



Effect of Siliconizing (Thermochemical Treatment) on the Corrosion and Wear Behaviour of Heat-Treated Low Carbon Steel

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Abstract

The effect of siliconizing on the corrosion behavior of heat-treated low carbon steel was analyzed. The steel was siliconized from 800°C to 1000°C with siliconizing time of 1 to 5 hours. Hardness test was carried out to determine the optimized condition. The corrosion behavior was studied by varying HCl from 0.5 to 2.5M with time of 15 to 90 days. The results obtained showed that optimized hardness values were obtained by siliconizing at 1000°C for 3 hours. Corrosion rate increased with increase in concentration of HCl from 0.5 to 2.0M. The siliconized sample showed lower corrosion rate when compared with the unsiliconized sample. The surface treatment (siliconizing) offer some corrosion protection to the mild steel. The wear rate was raised with increase in applied load and sliding speed.

1. Introduction

Corrosion is the gradual deterioration of materials due to interactions with their environments. Corrosion of most metals and many materials for that matter is inevitable. While primarily associated with metallic materials, all types of materials undergo corrosion or degradation, and this is a function of time, the circumstances and environment where the material is put to use [1]. Thus, polymeric materials, ceramics, noble metals such as platinum, gold, silver e.t.c all undergo corrosion processes. While some are very slow to corrosion process as a result of their inertness, some form protective covering around themselves and hinder further corrosion by a mechanism called passivation. Corrosion is both costly and dangerous. Billions of dollars are spent annually for the replacement of corroded structures, machinery, and components. Premature failure of bridges or structures due to corrosion can also result in human injury, loss of life, and collateral damage. Taking all these factors into account, it becomes obvious why those persons involved with the design and/or maintenance of structures and equipment should have a basic understanding of the steel corrosion process [2]. Steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions.

Surface hardening is a process which includes a wide variety of techniques for improving the wear resistance of parts without affecting the softer, tough interior of the part. This combination of hard surface and resistance to breakage upon impact is useful in parts such as a cam or ring gear that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Furthermore, the surface hardening of steel has an advantage over through

hardening because less expensive low-carbon and medium-carbon steels can be surface hardened without the problems of distortion and cracking associated with the through hardening of thick sections [3]. There are two distinctly different approaches to the various methods for surface hardening [4]:

- i. Methods that involve an intentional build up or addition of a new layer
- ii. Methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions

Surface hardening methods includes the use of thin films, coatings, or weld overlays (hard facings). Films, coatings, and overlays generally become less cost effective as production quantities increase, especially when the entire surface of work pieces must be hardened [5]. The fatigue performance of films, coatings, and overlays may also be a limiting factor, depending on the bond strength between the substrate and the added layer. Fusion-welded overlays have strong bonds, but the primary surface-hardened steels used in wear applications with fatigue loads include heavy case-hardened steels and flame- or induction-hardened steels. Nonetheless, coatings and overlays can be effective in some applications [5]. With tool steels, for example, TiN and Al₂O₃ coatings are effective not only because of their hardness but also because their chemical inertness reduces crater wear and the welding of chips to the tool [5]. Surface hardening focuses exclusively on the second group of methods, which is further divided into diffusion methods and selective hardening methods [6]. Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen, or boron [7]. Diffusion methods allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened. In contrast, selective surface hardening methods allow localized hardening. Selective hardening generally involves transformation hardening (from heating and quenching), but some selective hardening methods (selective nitriding, ion implantation and ion beam mixing) are based solely on compositional modification [8].

Siliconizing involves the diffusion of silicon into metal surfaces for the enhancement of hardness and wear resistance. Siliconizing is most often applied to tool steels that have already been hardened by heat treatment. Siliconizing techniques include metallizing, chemical vapor deposition, and pack cementation [3]. The siliconizing process can be separated into three interconnected systems: a thermodynamic equilibrium condition and the depositions between mild steel substrate surface and the Si powder pack is driven by chemical potential gradients in the solid-state phase and surface reactions at the mild steel substrate to deposit the siliconizing coating elements. The pack powder (TPP) siliconizing process, i.e. Fe + Si is thermodynamically more stable at temperature 1000°C for 4 hours as stated in Equation (1).



2. Methodology

The materials used for the work was, RST 35 grade steel rods of 18 mm diameter and it was obtained from National Metallurgical Development Centre, Jos (see Table 1). The silicon and HCl acid were obtained from a chemical shop in Onitsha. Equipment used in this work were: Meter balance, Tong, muffle type furnace, Pyrometer, Rockwell hardness Testing Machine Model MHT-1 No: 8331, Pin on disc machine (make: SD scientific industries), Grinding and Polishing machine, Scanning Electron Microscopy (SEM)/Energy dispersive system (EDS), Optical Metallurgical Microscope.

2.1. Siliconizing of mild steel samples

Pack siliconizing was used in this research. Pack siliconizing is an easy technique which can be adapted to components of any dimension provided furnaces and retorts of bigger dimensions are available. In the pack process the mechanism of casing depends on in-situ reaction and partly on

reduction as well. The mild steel sample's surface was ground with series of SiC paper of 600 grit and cleaned in acetone baths and dried in air. Silicon powder of 95% purity was used in siliconizing experiments of average size below 150 μm. The cleaned mild steel substrates were assembled in packs consisting of the silicon powder inside a graphite crucible. The crucible was placed inside a muffle furnace and then maintained at the different required siliconizing temperatures (1000, 950, 900, 850 and 800°C) and times (1, 2, 3, 4 and 5hours), by this way the mild steel samples gets siliconized and then quenched in water.

2.2. Hardness determination

The hardness values of the samples were determined according to the provisions in American Society of Testing and Materials (ASTM E18-79) using the Rockwell hardness tester on "C" scale (Frank Welltest Rockwell Hardness Tester, model 38506) with 1.56mm steel ball indenter, minor load of 10kg, major load of 150kg and hardness value of 125HRC as the standard block. Before the test, the mating surface of the indenter, plunger rod and test samples were thoroughly cleaned by removing dirt, scratches and oil and calibration of the testing machine using the standard block. The samples were placed on anvils, which act as a support for the test samples. A minor load of 10kg was applied to the sample in a controlled manner without inducing impact or vibration and zero datum position was established, and then the major load of 150kg was then applied, the reading was taken when the large pointer came to rest or had slowed appreciably and dwelled for up to 2 seconds. The load was then removed by returning the crank handle to the latched position and the hardness value read directly from the semi-automatic digital scale. Three indentations were taken for each sample and the average values were used.

2.3. Corrosion Test

Before the corrosion test sample was cleaned in acetone baths, dried in air and stored in the desiccator to avoid oxidation. The solution was prepared from analytical grade reagent HCl (98% pure) and distilled water. The HCl solution of 0.5, 1, 1.5, 2 and 2.5M was prepared and used in this research. The weight (mass) of each specimen was taken before immersion and recorded as initial weight (w_0). The solutions were put into separate beakers and the samples were completely immersed in them (see Equation 4)

The experiment was monitored from 15 to 90days. The samples were brought out of the solution, cleaned, washed in distilled water, rinsed in acetone and dried. After which they were weighed and the weight recorded as final weight W_1 . Electronic digital weighing balance Mettler Toledo which has a sensitivity of 0.01mg and a standard deviation of ± 0.02 mg was used for the weight measurements. The weight loss (W) is evaluated using the equation:

$$W = W_0 - W_1 \quad \dots \dots \dots \quad (2)$$

The corrosion rate was obtained from standard expression for measurement of corrosion rate in mills per year (mpy) [8].

$$\text{Corrosion rate (mpy)} = \frac{534w}{DAT} \quad \dots \dots \dots \quad (3)$$

Where w is the corrosion weight loss of the sample (mg), A is the area of the coupon (49mm), t is the exposure time (h) and D is the density of mild steel (g/cm^3) (ASTM, 1987) ...

The protection efficiency was computed using the relationship:

$$\text{Protection efficiency} = \frac{r_o - r}{r} \times 100\% \quad \dots\dots\dots (4)$$

Where: r_o = corrosion rate of unsiliconized sample, r = corrosion rate of siliconized sample.

2.4 Microstructural studies

The microstructures of corrosion surfaces after immersion were observed using scanning electron microscope (SEM). The SEM was applied at different magnifications using secondary electron detector to obtain high quality images at voltage of 20kV electron beam energy. The SEM was coupled with energy dispersive X-ray spectroscopy (EDX) to determine the surface elements composition.

2.5 Wear testing

A tribometer test apparatus was used to investigate the dry sliding wear characteristics of the samples as per ASTM G99-95 standards (ASTM Standards, 1990) (see Figure 6). Wear tests were conducted with loads ranging from 5 to 20 N and sliding speeds of 1.26 to 5.02m/s for a constant sliding distance of 2000m. All tests were conducted at room temperature. The initial weight of the specimens was measured using a single pan electronic weighing machine with an accuracy of 0.01g. During the test, the pin will be pressed against the counterpart rotating against an EN32 steel disc (hardness 65 HRC) of counter surface roughness of 0.3 μ m by applying the load. A friction-detecting arm connected to a strain gauge held and loaded the pin sample vertically into the rotating hardened steel disc. After running through a fixed sliding distance, the samples were removed, cleaned with acetone, dried, and weighed to determine the weight loss due to wear. The differences in weight measured before and after tests give the wear of the sample. The wear of the samples was studied as a function of the percentage volume of reinforcement, applied load and sliding velocity. The formula used to convert the weight loss into wear rate is:

$$\text{Wear rate} = \frac{\Delta W}{S} \quad \dots\dots\dots (5)$$

where ΔW is the weight difference of the sample before and after the test in g, S is total sliding distance in m.

3. Results and Discussion

Table 1: The chemical composition of the mild steel

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Sn	Cu	V
Percent	0.13	0.15	0.47	0.043	0.006	0.01	0.01	0.01	0.001	0.03	0.002

Table 2: Wear test result at varying load with constant speed and sliding distance

Sample condition	Δm (mass loss) Grams	F_f (Frictional force) kg	μ (Co-efficient of friction)	Specific Wear rate($\times 10^{-6}$) kg/m
5N				
Control	0.90	0.35	0.70	1.80
Siliconized	0.27	0.59	1.18	0.54
10N				
Control	1.11	0.82	0.82	2.22
Siliconized	1.10	0.94	0.94	2.20
15N				
Control	2.00	0.68	0.45	4.00

Siliconized	1.30	0.84	0.56	2.60
20N				
Control	1.20	0.89	0.59	2.40
Siliconized	1.13	0.96	0.64	2.26

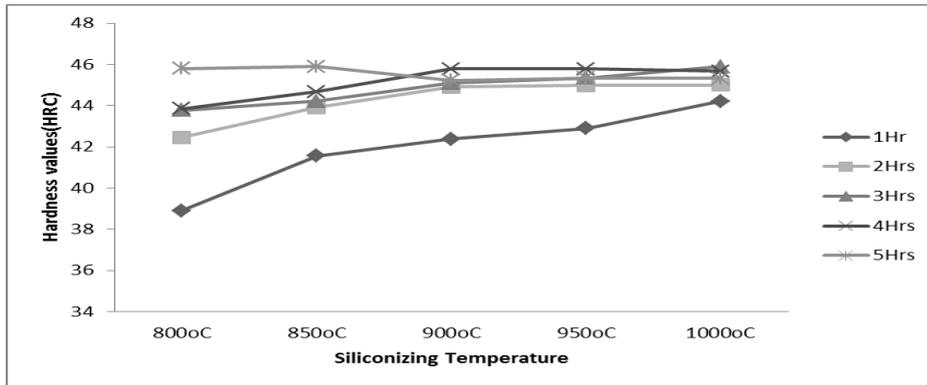


Figure 1: Variation of hardness values with siliconizing temperatures

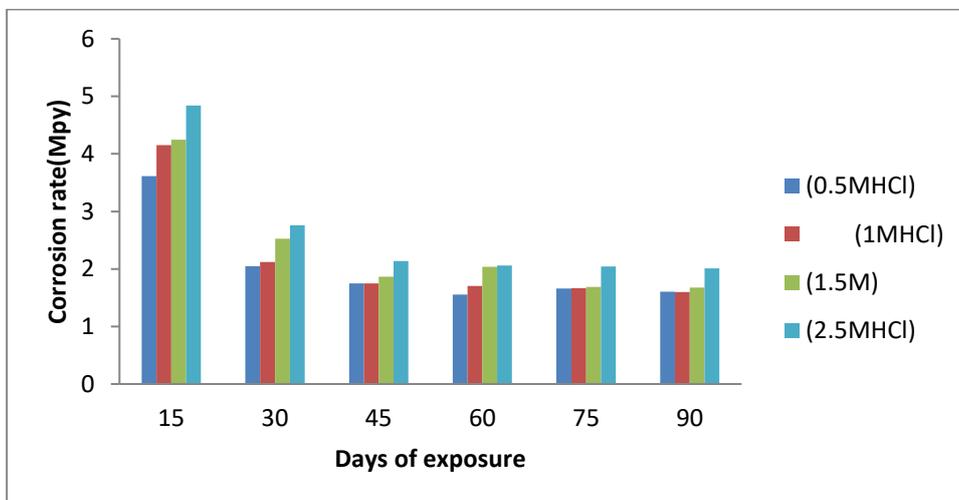


Figure 2: Variation of corrosion rate with exposure time for the unsiliconized sample

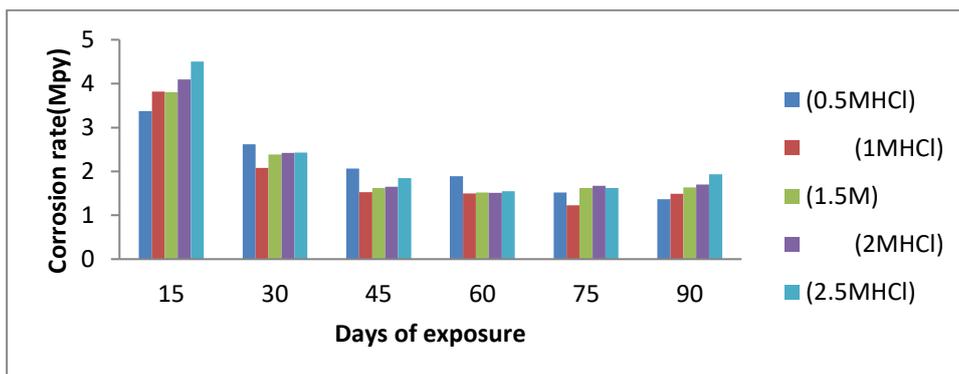


Figure 3: Variation of corrosion rate with exposure time for the siliconized sample

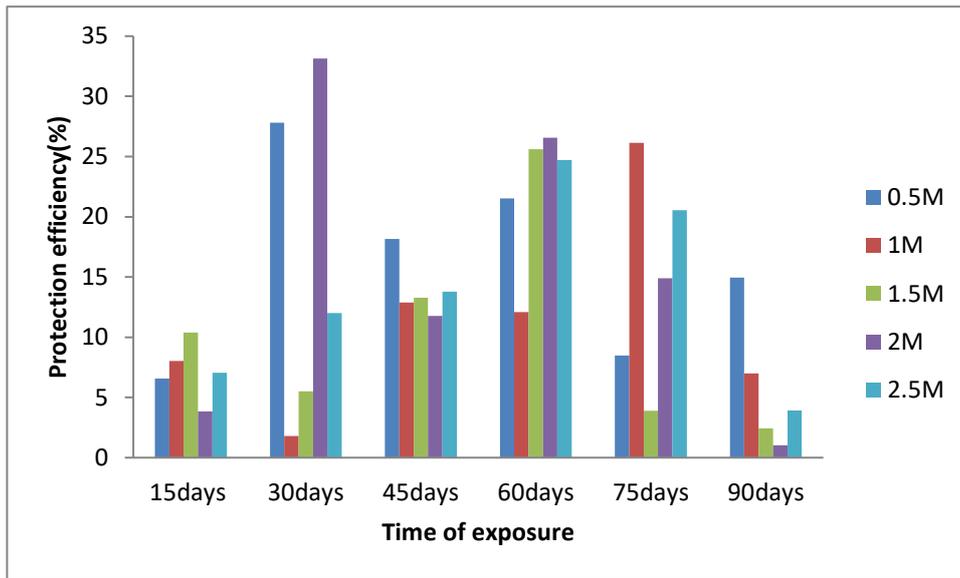


Figure 4: Variation of protection efficiency with exposure time

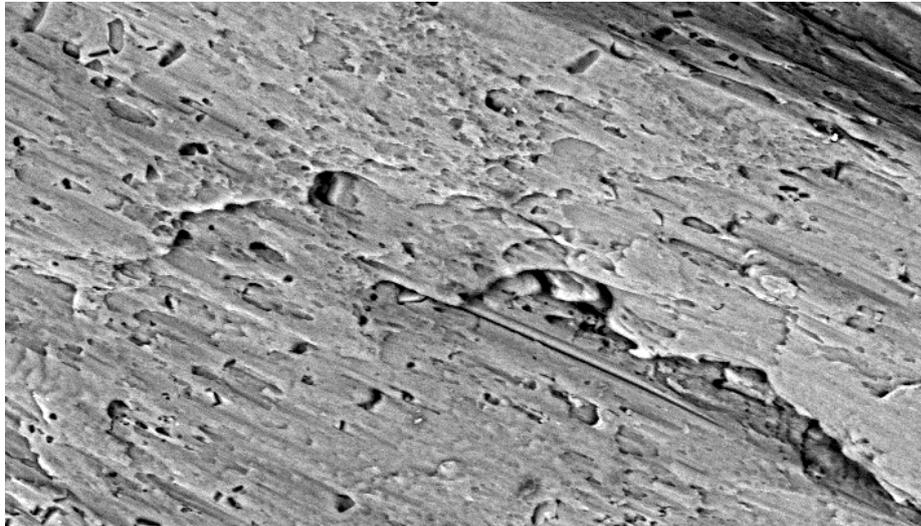


Plate 1: SEM corroded surface of the unsiliconized samples after 90days in 2.5MHCl at 1000X



Plate 2: SEM corroded surface of the siliconized samples after 90days in 2.5MHCl at1000X Magnification

As the siliconizing temperature increase from 800 to 1000°C, the hardness values increase linearly. Siliconizing time shows similar results as that of siliconizing temperature increases. As the siliconizing time increases from 1hours to 5hours, the hardness values of the siliconized mild steel also increased. The improvement in hardness values obtained can be attributed to hard phases of Iron Silicon (Fe Si), Fersilicite (Fe Si), martensite ($C_{0.12} Fe_{1.88}$), Stishovite ($Si O_2$), Manganese Silicon (Fe Si) form after siliconizing. The hardness value of the mild steel is lower than all the siliconized samples. It can be seen that siliconizing of mild steel led to an improvement in hardness values no matter the operating condition shown in Figure 1. An improvement of 49.13times the hardness of the mild steel was achieved at siliconized temperature of 1000°C for 3hours. The decrease in hardness values at low siliconizing time was as a result of low rate of diffusion of silicon as similar observation was obtained in the work of [9]. Also, as siliconizing temperatures and time increases, the lattices of the austenite phase were saturated and resulted in the formation of hard Fe_2Si in the steel sample. This observation agrees with previous works carried out by the authors [10]. So, the sample siliconized at 1000°C for 3hours gave the best results and was used for the corrosion and wear test. The results observed in Figures 1 & 2 shows that the samples were found to corrode in different concentrations of HCl. This was evidenced by the decrease in the original weight of the metal coupons. Un-siliconized mild steel was found to lose weight more than the siliconized mild steel. The Figure 1&2 also revealed that the weight loss of samples increased with time and concentration. This observation is attributable to the fact that the rate of a chemical reaction increases with increasing concentration, it clear that the corrosion resistance of the siliconized sample is higher than the unsiliconized sample e.g corrosion rate of 2.012 and 1.933 mpy was obtained after 90days exposure at 2.5MHCl for unsiliconized and siliconized sample respectively. This may be attributed to the fact that the hard case formed after siliconizing offer more corrosion protection than control samples. The decrease in the corrosion rates with increasing numbers of days observed for all the two categories of coupons is probably due to the deposition of corrosion products which tends to shield the corroding surface from further corrosion attack thereby

depressing the rate of the corrosion [11]. Table 2 shows the variation in wear rate with applied load at constant sliding distances and speed, the wear rate of the sample increases as the applied load increased. From Tables 2, the positive effect of the siliconized samples in reducing the wear rate of mild steel can be seen. When load applied is low, the wear loss is quite small, which increases with increase in applied load. It is quite natural for the wear rate to increase with applied load. A similar trend was also observed independently for different wear distances as a function of load and speed [12]. He observed that the siliconized sample exhibited significantly higher wear resistance than did the unsiliconized sample due to the harder phases formed after siliconizing which acts as a load bearing constituent. A siliconized mild steel restricts deformation of the matrix material with respect to load, hence the wear rate siliconized sample is lower. The SEM of the corroded surfaces is shown in Plates 1-2. The SEM images reveal that the siliconized sample has a better appearance; it had a smooth surface while the unsiliconized sample was rough. Its surface was covered with corrosion products and appeared to have many pits and cavities.

4. Conclusion

The results showed that the optimized hardness values were obtained by siliconizing at 1000°C for 3hours and corrosion increases with increase in concentration of HCl from 0.5 to 2.5M in which surface treatments (siliconizing) offer some corrosion protection to the mild steel and the wear rate was raised with increase in applied load and sliding speed.

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