al. (2019), the solar molten salt (60 wt.% $NaNO_3$ + 40 wt.% KNO_3) contains nitrate salt has impurities which will enhance the corrosion. This impurity can lead to an initially high corrosion rate until the impurities are exhausted and corrosion becomes driven by different mechanism.

The corrosion rate on the metal surface can be minimized if the coating layer is applied on the layers of the substrate metal. Coating is the process of covering a surface or substrate with another substance to temporarily or permanently protect it from deterioration or degradation because of its reaction with the environment or corrosive agents. Coatings come in a variety of forms, including liquids, gases (vapour deposition), and solids. There are several factors to consider when selecting the corrosion coating. In general, corrosion is known to be caused by a combination of various conditions and material relationships (Dorcheh et al., 2016). Thus, before deciding on the type of coating that can be applied to the metal surfaces, the type of corrosion that the part is most likely to develop (such as stress-corrosion cracking, uniform, galvanic, pitting, crevice, or graphic corrosion) must first be identified. Information on how the coating part may be utilized, how long the coating part will be exposed to the corrosive environment, and the materials' strength must also be determined. Following that, the coated portions exposure to external factors such as temperature and humidity must be evaluated. Furthermore, the coated part's surface quality must be examined by assessing if it is free of surface porosity and other flaws since small holes might allow the corrosive agent to penetrate below the surface.

Aluminide coating is a high-temperature chemical process where aluminum diffuses into the surface of the substrate metal to form an aluminide coating layer. This coating is often applied on 304 stainless steel as a corrosion protective layer. Aluminized steel is more corrosion resistant than carbon steel or even pure aluminium. According to Dai et al. (2016), aluminide coatings provide excellent oxidation resistance due to its ability to form protective scales. Attempts to increase the oxidation resistance of boiler tube steels with aluminide coatings have been made utilizing a variety of processes, including CVD, pack aluminizing, and slurry aluminizing (Grégoire, B. et al., 2021). The creation of an Al_2O_3 layer protects the base metals. A hydrated aluminium sulphate protective layer is formed. The aluminide coating method is also known as the aluminizing process, which is a thermo-chemical process that diffuses aluminium onto the surface of the parent metal. The most common material to be aluminized is steel. As a result, the slurry aluminizing coating composition is ideal for aluminizing a metal-based substrate's surface region. The slurry aluminizing method also results in a very homogenous distributed aluminide coating layer. As a result, aluminizing the metal surface for greater corrosion resistance in structural alloys may be explored (Galedari et al., 2019).

1.2 Problem Statement

Aluminizing Molten salts are a phase transition material that is extensively employed in Thermal Energy Storage (TES) and Biomass Superheater Boiler Tubes where TES was applied for solar energy technology while Biomass Superheater Boiler

Tubes were applied for biomass energy technology. The molten salt was used in thermal storage because it can be heated to 565°C, allowing high-energy steam to be produced at utility standard temperatures of 551°C, resulting in high thermodynamic cycle efficiencies. When thermal energy is transmitted to the storage medium, molten salts transform from a solid to a liquid at room temperature and atmospheric pressure. When heated to a very high temperature, molten salts can be very corrosive due to thermodynamics, impurity effects, activity, and temperature gradients. In those conditions, the steel can corrode and melt. Next, during biomass combustion, the volatile alkali chlorides, and corrosive flue gas species deposit and condense on a biomass superheater boiler tube, causing fast corrosion. Burning agricultural leftovers releases biomass molten salts such as KCl and NaCl which can lead to higher corrosion rate inside biomass superheater boiler tubes.

The corrosion in TES and biomass superheater boiler tubes will occur when the stainless-steel material on it is exposed to a molten salt environment at a high temperature where the molten salt will become very corrosive during this condition. The corrosion will become worse when the protective coating layer were not applied to the substrate material surface layer. Iron is a very robust metal that does not corrode quickly but does result in the creation of rust. Rust causes metals to become brittle, which can accelerate corrosion. Iron must be coated with other metals that do not corrode easily, such as aluminium to generate rust resistance layer. The Aluminide coating will protect the 304 stainless steel surfaces from deterioration by reducing the corrosion impact. Slurry Aluminizing, Pack Cementation, Chemical Vapour Deposition (CVD) and Hot Dipping Aluminizing are some of the aluminide coating processes.

The Slurry Aluminizing coating process was chosen for this study because of its low cost, environmental friendliness and ability to cover practically any shape and size by spraying, brushing or dipping as mentioned by Segure-cedillo (2011). According to Syamimi et al. (2021), the pre-oxidation in air promoted the generation of a compact and protective Al_2O_3 layer, which could efficiently prevent the aggressive species from attacking the substrate and rapid consumption of the aluminizing coating. The study also supported by Hu et al. (2020) that a dense and continuous inner layer made up of FeAl-base intermetallic is believed to improve the corrosion resistance of stainless steel. For this study, the raw 304 stainless steel and aluminide-coated 304 stainless steel were prepared for the corrosion test. The corrosion test for both sets of samples was conducted in a biomass agricultural molten salt environment which consists of 95.5 wt.% KCl + 4.5 wt.% NaCl and solar energy molten salt environment which consists of 60 wt.% $NaNO_3$ + 40 wt.% KNO_3 at the temperature of 700 °C for 100 hours. After completing the corrosion test, the weight loss and corrosion rate for both sets of samples were determined.

1.3 Research objectives

The objectives of this project are as follows:

1. To evaluate aluminide coating on 304 stainless steel substrates using the slurry aluminizing coating technique.
2. To evaluate the corrosion behaviour of aluminide coating in various molten salt compositions.

1.4 Scope of research

This thesis is divided into five chapters. Chapter 1 describes a brief overview of the study, including a problem statement and objectives for this project. Chapter 2, a comprehensive review of the aluminizing techniques, slurry aluminizing, problems faced by aluminide coating are present, the method of corrosion test, and the type of molten salt used during the corrosion test. Next, Chapter 3 describes the methodologies used in this project, including sample and slurry preparation, coating procedure, coating characterization techniques, and corrosion test procedure. Chapter 4 presents the experimental results of the aluminide coating as well as a discussion of the corrosion rate of aluminide coating. Finally, Chapter 5 summarizes the findings of the research and makes recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of renewable energy storage system

Over the last five decades, the world's collective greenhouse gas emissions have grown rapidly, even as greater efficiency has resulted in more people having access to energy. Many argue that we should increase energy efficiency and save resources in order to reduce greenhouse gas emissions and prevent a climatic disaster. According to Foster et al. (2019), burning fossil fuels more efficiently has not cut overall greenhouse gas emissions for several reasons, and such initiatives are unlikely to have a discernable effect on atmospheric greenhouse gas composition.

Although the relationship between energy usage and greenhouse gas emissions is questionable. Emerging technologies and artificial alternatives will also be utilized to manage the composition of the atmosphere. but will require extensive expertise and energy management. Thus, enhancing renewable energy sources has been driven largely by lowering their negative consequences of the creating greenhouse gas emissions. Solar energy stands out among renewable energy option due to the abundance of solar radiation reaching earth's surface (Walczak et al., 2018).

2.2 Solar energy power plant

Solar energy is a sustainable and renewable energy source since it is predicted that the sun will continue to provide solar energy for the next 4 billion years according to current predictions. Solar energy released by the sun is accessible on the earth's surface at an estimated intensity of 1000 Wm^{-2} during clear sky circumstances (Guruprasad et al., 2018). This intensity is adequate to fulfil the needs for thermal energy needed for applications operating at low temperatures, such as the provision of hot water.

When dealing with high temperatures, solar radiation must be concentrated with the help of the proper reflectors. Solar radiation may be converted into energy via the use of photovoltaic, often known as PV, cells or concentrated solar power plants (CSP). Solar radiation may be used for a variety of purposes, including space heating, the provision of hot water, absorption refrigeration, and so on and so forth if the appropriate solar thermal equipment is utilized. Energy storage systems, such as Thermal Energy Storage (TES) systems or battery-based electricity storage technology, are intended in order to compensate for the intermittent nature of the resource and its lack of availability during times of peak demand.

2.3 Biomass energy power plant

Biomass energy is a renewable energy that were created by living or once-living organisms. For biomass energy application, the plant-based substance utilized as fuel to create heat or power. Among the common biomass material used for energy are woods, plants and biomass waste. These materials are also known as biomass feedstock. This feedstock may be burnt via thermal conversion and utilized for energy. Biomass fuels are considered ecologically favorable for numerous reasons. There is no net increase in CO_2 as a consequence of using biomass fuel.