©2021 Published in 9th International Symposium on Innovative Technologies in
Engineering and Science 15-17 October 2021 (ISITES2021 Sakarya - Turkey)
https://doi.org/10.33793/acperpro.XXXX

Characterization of Zinc Coating by Sherardizing Process

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Abstract

Sherardizing process is a common industrial surface treatment technology that provides protection against corrosion by forming a zinc-iron based layer on steel surfaces by thermo diffusion mechanism. Sherardizing is much more reliable, environmentally friendly and cost effective than many paint and zinc based coatings. Sherardizing is in the interest of many industries with the advantages it provides. For this reason, it is very important to understand and characterize the properties of sherardized surfaces. In this study, the cross-sectional and top surface morphology of the coating was investigated by scanning electronic microscopy (SEM). The thickness of coating were analyzed using nondestructive test methods. Surface properties are discussed and wetting angle measurements were carried out and analyzed. Sherardizing process provides a very strong and long-term protection against corrosion and wear. It is an indispensable surface treatment especially for fasteners and bolts that require high strength and service life.

Key words: Zinc coating, Sherardizing, Corrosion, Surface Treatment, Coating Thickness, Coating Thickness Measurement.

1. Introduction

The economical losses by atmospheric, offshore and soil corrosion of steel and its alloys is in the range of several hundred billion dollars every year. For this reason, the excellent protective properties of zinc and zinc alloys have been used in many industrial areas to protect steel alloys for a long time. The zinc coating acts as a diffusion barrier and sacrificial anode against steel, providing long-term active protection. Several protective surface treatment methods have been used to zinc coat steel, such as hot-dipping, electroplating, thermal spraying, mechanical plating or zinc flake painting. Table 1 compares zinc coating processes at process temperatures, thickness, homogeneity and coating ability. Like hot dip galvanizing, sherardizing is a zinc diffusion coating process, creating diffusion bonded zinc-iron layers with the steel. Other zinc coating methods are mostly batch type applications. As can be seen from Table 1, sherardizing process provides both high hardness and corrosion resistance [1-3].

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Table 1. Comparison of zinc coating processes [1]

Zinc Coat Process	Sherardizing	Hot dip galvanizing	Electro-plating	Protective paint	Thermal spraying
Hydrogen embrittlement	No	Possible	Possible	No	No
Surface hardness	Hard	Soft	Soft	Soft	Soft
Process temperature	320–500°C	> 440°C	< 100°C	< 200°C	–
Paintable	Yes	Yes*	Yes*	–	Yes*
Uniformity	Good	Good	Good	Good	–
Layer thickness	10–120 μm	> 30 μm	< 30 μm	< 15 μm	> 70 μm

Sherardizing is a zinc diffusion based thermochemical coating process (dry galvanizing), which uses zinc vapor to form zinc-iron contented layers on the steel parts. It is necessary to have the process media (furnace inside) close and contact to the steel surface, because of the low partial pressure of zinc powder mixture for vaporizing (Figure 1.). The process allows the surface treatment of complex shaped parts, so that even hollow parts like pipes, tubes can be coated, and threads do not fill. Because of the lower sherardizing temperatures, hardened and tempered steels can be processed without losing their hardness and mechanical properties. Today, sherardizing process is mostly applied to ferrous parts, but it can also be used on any substrate that forms an alloy with zinc such as copper-based materials. The process is internationally specified in DIN EN ISO 17668 and EN 13811 Sherardizing/Zinc diffusion coatings [1-4]. The standards subdivide the layer thickness into three classes: Class 15 (min. 15 μm), Class 30 (min. 30 μm), and Class 45 (min. 45 μm). Classes 30 and 45 are specified for outdoor applications, while Class 15 is sufficient for indoor applications. The corrosion resistance is proportional to the thickness of the zinc layer.

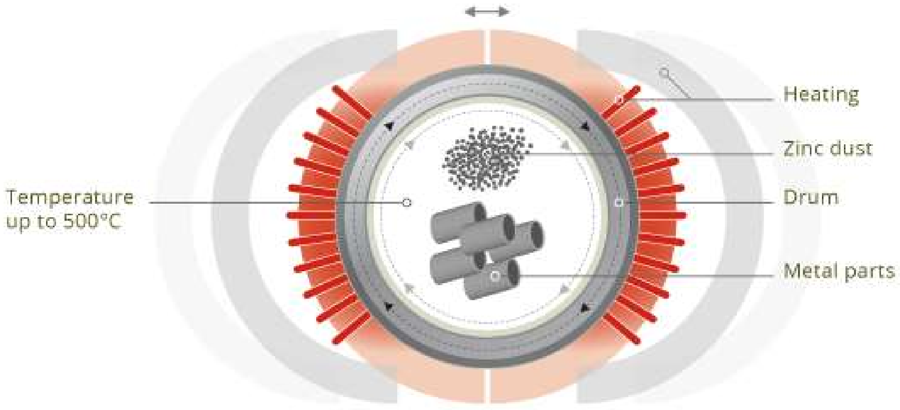

Figure 1. Sherardizing process (schematically) [4]

The process is named after the British metallurgist Sherard Osborn Cowper-Coles who invented and patented the method ca. 1900. This process involves heating the steel parts up to ca. 500°C in a closed rotating drum that also contains metallic zinc dust and possibly an inert filler, such as sand. At temperatures above 300°C, zinc evaporates and diffuses into the steel substrate forming diffusion bonded Zn-Fe-phases [4]. A variety of ferrous materials can be treated, such as structural steel, heat-treatable steel or cast iron. In case of heat-treatable steel the sherardizing temperatures can be adjusted to the tempering temperatures of the heat treatment to prevent a significant change in properties [1-7]. The main benefits of a sherardizing layer are: uniform diffusion coating, low process temperature, hard and wear-resistant layer, good bonding between paints or polymers and substrate, no hydrogen embrittlement [1]. Some of the main advantages are that the sherardizing process is non-toxic, free of heavy metals, it has almost no discharges to the environment, and additional an extremely low water consumption - a critical issue for the galvanizing industry. Sherardizing suits perfectly for small metal parts like springs, nails, screws, nuts and bolts, chain link. Especially for components used in aggressive salt water atmosphere sherardized parts are long-lasting and continue to function [5-7]. Within the scope of this study, the surface properties of sherardized steel plates due to different process times were examined and the coating thicknesses were examined by ED-XRF. The ED-XRF measurement method is indispensable for the easy/non-destructive measurement of small surfaces and complex geometries (such as screws, nails, nuts) in industrial applications. Measurements with XRF are used by correcting the density with the help of witness samples (arbitration specimen).

2.Experimental Details

In all surface technologies a pretreatment is essential for high quality coatings. For the sherardizing process, impurities such as rust, oxide or grease on the surface of the samples are strictly not desired. Layers will not grow on rust, scale, oxide layers or grease. Because of this, it is of great importance that the work part is thoroughly cleaned before it is treated. There are mainly three kinds of pre cleaning technics; shot blasting, degreasing in organic solvent, or hydrochloric acid pickling. The kind of method used is dependent on the surface contamination and the type of component. After the samples has been cleaned to an acceptable level (acid pickling, rinsing and ultrasonic cleaning and drying), it is loaded into a container together with a zinc powder (minimum of 95% zinc and the particle size: 5–40 µm.) mixture. An inert filler, often silica sand, is added with the purpose of distributing the zinc evenly as well as preventing damage to the steel surface. The filler has several functions: on the one hand, it supports the distribution of the zinc powders and prevents it from sintering, while on the other hand it cushions colliding parts in the rotating container. The sherardizing process was done by mixing zinc powder with sand at ratio (50:50) % the mixer was done for 30 minutes period. The samples and mixture are placed inside containers. The container is closed, air tightened and placed in a furnace at temperatures ranging from 380-450 °C. A sherardizing furnace should be able to rotate the container and provide temperature uniformity. The sherardizing method can also be carried out at temperatures around 300 °C at the cost of longer processing time. This low temperature range does not usually affect the physical properties of most parts. During the heating process a sequence of zinc-iron compounds with decreasing zinc concentration ranging from the outer surface to the ferrous substrate is built up on the samples. The diffusion coating layer grows by a reaction of zinc with the iron on the steel surface. The cylindrical container is not fully loaded in order to allow even distribution of heat and materials by rotating in the furnace at approximately five or four rounds per minute. Zinc vapor is generated by sublimation due to the increased temperature in combination with the presence of catalysts. After sherardizing the process containers are cooled down to room temperature. This can be done in a separate cooling station. After cooling the load is screened and post-treated [5]. Coating thickness and surface roughness are important for paint, adhesion and lacquer applications. According to the standards the layer thickness can be determined by nondestructive and destructive methods. In this study; thickness measurements were measured both by nondestructive methods and by image analysis method under electron microscope (SEM) after metallographic (sectioning, hot moulding, grinding, polishing) preparation. Contact angle measurements were carried out for the effect of thickness and surface morphology on wetting angle and adhesion.

3.Results and Discussion

The sherardized samples (400 ºC/60-240 min.) have matt grey appearance in Figure 2. The increase in thickness changes the color from light gray to dark gray (right). In the magnetic induction measurements made with the Deltascope FMP30 (with FGAB1.3 probe) thickness measuring device (Helmut Fischer GmbH), coating thickness measurement (DIN/ EN ISO2178) results were obtained in the range of 10-85µm. Measurements were made at 9 different points on the entire 1020 grade steel plate (40x40x2mm) surfaces (Table 1.).

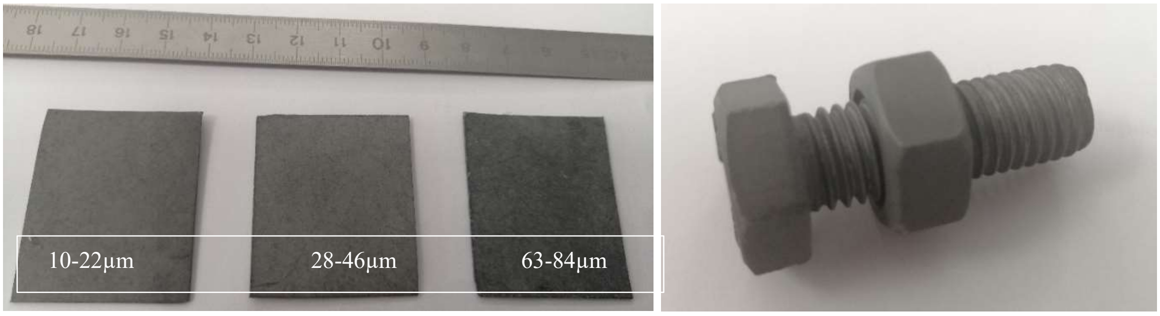

Figure 2. Sherardized samples and fastener

Table 1. Thickness Measurement by Deltascope, Helmut Fischer GmbH

Process	400 ºC/60 min.	400 ºC/ 120 min.	400 ºC/240 min.
1	12	35	74
2	16	38	80
3	18	40	84
4	14	36	76
5	20	42	68
6	22	45	73
7	15	34	65
8	17	39	78
9	19	43	82
Mean (µm)	17	39,11	75,555
Standard Dev.	2,792	3,359	5,623

The thickness of sherardizing process increases with increased treatment time as shown in Figure 3. The average thickness increase from 17µm when treatment time 60 min. to 75 µm when the time reach to 240 min. at 400°C that due to diffusion of zinc increase as time. Required sherardizing thickness can achieved by combination of time and temperature.

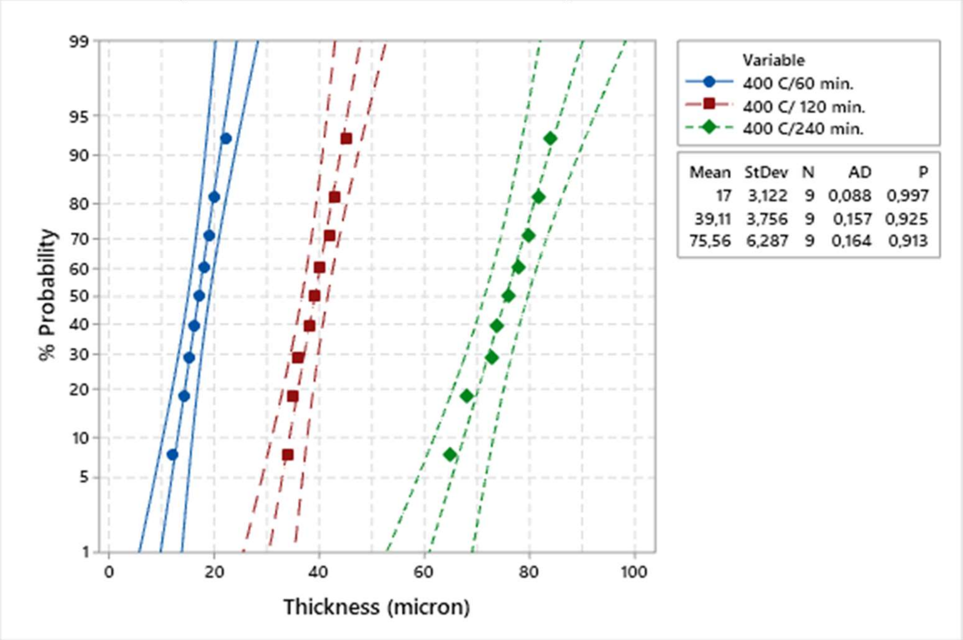

Figure 3. Thickness change of sherardizing as a function of treatment time

Coating top surface morphologies were examined under scanning electron microscope (SEM) in SE mode. As can be seen in figure 4, there is a difference between the surface topologies depending on the coating thickness and the process time. It was determined that the surface roughness (Ra) decreased from 6µm to 4.5µm with increasing process time. It is observed that the morphology of the crystallites on the surface has changed. It is observed that sharp, thin and short crystallites turn into spherical agglomerated form with increasing time. It can be clearly seen that the surface roughness has decreased.

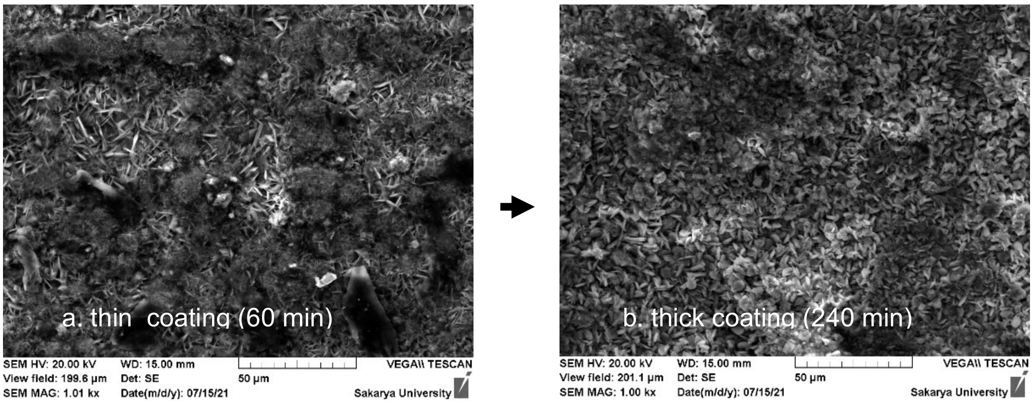

Figure 4. Top surface SEM micrographs of sherardized samples

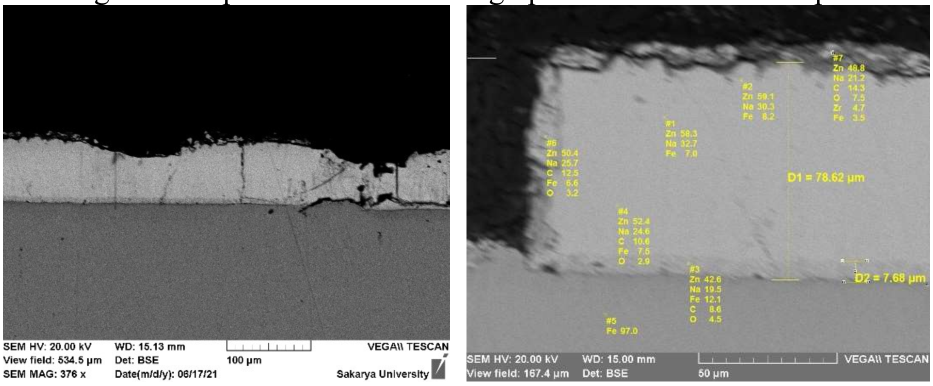

Figure 5. Cross section SEM micrograph of thick sherardized sample (left), thickness measurement and EDX analysis (right)

The effect of the sherardizing time on microhardness values is shown in Figure 6. Although the effect of thickness increase on hardness increase is not fully explained, a significant increase is observed. It is thought that the increased processing time allows the formation of hard phases with the effect of zinc diffusion. The red solid line represents the low carbon steel microhardness. Above this red line, the microhardness increases towards the surface along the diffusion layer. It consists of Fe-Zn phases with different stoichiometry across the diffusion layer. As can be seen from the Figure 6, the highest hardness values were obtained at the end of the longest processing time (at 240 min). The hardness change in the region between the substrate and the upper surface changes with the effect of the phases formed due to the diffusion mechanism. The sherardized coating is composed of the ζ—FeZn13 phase at outer layer and the δ—FeZn7 phase inner layer.

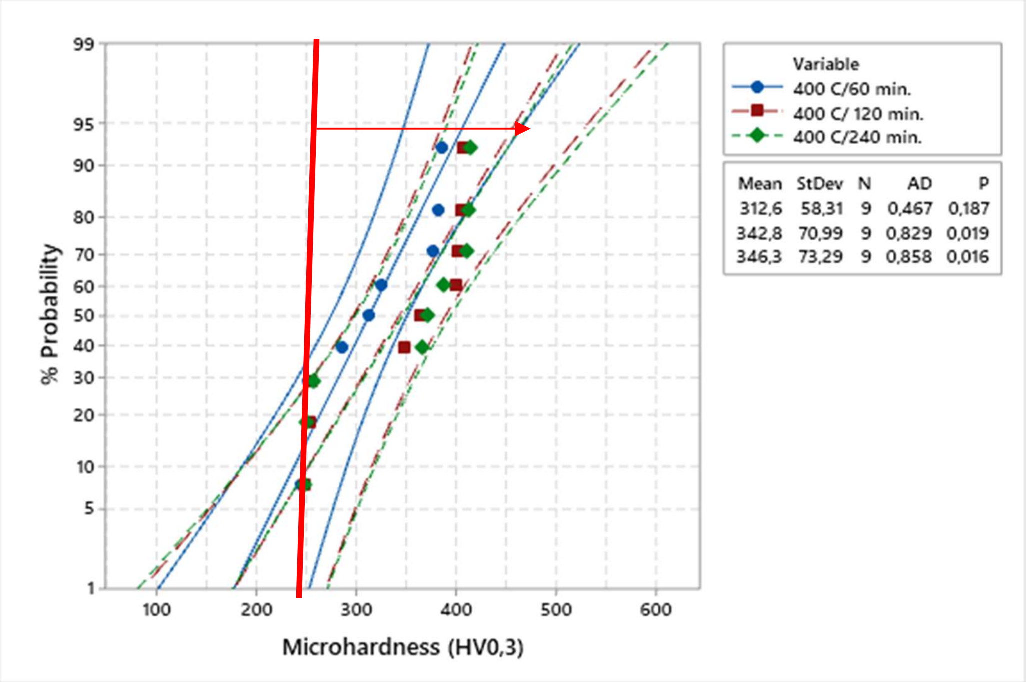

Figure 6. Microhardness change as a function of sherardizing time

Wetting angle is an important key parameter for the adhesion of paint and different organic coatings after sherardizing. Wetting angle measurement results are displayed depending on the thickness variation (Figure 7.). If the wetting angle is high, the adhesion is weak, if it is low, the adhesion is better. The surface wetting angle is higher (CA:85°) in thin coating thicknesses and decreases (to CA:48°) as the coating thickness increases. Therefore, the decrease in surface roughness as a result of both the increase in the process time and the increase in the coating thickness causes a decrease in the wetting angle. This indicates that an optimum coating thickness will provide better adhesion.

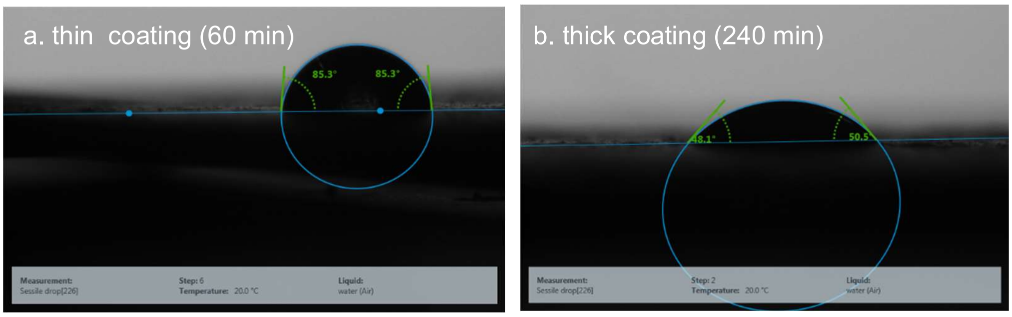

Figure 7. Contact change as a function of sherardizing thickness

X-ray fluorescence (ED-XRF) analysis is a fast and non-destructive method for measuring coating thickness and composition of plating deposits of a broad range of materials with high accuracy [8,9]. ED-XRF coating thickness measurements were performed with Fischerscope X-Ray XDAL 237 PIN (Helmut Fischer GmbH) device within the scope of DIN ISO 3497 standard. You can see the test results in Table 2.

Table 2. ED-XRF thickness measurement results
(Fischerscope, XDAL237 PIN, Helmut Fischer GmbH)

Process	400 °C/60 min.	400 °C/ 120 min.	400 °C/240 min.
1	11,89	33,21	74,30
2	9,76	35,10	75,90
3	12,12	30,11	77,70
4	11,56	36,15	78,13
5	8,12	34,33	69,70
6	13,25	38,10	71,45
7	11,56	31,82	76,33
8	10,36	33,40	75,56
9	9,67	28,30	77,63
10	9,97	27,10	70,12
Mean (µm)	10,83	32,76	74,68
S. Deviation	1,51	3,47	3,18

4.Conclusions

The sherardizing coating thickness increases with treatment time. The coating thickness increases from 17 µm to 75 µm when treatment time increased from 60 min to 240 min at 400 ºC. Thickness measurements were carried out successfully with both methods and consistent results were obtained. ED-XRF method is a more systematic and effective solution for precise thickness measurements. Both thickness measurement methods can be used in industrial conditions. For further analysis, electron microscopy (SEM) studies after metallographic preparation are useful. Microhardness values of sherardizing coating surface are increased with treatment time. Depending on the increasing diffusion time, the surface morphology and crystallites changed and the surface roughness decreased from 6µm to 4.5µm.

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