Siliconizing Process of Mild Steel Substrate by Using Tronoh Silica Sand (TSS): An Experimental Investigation

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Abstract

Siliconizing is one of the surface hardening treatments where silica diffuses into a metal substrate forming a thin layer coating material. This paper discussed on appropriate Design of Experiment (DOE) involved in performing siliconizing process onto mild steel substrate using Tronoh Silica Sand (TSS). Available knowledge on the siliconizing related parameters, material selection issue, temperature-time dependence and effects on the interface, structure and properties of siliconized substrate were critically reviewed. Critical parameters for the siliconizing process on mild steel substrate by using TSS were established. In order to enhance formation of the thin film coating, simultaneous TSS powder pack for siliconizing process was designed. Associated siliconizing mechanism in producing the thin film coating will be discussed and established.

Keywords: Siliconizing; Silica sand; Thin Film Coating; Pack Powder; Diffusion; mild Steel; Surface Hardening Treatment

1. Introduction

The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative coating processing technologies. The coating nowadays for high temperature applications include mainly diffusion coatings, overly coatings and thermal barrier coating [1]. Diffusion coatings have first been developed and still are the most used coatings. Silicides diffusion coatings are proved to be the cost-effective solution for high oxidation because of their properties. Tronoh Silica Sand (TSS) is found abundantly in Malaysia especially in Tronoh, Perak where previous tin mining activities were actively progressed for last 50 years ago. Except for housing construction foundation there was no efforts or initiatives taken in converting the natural silica sand to a different particle form, size or for other potential technical applications especially in coating processing technologies. Utilization of TSS in high technology application such as in protection of metal surfaces against corrosion is still an active area of research. Hence continuous support from the local government is necessary for ensuring better development of relevant industries and the nation.

The processes for material surface changes can be defined as the treatments in which the surface and matrix materials are designed together thereby providing properties that cannot be provided by each material alone [2]. Therefore, in recent years the importance of surface treatments based on both classical and modern technologies has been increasing tremendously. The material should have acceptable surface properties in order to be used efficiently. Among the important properties are electrical, optical, thermal, mechanical and electrochemical [1]. It is still remained as challenges in inventing a material or process that offering superior properties.

Available processes for producing silicon diffusion coatings on the metal’s surfaces include ion implantation [3], molten metal/salt baths [5], slurry/sinter, and/or chemical vapor deposition (CVD) [6] and pack cementation [8-9]. Each of the process offering unique advantages. Pack method (pack siliconing) for instance, is able to produce uniform coating of the substrate, minimum cleaning of parts after treatment, in situ treatment of fabricated parts, ease of...
surface cleaning, and capability for thermal treatment deposition. The surface modification have been improvement. Promising research findings to this siliconizing process were incorporating various elements such as stainless steel/alloying Si [4], steel/liquid Na₂O-SiO₂ [5], iron/precacuribarized iron[7], steel/Si+NH₄Cl+alumina [8] etc. However, a simpler and less expensive method is still required. Among the various surface hardening treatments, the siliconizing process is selected in this research because it is much simpler and cheaper compared with other expensive advanced techniques such as CVD and PVD. Studies on multiple diffusion of silicon [10], chromium [11], boron [12] and aluminum [13] were reported. All findings agreed to the conclusion that at high temperatures siliconizing process is a diffusion-controlled process. Hence it is very important to establish and select the process parameters that effect the siliconizing process to attain the desired thickness and properties of the coating. This is aiming for utilizing the advantages of the coating such as chemically inert and able to function as a barrier layer in preventing the diffusion of the active species into the substrate’s surface.

In recent years several metal oxide and organic (natural) coatings including silica sand were reported as corrosion protection of metals [2]. The silica coating provides corrosion resistance of steel without changing the mechanical properties of the bulk material (substrate). In addition silica sand could improve steel high temperature oxidation resistance [10, 11, 14, 15]. The coating can serve as protection either by a barrier action from the layer or from active corrosion inhibition supplied by pigments in the coating which give protection to the underlying substrate [3]. Therefore, usage of the silica sand in engineering applications is strongly depends on ability of the silica to diffuse into the metal’s surface (substrate). The substrate used in this research is mild steel. Since this steel is subjected to corrosion, outcomes from this research will undoubtedly offering solution as means of potential corrosion’s mitigation approach. The research is aiming at forming a thin layer of fine TSS coating onto mild steel via siliconizing process. Relevant siliconizing mechanism involved in transforming TSS particles into thin film coating on mild steel substrate is expected to be established.

2. Experimental Set-up Approach

2.1 Tronoh Silica Sand Jacket (TSSJ)

Fireclay is a heavy dense and heat resistance ceramic materials. It has an excellent thermal conductivity and stable even after exposed to multiple heating and reheating cycle.

Such excellent refractory properties meeting requirements of the thermal jacket needed by the research. Hence, the Tronoh Silica Sand Jacket (TSSJ) made from fireclay will be fabricated. The construction model of the TSSJ is shown in Figure 1.

3. Overall Research Flow and Apparatus

An overall research flow taken in this study is illustrated in Figure 2.

4. Experimental Results Evaluation: Review of Parameters

4.1. Material Selection

In multi-component diffusion the hardened surface is due to formation of solid solution and complex compounds. Similar effect can also be achieved with siliconizing. Fitzer (1978) [17] conducted one of the siliconizing of pure Fe and steels using ferrosilicon master alloys containing 6-20wt%Si, with NH₄Cl activator, at coating temperature of 1500°C, and diffusion times ranging from 5 to 30 hours. The initial study showed that adherent, nonporous coatings containing 6-11wt% Si could be produced. However it was not possible due to excessive outward growth occurred during the coating process [17]. Several authors reported that silica coating bind strongly on the iron surface [16, 18]. Thus siliconizing using pack cementation has not been adopted on any considerable
process. Many authors describe the siliconizing process as a hard silicide layers with excellent chemical resistance at high-temperatures [28, 29]. The properties of the silicides coating can be improved. Furthermore, less expensive low-carbon steels showed that type 304, 316 and 310 steels are much higher than iron, copper etc and is a reason why it is used as source of Silica sand coating. Mild steel is use in different industries in the merit of its good structural properties, good mechanical workability and cost. Mild steel is selected because of its mechanical properties and machine-ability at a low price, while at the same time, their corrosion resistant can be improved. Furthermore, less expensive low-carbon steels can be surface hardened without having problems of distortion and cracking associated with the through hardening of thick sections. This material was used for the substrate material to take advantages of its easily adjustable mechanical properties of the core on subsequent treatment processes [40].

4.2. Temperature and Time Dependence

Temperature is the most important parameter in solid-state diffusion (e.g. siliconizing). It controls kinetic of the thermally activated process involved in diffusion bonding. In fact, all diffusion mechanisms are sensitive to temperature. The temperature required to obtain sufficient joint strength is typically between 0.5 T_m and 0.9 T_m, where T_m is the absolute melting point of the base metal [28]. To a certain extent, increasing the temperature enhances bonding, provided that time (bonding time) is controlled to prevent the development of detrimental reaction products in reactive systems. The bonding times may vary from one second to several hours depending on the silica sand-metal combination and the joining temperature [27]. At each temperature, there is a corresponding minimum time required to achieve complete bonding. Normally this value decreases when the temperature or pressure increases. As for the reactive systems, bonding time have to be controlled to promote bonding with limited reactions. Due to the fact that solid-state diffusion is frequently described by non-equilibrium thermodynamics, the time involved may not only effect the amount of reaction, but also the nature of the reaction products [27].

The temperature and time parameters have been extensively studied especially at high temperature of the siliconizing process. Many authors described the siliconizing process as a heterogeneous solid/liquid reaction followed by a mechanism of diffusion of the reactant [12, 24]. This process produced hard silicide layers with excellent chemical resistance at high-temperatures [28, 29]. The properties of the silicides coating depending on the process methodologies (parameters) used to deposit the coating, the substrate composition and the associated treatments. Meanwhile the coating rate and morphology depends on the process temperature and time. Processing temperature influences the rate of solid diffusion, at which silica sand coating elements may diffuse, thus, it is a critical parameter in the processing and manufacturing of coatings. Such findings led to a concluding remarks about the coating time at temperature defines the thickness of the coating formed during the solid diffusion step [27]. A good of prediction of the temperature is important, because the solid diffusion depends strongly on temperature and too high temperature may cause degradation or too early cross-linking of the substrate. Relatively little attention has been paid to thermal boundary condition. The temperature is usually controlled at some distance from the wall to the substrate’s interface before diffusion. This temperature is then assumed as boundary condition on that surface. Some researchers showed that such a temperature boundary condition resulted in a considerable temperature rise at the substrate interface [43].

However, recent findings in siliconizing researches shows that the best temperature and time ranges to form a thin layer coating are 1000°C-1500°C and 2-6 hours, respectively. However the optimum parameters are strongly depending on composition of mixture pack and substrate type as shown in Table 1.

| Parameter Siliconizing Process | Treatment temperature (°C) | Treatment time (hr) | Reference |
|-------------------------------|-----------------------------|---------------------|-----------|
| Stainless steel/Powder mixture-silicon, aluminium chloride and alumina | 1323-1423 | 2-6 | [35] |
| iron and precarburized iron | 1000 | 4 | [8] |
| Armco iron, steels 45 | 1050 | 3 | [52] |
| pulverized Si-45 grade ferrosilicon powder | 1000 | 4 | [21] |
| Carbon Steel | 1000-1050 | 3-6 | [25] |

Several works have been studied on the depth of siliconized layer as a function of time and temperature. They found that the diffusion coefficient of the process increased with treatment time [33-37]. For applications where higher temperatures are involved, silicide coatings provide the most efficient protection. MoSi_2, for instance, melts at temperatures above 2000°C, and its resistance to oxidizing environments results in service temperatures of the order of 1900°C [29, 30]. Siliconized layers on steels and alloys exhibit high resistance to various chemical effects. Moreover, the ferrite of the siliconized layers, which can be hardened to a greater degree by silicon than by other alloying elements, is distinguished by...
good stability. Thus, complex saturation of a surface on a siliconized base makes it possible to a) produce a broad spectrum of wear-resistant structures on the surface; b) improve the damping properties of the surface when subject to various mechanical effects causing failure; c) increase the bearing capacity of the component due to the presence of a region of increased hardenability in the sub-layer zone [22]. Khisaeva showed that in order to prevent sintering of the mixture and sticking of powder to substrate, inert additives of Al₂O₃ or Mn₂O₃ is proposed [23]. Other researchers have observed that thickness and structure of the diffused siliconized coating depends on the mixture composition [25, 26].

4.3. Effects on the Interface, Structure and Properties

Over the years several methods to form a thin layer of silica on metals have been developed. The appropriate approach is depending on the material to be diffuse, design and the anticipated operating conditions. Solid-state diffusion bonding arises as an alternative method to produce temperature-resistant interfaces. Diffusion bonded joints are able to withstand higher service temperatures and to resist chemically hostile environments. Solid-state joining requires the application of pressure at high temperature in order to promote intimate contact between the parts, which is essential for high-quality bonding. Therefore, in order to assess the potential of a specific silica sand-mild steel combination for structural applications, the physical and mechanical properties of the diffusion materials is an important aspect. However, it is also relevant to understand the mechanism of interface formation between the metal and silica sand. In solid-state diffusion, the aim of the process is to produce an interface joint (bonding) without melting any of the components. Bonding occurs with or without mass transfer across the interface. In the latter case, bonding is a result of change transport across the interface with the established of van der Waals forces between the materials (physical bonding). Mass transfer occurs when the atomic species of the original materials diffuse across the interface (chemical bonding). The resulting interface can have a diffusion layer (diffusive interface) or a reaction layer (reactive interface), depending on the heat transfer of the system and the joining conditions [31].

Several variables (parameters) dictate the choice of application method which are geometry and size, appearance of the coating finish, and production rate. Facility constraints will also determine the choice of application method. The configuration of the application equipment is dependent on space or climate. Similar application systems may operate at different parameters. The viscosity of the coating material, the desired thickness of the final coating, and the complexity of the part will determine the best operating parameters for the application method [49]. Concurrently the dip times or number of coats are also need for further consideration. Another important factor is the transfer efficiency of coating material onto the substrate. This transfer efficiency is the percentages of solid coating material used that actually deposited on the surface of the part. The solid content of a coating determines some other important parameters of the coating such as the density, viscosity, thickness, coverage [50].

Numerous research works has been focused on surface modification attempting to improve the surface property (e.g. toughness and wear resistance) and some good results have indeed been achieved. However, so far, long-time treatment with a special equipment needed for surface hardening treatment hindering further development. Therefore, the main concern in the surface treatment field now is how to enhance the formation of a protective layer (siliconized layer). It should be noted that directly adding the element individually or in combination with another element at the surface can favor the formation of the protective steel scale and therefore retard the diffusion rate during forming coating layer [27]. On the other hand, the formation of silica at the surface also plays an important role in improving the thin layer onto substrate. It has been reported that alloying addition of few percent silica is effective to decrease the oxidation rate to some extent by forming discrete silica in the oxide layer. Once the silica was formed in the layer it became a good barrier against oxidation (corrosion) [32, 33].

5. Conclusion

A systematic approach to the experimental evaluation of the siliconizing process has been outlined. The assessment is based on the most critical process parameters covering relevant physical and chemical contact mechanisms and material transfer. The use of thin coating layer offers an excellent possibility for surface design to achieve the required surface properties. The main process parameters in siliconizing process (diffusion bonding) are temperature and time. Temperature is, however, the most important one due to the fact that the siliconizing is thermally activated processes. A small change in temperature will result in a significant change in process kinetics compared with other parameters. Furthermore diffusion is sensitive to temperature. In general, increasing the bonding temperature resulted in a faster growth of the reaction zones and longer times were necessary to increase the thickness of the interface. The effect of a reaction layer on the interface strength depends on a number of factor such as the mechanical properties of the reaction layer, its thickness and morphology, the strength of the interfacial condition and the mode of loading at the interface. Possible reactions that might be formed at mild steel/TSS interface include solid solutions, amorphous and crystalline phases. Each of these reaction producing different types of interface between the metal and ceramics. Relative efficiency of similar type of reaction products on the strength of mild steel/TSS interface is not fully understood.

However, most reaction layers are brittle and therefore potentially detrimental to the interface properties. Reaction products are generally brittle and as the thickness of these phases’ increases, the joint strength, at first arises and then reaches a maximum at a certain thickness and then decreases as the interface continues to grow. Therefore, the reaction layer thickness must be controlled to enhance joint strength. The choice of suitable conditions to prepare TSS/ mild steel
joint requires a knowledge about the mechanism of the reaction between the materials and the evolution of the interface. This review can be concluded that critical parameters for the siliconizing process on mild steel substrate by using TSS can be established. In order to enhance formation of the thin film coating, simultaneous TSS powder pack for siliconizing process was designed. Associated possible siliconizing mechanisms due to the coating formation have been discussed.

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