Enhancement of Materials Surface Properties via Case Hardening Process:
Metals Substrate in Silica Sand Bath

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
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(MECHANICAL ENGINEERING)

Approved by,

____

(DR OTHMAN BIN MAMAT)

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TRONOH, PERAK
Sept 2013

CERTIFICATION OF ORIGINALITY

This is to certify that i am responsible for the work submitted in this project, that the original project is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

FATIN AMALINA BINTI ROSDI

ABSTRACT

This report is compilation of work about a study concerning case hardening process. This study, Enhancement of Material's Surface Properties via Case Hardening Process: Metals Substrate in Silica Sand Bath aims to introduce simplicity in case hardening concept; focusing on siliconizing using silica sand bath. This study is proposed as the process of case hardening was always complicated, examples including pack carburizing, flame and induction hardening and also heating and quenching in carbon-rich medium.

Using silica sand bath concept, the siliconizing steps were simple and economical as it just needed sand and brick which was easily available. Apart from that, the objective is also to characterise and analyse the microstructure and surface properties of the metal after siliconizing using silica sand bath in order to look in the difference before and after the experiment.

Using only mild steel, silica sand and brick as the container; the siliconizing process started with sample preparation of the mild steel, preparation of sand and brick for siliconizing, siliconizing experiment which focused on heating the sample in furnace with designated working temperature and time and also microstructure evaluation and analysis after the experiment. After experiment, there is coating layer produced. The layer produced was brittle, weakly adherent to substrate, porous and easily removed after sectioning. However, the interesting part is that the thickness layer was even and homogeneous. Thus, the siliconized sample is evaluated using optical microscope and FESEM testing. The evaluation focused on microstructure and analysis of the coating layer formed at the front layer of the coating and interface of the coating and sample. At the end of the report, the study is concluded and recommendations in order to carry out this project were identified.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious, the Most Merciful. Praise to Him the Almighty that in his will and given strength, the study of Enhancement of Material's Surface Properties via Case Hardening Process: Metals Substrate in Silica Sand Bath is completed successfully within the allocated two semesters.

Upon completing the study, I owe a great many thanks to a great group of people for their support and kindness, as well as their contribution in terms of time, effort, advice, supervise and help during the study period. As a token of appreciation, deepest heartily thank goes to my supervisor, Dr. Othman Bin Mamat who had helped me a lot throughout the study period. Without his guidance and support, I would not have been able to complete the project. I would also like to express the thanks to all the lab technologists at Mechanical Engineering Department for their help in facilitating me throughout the preparation and experimentation.

Last but certainly not the least; million thanks would have not been able to recompense all the help and support that had been given to me by all of my families and friends. Without all the help, support, advice, knowledge and encouragement i would have not been able to complete this study. Thank you once again.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND STUDY

The objective of case hardening is to form a thin layer of harder metal, like a case at its surface. The surface of a metal is hardened while deeper underneath or at its core; it remains soft. Case hardening is important in order to have two different kind of steel at two different points in time. Soft steel is preferable during manufacturing as it will be easy to bend and machine. After the steel has been turned into products, soft steel is not desired because it is not strong, scratchable and plus, it corrode easily. Because of that, case hardening is performed to make the outer layer harder. This is done by diffusing carbon**,** nitrogen or silicon into the outer layer of the steel at high temperature. By case hardening, the metal will be harder, not easily scratch and corrode.

1.2 OBJECTIVE

1. To introduce simplicity in case hardening concept; focusing on siliconizing using silica sand bath.
2. To characterise and analyse the microstructure and surface properties of the metal after siliconizing

1.3 PROBLEM STATEMENT

For common heat treatment process, the whole sample will undergo heat treatment where there will be microstructural alteration and changes in property as a whole. However a sample that increased in hardness will also experience reduce toughness. This can lead the sample prone to failure. Thus it is desirable to have alteration only to the surface properties. This can be done by case hardening.

There are various types of case hardening such as carburizing, nitriding and siliconizing. However, the process of case hardening such as pack carburizing, flame and induction hardening and also heating and quenching in carbon-rich medium are always complicated. Thus for this project, a simple concept of siliconizing using silica sand bath is introduced. A metal sample immersed in sand will be heated using bath technique in a furnace. The microstructure and surface properties after the experiment will then be analysed.

1.4 SCOPE OF STUDY

In order to carry out the project, there are certain scopes of study that will be focused on including:

- Literature review on siliconizing.
- Conducting experiment on siliconizing.
- Conducting microscopic examination on sample after siliconizing process.
- Perform analysis on the siliconized sample.

CHAPTER 2: LITERATURE REVIEW

2.1 CASE HARDENING

The failure of engineering materials is a problem that needs to be avoided as it can later risk human life and results in loss in terms of economic value. Callister (1940) discussed that the common threats of failure such as creep and fatigue often starts from cracks or scratches during machining operations. In order to remove the cracks and scratches, surface treatment such as surface finishing is needed. Surface treatment can improve the surface as residual compressive stresses are applied within the outer surface layer. The residual compressive stresses will lower the surface tensile stress of the external origin; resulting in reduce potential of crack formation and fatigue.

There are many techniques of surface treatments. As for this study, the focus will be on case hardening. Case hardening is a process in which its surface hardness, fatigue life and reliability are improved by carburizing, nitriding or siliconizing. As for this process, the material is exposed to the carbonaceous, nitrogenous or siliconaceous atmosphere (depending on the substance used) at higher temperature. An outer surface which is harder than the materials inner core; more like a case in which rich of either carbon, nitrogen or silica is formed due to the diffusion of the atoms (diffusion coating).

2.2 DIFFUSION COATING

Diffusion is a case of material transport by atomic motion. For that to happen there must be empty adjacent site and the atom must possess enough energy to break the bonds. Factors that affect diffusion include diffusion species and temperature.

Diffusion coefficient is the diffusion rate. As for the temperature, it affects the coefficients and diffusion rate for the coating.

Diffusion coating is discussed in details by V.I.Pokhmurskii (1977) in his study, Effect of Diffusion Coatings on the Service Properties of Metals and Alloys. He emphasized that new material is formed as the diffusion impregnation of materials with aluminium, nitrogen, boron, beryllium, vanadium, tungsten, silicon, titanium, chromium, carbon and also combined two or more elements resulted diffusion coatings that will alter the properties of the surface.

2.3 SILICONIZING

2.3.1 Importance of siliconizing

Siliconizing is a process of diffusion coating on metals using silicon. Silicon is the fastest diffusing species in the ferrite surface and because of that, the coating further moves inward resulting in dense layer without affecting pack particles. He also stressed that silicon deposition enhance steel resistance to oxidation, sulfidation and erosion better that chromized steel. Apart from that, as compared to chromizing coating and coating with Cr + Si, a little amount of Si improve the perfection of diffusion layer and lower the decarburization depth.

Z.S. Broide and V.I. Udovitskii (1981) states that siliconized surface give high resistance to chemical effects. This is in agreement with study conducted by V.I. Pohmurskii (1977) who announced that siliconizing of steels will give high resistance from mineral, organic acids and also salts and alkalis for a broad temperature range.

Broide and Udovitskii (1981) also discussed on the prospects for the commercial use of diffusion siliconizing coatings. Among them are siliconized layer saturated with polymer on the carbon steels can be apply to food and chemical industries as rubbing components. Siliconized layer with chromium plating on carbon or low alloy steels can be used as transmission components for agricultural engineering. As for siliconized layers saturated with lubricants, it has broader applications comprising molds, bearings, machinery and also components that subjected under corrosion and high temperature.

In other study by A.I Negadailov, V.V.Matyash and V.I.Udovitskii (1975), they found out that it is possible to have controlled porosity coating and self-lubricating effect in porous layer by siliconizing. Thus it can be use for hardening parts in expansion tools.

Siliconizing also has been proved to improve the corrosion resistance (Nogtev & Koskov,1981). This is because of dense pore-free silicon layer formed on the metal surface. S.Motojima,M. Kohno and T.Hattori (1987) also agree that diffusion coating using silicon on the metal resulted in a layer that protect against hot corrosion and oxidation as their physical and chemical properties improved. Improved oxidation resistance is due to formation of protective scale such as SiO_2 (Alam, Rao & Das, 2010).

2.3.2 Experimentation Procedures of Siliconization

From several studies conducted, there are some methods used to siliconize steels including gas siliconizing, molten siliconizing and powder siliconizing.

From a study conducted by Lyakhovich, Voroshnin and Scherbakov (1971), they found out that steel siliconizing is possible by using pure silicates at high temperature. For that experiment, they siliconized metal using molten silicate through electrolysis. The liquid bath Na_2O and SiO_2 is prepared by melting quartz sand with soda. For this experiment, the parameters used to siliconize steel including temperature of 1050°C and 1 hour of experimentation time. In order to lower the siliconizing temperature to $1000^\circ C$- $950^\circ C$, NaCl is added.

There was a study conducted on the powder siliconizing on the noncontact siliconizing and contact siliconizing. Test on powder siliconizing (contact siliconizing) was conducted in such a way that samples were placed in a container of silicates bath. To speed up the process, magnesium and calcium oxides were used.

Another experiment on powder siliconizing is conducted by Khisaeva and Kuzeev (2004). Powder mixture of SiC was used. Inert additives of Mn_2O_3 and Al_2O_3 are used to avoid mixture sintering and powder sticking to the metals while to speed up the process, NH_4F was used. The specimens and the powder mixture were placed in unpressurized containers because from their preliminary finding, siliconizing is not affected by degree of air-tightness of the container. The container is then put into the furnace. After that, the container was cooled in air before being tempered for 4 hours at 720°C. In order to see the result of the siliconized and heat treatment layer, specimens were studied under scanning electron microscope. Besides that, microhardness test and low-cycle fatigue test was perfomed too on the specimens.

Other studies on powder siliconizing using different experimental procedures were conducted by Mottojima, Kohno and Hattori (1987). As for their experiment, metal plates were put in quartz boat before being placed in central part of the diffusion reaction tube. Hydrogen saturated with hexachlorodisilane was released inside the reaction tube as it can dissolve in the steel lattice effuses to avoid embrittlement.

Based on founding by Alam, Rao and Das (2010) on silicide coating of niobium, there are many techniques can be used for siliconizing including hot dipping of niobium into molten silica, silica electroless plating in molten halide salt bath and also pack cementation. Focusing on pack cementation, it is chemical vapour deposition technique (CVD) whereby the specimen is lumped in a powder pack and heated in elevated temperature. In preparing the specimen, they ensure that the surface undergo grit blasting for cleaning and degreasing in acetone.

Pack cementation for siliconizing also being carried out by Bianco and Rapp (1996). According to them, important components in pack cementation are the parts to be coated; the powder to be deposited on the parts; halide salt activator (energizer) and also inert filler powder. The parts to be coated are immersed in the mixture of other components. In their experiment, for the retort they use a cylinder of pure alumina with one end closed. The cylinder retort is then closed with lid from alumina too before sealed with alumina-base cement. The retort is then placed in furnace of 800°C to 1100°C for 4 to 12 hours. They explained that at high temperature, the coating powder will react with energizer, resulting in volatile metal halides that will diffuse the porous mixture in gas phases before deposit and diffuse into specimens.

2.3.3 Result of siliconizing

From the study by Negadallov, Matyash and Udovitskii (1975) regarding diffusion siliconizing in expansion tooling; they found out that the siliconized expansion tool part have better service life by a factor of two besides decrease in porosity.

As for Nogtev and Koskov (1981), they have done a research in pore-free siliconizing in solids by means of contact and noncontact siliconizing. From their finding, the noncontact siliconizing layer has lower porosity as compared to contact siliconizing.

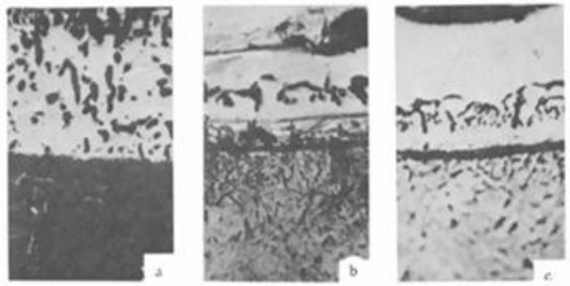
Klam, Millet and Mazille (1991) in their finding (with respect to their parameters) states that siliconizing of Armco iron (mixture of Ar-SiH_4-H_2) gives out a non-porous and adherent soild solution layer with maximum silicon content of 6%.

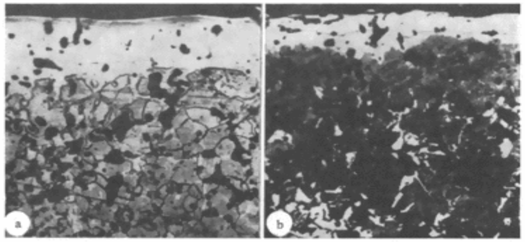
2.3.4 Summary of siliconizing study based on years

Research in siliconizing has been carried out back in 1960's. Table 1 below summarized all the research regarding siliconizing based on years.

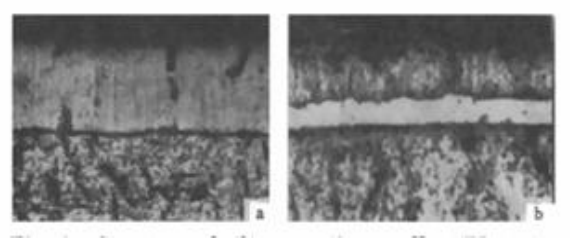
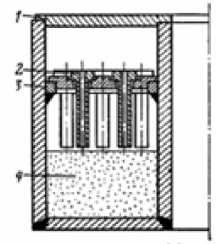
Table 1 Summary of research in siliconizing based on years.

Name & year	**Study**	**Parameters**	**Methods**	**Findings**	**Comments**
Zemskov and Kaidash (1964)	Barosiliconizing iron and steel	-Armco iron, steels 45 -1050°C -3 hours	-Using powders -Impregnation with boron and silicon in a tube furnace	-Thickness and structure of the diffused borosiliconized coating depends on the mixture composition	-Increase temperature, process time – increase thickness of layers
Kidin, Andryusheckkin, Kholin (1967)	Siliconizing steel with rapid electrical heating	-Steel 45 -Different heating rate (10 deg/sec, 100 deg/sec and 3000 deg/sec)	-Heating in the furnace	-Porous coating are formed at all heating rates -Slow heating and rapid heating at 10 deg/sec – Pores distributed irregularly throughout the coatings.	-Heating rates influence porosity of the coating (due to intensity of diffusion process)

				-Higher heating rate – linear pores parallel to the surface of the sample -Higher heating rate, nearer the linear pores to the base metal (further from coating surface)  Figure 1 Microstructure of silicon coating after gas siliconizing of steel 45 at 1100°C (x400) a) heating rate 10 deg/sec; b) 100 deg/sec; c) 3000 deg/sec) . Taken from Kidin, Andryusheckkin, Kholin (1967) -Figure 1 shows the microstructure of the findings.	

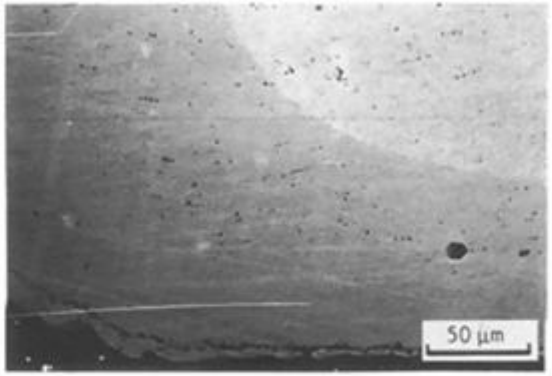
Protasevich, Voroshnin, Lyakhovic and Devoino (1971)	Chromosiliconizing of sintered iron	-Iron and precarburized iron	-Impregnation in electric furnaces with silicon carbide heating elements, using ceramic crucibles.	-Iron : diffusion layer consists of α solid solution of silicon and iron -Precarburized iron: 2-phase layer is formed composed of carbide zone on the surface and layer consists of α solid solution of silicon and iron below it. -Figure 2 shows the chromosiliconized layers.  Figure 2 Structures of chromosiliconized layers, x340: a) iron(1000°C, 4 hours) b) precarburized sintered material (1100°C, 4 hours). Taken fom Protasevich, Voroshnin, Lyakhovic and Devoino (1971)	-Gives high wear resistance, increase resistance to oxidationand corrosion
Lyakhovich, Voroshnin and Scherbakov	Chemicothermal treatment – Siliconizing	-Steel -Bath of liquid Na_2O - SiO_2 with 44-75 wt	-Siliconizing bath with electrolysis	-Dense layer of silicon ferrite is formed on the surface - To obtain pore-free siliconized coating	-Addition of NaCl lowers the siliconizing

(1971)	steel in liquid media	% silicon dioxide -Temperature above 1050°C -Current density 0.3 A/cm^2		(recommendation): • 100% Na_2SiO_3 or 95% Na_2SiO_3 + 5% NaF. • Processing condition: 1050-1070°C, 1.5-2.0 hours, 0.2-0.25 A/cm^2	temperature to 1000-950°C
Belyaeva,Anfinogenov and Ilyushchenko (1971)	Structures and properties of silicon coatings on alloy VN-2	-Niobium and niobium alloy VN-2 -Temp = 800, 850, 900, 950°C	-Siliconizing in mixtures of molten halides and powdered silicon (Composition : equimolar mixture of KCl-NaCl -72wt%, NaF-14%, and Na_2SiF_6-14% with silicon powder- 10wt% of salt.	-Silicon coating consists of of single phase ($NbSi_2$) with microhardness of H1080 -Heat resistance increase proportionally with coating thickness. -Silicon coatings with thickness 30µ protect the alloy against oxidation for 80h at 1100°C and 40h at 1200°C -The silicon coating is shown in Figure 3	-This method is suitable for thick-walled and complex part as it is conducted at low temperature and resulted in even coating. -Oxidation results in the formation of glassy surface film of α SiO_2 , with $NbSi_2$ below it. -If the coating cracks

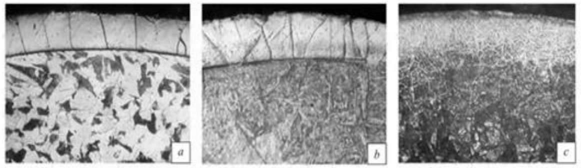
				 Figure 3 Structures of silicon coating on alloy VN-2: a) original (x615) b) after siliconizing (x700). Taken from Belyaeva,Anfinogenov and Ilyushchenko (1971)	during thermal cycling then nodules β Nb_2O_5 form on the surface.
Negadallov, Matyash, Udovitskii (1975)	Industrial experience in acceptance of diffusion siliconizing of expansion tooling in production	-Basic constituent of mixture: pulverized Si-45 grade ferrosilicon powder -Ammonium chloride as process intensifier -Additive: aluminium oxide	-Siliconization in basket as shown in Figure 4  Figure 4 Layout of basket for simultaneous siliconizing of 50 bodies of expansion tools: 1) cover; 2) body of expansion tool;	-When siliconized parts are air-cooled, increase (by 2.5 times) results in the useful service life of the expansion tools due to more abrupt cooling of α solid solution of silicon in iron that takes place in air. -Silicon ferrite, it not facing allotropic changes during quenching will contribute to enhance hardness of the material during cooling. -When the siliconized parts are oil-quenched or water-quenched, severe internal stresses	-Siliconizing 30-60 products at a time -Before siliconization, the expansion tools bodies were degreased by applying gasoline, etched with concentrated hydrochloric acid

		-Temperature : 1000°C -time: 4 hours	3) body of basket; 4) reaction moisture. Taken from Negadallov, Matyash, Udovitskii (1975)	are generated in diffusion layer due to rapid cooling rate. -Later it can form cracks on the surface of the parts.	and finally rinsed off with water and acetone.
Nogtev and Koskov (1981)	Pore free siliconizing in soilds	-Sample: carbon steels -Temp:,1000 to 1050°C -Time: 3-6 hours	-Mixture and samples were placed in a container with reaction chamber sealed with lumps of silicate. -Noncontact siliconizing (parts were placed on the mixture with inert powders (layer of quartz sand) used as filters between mixture and parts) -Incontact siliconizing (inert additions were replaced with	-After noncontact siliconizing- surface was clean (a layer without skin),dimensions did not change, porosity decreased, but thickness layer varied even on the same sample (indicating siliconizing in powders occur by gaseous phase) - Greater thickness but lower in porosity as compared to contact siliconizing -After contact siliconizing – thickness increases with temperature and time -To have dense (pore free) silicon layer add magnesium and carbon oxide (for both siliconizing types) – increase carbon content in steel, decrease thickness layer and increase microhardness.	-Corrosion resistance increase with a dense pore-free silicon layer on the surface -Contact method produce brittle surface layer,weakly adherent to substrate, porous (lower corrosion resistance) and easily removed during microsection.

			magnesium and calcium oxides – affect the gaseous siliconizing)		
Motojima, Kohno and Hattori (1987)	Vapour-phase siliconizing of some nickel based alloys and transition metals using Si_2Cl_6 as a source of silicon	-Hexachlorodisilane Si_2Cl_6 as silicon source -Temp :500-1000°C -Time – 1 hour -Sample: nickel base-alloys (Inconel No.600 and Monel)	-Chemical vapour diffusion (CVD) or silicon diffusion. -Sample was set horizontally in quartz boat and then put into horizontal diffusion reaction tube. - Si_2Cl_6 was saturated into hydrogen and introduced into reaction zone. -X-ray microanalysis carried out on a cross-section of siliconized plate	-Using Si_2Cl_6, weight gain on nickel-base alloy plates was observed around 500°C while for $SiCl_4$,(common silicon source for CVD) weight gain for nickel-base alloy plates observed at 700°C -Above 800°C same weight gain is attained despite of different silicon source.	For nickel – siliconizing temperature can be lowered to 200-300°C using Si_2Cl_6 instead $SiCl_4$ -

			-The siliconized sample then were immersed for 30 mins in sulphuric acid/nitric acid solution maintained at 100°C and the weight decreased was measured.		
Klam, Millet, Mazille and Gras (1991)	Chemical vapour deposition of silicon onto iron: influence of silicon vapour phase source on the composition and nature of	-Sample; Armco iron -Temp: 750-1100°C -Silicon source: argon-tetrasilane-hydrogen mixture (Ar- SiH_4- H_2)or Argon-tetrasilane-tetrachlorosilane-hydrogen mixture (Ar- SiH_4-$SiCl_4$- H_2)	- Chemical vapour diffusion (CVD) or silicon diffusion. -Samples were first polished in oxalic aci-hydrogen peroxide aqueous solution. -Annealing treatment of 2 hours at 800°C in pure hydrogen were carried out first	-SEM image of siliconized sample is shown in Figure 5  Figure 5 Backscattered electrons image of cross-section of siliconized sample after 1	Whatever the parameters, siliconizing always lead to formation of non-porous and adherent solid solution with max silcon content of 6% by weight at outer surface.

	the coating		- For argon-tetrasilane-hydrogen mixture, Ar-3% SiH_4 gas is used and diluted with pure hydrogen. -For second mixture it is obtained by bubbling , Ar- 3% SiH_4 in saturator containing silicon tetrachloride. -The structures are anaysed by X-ray diffraction,SEM, Vickers microhardness test.	hour CVD treatment at 1000°C. Taken from Klam, Millet, Mazille and Gras (1991)	
Bianco and Rapp (1996)	Pack cementation diffusion	-Masteralloy/ powder to be deposited - Cr	-CVD process -The masteralloy powder, halide salt	-Produce corrosion and wear resistant coating	-At elevated temperature, the masteralloy reacts

	coatings	and/or Si -Halide salt activator/ energizer (NaCl, NaF etc) -Inert filler powder (SiC, $Si0l_2$, Al_2O_3) - Temp: 800-1100°C -Time: 4-12 hours	activator, inert filler are mixed thoroughly and parts to be coated are buried in this mixture within heat-resistant retort (alumina retort). -The alumina retort is closed by alumina lid and sealed using alumina-base cement. -The retort is heated.		with halide salt activator to produce volatile metal halides that diffuse through the gas phase of porous pack, before deposited and diffuse into substrate.
Khisaeva and Kuzeev (2004)	Effect of siliconiing on the low cycle fatigue of steel	-Sample: Steels 15Kh5M and 10Kh23N18, steel 09G2S	-Powder mixture based on SiC -Containers with specimens were placed into the furnace and heated. -The containers were cooled in air in	 Figure 6 Microstructures of surface layer of steels after siliconizing a) 09G2S; b) 15Kh5M and c) 10Kh23N18 . Taken from Khisaeva and Kuzeev (2004)	-Majority of known experiments on siliconizing have been performed for low alloy steels. -In order to prevent sintering of the mixture and sticking

			accordance with heat treatment process. -Metallography is carried out to determine thickness of siliconized layer. -Hardness test is also carried out. -Apart from that, the specimens is also subjected to low-cycle fatigue. (Lateral bending with rotation of specimens fixed in cantilever mode until failure). Loading frequency = 10 cycles/min	Figure 6 above shows microstructure after siliconizing for all the sample	of powder to specimens inert additives of Al_2O_3 or Mn_2O_3 is introduced. - Nh_4F to accelerate the process. -Degree of air-tightness of the container did not have noticeable effect on siliconizing.

CHAPTER 3: METHODOLOGY

3.1 RESEARCH METHODOLOGY

To carry out study of Enhancement of Materials Surface Properties via Case Hardening Process: Metals Substrate in Silica Sand Bath, the first step was to understand the rationale behind the study and identify the problem. As being discussed before, this study aims to improve the microstructure and surface properties of metals. Next step was to carry out related literature review on case hardening, siliconizing etc. As the author has already learnt on what other people had done on the related field, the next step was to take that as her references for designing her own experiment parameters including working temperature needed, time needed for siliconizing and so on.

After the parameters of the experiment have been figured out, the experiment is conducted. The metal specimen is ground and polished in order to remove outer corroded layer. After that, the metal specimen is put in a ceramic container, covered with ceramic lid too. This container is placed inside a furnace for designated time and temperature. Later, the metal specimens underwent microscopic examinations and FESEM testing to get the result after the experiment. Both results before and after the experiment were compared and analysed. The final step was identification of the limits in the study and recommendations for further research.

The summary of the research methodology is shown in Figure 7.

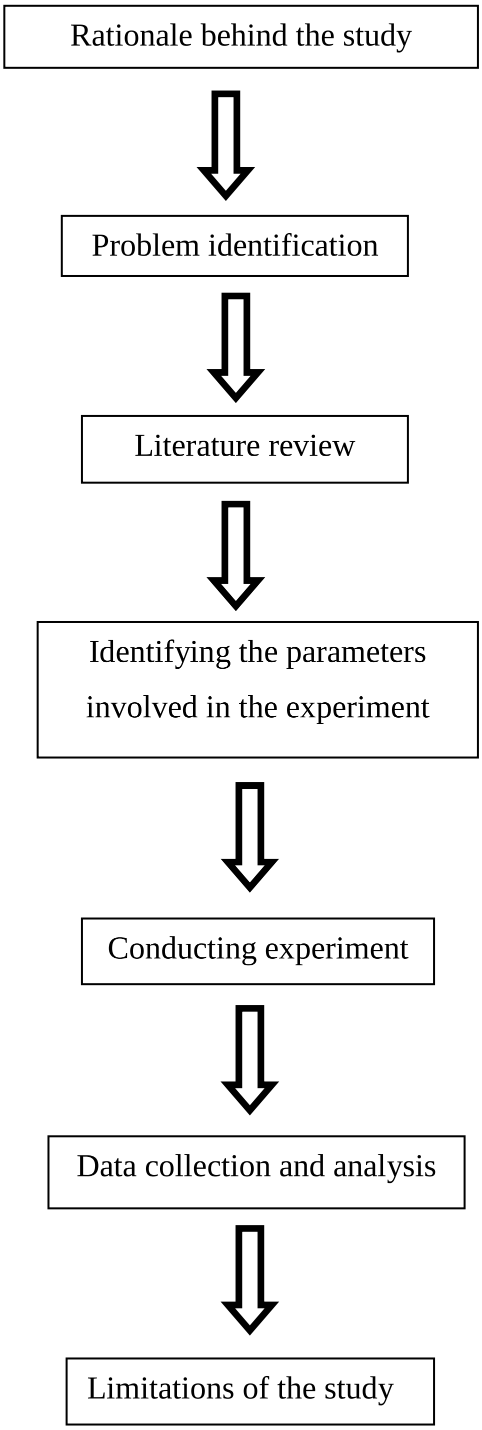


Figure 7 Research methodology of the study.

3.2 PROJECT ACTIVITIES

3.2.1 Materials and testing.

The materials that are used in the siliconizing experiments are listed as follows:

1. Sample : mild steel (2.6 x 2.7 x 0.3 cm).
2. Silica sand (212µm).
3. Brick as the ceramic container.

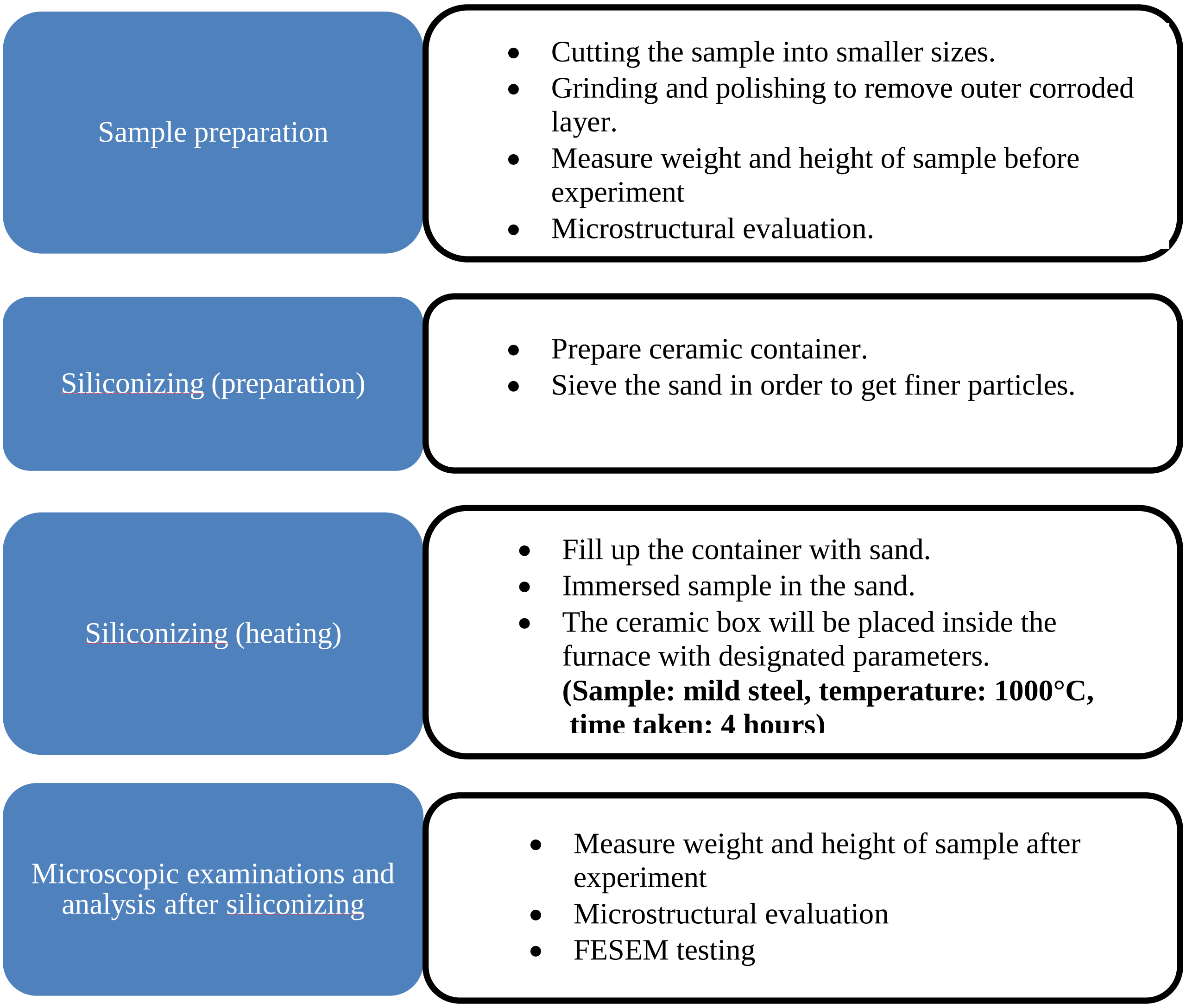
The testing that were conducted for this study:

1. Microstructure analysis using optical microscope
2. Field Emission Scanning Electron Microscope (FESEM) Testing.

Mechanical testing such as hardness test and scratch test were planned to be conducted at the initial stage of the study. However due to nature and condition of the coating layer, the mechanical testing cannot be carry out.

3.2.2 Siliconizing process

In order to carry out the siliconizing, the author designs the experimental procedure of the experiment as shown in Figure 8 below.



Sample preparation

- Cutting the sample into smaller sizes.
- Grinding and polishing to remove outer corroded layer.
- Measure weight and height of sample before experiment
- Microstructural evaluation.

Siliconizing (preparation)

- Prepare ceramic container.
- Sieve the sand in order to get finer particles.

Siliconizing (heating)

- Fill up the container with sand.
- Immersed sample in the sand.
- The ceramic box will be placed inside the furnace with designated parameters. **(Sample: mild steel, temperature: 1000°C, time taken: 4 hours)**

Microscopic examinations and analysis after siliconizing

- Measure weight and height of sample after experiment
- Microstructural evaluation
- FESEM testing

Figure 8 Design experimental procedure of siliconizing

The details on the siliconizing process are discussed as follows:

3.2.2.1 Sample preparation

As for the sample, mild steel will be used for the experiment based on the literature review as it is familiar with siliconizing. The mild steel was cut according to the slot size of the bricks. Next, the mild steel is ground and polished in order to remove outer corroded layer. Later the mild steel sample is weighed and its height is measured in order to be compared with the data after the experiment.

Figure 9 Process of cutting mild steel plate

Figure 10 Process of preparing mild steel

Figure 11 Mild steel sample that will be used in experiment

3.2.2.2 Siliconizing (preparation)

For the experiment, brick is used as the container. The brick is milled and chiselled to form slots as shown in Figure 12. Brick is chosen as it is easily available and able to withstand high temperature. Apart from that, it is a good insulator where heat trapped inside will not easily escape.

Figure 12 Slotted brick that will be used in the siliconizing process

The author used sand as the source of the silica. In order for easy diffusion coating, the sand must be fine in size. In order to get finer and homologous particle size distribution, sieving is carried out. The sand is sieved until 212µm. This is because for the next sieve opening (150µm), there was hardly any sand that the author can get. As compared to other materials preparation, most of the time spent is on sand preparation as it takes quite some time to get sand with the desired size particle and right amount. Apart from that, the sand that is going to be sieved needs to be dried first for easy separation.

Figure 13 Sieving process

Figure 14 Sieve shaker

3.2.2.3 Siliconizing (heating process)

To carry out the siliconizing experiment, the brick slot is filled up with sieved sand and the sample is immersed in the middle of the sand lump. The furnace is set to have working temperature of 1000°C for 4 hours. The parameters used are based on the literature review.

3.2.2.4 Microscopic examinations and analysis after the experiment

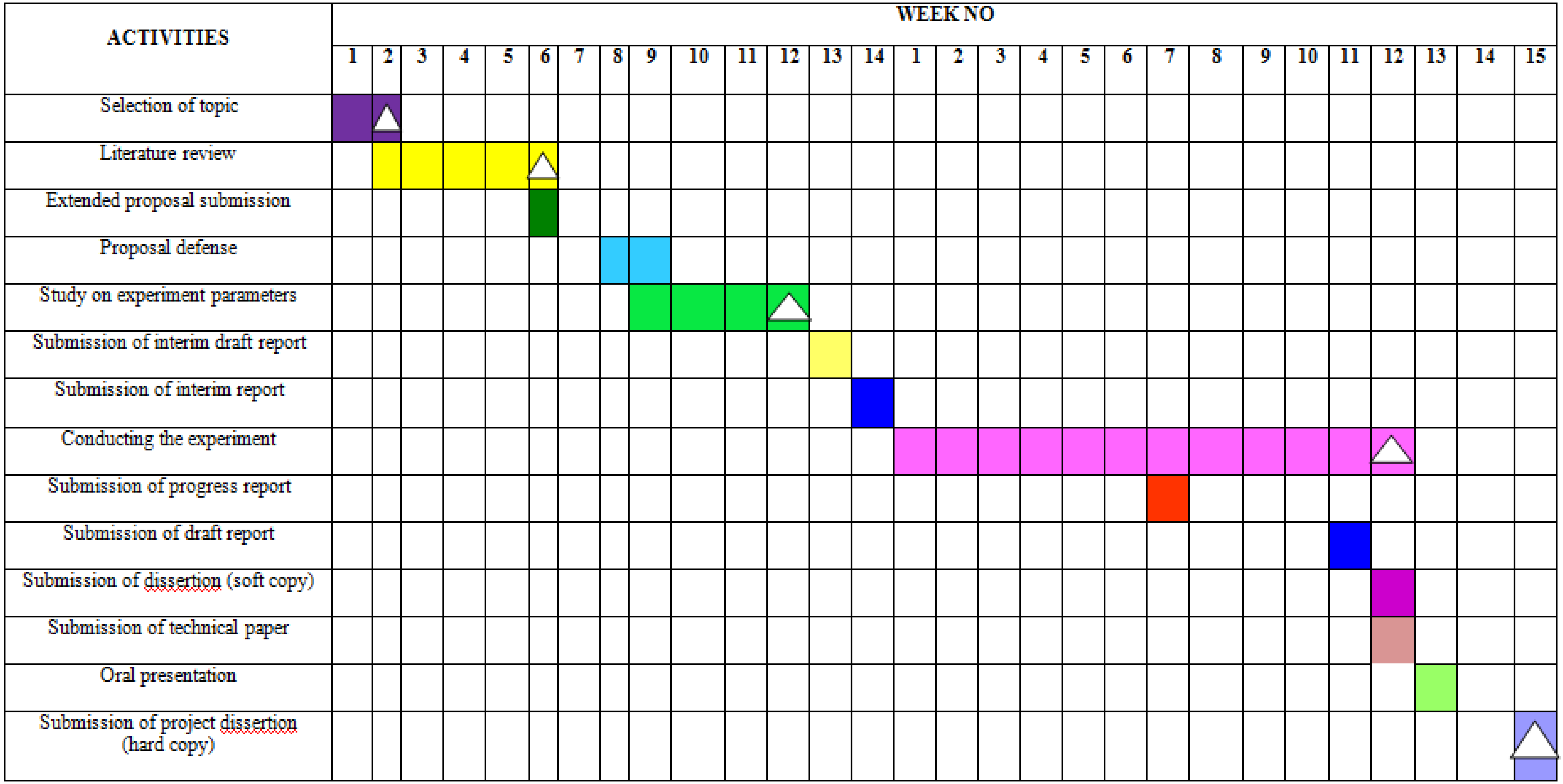
After the siliconizing, the weight and height of the sample is measured. The sample is cross-sectioned and the microstructure is evaluated using optical microscope. Apart from that, the sample also undergoes FESEM testing for further analysis on microstructure and its chemical composition. All the data result can be referred in next section of Results and Discussion.

3.3 KEY MILESTONE AND GANTT CHART

Based on the university guideline, the final year project must be carried out in two semesters, which is around 29 weeks. The author allocated first semester as the period where research and literature study is carried out. All the paperwork such as project proposal also was done in the first semester. The second semester was for sample preparation and experimental time. To keep up with the time frame, the author had set a key milestone as benchmark in doing the study. The key milestone was marked by white triangle in the Gantt Chart as shown is Table 2.

Table 2 shows the Gantt Chart of the study, showing much more details of the activities division and paperwork datelines in terms of week. Week 1 to week 14 of the first half of the Gantt Chart referred to first semester while the second half, from week 1 to week 15 showed the second semester of the study.

Table 2 Gantt Chart and key milestone of the study



ACTIVITIES	WEEK NO																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Selection of topic	■	△																											
Literature review		■	■	■	■	△																							
Extended proposal submission						■																							
Proposal defense								■	■																				
Study on experiment parameters									■	■	■	△																	
Submission of interim draft report													■																
Submission of interim report														■															
Conducting the experiment															■	■	■	■	■	■	■	■	■	■	■	△			
Submission of progress report																					■								
Submission of draft report																									■				
Submission of dissertion (soft copy)																										■			
Submission of technical paper																										■			
Oral presentation																											■		
Submission of project dissertion (hard copy)																													△

CHAPTER 4: RESULT AND DISCUSSION

This section is further divided into four categories, which are

- The sample before and after the siliconizing.
- Comparison of the height and weight of the sample.
- The microstructure of the sample using optical microscope.
- FESEM testing and analysis.

4.1 THE SAMPLE BEFORE AND AFTER THE SILICONIZING

Before the experiment, the metal sample is ground and polished to remove outer corroded layer. Figure 17 shows sample before the siliconizing process takes place. After siliconizing, coating layer is produced as shown in Figure 18 and 19. The coating layer produced is just like what being described in the literature review. The layer produced was brittle, weakly adherent to substrate, porous and easily removed after sectioning. However, the interesting part is that the thickness layer was even and homogeneous.

Figure 15 Sample before siliconizing

Figure 16 Sample after siliconizing (front)

Figure 17 Sample after siliconizing (back)

Figure 18 Sample after cross-sectioned

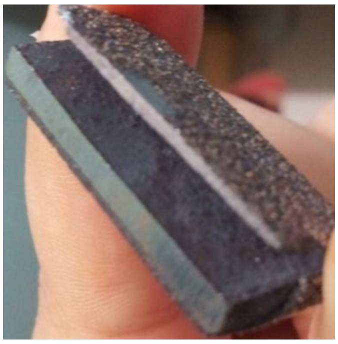


Figure 19 Detached coating layer

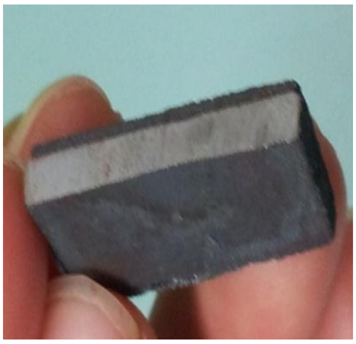


Figure 20 Top metal layer after coating layer is detached

In the beginning, it is proposed to carry out mechanical testing on the coating layer which is hardness test and scratch test. However due to natural of the coating layer, (porous and uneven surface), the scratch test and hardness test cannot be carried out.

4.2 COMPARISON OF HEIGHT AND WEIGHT OF THE SAMPLE

The height and weight of the sample before and after the siliconizing process is measured in order to know the weight and thickness of the coating layer produced. The weight is measured using analytical balance while the thickness is measured using vernier caliper. The values are summarised as follows:

- Weight before siliconizing: 15.89g
- Weight after siliconizing: 17.73g
- Weight of the layer produced: 1.84g

- Height before siliconizing: 2.96mm
- Height after siliconizing: 4.48mm
- Height of the layer produced: 1.52mm

4.3 THE MICROSTRUCTURE OF THE SAMPLE USING MICROSCOPE

In order to evaluate the microstructure of the coating layer produced, optical microscope is used.
Figures below show some microstructures of the layer.

Figure 21 Circle shows sample point at the interface

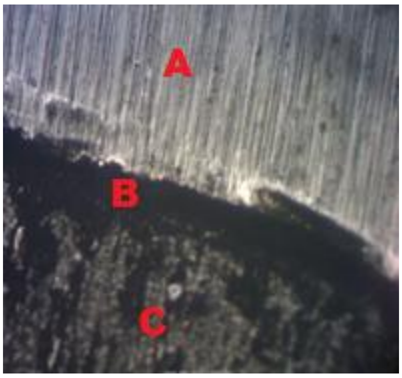


Figure 22 Microstructure of the sample at the interface of metal and coating layer where microstructure is evaluated (50x)

Based on Figure 24, it can be seen that at the interface of the metal and coating layer there are three sections. Section A is the metal itself, section B is the oxide layer formed due to high temperature and section C is the coating layer.

Figure 23 Circle shows sample point on coating layer where microstructure is evaluated

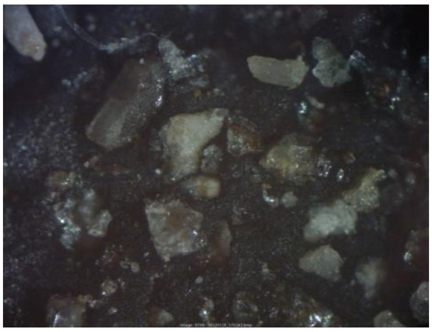


Figure 24 Microstructure of the sample at the top of the coating layer (50x)

The top coating layer contains sand grains that also diffuse during formation of coating layer. This explains why the top coating layer surface is rough.

Figure 25 Circle shows sample point without the coating layer where microstructure is evaluated

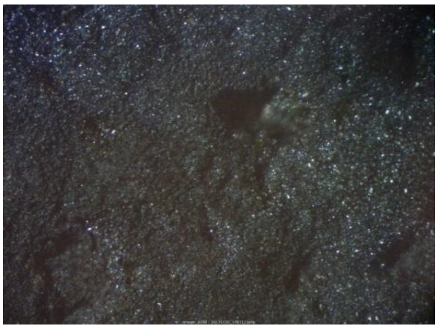


Figure 26 Microstructure of the metal sample when the coating layer is detached.(50x)

The surface region at the back of the coating layer and at the top of the metal when the layer is detached is quite same; the surface is smooth compared to the top coating. This region is the oxide region that formed due to high temperature heating.

Figure 27 Circle shows sample point on chipped coating layer where microstructure is evaluated

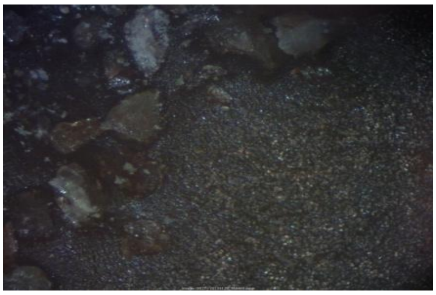


Figure 28 Microstructure of the sample at chipped coating layer (50x)

4.4 FESEM TESTING AND ANALYSIS

In order to know the surface features, size and shape of the features, chemical composition and crystalline structure, FESEM testing is used as it can visualize very small topographic details on the coating layer surface. Figures and tables below show the microstructures and chemical composition of the coating layer.

4.4.1 Surface of the metal without the coating layer (detached layer).

Figure 29 Surface of the metal without the coating layer (detached layer)

For the surface of the metal without the coating layer (as shown in Figure 29), the microstructure of the surface features with magnifications of 200x and 1000x are shown in Figure 30 and Figure 31 respectively.

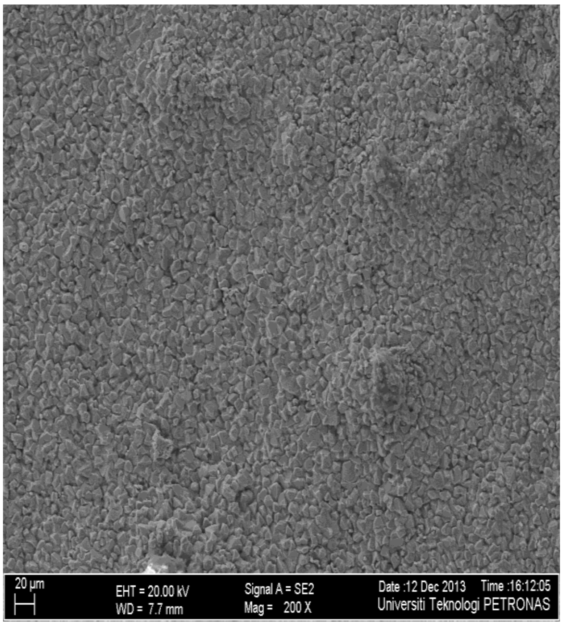


Figure 30 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the surface of the metal with detached coating layer . Magnification: 200x.

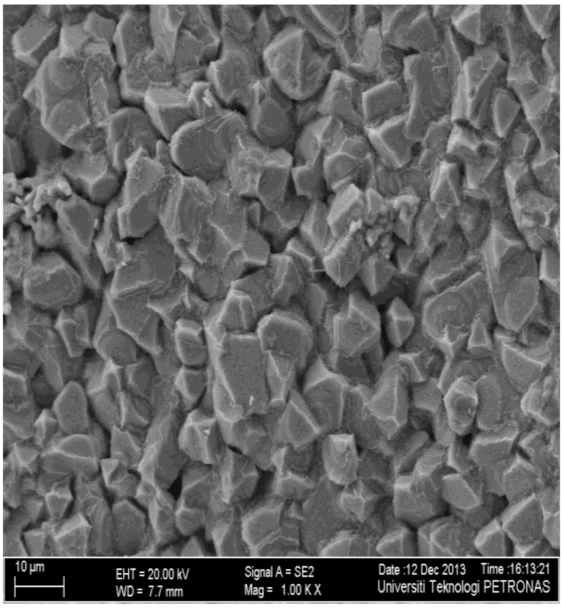


Figure 31 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the surface of the metal with detached coating layer. Magnification: 1000x.

In order to know about elemental information and chemical composition of the metal surface without the coating layer, Energy Dispersive x-ray spectroscopy (EDX) which is coupled with FESEM is used. Graph and table below show the element and chemical composition for Spectrum 1 of the metal surface with detached coating layer.

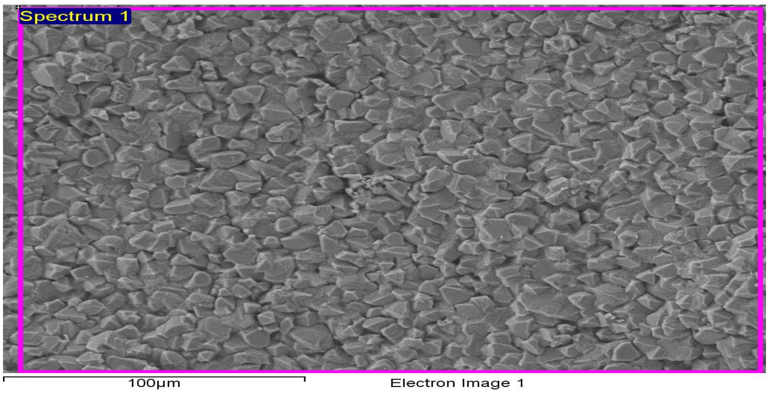


Figure 32 Spectrum 1 shows the surface region of the microstructure where the EDX is performed.

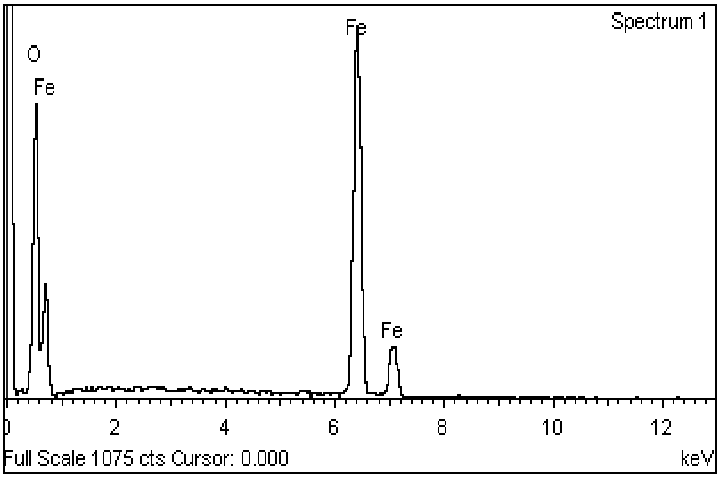


Figure 33 EDX result for Spectrum 1.

Table 3 Element present in Spectrum 1 together with their respective weight% and atomic%

Element	**Weight%**	**Atomic%**
O K	29.47	59.33
Fe K	70.53	40.67
Totals	100.00	

EDX line profile analysis in Figure 33 indicated that there are presences of Fe and O, coming from SiO_2 in the metal surface with detached coating layer. Fe and O element confirmed the surface is an oxide layer. The weight% and atomic% of the elements are shown in Table 3.

4.4.2 Coating layer (Front)

Figure 34 Front side of the coating layer where testing is carried out.

Both figures below are field emission scanning electron micrograph of front side of the coating layer (as shown in Figure 34), which shows its surface morphology. For the front side coating layer, the microstructure of the surface features with magnifications of 100x and 1000x are shown in Figure 35 and Figure 36 respectively. In Figure 35, we can see the sand grain also diffuse and form the front side of the coating layer.

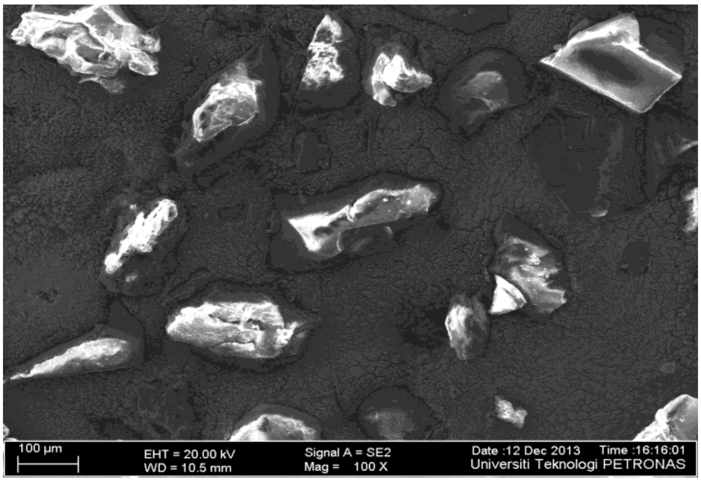


Figure 35 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the front side of the coating layer. Magnification: 200x.

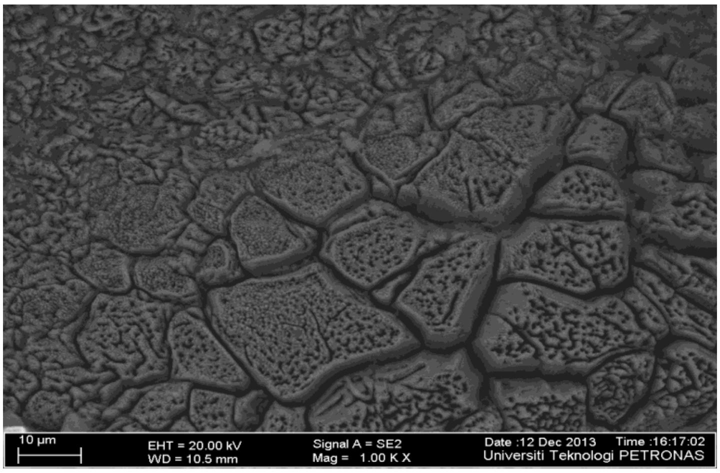


Figure 36 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the front side of the coating layer. Magnification: 1000x.

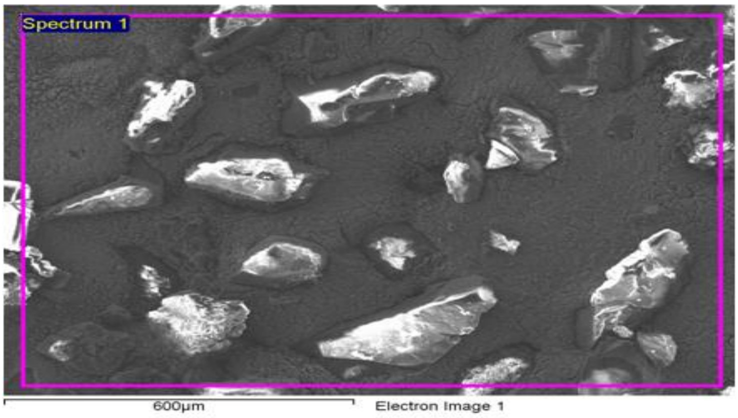


Figure 37 Spectrum 1 shows the surface region of the front coating layer microstructure where the EDX is performed.

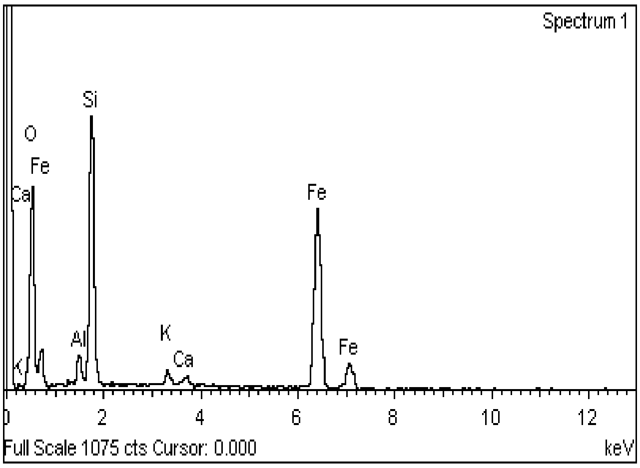


Figure 38 EDX result for Spectrum 1.

Table 4 Element present in Spectrum 1 together with their respective weight% and atomic%.

Element	Weight%	Atomic%
O K	35.32	59.16
Al K	1.72	1.71
Si K	17.99	17.17
K K	1.13	0.78
Ca K	0.81	0.54
Fe K	43.02	20.65
Totals	100.00	

EDX line profile analysis of the front side coating layer (Figure 40) indicated that there are presences of O (from SiO_2), Al (from Al_2O_3), Si (fromSiO_2), K (from MAD-10 Feldspar), Ca (from Wollastonite) and Fe. The elements present are consistent with the chemical composition of silica sand in Table 5 and thus, it proves that sand grains also diffuse and form coating layer at the front side.

Table 5 XRF composition of silica sand. Retrieved from Taher and Mamat (2011)

Al_2O_3 (wt.%)	SiO_2 (wt.%)	P_2O_5 (wt.%)	K_2O (wt.%)	CaO (wt.%)	TiO_2 (wt.%)	Fe_2O_3 (wt.%)
2.99	95.22	0.77	0.095	0.139	0.16	0.121

EDX testing are carried out at several other points inside the Spectrum 1 region, namely Spectrum 2, Spectrum 3 and Spectrum 4 in order to know the chemical composition at that exact point. Location of Spectrum 2, Spectrum 3 and Spectrum 4 can be referred in Figure 40, Figure 42 and Figure 44 respectively.

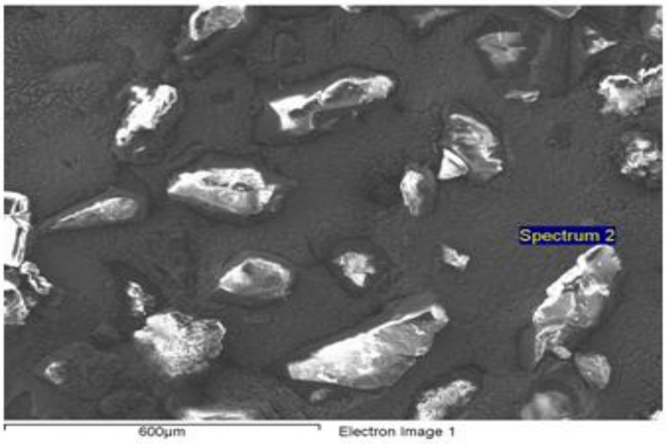


Figure 39 Spectrum 2 shows the surface point of the front coating layer microstructure where the EDX is performed.

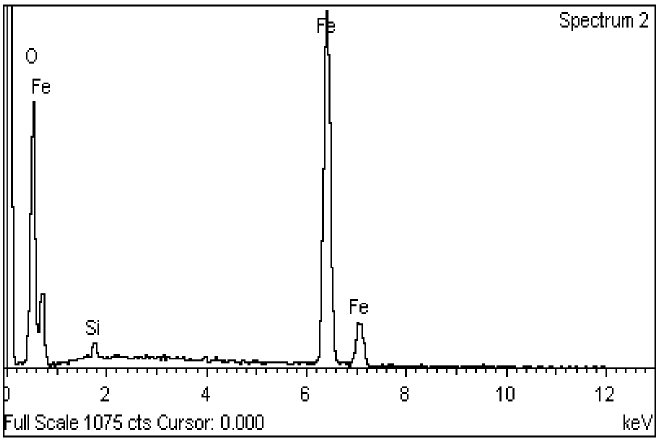


Figure 40 EDX result for Spectrum 2

Table 6 Element present in Spectrum 2 together with their respective weight% and atomic%

Element	Weight%	Atomic%
O K	28.01	57.28
Si K	0.96	1.12
Fe K	71.02	41.60
Totals	100.00	

Figure 41 and Table 6 show the elements present in that Spectrum 2 and its respective weight% and atomic%. For Spectrum 3, the details of element in that spectrum are discussed in Figure 43 and Table 7.

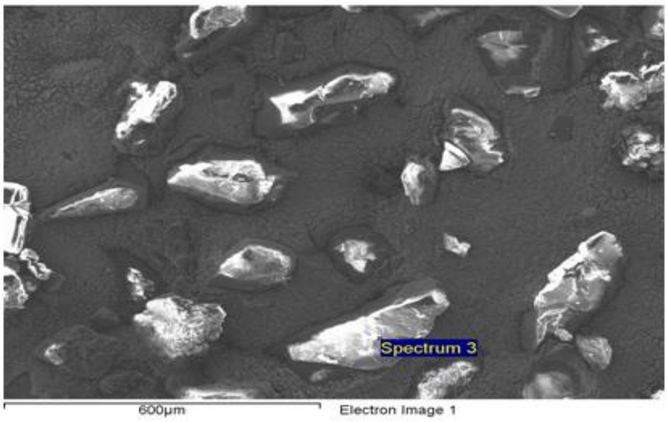


Figure 41 Spectrum 3 shows the surface point of the front coating layer microstructure where the EDX is performed.

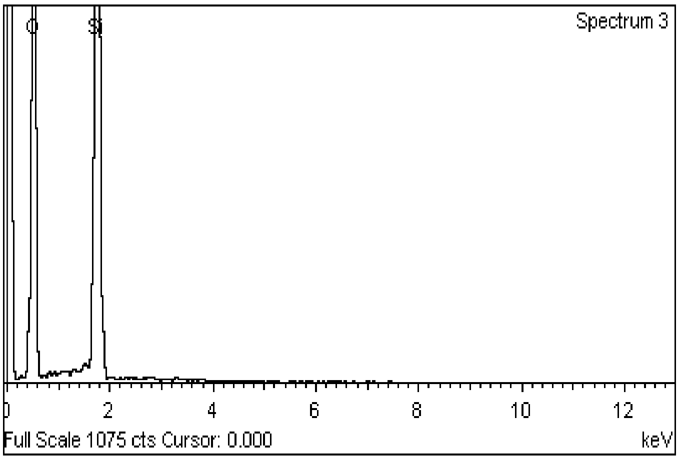


Figure 42 EDX result for Spectrum 3

Table 7 Element present in Spectrum 3 together with their respective weight% and atomic%

Element	Weight%	Atomic%
O K	65.68	77.06
Si K	34.32	22.94
Totals	100.00	

Figure 45 and Table 8 show the elements present in Spectrum 4 (can be referred to Figure 44) together with its respective weight% and atomic%.

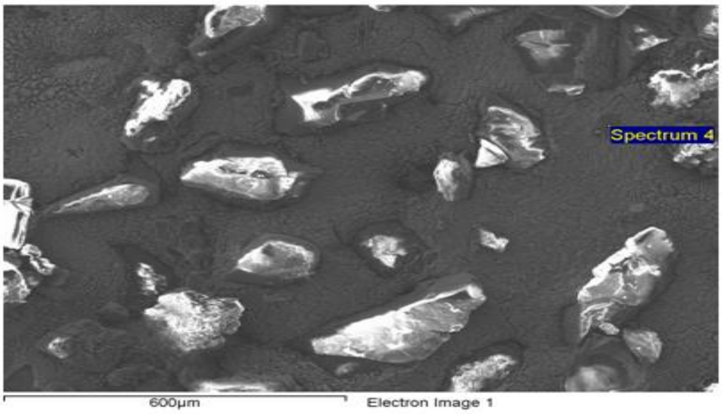


Figure 43 Spectrum 4 shows the surface point of the front coating layer microstructure where the EDX is performed.

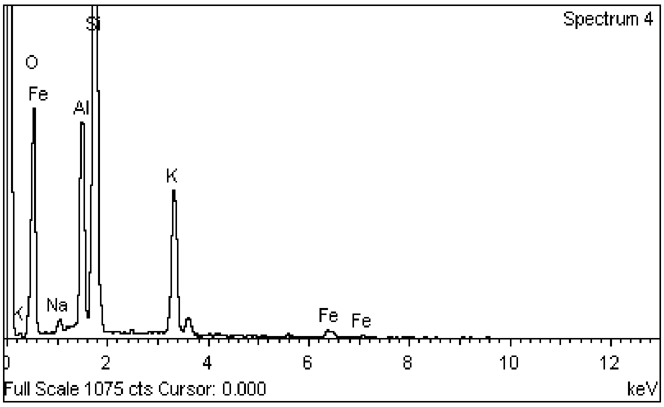


Figure 44 EDX result for Spectrum 4

Table 8 Element present in Spectrum 4 together with their respective weight% and atomic%

Element	Weight%	Atomic%
O K	49.42	64.60
Na K	0.94	0.85
Al K	8.71	6.75
Si K	29.23	21.77
K K	10.30	5.51
Fe K	1.40	0.52
Totals	100.00	

4.4.3 Coating layer (Back)

Figure 45 Back side of the coating layer where FESEM testing is carried out.

Both figures below are field emission scanning electron micrograph of back side of the coating layer(Figure 48) which displaying its surface morphology. For the back side of the coating layer, the microstructure of the surface features with magnifications of 100x and 1000x are shown in Figure 49 and Figure 50 respectively.

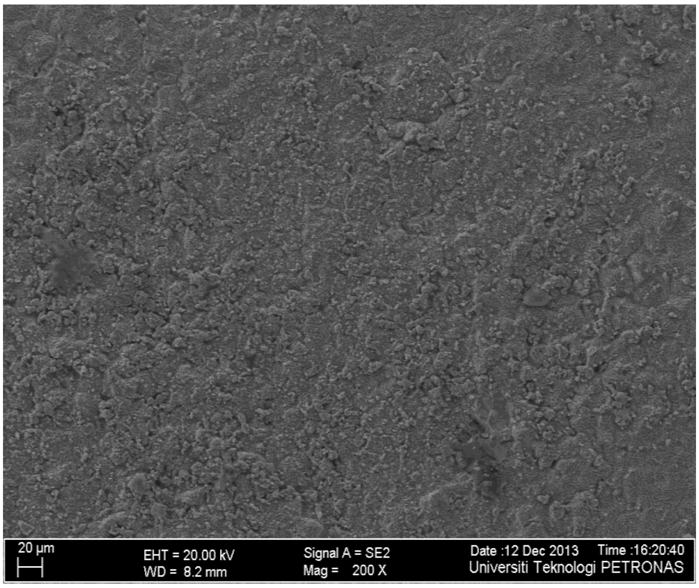


Figure 46 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the back side of the coating layer. Magnification: 200x

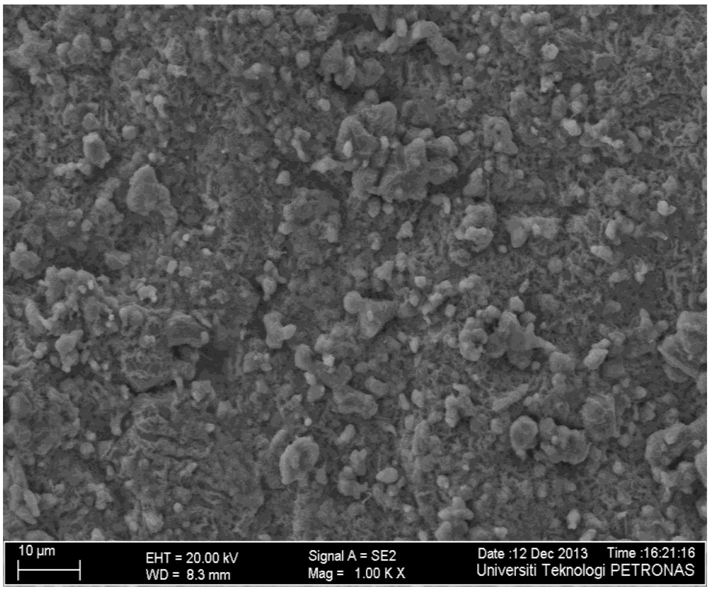


Figure 47 Morphology of mild steel after siliconizing at 1000°C for 4 hours, at the back side of the coating layer. Magnification: 1000x.

Spectrum 1 in Figure 49 indicate the region of testing while Figure 50 and Table 9 show the elements present and its respective weight% and atomic%.

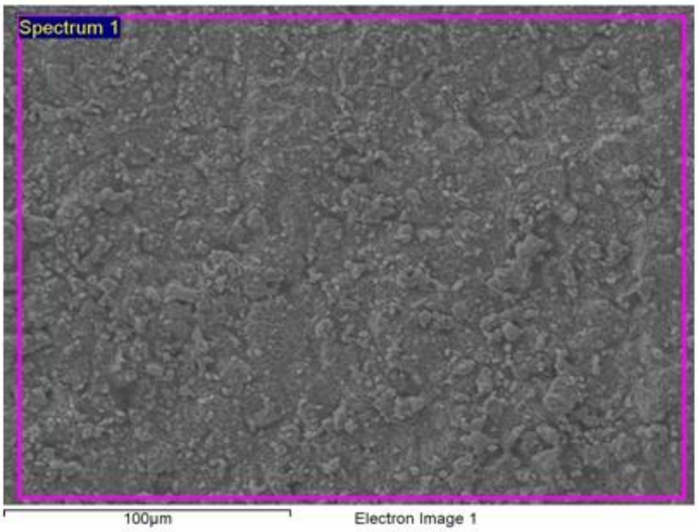


Figure 48 Spectrum 1 shows the surface region of the back coating layer microstructure where the EDX is performed.

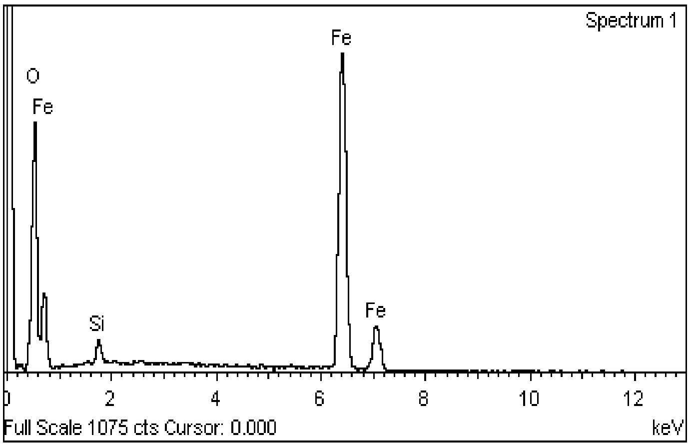


Figure 49 EDX result for Spectrum 1

Table 9 Element present in Spectrum 1 together with their respective weight% and atomic%

Element	Weight%	Atomic%
O K	29.16	58.44
Si K	1.56	1.78
Fe K	69.28	39.78
Totals	100.00	

From the analysis of microstructure and composition of FESEM testing, it showed that the diffusion of the silica only occurred at the coating layer and it did not diffuse into the metal. Thus, the metal is protected and hardened by having outer case formed by silica and oxide layer.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Siliconizing using silica sand bath depended only on sample, sand as source of silica and brick as the container. The experimental steps of this technique such as sample preparation, sieving, creating slot on the brick and heating showed that silica sand bath is the simplest method of case hardening (siliconizing) as compared to other methods such as pack carburizing, flame and induction hardening and also heating and quenching in carbon-rich medium.

The outcomes of this study showed that there was coating layer produced after the experiment. The layer produced was brittle, weakly adherent to substrate, porous and easily removed after sectioning. However, the interesting part is that the thickness layer was even and homogeneous. In order to characterise and analyse the microstructure and surface properties of the metal after siliconizing using silica sand bath, evaluation using optical microscope and FESEM testing were carried out. The result showed that the diffusion of the silica only occurred at the coating layer and it did not diffuse into the metal. Thus, the metal is protected and hardened by having outer case formed by silica and oxide layer.

5.2 RECOMMENDATIONS

There are many limitations in this study, mainly due to time constraint. In order to carry out further study on this project, use of software in determine rate of heat transfer and the temperature inside the bricks can be done for more thorough analysis. It is also recommended that during the siliconizing, apply higher pressure and higher temperature so that the silica will diffuse into the metal and binded instead of become outer case of the metal. Higher temperature and longer working time also can be used in order to increase the coating layer thickness. Apart from that, it is recommended to add in inert additives and catalyst in order to prevent sticking of grain to the sample, accelerate the process and also for dense and pore-free coating. In order to know more about the potential of the coating layer produced, mechanical testing such as hardness test and scratch test can be carried out. This is possible once the coating layer produced is dense, pore-free and has even surface.

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