



THE MECHANISM AND MICROSTRUCTURE OF SILICANIZING PROCESS ON MILD STEEL SUBSTRATE IN THE MEDIUM OF SILICA SAND

Yusnenti Fmy and Othman M.

Mechanical Engineering Department, Universiti Teknologi Petronas, Bandar Seri Iskandar, Perak, Malaysia

E-Mail: drothman_mamat@petronas.com.my

ABSTRACT

This paper presents the work carried out to determine the morphology and mechanical properties of coating deposited layer that formed onto mild steel substrate using a new silicanizing method. The result shows that the coating silicanized layer consisting of FeSi, Fe₂SiO₄, FeSiO₃ and SiO₂ phase was successfully formed on the mild steel after subjecting to heat treatment process of 1000 °C for 4 hours. This layer of ≈500µm thickness and also established that higher temperature and elongated deposition/adhesion time resulted an increase in SiO₂ concentration on the substrate (mild steel).

Keywords: silicanizing, silica sand, thin film coating, pack powder, mild steel, diffusion, deposition, adhesion.

INTRODUCTION

Surface Engineering especially surface heat treatment contributes an opportunity to improve the surface substance of mild steel and at the same time the bulk characteristics relatively unchanged. The deposition or at least an awareness of the physical, chemical properties of materials (coating-TSS/Substrate-Mild steel) and their mechanical properties and especially structure/property relationship in material substrates. Therefore, in an endeavour to establish the adequate process to deposit/adhesive coatings or alter the chemical composition of its surface, a number of experimental have been conducted in the over decade. Among these expert ways of art and so on, a diffusion process (pack siliconizing), extensively used to deposit/adhesive high-temperature corrosion-resistance coatings especially on low carbon steels [1-2]. To the knowledge of the authors, in comparability with another statement procedures of thin coating layer on metal substrates, the pack silicanizing process has the consequent characteristic benefits: large volume and inexpensive formation of diffusion coating with simply controllable thickness (temperature/time); concurrently formation of various elements such as Al, Si, Cr and Ti; distinctive deposition/ adhesion amongst the coating and metal substrate; appropriate for a broad range of shapes and size and not required to line of vision limitations [3-4].

Between miscellaneous thin coating systems, silicide coatings can acquire a compact SiO₂ scale for oxidation avoidance. In 1965, Priceman and Sama successfully developed a type of silicide coating R512E with a high level of quality and reliability, which has been operated in gas engines for the short-time high temperature applications [5-7]. Fterwards, Vilasi *et al.* [5-6] developed quaternary Nb(Ti)-T-Cr-Si (T=Fe or Co or Ni) silicide coating systems by pack cementation process, and inspected the oxidation performances of two of them. Currently, some silicide coatings altered with active elements have also been successfully developed.

Many researcher observations have been managed over many years in an endeavour to evolve a process and method that would allow significant enhancement in toughness accomplish at minimum amount of mechanical properties [2-10]. As regards the character of the processes taking place on contact surfaces during the interaction of specimens, however, there are a number of points which require clarification. As a result of examinations of contact surfaces with a scanning electron microscope it was established that, after the interrelation between the silicide coating, sample detachment occurred as the result the coatings and the interaction amongst the coatings and mild steel was attended by the coatings tend to be discrete against the basis metals. A necessary condition for adhesion properties of a material can be expected to depend on its mechanical characteristic (e.g., hardness, tensile strength, modulus of normal elasticity and elongation) at high temperature. Comparing data on the effect of temperature on hardness HV and tensile strength for uncoated substrate and coated substrate and on the coefficients of adhesion of these metals, it will be seen that the beginning of adhesion interaction between similar metals coincides with their temperature of sharp strength loss.

The aim of the work reported in this paper was investigate at forming a thin layer coating of fine TSS powder pack onto mild steel via silicanizing process at optimum temperature and time. Accordant silicanizing mechanism (chemical reaction) immersed in transforming TSS particles into thin film coating on mild steel substrate is expected to be established.

EXPERIMENTAL PROCEDURES AND APPARATUS

The rectangular mild steel of 98% (Table-1) specimen of dimension 18 mm (length) x 18 mm (width) x 5mm (thickness) were embedded in silica sand using fire clay jacket as crucible which subjected to surface hardening treatment and samples surface was ground with



series of SiC paper of 600 grit. The sample were cleaned in acetone baths and dried in air. TSS powder of 80%-90% (Table-2) purity was used in silicizing experiments with below 150 μm in size. The specimen was subjected to heat treatment in furnace at 1000 $^{\circ}\text{C}$ in 4 hr hour. After the scheduled heat treatments, the sample was cooled in situ about 25 $^{\circ}\text{C}$ in furnace.

Table-1. Chemical composition of mild steel substrate.

Element	Fe	Mn	Other
%wt	98	2.5	0.5

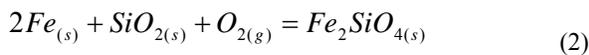
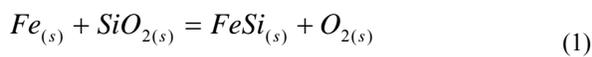
Table-2. Chemical composition of TSS.

Element	Si	P	Fe	Al	Ca	K	Other
%wt	87.2	2.99	2.98	2.87	1.11	1.03	1.52

RESULTS AND DISCUSSIONS

Mechanisms of chemical reaction of silicizing process

The silicizing process can separated into three interconnected systems: a thermodynamic equilibrium condition and the depositions between mild steel substrate surface and the SiO_2 powder pack is driven by chemical potential gradients in the solid state phase and surface reactions at the mild steel substrate to deposit the silicizing coating elements. In the pack powder (TSS) silicizing process, as $\text{Fe} + \text{SiO}_2$ is thermodynamically more stable at temperature 1000 $^{\circ}\text{C}$ for 4 hours as presented in reaction in Equation below:



Where, Fe is the metal and SiO_2 is the oxidant species. Relevant assumption for the above reactions is the chemical reaction of the system promptly reach equilibrium state and mixing the solid state atom constituents is complete is shown in Figure-1. Along continuing treatment time, some of elements react with Fe to form Fe-containing coating. As mentioned early, SiO_2 can improve the oxidation resistance of substrates by forming a vitreous SiO_2 in the surface substrate. This vitreous layer of SiO_2 has a much low density of defects, which thus acts as barrier for cations (Fe) and anions (SiO_2) produced by the ionization reactions taking place at the substrate surface.

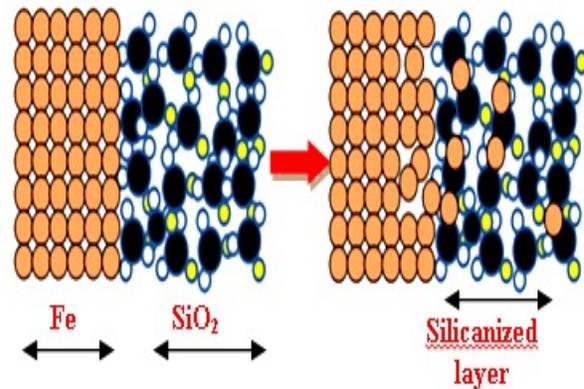


Figure-1. Model of evolution of Fe- SiO_2 growth dislocation molecules of SiO_2 into Fe compound forming silicized layer.

Mechanisms - Microstructure of silicizing process

Ideally, when SiO_2 molecules are brought into contact with substrate, the interface is very sharp. However, under sufficiently high temperature and time (1000 $^{\circ}\text{C}$ for 4 h), the lower density of vitreous silica sand (operating conditions-1000 $^{\circ}$ -1400 $^{\circ}$) and reduced of particles size as compared to crystalline form might well due to an increased concentration of such larger voids shown in Figure-2. For SiO_2 , the number and distribution of such voids depend on the time, temperature and ambient conditions in the growth process. The density of thermal silica has been shown to vary with these conditions [21]. In this study, an amount of SiO_2 deposited and diffused layers of various composition deposited on Fe (mild steel) and silicized at 1000 $^{\circ}\text{C}$ for 4 hr. Based on these results, the presenting picture of structural changes occurred (Figure-1).

The fine-particles structure of coating layers quickly recrystallines and form large particles/grains of FeSi , Fe_2SiO_4 and FeSiO_3 solid state diffusion reaction. Fe reacts with SiO_2 and nucleates particles of the phase transformation (silicates) along the silicized layer interface. In consideration of the amorphous character of SiO_2 and the requirement of structure relationship between bcc in Figure-3 and silicates phases, the position of the nucleated phase is random. The phases grain combines and form a constant layer disjoint the SiO_2 and thin coating (silicized layer). The Fe- SiO_2 reaction releases (Figure-4) unbroken Si and O that diffuse into unreacted thin layer. Considering solubility of oxygen in Fe is very low, deposition of the phase transforming occurs throughout the thin silicized layer, increasing forms round particles of the oxide.

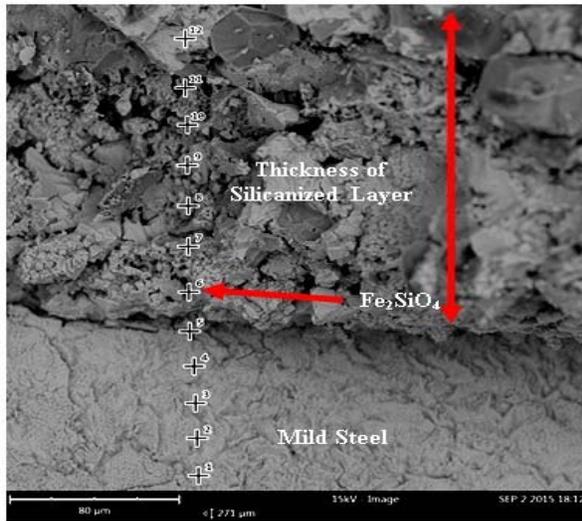


Figure-2. Spot line SEM cross-section view of the thickness silicizing layers on mild steel substrate at 1000 °C for 4 h.

Reaction product can provide adequate protection for the substrate if they are uniform and adherent; but the depletion of the protective element can degrade the mechanical properties, leading to a chemically-assisted premature failure. For this reason, most heat-resistant metal are designed or coated to produce a surface composition which upon exposure develops a protective external substrate surface, usually an oxide. The oxide acts as a diffusion barrier to the oxidant, eliminating and/or reducing the rate of reaction or scale growth by the silicizing process. When exposed to high-temperature oxidizing environments, heat-resistance mild steel initially forms small oxide nuclei of all its reactive elements. In time, however, a steady-state protective oxide overgrows the initial transient oxide to reduce the rate of further oxidation. Not all thermally grown oxides are equally protective. Various external oxides suffer cracking from stresses induced during their formation and growth (e.g., Fe_2SiO_4) allowing molecular oxygen to the mild steel surface.

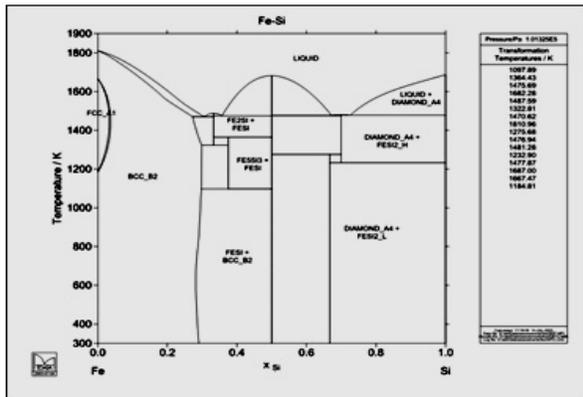


Figure-3. Fe-Si phase diagram.

Furthermore, in enhancing the thin silicized layer onto mild steel substrate, the deposition of SiO_2 at the surface layer also take the role of an important behavior. The alloying enhancement of few percent SiO_2 is persuasive to reduce the oxidation percentage to some limit by forming detached SiO_2 in the oxide layer has been reported and when SiO_2 was deposited in the layer it evolves into a good barrier in contrast to oxidation (corrosion) [19-20]. SiO_2 has no acidic solute and thereby is not attacked by an acidic melt; therefore, SiO_2 offer the potential for the resistance to acidic high temperature.

Deposition at 1000 °C for 4 hours is the optimization of experimental parameter for this work, a large number SiO_2 deposited and diffused layers of various composition deposited on Mild steel (Fe) become uniform, stable and thin silicized layer were form on the mild steel substrate. The average thickness of the pack powder mixture containing 80-90 wt.% SiO_2 resulted in deposition of $Fe-SiO_2$ is around $\approx 500\mu m$. The as-formed thin layer silicized were very amorphous but low porosity and more homogeneously (Figure-2). The $Fe-SiO_2$ gain on the substrate activates with the chemical reaction activities of the donor SiO_2 powder at the high temperature operated, generating phase transformation. When SiO_2 attain into contact with the mild steel substrates and decrease, producing in formation of SiO_2 on the surface layer of the substrate. SiO_2 compound being predominant moving species with thermal diffusion then occurs. The result of reaction of the SiO_2 with the chemically deposited mild steel substrate and their concentration is the formation of the thin silicized layer compounds is shown in Table-3. The deposited of SiO_2 in steel is very fast under this conditions which has been reported.

Therefore, Silicized deposition is an interface-limited process at the $Fe-SiO_2$ interface. The cross-sectional view SEM micrograph of the silicized layer is presented in Figure-4. The as-formed silicized layer are very brittle, and cross-sectional sample preparation for microscopic observation was not possible approximately.

Table-3. Chemical composition of Silicized Layer at 1000 °C for 4 h.

Element	Fe	Si	Al	K	P	Other
%wt	47.4	43.8	3.16	1.83	1.22	1.52

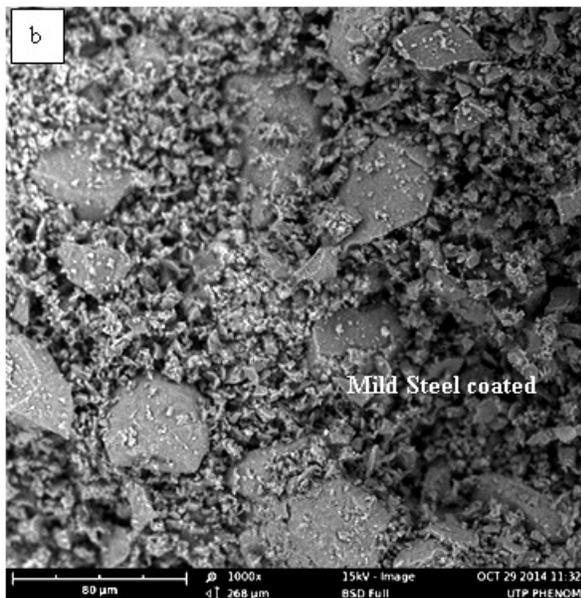
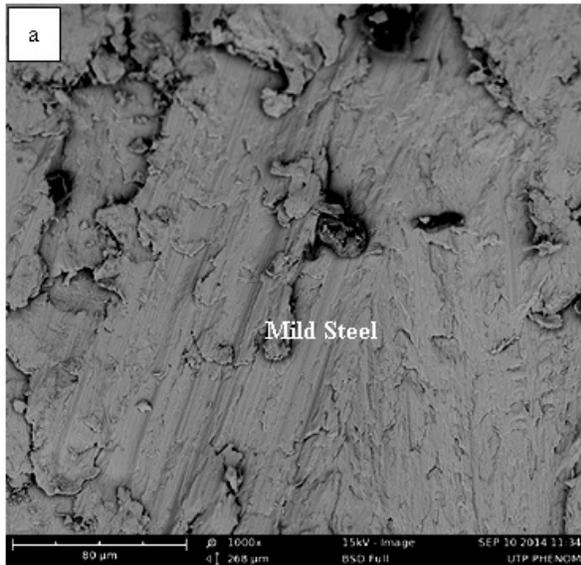


Figure-4. Surface morphology view of (a) raw material (b) the bare silicized layers on mild steel substrate at 1000 °C for 4 h.

For certain recognition of the as-formed structure, EDS-SEM analysis of several regions of the final thin silicized layer was achieved and the results it was analyzed that three different Fe-SiO₂ elements were formed. The scan-line EDS analysis in Table-4 presented the %wt elements was found to consist of 91.0 wt% Fe, 1.8 wt% Si and insignificant amounts of O₂ (less than 7.2 wt%) which can be associated to the amounts of oxygen in the mixture of SiO₂ pack powder. The above-mentioned results are in concurrence with the XRD pattern (Figure-6) obtained from the same sample. By combining the results of EDS-SEM analysis (Figure-5) and XRD

characterization it was analyzed that areas correspond to FeSi, Fe₂SiO₄ and FeSiO₃ respectively (Figure-6). Increasing the time of silicizing process resulted in the deposition of greater Fe-SiO₂ coatings. These results provide for the suggested coating mechanism: at the creation of the process there is great gradient in the Si activity that acts as the driving force for the formation of Si solid solution on the mild steel [16]

Table-4. Scan line EDS-SEM analysis cross-section %wt concentration silicizing layer at 1000 °C for 4 h.

Scan line/Element	Fe	Si	O
%wt	91	1.8	7.2

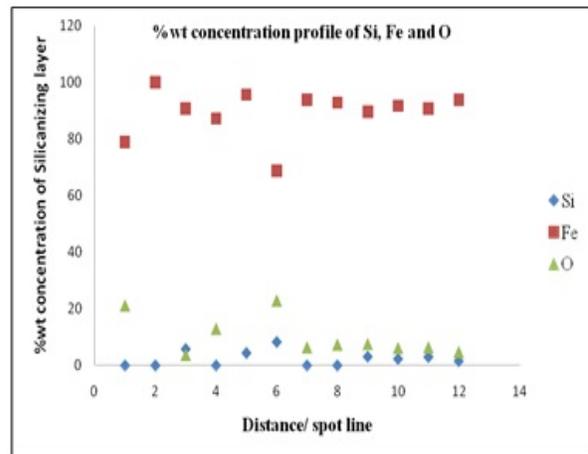


Figure-5. %wt concentration of silicizing layer of spot line EDS-SEM analysis.

Deposition at this temperature and time (1000 °C/4h) resulted in complete transformation of SiO₂ into substrate. The cross-sectional view SEM micrograph of the as deposited silicized layer is demonstrated in Figure-4. The EDS analysis results were mostly related to those acquired from previous sample for both determined regions. The only dissimilarity was that in spotted areas, the quantity of Si, Fe and O were detected (Table-4), which indicate establishment of a new Fe-SiO₂ mixture. This was confirmed by XRD analysis of the surface region (Figure-6), which showed the presence of four different phases. There were at the same as earlier (FeSi, Fe₂SiO₄ and FeSiO₃) and the fourth was SiO₂, which thermodynamically prefers its establishment. In bottom line, as stated for mechanical properties of Fe and SiO₂, all four equilibrium phases in the Fe-SiO₂ system can be created, contingent on the Fe/SiO₂ atomic (mole) ratio.

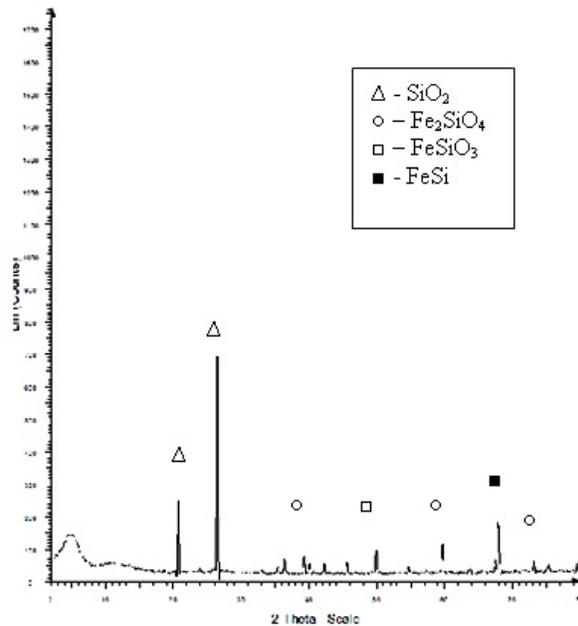


Figure-6. XRD analysis of the silicizing process showing the FeSi, Fe₂SiO₄, FeSiO₃ and SiO₂ phase at 1000 °C for 4 hours.

CONCLUSIONS

A simple and economical to alter the surface of a mild steel by silicizing process (solid state diffusion) has been proposed. The experimental test at 1000°C for 4 hours was performed, the microstructure and kinetic growth mechanism of the silicized layers were examined. The silicized layer was very adherent, homogeneous and uniformly to substrate. The results are summarized as follows.

- The Si composition concentration in the silicized layer attain 43.8 wt% in the silicizing temperature and time at 1000 °C for 4 hours. The surface layer of the sample silicized is mainly composed of FeSi, Fe₂SiO₄ and FeSiO₃ phase.
- The thickness of the silicized coating is range ≈500μm.

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REFERENCES

- [1] He D. Zhou A. Liu Y. *et al.* 2000. Cavitation Erosion and Pitting Corrosion Behaviour of Laser Surface-melted Martensitic Stainless Steel. UNS S4[J] Surface and Coating Technology, 2000, 126 (2/3): 238-255
- [2] Flis J. Tobiyama Y. Mochizuki K. *et al.* 1997. Characterisation of Phosphate Coatings on Zinc, Zinc-nickel and Mild Steel by Impedance Measurements in Dilute Sodium Phosphate Solution [J]. Corrosion Science, 39(10/11): 1757-1770
- [3] Huang, H.L., *et al.* 2006. The microstructure of siliconized type 310 stainless steel. Materials Science and Engineering, A 422(1-2): 259-265.
- [4] Ugur S. Azkan O. Senol Y. and Saduman S. 2013. Kinetics of Iron Silicide Deposited On AISI D2 Steel by Pack Method. Metal, 15:17.5.2013, Brno Czech Republic.
- [5] Vilasi M. Francois M. Brequel H. Podor R. Venturini G. Steinmetz J. 1998. Phase equilibria in the Nb-Fe-Cr-Si dydtem. J.Alloys Compd. 269 187-192
- [6] Yoon J.K. Kim G.H. Shon I.J. Doh J.M. Hong K.T. 2005. Microstructure and oxidation property of NbSi₂/Si₃N₄ nanocomposite coating formed on Nb substrate by nitridation process folled by pack silicizing process. Intermetallics, 13 1146-1156 J
- [7] Vilasi M. Francois M. Podor R. Steinmetz J. New silicides for new niobium protective coatings, J.Alloys Compd. 264 (1998) 244-251
- [8] Burnett P.J. Rickerby D.S. 1987. The relationship between hardness and scratch adhesion. Thin Solid Films, 154, 403-416
- [9] Wang J.D. *et al.* 2009. Progress in Organic Coating. 64 pg 327-338
- [10] Propovic M.M. *et al.* 2005. Corrosion studies on electrochemically deposited PANI and PANI/epoxy coating on mild steel in acid sulphate solution. Prog. Org. Coat, 52:359-365
- [11] ASM Handbook: Alloy Phase Diagrams, ASM International, Materials Park, OH, 1992
- [12] Huang H. L., *et al.* 2006. The microstructure of siliconized type 310 stainless steel. Materials Science and Engineering, A 422(1-2): 259-265
- [13] Yoon J.K. Kim G.H. Shon I.J. Doh J.M. Hong K.T. 2005. Microstructure and oxidation property of NbSi₂/Si₃N₄ nanocomposite coating formed on Nb substrate by nitridation process folled by pack silicizing process. Intermetallics 13 1146-1156 J
- [14] Fukomoto M. *et al.* 2012. Formation of Si diffusion layer on stainless steels and their high temperature corrosion resistance in molten salt. Corrosion Science 56(0): 105-113



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- [15] Matychak Y. S., *et al.* 1998. Diffusion processes and mechanics of materials. *Materials Science* 34(3): 304-314.
- [16] Udovitskii V. 1990. Mechanism of pore formation in diffusion layers. *Materials Science* 25(5): 543-546.
- [17] Lyakhovich L. S., *et al.* 1971. Siliconizing steel in liquid media. *Metal Science and Heat Treatment* 13(8): 647-649.
- [18] Chen F.S. and Wang K.L. 1999. The kinetics and mechanism of multi-component diffusion on AISI 1045 steel. *Surface and Coatings Technology* 115(2-3): 239-248.
- [19] Ivanov V.E. and Samsonov G.V. 1995. Vacuum Siliconizing of Refractory Metals. *Diffusion Cladding of Metals*. Springer US; 29-35.
- [20] Hai Li Yang. 2011. Growth Kinetics and Microstructure of Siliconized Layer by Molten Salt Electrodeposition. *Advanced Materials Research*; 214; 434.
- [21] Taft E.A. 1978. *J. Electrochem.Soc.* 125,968