

## Improving the Corrosion Resistance of Carbon Steel Cylindrical Pipe by Nano-Materials Coating, Part -1.

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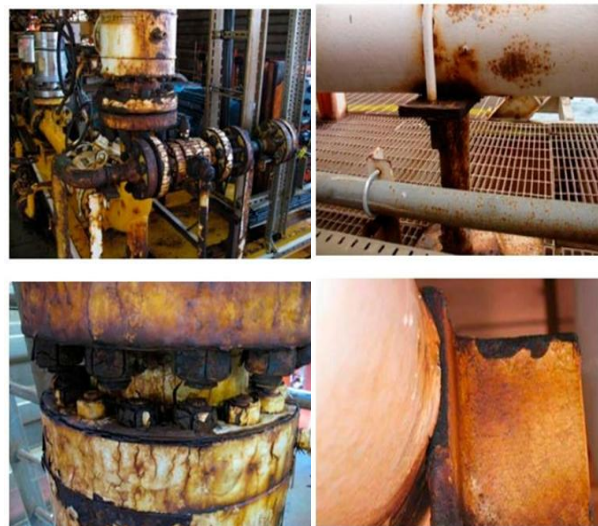
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**Abstract:** Recent research has shown that the Nano coating materials play a vital role in improving performance of corrosion resistance in hostile environment and enhancing the mechanical properties and reducing the dimension changes. Due to the superior capabilities of Nano coating in many benefits which can be achieved, in addition to corrosion resistance, mechanical properties, make it smoother, stronger and improves its adhesive properties. In this work, the effect of anti-corrosive nanomaterials (Cobalt and Zinc) coating on chemical corrosion behavior and mechanical properties of carbon steel cylindrical pipe were studied in detail. The Nano-coating was done with different thicknesses (300nm,600nm,900nm and 10  $\mu\text{m}$ ), then analyzed using ANSYS software technology (version .19).The results showed that there is a strong relationship of corrosion improvement with improving mechanical properties, especially surface deformation resistance, elastic strain and stresses reduction of the inner pipe surface which contains a pressurized corrosive fluid. The maximum improvement was with the thickness of the cobalt coating (10  $\mu\text{m}$ . The result of improvement in corrosion resistance of the cobalt-coated surface is approximately (5.165%) compared to the uncoated surface, also, the results showed an improvement in mechanical resistance and corrosion resistance because of deposition of cobalt particles better than zinc particles in all different thicknesses, with a maximum of about (66%) compared to zinc. Therefore, can conclude that the improving corrosion resistance due to coating with nanomaterials is very promising.

**KEYWORDS:** MECHANICAL PROPERTIES, NANO, COATING, ZN, CO, AND CARBON STEEL, ANSYS-19.

**List of Abbreviations:** ALD: Atomic Laser Deposition, CVD: Chemical Vapor Deposition, ISO: International Organization for Standardization, MWCNT: Multi-Wall Carbon Nanotubes, SEM: Scanning Electron Micrographs, SCC: Stress Corrosion Crack, Co: Cobalt, Ni: Nickel, nm : nanometer, Zn : Zinc,  $\mu$ : surface Roughness,  $E$ : Modulus of elasticity,  $\nu$ : Poisson's ratio,  $\sigma$ : Sigma (tensile stresses),  $P$ : Fluid pressure

**Background:** A relationship formed between corrosion and the degradation of metals' mechanical properties. The further corrosion the metal undergoes, and both the tensile strength and fracture strength of the metal are diminished by the corrosion. Corrosive wear is also known as chemical wear or oxidation. Due to the chemical and electrochemical interaction of the surface and the environment, this form of wear can occur. In corrosive wear, the fine corrosive products on the surface reflect the wear debris. As the shaped layer is broken or removed by sliding and abrasion because of corrosion, another layer starts to form, and the process of removing a new corrosive layer formation repeated. The most common corrosive media are water, seawater, oxygen, acids, chemicals, atmospheric hydrogen sulfide and sulfur dioxide. Corrosion can have a variety of negative effects on metal. When metal structures suffer from corrosion, they become unsafe which can lead to accidents, such as collapses. Even minor corrosion requires repairs and maintenance [1]. Corrosive wear can be minimize by selecting the right materials that will resist environmental attack, by applying different coating methods. This can Control the environment, and reducing operating temperatures in order to lower the rate of chemical reaction. Researchers distinguished by being a corrosive complex medium due to the high salt content, dissolved organic substances, such as carbohydrates and amino acids, and dissolved gasses such as (chiefly nitrogen, oxygen, argon, and carbon dioxide). The presence of carbonates, chloride and other component will influence seawater chemistry significantly and lead to the formation of scale at the membranes and in piping structures. This lead to severe corrosion of alloys, especially carbon steel, and with high level of presence of dissolved oxygen, corrosion will accelerate [2], as can be seen in figure (1) shows an example of corrosion effect on bolts, valves, flanges, piping, and pipe support.



**Figure (1)** Example of corrosion effect on bolts, valves flanges, piping, and pipe support [2]

One of the most important problem of damage that contribute to reduce both the static and cyclic strength of a performance of thin-walled structures that immersed in seawater such as pipelines is corrosion problem. It is a process depend on a time, local environment inside or near the pipeline and occur on the internal and external surfaces in the pipe, in the base material and contact welding. As such, protection of metal equipment in a seawater environment will give prime consideration [3].

Predicting the rate of corrosion of a steel structure in seawater is one of the difficult tasks facing design and corrosion engineers. The main parameters that effect on the rate are dissolved oxygen, salinity, temperature, ph and Sulphur [4]. Protective coatings are one of the most important methods used to reduce metal waste caused by surface corrosion, which leads to extend the life of metal equipment. Example of these coatings are chromized or aluminized coatings [5]. Chromatid zinc deposits give a better protection against corrosion compared to unprotected zinc that was corrodes quickly in chloride medium [6]. In present work a more advanced coating will be used which is a Nano-coating.

## Corrosion and Nanomaterial:

The field of nanomaterial have found one of the most promising topics in different applications such as chemistry, engineering, physics, biology that will change the direction of nanotechnology advances in wide range of fields. The term "nanomaterials" employed to describe of the creation and exploitation the materials where at least one dimension in the range from approximately 1-100 nanometer. Due to their unique properties in nanoscale, observations showed that nanomaterial's are different from their bulk moieties and cannot be studied as same as from their bulk molecules [7]. The use of nanomaterials reduces the content of costly and toxic elements in alloy components, which gives high profitability in material cost, excellent performance, and enhances the mechanical properties of the coating. Electrodeposition and sol-gel chemistry method are attractive techniques in Nano-coatings applications, as it is cheaper and novel strategies [8]. Nano coatings have significant potentials to resistance the corrosion performance of surfaces compared to micro material coatings. Due to their fine grain sizes, nanocrystal line structures are superior over microstructures for corrosion resistance .where provide a better filling ,a higher integrity of the coated surface and it also called for the availability of chromium-toxic coating replacements . However, the coating thickness and composition should optimize to avoid decrease its protective characteristics towards corrosive and eroding influences [9]. Corrosion induces changes in the composition of the elements and decreases in grain size, contributing to the deterioration of corroded materials' mechanical properties (yield strength, ultimate strength, and failure strain). Applied stress accelerates corrosion and the loss of ultimate strength and failure strain of corroded materials exacerbated by its interaction with corrosion [10]. The tribo-corrosion behavior does not depend on the electrochemical environment only. There are other factors that play it's role in the corrosion process, such as design, equipment, and operating conditions, these factors do not affect independently, but depend on each other. Anti-corrosion nanomaterials and their coatings play an important role in improving mechanical properties such as ductility, high hardness, etc. in addition to surface properties such as residual stresses, surface roughness and distribution of particles on surface [11].

**Research Objectives:** In present study the following main objectives will achieved:

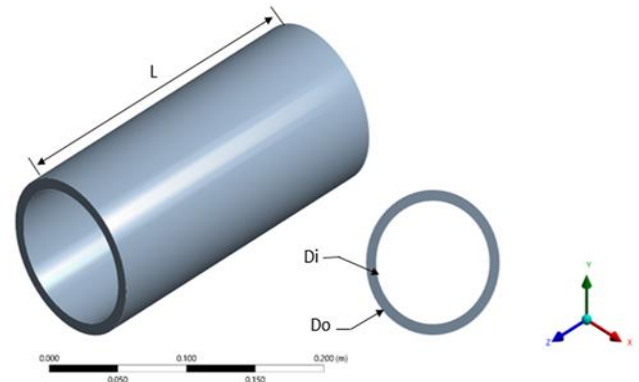
1. Study and analyze the improvement of corrosion properties when using a Nano coating for carbon steel cylindrical pipe subjected to sever corrosive environment with relationship of mechanical properties improvement.
2. Selection nanomaterials that have shown better properties for anticorrosion resistance especially in salty water.
3. Study and analyze the surface roughness before and after deposition of nanomaterials of different thickness and recommending the best one.
4. Analyze the improvement of mechanical properties of the study materials after coating by anticorrosion nanomaterials and find a relationship between these improvement and corrosion resistance.

## Research Methodology:

A comprehensive review of the literature pertaining to Nano materials and their applications in the field of corrosion has undertaken in order to achieve the above objectives for this

research. Then a group of nanomaterial's with corrosion-resistant properties will be selected and simulated the effect of apply Nano coating technology using ANSYS software on a thick-walled cylindrical pipe that carries salty water under internal pressure, using electrodeposition Nano coating method. After that will study and analyze the results and compare the changes in corrosion mechanical and wear properties before and after applying coating by nanomaterials of different thickness.

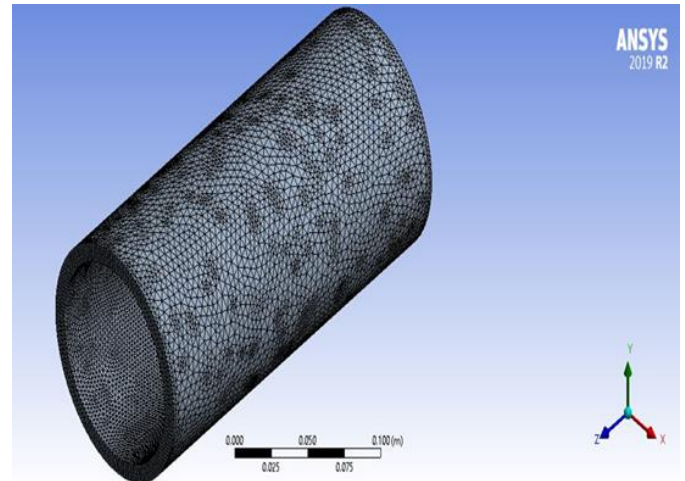
The Geometric modeling of the study: One finite element model has created. Thick walled cylindrical pipe coated with different Nano thickness of Zinc and Cobalt materials separately, as in figures (2 to 5), which show the pipe specimen will analyze and coated during this work. At the beginning, the CAD geometry built using space claim in ANSYS with the given dimensions. Geometry transferred into ANSYS mechanical and thin Nano layer defined on the inner surface wall using surface coating from ANSYS.



**Figure (2)** Front and ISO views of thick-walled cylindrical pipe specimen with dimensions.

Where:  $L=0.25\text{m}$   $Do=0.1143\text{m}$   $Di=0.0971804\text{m}$

**Mesh Details:** Parts was converted to small elements in order to use FEA methods for solving the problem, refinement of mesh was done on the inner wall where the Nano coating is located in order to get more accurate results, number of Nodes is 143620 and elements is 71929.



**Figure (3)** Thick-walled cylindrical pipe with 4.5 mm on outer and side faces and 3.5 mm on inner face elements size of mesh.

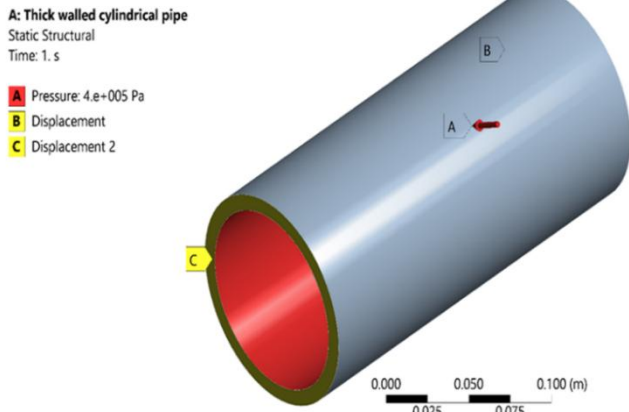


Figure (4) Boundary Condition of thick-walled cylindrical pipe specimen.

**Materials:**

In the present work cobalt and zinc which are anticorrosion nanomaterial's will be used to apply coating on a thick-cylindrical pipe made from carbon steel, the physical, chemical and mechanical properties of the materials will be analysis before and after coating by Nano-materials.

**Carbon Steel:**

Carbon steels defined as those containing iron, carbon, and manganese. There are three type of carbon steel depend on the amount of carbon content is low carbon, medium carbon, and high carbon steel which contains 0.6–1.4% carbon [14]. It is the most widely used engineering material for service in seawater and many engineering applications in high temperature conditions such as power plant, chemical treatment, mining, mineral equipment Processing and other industrial fields, it offers many advantages of low price, easy availability, ease of fabrication, and a satisfactory rate of corrosion [15]. Carbon steel piping and tubing because of their minimal resistance to corrosion there are limits on their operating time [16].

**Zinc:**

Zinc is the fourth most used engineering metal in the world, a bluish-white metal, and one of the main uses for zinc is steel coating to protect against corrosion in the presence of an electrolyte such as moist soils or seawater.

**Cobalt:** Cobalt is one of the rare elements in the Earth's crust of about 0.100%, usually distributed in conjunction with nickel, lead, silver, iron, etc. It is a white, hard-bluish, ferromagnetic metal, relatively unreactive and slowly dissolves in mineral acids without union with hydrogen or nitrogen [12]. Cobalt is now widely used in the production of alloy steel, which is the base metal in most of them. Cobalt alloys distinguished by being strength, high melting point, and high resistance to oxidation [13].

**Results and discussions:** Mechanical properties including the principle stresses, deformations, linear stress resistance and the consequence on corrosion resistance were studied for carbon steel [ASTM A53 (ASME SA53)] thick walled cylindrical pipe, the pipe is coated with different Nano thicknesses of Cobalt (Co) and Zinc (Zn) with different thicknesses. The study was conducted and running through surface coating technique using ANSYS Software, Product Release 19.2. Uniformly distributed pressure (4 bars) applied on the inner walls of the pipe this is the same. Initially the boundary conditions were applied before coating the pipe and then the same conditions applied after the pipe coated by Cobalt or Zinc at different thicknesses (300nm, 600nm, 900nm and 10 μm), then the mechanical properties on the pipe were measured.

**a) Total Deformation:** Deformation in X,Y, and Z directions was measured using total deformation resulted due to applying uniformly distributed internal pressure, figures (14) and table (1) show the values of the total deformation before and after

coating thick-walled cylindrical pipe with different Nano thicknesses of Cobalt and Zinc separately.

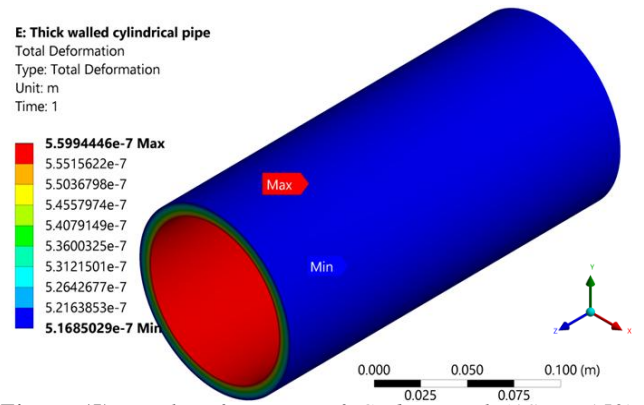


Figure (5) Total Deformation of Carbon steel (ASTM A53) without coating.

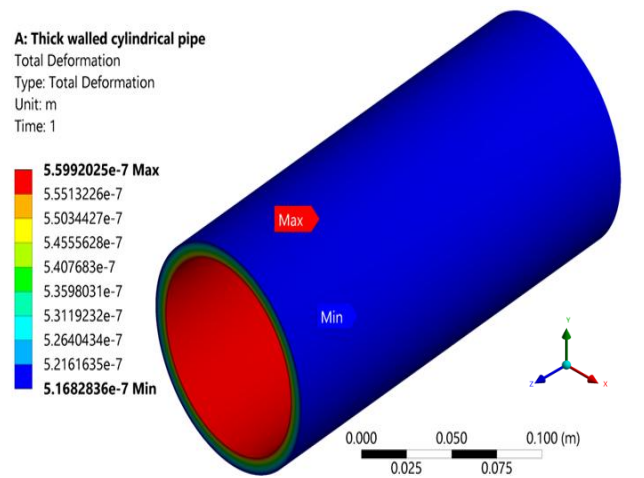


Figure (6) Total Deformation of Carbon steel (ASTM A53) with 300 Nanometers of Cobalt.

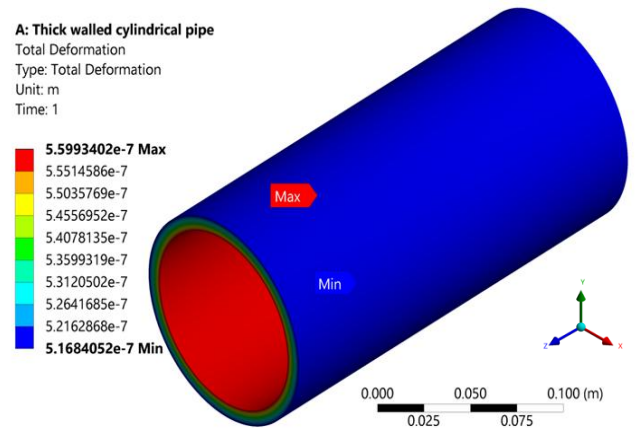
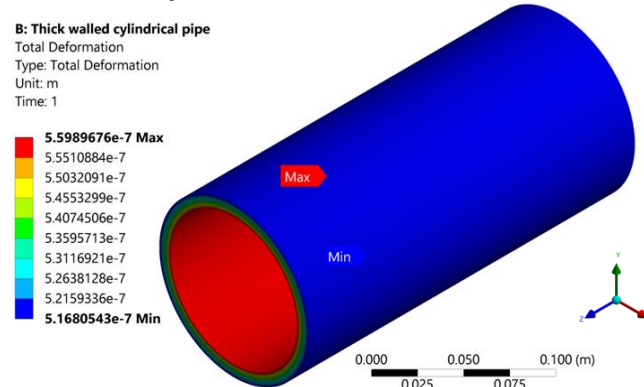
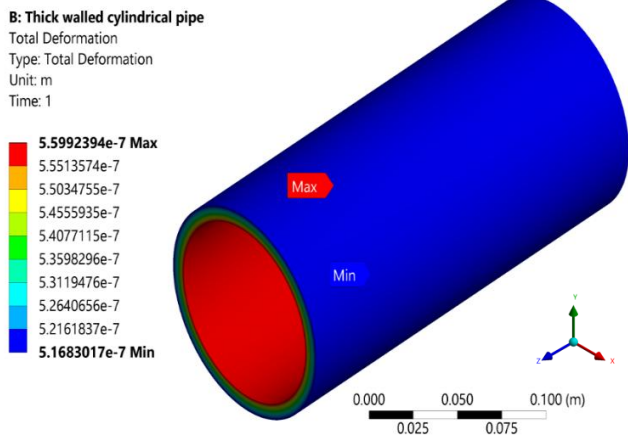


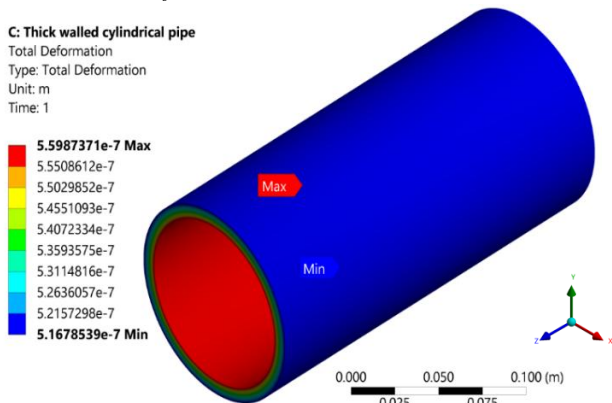
Figure (7) Total Deformation of Carbon steel (ASTM A53) with 300 Nanometers of Zinc.



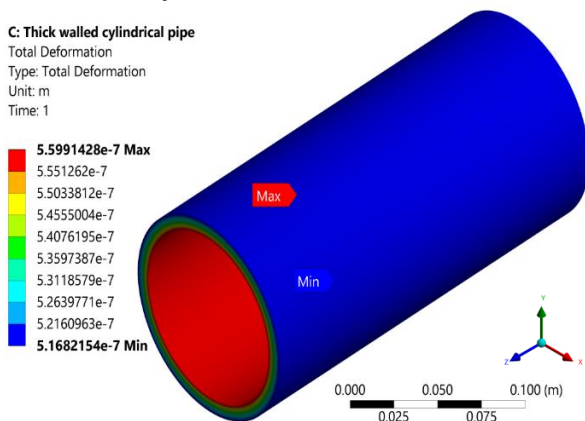
**Figure (8)** Total Deformation of Carbon steel (ASTM A53) with 600 Nanometers of Cobalt.



**Figure (9)** Total Deformation of Carbon steel (ASTM A53) with 600 Nanometers of Zinc.

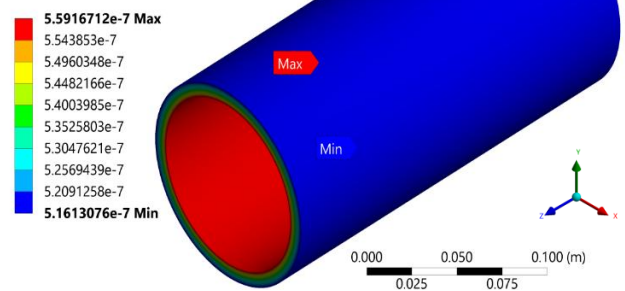


**Figure (10)** Total Deformation of Carbon steel (ASTM A53) with 900 Nanometers of Cobalt.



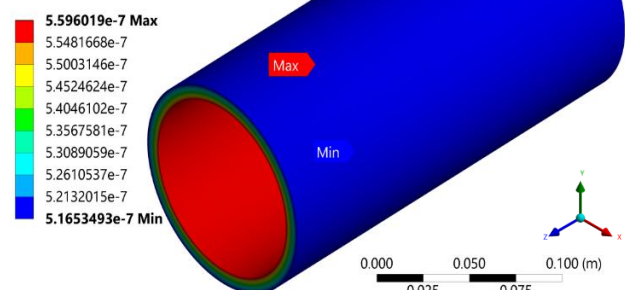
**Figure (11)** Total Deformation of Carbon steel (ASTM A53) with 900 Nanometers of Zinc.

**D: Thick walled cylindrical pipe**  
Total Deformation  
Type: Total Deformation  
Unit: m  
Time: 1



**Figure (12)** Total Deformation of Carbon steel (ASTM A53) with 10 Microns of Cobalt.

**D: Thick walled cylindrical pipe**  
Total Deformation  
Type: Total Deformation  
Unit: m  
Time: 1



**Figure (13)** Total Deformation of Carbon steel (ASTM A53) with 10 Microns of Zinc.

**Table (1)** Percentage change in maximum values of total deformation ( $\Delta$ ) and corrosion resistance at different thicknesses.

Coating Thickness	Cobalt (Co)			Zinc (Zn)		
	Absolute Value of $\Delta$ (m)	improvement %	Corrosion Resistance %	Absolute Value of $\Delta$ (m)	improvement %	Corrosion Resistance %
0.0 nm	5.5994446E-07	0	0	5.5994446E-07	0	0
300 nm	5.5992025E-07	0.004323643	0.658	5.5993402E-07	0.001864471	0.432
600 nm	5.5989676E-07	0.008518702	0.923	5.5992394E-07	0.003664649	0.605
900 nm	5.5987371E-07	0.012635182	1.124	5.5991428E-07	0.00538982	0.734
10 $\mu$ m	5.5916712E-07	0.138824483	3.726	5.5960190E-07	0.061177496	2.473

Improvement percentage =  $|(original\ value - new\ value) / (original\ value)| * 100\%$   
Original value: value before coating. New value: value after coating.

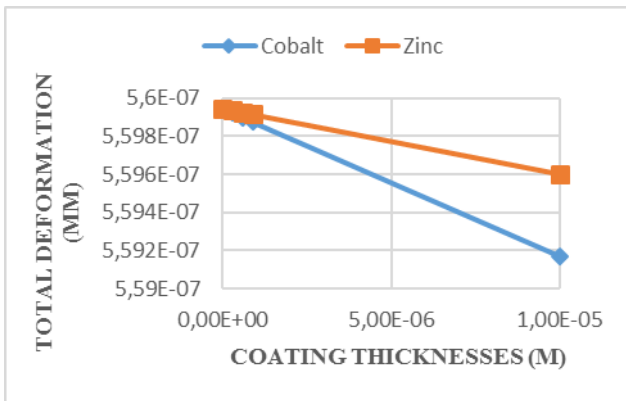


Figure (14) Comparison of maximum total deformation values (mm) at different thicknesses (m) for Cobalt and Zinc

**b) Normal Elastic Strain:** Normal elastic strain is the line segment elongation or contraction resulted from normal stress perpendicular to the face of an element and is equal to change on length over the original length.

**1, Normal Elastic Strain  $\epsilon_L$  (longitudinal Strain)**

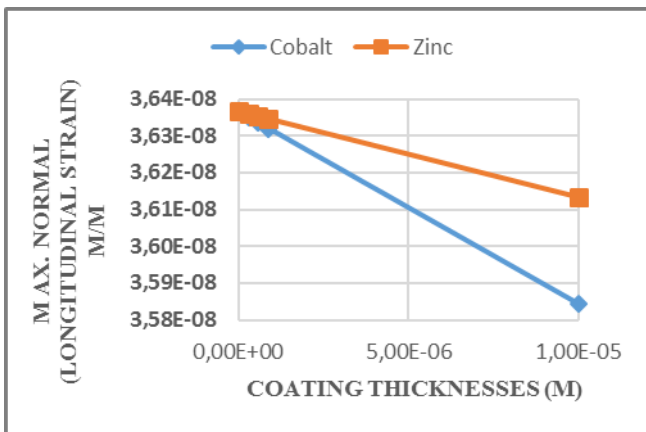


Figure (15) Comparison of maximum normal elastic strain (Z-axis) values at different thicknesses (m) for Cobalt and Zinc.

**2. Normal Elastic Strain (hoop strain)**

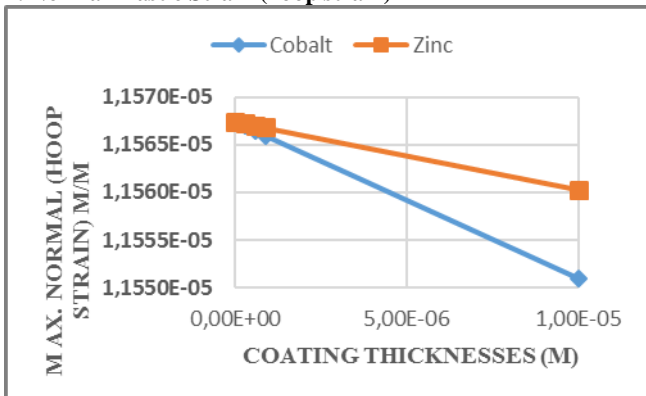


Figure (16) Comparison of maximum normal elastic strain (X-axis) values at different thicknesses (m) for Cobalt and Zinc.

**c) Normal Stress  $\sigma$ :** A normal stress occurs when a part loaded by an axial force and hence tension or compression stresses are resulted. The value of the normal force represent by force divided by the cross sectional area.

**d) Equivalent Stress  $\sigma_e$  :**

Equivalent stress (Von misses stress) usually utilized in design because it is able to represent any three-dimensional stress state as a single positive stress value Equivalent Stress represented as results of applying uniformly distributed internal pressure, figure (19) and table (2) show the values of improvement equivalent stress after coating with different Nano thicknesses of cobalt and zinc separately. It can notice that maximum value of stresses are located at the inner surface of the pipe and it is gradually decrease through thickness to outer surface, which have minimum values of stresses.

**1-Normal Stress  $\sigma_L$  (longitudinal stress):** Normal stress (Z-axis) direction is represented as results from applying uniformly distributed internal pressure along the longitudinal axis; figures (15-18) show the values of normal stress (Z-axis) after coating with different Nano thicknesses of Cobalt and Zinc separately on thick-walled cylindrical pipe.

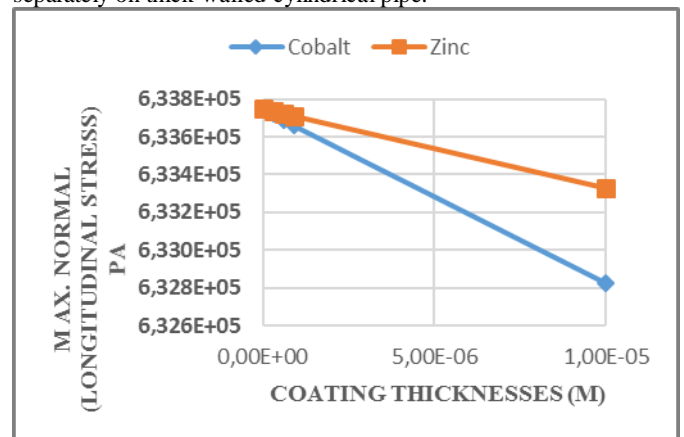


Figure (17) Comparison of maximum normal stress  $\sigma_L$  (Z-axis) values at different thicknesses (m) for Cobalt and Zinc.

**2. Normal Stress  $\sigma_h$  (hoop stress)**

Hoop stress is the stress on a cylindrical pipe wall that works in a plane perpendicular to the pipe's longitudinal axis. Normal stress (X-axis) direction represented as results of applying uniformly distributed internal pressure; figure (15-17) and table (2) show the values of normal stress (X-axis) that improved after coatings.

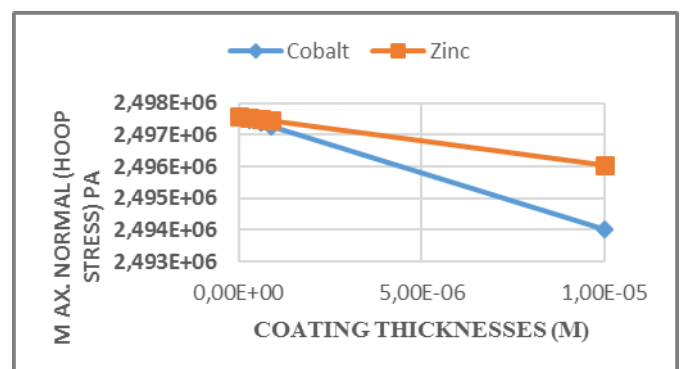


Figure (18) Comparison of maximum normal  $\sigma_h$  stress (X-axis) values at different thicknesses (m) for Cobalt and Zinc.

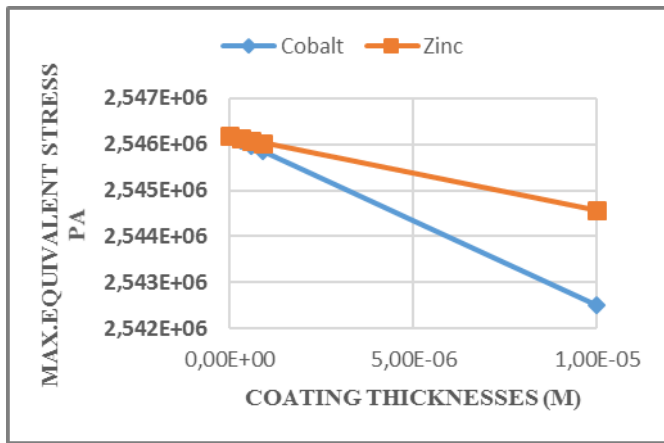


Figure (19) Comparison of maximum equivalent stress  $\sigma_e$  values at different thicknesses (m) for Cobalt and Zinc.

shear stress (XY plane) after coating with different Nano thicknesses of cobalt and zinc separately.

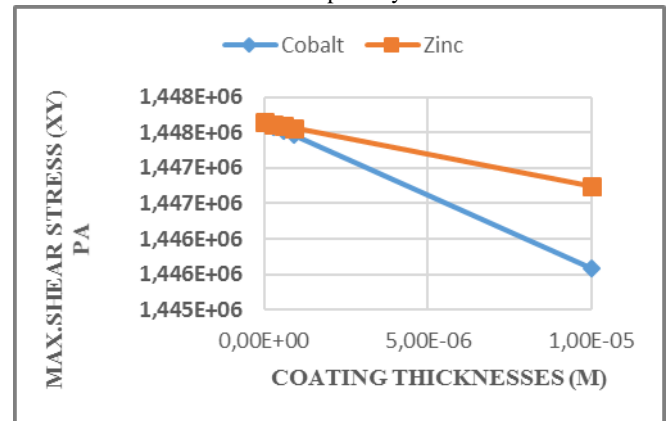


Figure (20) Comparison of maximum shear stress (XY plane) values at different thicknesses (m) for Cobalt and Zinc.

**e) Shear Stress  $\tau$  :**

Shear stress is the stress caused by two equal and opposite forces in a body, which work tangentially across the resistant portion [17].

**1. Shear Stress in XY plane:** Shear stress in XY plane is represented as a results of applying uniformly distributed internal pressure, figure (20) and table (2) show the values of maximum

Table (2) Summary of improvement percentage with different coating thicknesses and materials

	Improvement of Cobalt (Co) %				Improvement of Zinc (Zn) %			
	300 nm	600 nm	900 nm	10 $\mu$ m	300 nm	600 nm	900 nm	10 $\mu$ m
Coating thickness								
Total deformation	0.0043	0.0085	0.0126	0.1388	0.0018	0.0036	0.0053	0.0611
Normal Elastic Strain X axis	0.0042	0.0085	0.0128	0.1423	0.0018	0.0037	0.0056	0.0623
Normal Elastic Strain Z axis	0.0436	0.0872	0.1307	1.4330	0.0192	0.0384	0.0576	0.6367
Normal Stress X axis	0.0048	0.0096	0.0144	0.1453	0.0021	0.0042	0.0063	0.0663
Normal Stress Z axis	0.0042	0.0085	0.0128	0.1424	0.0018	0.0037	0.0056	0.0624
Equivalent Stress	0.0041	0.0085	0.0128	0.1431	0.0018	0.0037	0.0056	0.0627
Shear Stress XY plane	0.0042	0.0085	0.0128	0.1423	0.0018	0.0037	0.0056	0.0623
Shear Stress XZ plane	0.0224	0.0439	0.0655	0.7148	0.0103	0.0197	0.0292	0.3158
Average Corrosion Resistance	0.846	1.255	1.548	5.165	0.558	0.786	0.959	3.406

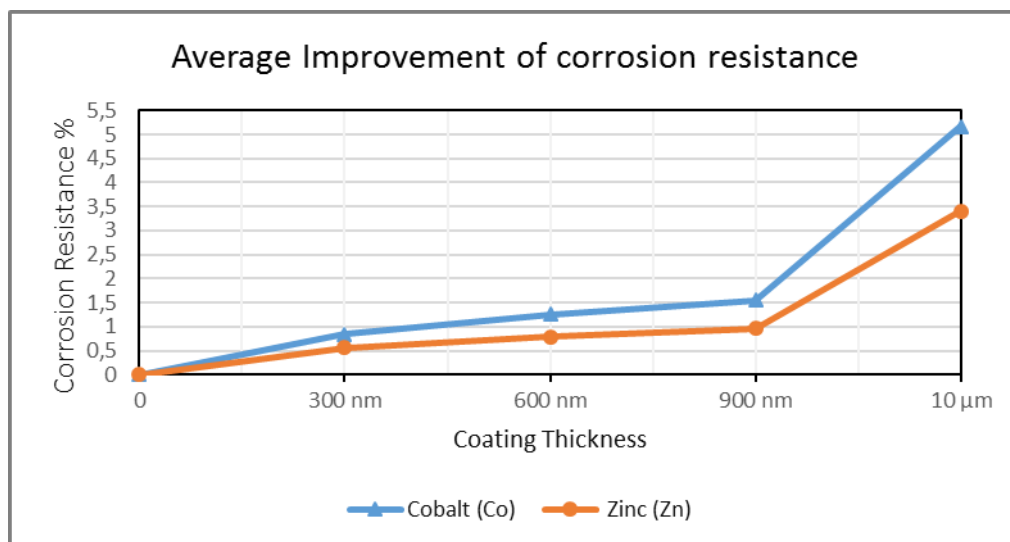


Figure (21) Average Corrosion Resistance Improvement with different Nano coating thicknesses of cobalt and zinc.

Table (2) shows a summary of improvement percentage of all deformations and stresses results with different coating thicknesses and coating materials, in addition to the rates of improvement in corrosion resistance is tabulated too. The maximum value of improvement in mechanical properties for all the studied cases is about 0.71% when coated with 10  $\mu$ m of Nano Cobalt material, while, the improvement in corrosion

resistance is about 5.2% . In other hand, the corresponding improvement for Zinc coating is 0.31% and for corrosion is 3.4%. In addition, the results showed that for the normal elastic Strain Z-axis and shear stress-XZ plane with the values of 1.4330 % and 0.7148 % respectively, when using cobalt coating. The rate of corrosion resistance, the maximum value was (5.165%) of cobalt as shown in the above figure (21).

## Conclusions:

From the analysis of the above results discussion, the following main points can be concluded:

- The Carbon steel (ASTM A53) thick walled cylindrical pipe was successfully coated theoretically with anticorrosion Nano particles of Cobalt and Zinc using ANSYS software (version .19 with different Nano thicknesses of 300nm, 600nm, 900nm and 10  $\mu\text{m}$  separately.
- The highest improvement in resistance of deformation is (0.1388 %) and corrosion resistance is (3.726%) when coated with 10  $\mu\text{m}$  of cobalt, while the minimum improvement is (0.0018 %) when coated with 300 nm of zinc. In addition, cobalt found to improve the deformation resistance by (44.0 %) and corrosion resistance by (66.3%) more than zinc.
- The maximum improvement in resistance for both longitudinal strain and hoop strain was (1.433%) and (0.1423%) respectively when coated with 10  $\mu\text{m}$  of cobalt. While the lowest value is (0.0018%) at 300 nm of zinc, that made cobalt outperform with zinc by a percentage of improvement (44.4%). Which accompanied by an improvement in the corrosion property by (11.971%), while zinc gave a good rate of improvement (7.979%).
- In both normal stresses (longitudinal stress and hoop stress) 10  $\mu\text{m}$  of cobalt gave better improvement than zinc with values (0.1453%) and (0.1424%) respectively.
- Comparing to all other coatings thicknesses, 10  $\mu\text{m}$  of cobalt has the highest percentage of change in reducing the equivalent stress (0.1535%).
- In shear stress 10  $\mu\text{m}$  of cobalt make a highest percentage of improvement in decreasing both shear stress in (XY plane) and ( XZ plane) with values (0.1423%) and (0.7149%) respectively compared to all other coatings, with rate of resistance to corrosion of (8.455%).
- The thick-walled cobalt-coated cylindrical pipe showed the largest percentage of improvement about (66 %) more in comparison with Zinc at 10  $\mu\text{m}$  thickness of coating.
- Cobalt and zinc are anti-corrosion Nano materials can help to protect and improve corrosive wear resistance, as well as rising a surface's thickness. So, the Nano-coating will be a promising solution to corrosion problems.

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