Silicanizing Process On Mild Steel Substrate by Using Tronoh Silica Sand: Microstructure, composition and coating growth

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Abstract. A new Silicanizing process on formation of coating on mild steel using Tronoh Silica Sand (TSS) is presented. The process was performed in the temperature range 1000-1100°C and with varying deposition time of 1-4 hours. Influence of the layer and the substrate constituents on the coating compatibility of the whole silicanized layer is described in detail. Morphology and structure of the silicanized layer were investigated by XRF, XRD and SEM. It is observed that diffusion coatings containing high concentrations of silica which profile distribution of SiO₂ in the silicanized layer was encountered and the depth from the surface to the substrate was taken as the layer thickness. The results also depicted that a longer deposition time have tendency to produce a looser and larger grain hence rougher layer. The silicanized layer composed of FeSi and Fe₂SiO₄ phases with preferred orientation within the experimental range. It is also found that longer deposition time and higher temperature resulted in an increase in SiO₂ concentration on the substrate (mild steel).

1. Introduction

Mild steel is used in large tonnages in marine applications, transportation, construction and metal-processing equipment. However these steels are vulnerable to very high corrosion rates in aggressive solutions and atmospheres due to their nature of limited alloying content [1-2]. Protective coatings are typically employed to protect the steel surface from corrosion. Because of its importance as an engineering material, there have been unending efforts by researchers to prevent its degradation caused by its susceptibility to corrosion attacks. Diffusion coatings and the corresponding industrial production processes such as siliconizing [3-5] were developed about 50 years ago for the purpose of preparing corrosion-resistant surfaces on unalloyed or low alloyed steels. Their composition did not exceed the limits of solid solutions. The preconditions for such a finishing process are that the alloying elements should have relative high diffusion rate into the substrate, the substrate should be insensitive to structural changes during the heat treatment preparation, and the diffusion rate of the coating components into the substrate during the application should be low. The last condition was fulfilled at that time because the coated substrate materials were not developed for long duration at high temperature applications. The coating then grows by solid-state diffusion of the deposited element through the substrate, which results is an excellent chemical compatibility with the substrate [6].

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Among various methods used for the diffusion coating, the surface siliconizing has been extensively studied. This process produces hard silicide layers with excellent chemical resistance at high-temperatures. The powder siliconizing (or pack cementation) is a relatively inexpensive method to modify the surface of mild steel. It simply consists of embedding the sample in a powder and of a heating to an appropriate temperature. It is known that siliconizing performed at high temperature is a diffusion-controlled process. It is very important to establish the process parameters that effect the siliconizing in order to select process parameters to attain the desired thickness of silicide layer and properties [7]. Depending on temperature and time of the process, as well as on the composition of the substrate, surface layers containing various phases can be formed [8].

This work is concerned with the depositing of SiO$_2$ using a pack siliconizing process using Tronoh silica sand (TSS) as a SiO$_2$ source. In this study, SiO$_2$ powders (TSS) is used as a depositing source, rather than their alloys, as using these powders was not only more economical, but also technically advantageous, providing an easy way to alter pack compositions and hence their depositing properties [9]. Pack siliconizing is an easy technique which can be adopted to components of any dimension provided furnaces and retorts of bigger dimensions are available. In the pack process the mechanism of coating depends on in-situ reaction and partly on reduction as well. Therefore, it is visualised that intimate contact of the coating element with the substrate will give rise to uniform and thick coatings besides other physio-chemical considerations.

2. Experiment Procedures and Apparatus
Mild steel substrates of 98.0% Fe (Table 1) were assembled in packs consisting of the TSS and Fire Clay Jacket as crucible were used in this "Siliconizing process". The mild steel substrates are rectangular specimen of 18 mm x 18 mm x 5mm dimension and sample’s surface was ground with series of SiC paper of 600 grit. The substrate was cleaned in acetone baths and dried in air. TSS powder of 80%-90% purity was used in siliconizing experiments of average size below 150 µm. The substrate was subjected to heat treatment in furnace at 1000°- 1100°C for 1-4 hr. After the scheduled heat treatments, the sample was cooled in situ to 25°C.

| Table 1. Chemical Composition Mild Steel substrate. |
|--------------------------------------------------|
| Element  | %wt |
| Fe       | 98  |
| Mn       | 0.25|
| Na       | 0.32|
| Si       | 0.242|
| Cu       | 0.239|
| Gd       | 0.155|
| Other    | 0.794|

3. Result and Discussion
Figure1 shows a typical SEM cross-sectional image of the coating layer and EDS analysis by siliconizing process at 1000-1100°C for 1-4 hour. It can be seen that considerable amount of SiO$_2$ has penetrated into the substrate to a depth of about 300-700µm. The coating is solid and free of voids.
except for a few flakes on the surface. The concentration profiles of SiO$_2$ is illustrated in Table 2. The table shows that the amount of SiO$_2$ at the edge of the coated layer is about 9.79 – 54.1 by weight. As can be seen, the SiO$_2$ concentrations vary steadily across of this layer to the surface and deposited into the substrate, which led to the formation of uniform coating layers rich in SiO$_2$. As the experimental temperature increases, more SiO$_2$ is coated on the substrate, resulting in an increase in film thickness.

During the deposition (adhesion) of SiO$_2$ in the mild steel, the relationship between the change in thickness of the silicide layers and the temperature and the duration of the deposition impregnation is shown in Fig.1a(i) -1c(i). With an increase in temperature and process time there is an increase in the thickness of the layers is shown in Table 2. An increase in the content of SiO$_2$ in the reaction, the thickness of silicide coatings diminishes. Deposition makes it possible to form a composition and structure corresponding to required properties in the surface layers of components at relatively low costs.

On the cross sections of silcanized layer, there are two distinct regions at silcanized surface layer. There are: (1) compact coating layer Figure 1a(i) and (ii) surface layer which includes porous structure (Fig. 1b(i)). After the interaction between SiO$_2$ coatings and mild steel, specimen separation occurred through the coatings, whereas the interaction between these coatings and mild steel was followed by the coatings becoming detached from the base metal [15-18]. The chemical potential gradients of the different elements across the coating-substrate interface, inherits interdeposition phenomena and these effects becoming dominant at elevated temperatures is shown in Figure 1a (i)-1c(i).
Figure 1. (a) SEM image and (ii) EDS analysis for Silicanized layers on mild steel at 1000 °C for 4 hours. 

Subsequently, elements from substrate may diffuse through the coating, reach the external surface and form protective layer. Conversely, interdeposition may also effect the structure of the subcoating zone in the surface substrate and alter its mechanical properties as shown in Fig. 1a(i) -1c(i) which were classified into two different phases; the substrate with FeSi and Fe₂SiO₄ phase. Based on these observations formation of such phases with signified brittle layer in nature becoming crack initiation sites during for propagation. These effects, can be very critical in the case of components with thin silicanized layer.

The phase diagram [13] is used to predict the propable phase composition in each individual case, assuming that there is a well-defined relation between the distribution of the saturating element in the zone, the probable phase-formation sequence and also possible formation of various compounds and solid solution that may exist, in principle, in the diffusion zone, and to determine the phase concentration. Fig 3-5 shows the presence of the FeSi and Fe₂SiO₄ structure in small peak at the XRD pattern. It is reported that further deposition of Si leads to progressive formation of Si-richer silicides (Fe₅Si₃ – FeSi – FeSi₂) [13]. A layer of greater thickness, but with a lower concentration of diffusing element SiO₂ is formed on the surface on substrate. It has been observed that a shallower depth of penetration and a higher concentration of SiO₂ was be deposited can been seen on Table 2. In our opinion, this associated with the presence of a stagnant zone which serve as the deposition-element carrier (adhesion), comes out of equilibrium. We observed that the probability conditions favour the deposition of silicanized layer which will deviate from the equilibrium conditions which increases with increasing SiO₂ content.
Table 2. Thickness of silicanized layer and SiO$_2$ wt% concentration profile in the mild steel substrate and process condition.

| Experiment | Holding Temperature (°C) /time (hour) | Thickness of silicanized layer (µm) | SiO$_2$ (%wt) |
|------------|---------------------------------------|------------------------------------|--------------|
| Experiment 1 | 1000°C/ 1 h | Non-uniform thin layer | 9.76 |
| Experiment 2 | 1000°C/ 4 h | ≈500 | 43.8 |
| Experiment 3 | 1100°C/ 1h | ≈700 | 53.7 |
| Experiment 4 | 1100°C/ 2h | ≈300 | 54.1 |

X-ray diffraction pattern of the layer of the silicanized samples, exhibit the presence of FeSi and Fe$_2$SiO$_4$ phases (Figures 3-5). According to the Fe-Si phase diagram [13], the infusion of Si first turns Fe into a phase of B2 structure with about 5wt% Si and then into FeSi of BCC_B2 structure (Fig.2). This was consistent with the present results. Although the substrate was mild steel, its characteristic peaks were small, indicating that a rather thick silicanized layer was formed. Two uniform and distinct layers can be observed. The phase composition starts to change from the surface and the changes spread into the depth in the deposition direction. The optimal temperature sand time of the process is between 1000-1100°C and 1-4 hour, respectively. The most stable phases are FeSi and Fe$_2$SiO$_4$. Under these conditions the thickness of the layer is in the range of 300-700µm. The structural stability of coatings is also an important factor if they are to maintain their protection qualities over extended period of time at high temperatures. Coating degrade not only by losing scale-forming elements to the surface, but also by deposition (adhesion) with the substrate. These can associating with substrate additional problems, such as the formation of topologically close-packed phases below the coating, which cause embrittlement of the substrate.
Figure 3. XRD pattern of the coating showing the FeSi and SiO$_2$ structure at 1000°C/4h.

Figure 4. XRD pattern of the coating showing the Fe$_2$SiO$_4$ at 1100°C/1h.

Figure 5. XRD pattern of the coating showing the Fe$_2$SiO$_4$ at 1100°C/2h.
4. Conclusion
A simple and inexpensive method to modify the surface of mild steel by silicanizing using Tronoh silica sand (TSS) has been established. The SiO$_2$ concentration in the silicanized layer reaches 4.79 – 54.1 wt% in the silicanizing temperature range of 1000°C to 1100°C for 1 hour to 4 hour. The thickness of the silicide coatings increases with silicanizing temperature and time. The measured silicanized layer from this study was 300 µm -700µm. Silicanized-coating layer formed on the mild steel substrate were compact, homogenous, smooth and porosity free, with significant regularities in their thickness. EDS analysis showed that the siliconized-coating layer comprised of FeSi and Fe$_2$SiO$_4$ phases.

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References
[1] Sindu T S, Agrawal R D, and Prakash S 2005 Surface Coating Technology Vol.198 pp. 441-6
[2] Qian M, McIntosh Soutor A, Hui Tan X, Ting Zeng X and Wijesinghe S L 2009 Two-part epoxy- silicone hybrid corrosion protection coatings for carbon steel Thin Solid Films 517 5237-5242.
[3] Fry A, Stahl Eisen 1923 Stahl Und Sonderstahl Kruppshre 43 1040
[4] Oknow M G and Moroz L S 1941 J.Tech.Phys 11 493-606
[5] Schneider A and Hesse H 1940 Z.Electrochem 46 279
[6] Negadailov A I, et al 1975 Industrial experience in acceptance of diffusion siliconizing of expansion tooling in production Chemical and Petroleum Engineering11(1): 53-55
[7] Khisaeva Z F and Kuzeev I R 2004 Effect of Siliconizing on the Low-Cycle Fatigue of Steel Metal Science and Heat Treatment46(9-10): 436-439
[8] Li X Y, Taniguchi S, Matsunaga Y, Nakagawa Y K, Fujita K 2003 Intermetallics 11 143
[9] Koo C H, Yu T H 2000 Surface Coating Technology 126 171
[10] Xiang Z D, Rose S R, and Datta P K 2003 Materials, Chemistry and Physics 80 482
[11] Wang J D, et al 2009 Progress in OrganicCoating 64 pg327-338
[12] 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
[13] ASM Handbook: 1992 Alloy Phase Diagrams, ASM International Materials Park OH
[14] Huang H L, et al 2006 The microstructure of siliconized type 310 stainless steel Materials Science and Engineering A 422(1–2): 259-265
[15] Yoon J K, Kim G H, Shon I J, Doh J M, Hong K T 2005 Microstructure and oxidation property of NbSi$_2$/Si$_3$N$_4$ nanocomposite coating formed on Nb substrate by nitridation process folled by pack siliconizing process Intermetallics 13 1146-1156 J
[16] Fukumoto M, et al 2012 Formation of Si diffusion layer on stainless steels and their high temperature corrosion resistance in molten salt Corrosion Science56(0): 105-113
[17] Matyuch Y S, et al 1998 Diffusion processes and mechanics of materials Materials Science 34(3): 304-314
[18] Udovitskii V 1990 Mechanism of pore formation in diffusion layers Materials Science25(5): 543-546
[19] Lyakhovich L S, et al 1971 Siliconizing steel in liquid metal Metal Science and Heat Treatment13(8): 647-649
[20] Chen F S and Wang K L 1999 The kinetics and mechanism of multi-component diffusion on AISI 1045 steel Surface and Coatings Technology115(2–3): 239-248