Siti Noor FitrianiMechanical Engineering Department
University of Brawijaya
Jl. Mayjend. Haryono 167
Malang, Indonesia 65145
fitrianiifety@gmail.com**Putu Hadi Setyarini**Mechanical Engineering Department
University of Brawijaya
Jl. Mayjend. Haryono 167
Malang, Indonesia 65145**Victor Yuardi Risonarta**Department of Industrial Engineering
University of Dharma Cendika
Surabaya, Indonesia

The Influence of Homogenization on Corrosion Rate of Zinc as Sacrificial Anode for API 5L X65 Steel

Corrosion is a material degradation due to electrochemical reactions involving electrical current. Corrosion cannot be avoided but it can be managed. This work investigated the influence of holding time and temperature variation for the homogenization process of Zinc (Zn) alloy. This zinc alloy is used as a sacrificial anode to decrease the corrosion rate of API 5L X65 steel. The investigation was performed with 3 varied holding times of 2, 4 and 6 hours of homogenization process while the temperature was varied at 150, 250 and 350°C. After that, a zinc alloy with a size of 40mm x 0.44 mm x 10 mm was connected to a cathode. Together with steel, both metals formed galvanic cells in this study. The metal with lower electricity potential became the anode and corroded. On the other hand, metal with higher electrical potential became the cathode and did not corrode. The lowest corrosion rate was obtained for homogenization at 150°C and 2 hours holding time. At this condition, the corrosion rate decreased by 38.36%. This occurred since higher temperatures and longer holding time of Zinc homogenization resulted in bigger and rougher grains.

Keywords: Homogenization; Zinc (Zn); corrosion; holding time; API 5L X65 Steel

1. INTRODUCTION

Corrosion is defined as material degradation due to the reaction between a metal and detrimental elements in the environment. Corrosion occurs due to electrochemical reactions involving spontaneous electrical current. Corrosion cannot be avoided but it can be managed although in many cases it is very expensive [1-3]. Corrosion is an electrochemical reaction that involves electrons movement as a result of a reduction-oxidation reaction [2]. In the oil and gas industry, corrosion may lead to detrimental effects, e.g. pipe damage pipe causing the production delay [4,5]. Various methods to control corrosion in water particularly for the piping system are therefore continuously investigated in many studies. Of these methods is the sacrificial anode which works based on the cathodic protection principle. Applying a sacrificial anode method delivers several advantages, e.g. simple, stable and low cost [6,7]. Considering the performance, Zinc and Aluminum are two typical sacrificial anodes generally used in the water environment.

Zinc is applied for corrosion protection or galvanizing on steel by forming a protecting layer on the steel surface. This formed layer prevents contact between steel and environment which then prevents steel corrosion. Zinc can reduce the corrosion rate of steel by 50%. In metallurgy, metal homogenization is generally worked out to increase the heat treatment ability of ingot casting products [8,9]. In this work, homogenization was applied to Zinc alloy to increase the effectiveness of Zinc as protective metal. API 5L X65 steel is usually used in the pipe system of manufacture as well oil and gas industry. Mechanical properties of the API 5L X65 steel pipe were responsible for the corrosion of this steel grade [10]. The corrosion occurred on oil and gas pipe are uniform corrosion, pitting corrosion, stress corrosion cracking, erosion-corrosion, galvanic corrosion, crevice corrosion and selective leaching [2,11,12].

One method to control corrosion is by applying for cathodic protection. Cathodic protection system

comprises of the impressed current system and a sacrificial anode system, usually named as a galvanic anode. In this system, the applied protection and current source are only due to the galvanic reaction of the metals. The electrolytes can be water, air or soil. Cathodic protection with sacrificial anode is usually applied in a structure with low soil resistivity and requires protecting current. Exemplary sacrificial anode protection can be seen in **Figure 1**[6,7].

Figure 1: Cathodic protection applying sacrificial anode [7]

2. METHODOLOGY

The specimens used in the study were Zinc alloys and 5L X65 API steel (**Table 1**). Major elements of Zinc alloy used are Zinc (79.97 %wt), Ferrous (12.70 %wt), and Yttrium (3.60 %wt) (**Table 2**). The chemical composition of API 5L X65 steel is presented in **Table 3**. In this study, homogenization was worked out for varied holding times and temperatures at 2, 4 and 6 hours and 150°C, 250°C and 350°C, respectively. After heating, the specimens were cooled down at room temperature.

Table 1: Dimension of Sacrificial Anode and steel

Specimen	Length [mm]	Width [mm]	Thickness[mm]
Zinc alloy	40	10	0.44
5L X65 API steel	40	10	5

Table 2: Chemical Composition of Sacrificial Anode

Element [%wt]	S	C	Cr	Mn	Fe	Ni	Zn	Y	Zr	La	Yb
	0.30	0.17	0.068	0.043	12.7	0.092	79.97	3.6	2.5	0.03	0.46

Table 3: Chemical composition of API 5L X65 steel

Element [%wt]	Fe	Mn	P	C	S
	99.20	0.60	0.05	0.12	0.04

2.1 Corrosion Rate Analysis

The method for simple corrosion rate calculation is by performing a weight-loss method. The method is conducted by immersing the sample of metal in particular corrosive media, e.g. NaCl. The test is usually called an immersion test and categorized as an accelerated test. Weight loss (W) [gr] was calculated through the difference between initial weight (W_i) [gr] and final weight (W_f) [gr] (eq. 1) [13]:

$$W = W_0 - W_A \quad (1)$$

Corrosion rate (CR) [mmpy] depends on metal density (ρ) [g/cm³], width of metal surface (A) [mm], weight loss (W) [gr], and homogenization time (t) [hour] (**eq. 2**).The corrosion rate in mmpy can be then converted into g/m².day (**Table 3**).

$$CR = K \times W / (A \times \rho \times t) \quad (2)$$

where: K = constant (87600)

Table 3: Conversion of corrosion rate unit [16]

	mA/cm ²	mmpy	mpy	g/m ² .day
mA/cm ²	1	3.28 M/nd	129M/nd	8.95 M/nd
mmpy	0.306nd/M	1	39.4	2.74d
mpy	0.00777nd/M	0.0254	1	0.0694d
g/m ² .day	0.112n/M	0.365	14.4/d	1

* mpy : mile per year

mmpy :milimeter per year

2.2 Microstructure Analysis

The microstructure of sacrificial anode was investigated after homogenization treatment. In the beginning, the sample was polished by sandpaper with a grit of 400, 100, and 2000 and being polished using a flannel cloth. After the specimen surface was smooth and shiny look, the specimen was then dried. After that, the surface of the polished specimen was deeply immersed into an etchant solution containing 15 mL of H₂O and 15 mL of HCl. After 5 to 10 seconds, the specimen was then rinsed with flowing water and then dried. After the sample preparation was finished, the sample was then photographed with 100x magnification.

2.3 Experiment of Cathodic Protection

After the specimen being cut and treated in the homogenization process, the specimen was cleaned. Every pair of anode and cathode was entirely immersed in a corrosive solution containing 3.4 %V NaCl(**Figure 2**). The experiment was conducted without stirring and electrolyte speed was neglected in this study. Anode and cathode were connected to an electric conductor until the galvanic cells were formed. The corrosion reaction was accelerated by the charging app. 350 mA current from an AC-DC adaptor. After immersion of the first 1 hour, the specimen was cleaned and weighed by using a digital scale with 0.001 gr of accuracy. After being weighted, the specimen was re-immersed again. The cleaning and weighing of the specimen were repeated 10 times with the sampling period was 1 hour. **Figure 3** shows the galvanic cell during the test. The red cable is for positive current connected to the Zn anode while the black cable is for negative current connected to the API 5L X65 steel cathode.

Figure 2. The schematic diagram of Galvanic cells for corrosion test in this study

Figure 3. Galvanic cell diagram during the Test

4. RESULT AND DISCUSSION

4.1 Electrochemical Test

Figures 4 - 5 and Tables 4 - 5 show the corrosion rate of Zn as sacrificial anode and API 5L X65 steel as cathode

Figure 4: The curve of polarization of API 5L X65 steel without treatment

Table 4: The Parameter of Specimen Polarization without Treatment

Specimen	I_{corr} [A]	Rate		Voltage [V]		
		Corrosion [mmpy]	Scan [V/s]	Start	Stop	Step
API 5L X65	3.85×10^{-5}	0.4475	0.001	-0.1	0.1	0.001
Zn Anode	8.00×10^{-6}	0.10884	0.001	-0.1	0.1	0.001

Figure 5: The Curve of Polarization of Zn Anode without Treatment

4.2 Weight Loss Method

Investigation of weight loss was worked out by immersing the specimen of zinc alloys and API 5L X65 steel into 3.5% NaClating as a corrosive solution. The surface width of the specimen for this test was constant at 8.44 cm². The zinc alloys and API 5L X65 steel were connected by 5 V voltage to accelerate the corrosion process. High weight loss, i.e. 0.460 gr, occurred for the homogenization process at 350 °C for 3 and 6 hours immersion duration (**Table 6**). The lowest weight loss is for the homogenization process at 150 °C and 2 hours holding time. For this case, immersion duration for 3, 6 and 9 hours resulted in a weight loss of 0.285 gr, 0.489 gr and 0.724 gr, respectively. This shows that the homogenization process of Zinc alloy achieved its optimum condition at 150 °C and 2 hours holding time. High weight loss occurred for the homogenization process at 350 °C and 6 hours holding time. This circumstance occurred since heat treatment changed the mechanical

properties of Zinc alloy, particularly grain size and hardness of this alloy. The data of weight loss and immersion duration are used as input values in **eq. 2** to determine the corrosion rate of each specimen.

Table 6: The Data of Corrosion Rate Test with Weight Loss Method

Sample	Weight [gr]			Test duration [hour]	Corrosion rate [g/m ² .day]
	Initial	Final	Loss		
X ₁₁	1.133	0.848	0.285	3	2701.69
		0.644	0.489	6	2317.77
		0.409	0.724	9	2287.75
X ₁₂	1.139	0.817	0.322	3	3052.44
		0.597	0.542	6	2568.98
		0.386	0.753	9	2379.38
X ₁₃	1.125	0.702	0.423	3	4009.88
		0.459	0.666	6	3156.71
		0.270	0.855	9	2701.69
X ₂₁	1.157	0.814	0.343	3	3251.51
		0.576	0.581	6	2753.83
		0.309	0.848	9	2679.57
X ₂₂	1.137	0.767	0.370	3	3507.46
		0.576	0.561	6	2659.03
		0.348	0.789	9	2493.14
X ₂₃	1.130	0.713	0.417	3	3953.00
		0.504	0.626	6	2967.12
		0.255	0.875	9	2764.89
X ₃₁	1.076	0.738	0.338	3	3204.11
		0.469	0.607	6	2877.06
		0.198	0.878	9	2774.37
X ₃₂	1.037	0.75	0.287	3	2710.65
		0.509	0.528	6	2502.62
		0.278	0.759	9	2398.34
X ₃₃	1.071	0.611	0.460	3	4360.63
		0.257	0.814	6	3858.21
		0.000	1.071	9	3384.22

X_{ij} = sample with variation temperature of *i* and holding time of *j* hours

Figure 6: The corrosion rate of the sacrificial anode of Zn

The highest corrosion rate of 4360.63 g/m².day was obtained at 350 °C in 3 hours of immersion duration (**Figure 6**). For 6 and 9 hours of immersion duration, the corrosion rate decreased to 3858.21 and

3384.22 g/m².day respectively. At 150 °C, the corrosion rate for 3 hours, 6 hours and 9 hours immersion duration are 2701.69, 2317.77 and 2287.75 g/m² respectively. This circumstance occurred since anode experienced oxidation which then increased the number of negative ions. On the contrary, the potential was always positive in the reduction process. This data shows that Zn served as a sacrificial anode that protected the steel in this study.

Figure 7. The difference of corrosion rate of anode and cathode during 10 hours immersion

The highest corrosion rate on Zn anode was also followed by the highest corrosion rate on API 5L X65 steel cathode (**Figure 7**). The highest corrosion rate, i.e. 3687.68 g/m².day, occurred for the homogenization process at 350°C and 6 hours holding time. On the other hand, the lowest corrosion rate, i.e. 2435.74 g/m².day, occurred for the homogenization process at 150 °C and 2 hours holding time. The highest corrosion rate on the cathode is 45,82 g/m².day. This occurred since Cl⁻ ions experienced difficulty to attach on the metal surface. The calculation shows that the highest corrosion rate of the anode was obtained after the specimen was immersed in 3 hours (**Figure 8**). The corrosion rate decreases for the specimen with 6 and 9 hours immersion duration which is due to the low weight loss rate of the specimen. **Figure 7** proves that Zinc anode protected API 5L X65 steel cathode and this is supported by the calculation of corrosion rate efficiency (**Table 7**).

4.3 Efficiency of Corrosion Rate

The highest efficiency is obtained for the homogenization process at 150°C and 2 hours holding time, i.e. 38.36% (**Table 7**). The efficiency of the corrosion rate is predicted due to the mechanical properties of both Zn and steel. For this reason, microstructure analysis and hardness tests are worked out in this study.

Table 7. The efficiency of corrosion rate

Sample	Corrosion rate [mmpy]		Efficiency [%]
	Without treatment	With treatment	
X ₁₁	202.01	124.50	38.36
X ₁₂		136.32	32.51
X ₁₃		168.14	16.76
X ₂₁		147.98	26.74
X ₂₂		147.55	26.95
X ₂₃		165.02	18.83
X ₃₁		150.88	25.31
X ₃₂		129.86	35.71
X ₃₃		197.70	2.13

X_{ij} = sample with variation temperature of *i* and holding time of *j* hours

4.4 Microstructure Analysis and Hardness Test

Microstructure analysis is important in this study to investigate the uniformity of grains on each specimen. Microstructure analysis was performed on the specimen of sacrificial anode Zn without treatment and with treatment for two treatment cases. The first is for the homogenization process at 150°C and 2 hours holding time while the second one for the homogenization process at 350°C and 6 hours holding time. The microstructure analysis showed that higher temperatures and longer holding time resulted in higher grain size (**Figure 8**).

Figure 8: Microstructure of sacrificial anode after being heated: (a) without treatment; (b) at 150°C and 2 hours holding time; (c) at 350°C and 6 hours holding time and room temperature cooling (200x); (d) how to take a sample to determine the number of grain.

Table 8: Grain Size Calculated based on ASTM E112-12

Specimen	Number of grain		NA [mm ²]	ASTM grain size [G]	Grain diameter [μm]	
	Inside	Intercepted			Average	σ
X ₁₁	118	46	1128	7.19	29.96	0.0039
X ₃₃	89	36	856	6.79	34.32	0.0044
Without homogenization	78	45	804	6.70	37.32	0.0045

X_{ij} = sample with variation temperature of *i* and holding time of *j* hours

Table 9. Hardness Test for Various homogenization process

Specimen	Hardness [HRT]
X ₁₁	71.17
X ₃₃	59.47
Without homogenization	32.47

X_{ij} = sample with variation temperature of *i*°C and holding time of *j* hours

Zn had a lower corrosion rate due to the smaller grain size (**Table 8**). This occurred since higher temperatures increase ductility and decrease hardness. When ductility increases, the corrosion rate increases. **Tables 8 - 9** show that the homogenization at 150°C and 2 hours holding time delivered the highest hardness, i.e. 71.17 HRT. At this temperature, grains size of Zn alloy became small which restricts Cl⁻ ion penetration into the metal surface. This decreases the corrosion rate. As a result, the efficiency increased, the corrosion rate decreased and the sacrificial anode has longer service time [14,15]. Although the weight-loss method is incomparable with the electrochemical method, both methods do not show any discrepancy in explaining the corrosion rate in this work.

5. CONCLUSIONS

This work shows that homogenization temperature and duration influences grain size which then influences hardness and corrosion rate. The lowest corrosion rate occurs for homogenization at 150°C and a holding time of 2 hours. At this condition, the grain size was only 29.964 μm . As a result, the corrosion rate decreases by 38.36%. For homogenization at 350 °C and 6 hours holding time, the corrosion rate is the highest since high temperature increases the grain size. This decreases hardness and increases the corrosion rate. A higher corrosion rate will shorten the service life of the sacrificial anode.

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