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EFFECT OF CORROSION ON MECHANICAL PROPERTIES OF COPPER-NICKEL ALLOY IN SEA WATER AND ACIDIC ENVIRONMENT

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Abstract

This paper examines the effect of corrosion on the mechanical properties of commercially available copper-nickel alloy in three different corrosive environments at room temperature. Commercially available constantan wires (Cu55%/Ni45%), 2cm diameter were cut into substrates of length 100mm and tested for hardness, strength, etc. before and after immersion in concentrated HCl, H_2SO_4 *and natural sea water. The immersion period for the substrates was one month. The results showed that the tensile strength, Young's modulus, stiffness and hardness of the specimens decreased after immersion in HCl and sea water with complete dissolution of the specimen in* H_2SO_4*. The tensile strength of the unsoaked copper-nickel alloy as evaluated from the Force – extension graph was 158 MPa, which differs from the 162 MPa based on the American Society of Materials Engineers standard by about 2.5%. With immersion in HCl, the tensile strength decreases by 8% of that of the unsoaked. Cu-Ni alloys thus have higher corrosion resistance in sea water than in HCl solution, with practically very little or no resistance to corrosion in concentrated* H_2SO_4 *solution.*

Keywords: Corrosion, Sea water, Alloy, Strength, Hardness, Passivation, Cupronickels.

1. Introduction

Copper-nickel alloys (also known as cupronickels) are generally known for their good corrosion resistance, excellent machinability, and outstanding thermal and electrical conductivity in marine environments (Alaba et al., 2018). They are used in electronics, for production of wires, sheets, tubes, and also to form alloys. A typical Copper – nickel based alloy wire is Constantan (55% Cu / 45% Ni) which has a high resistivity and is mainly used for thermocouples and electrical resistance heating. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. And its mechanical, physical and electrical properties are adversely affected by corrosion attack (Nwigbo, 2017).

The corrosion resistance of Cu-Ni alloys is attributed to their ability to form protective films of corrosion products on their surfaces. Among these corrosion products, Cu_2O plays a vital role in the corrosion protection of Cu-Ni alloys in sea water. The inner Cu_2O layer is able to incorporate foreign cations that affect its protective properties (Nageh et al., 2007).

Corrosion is known to be a problem normally associated with material deterioration in the field of oil and gas, construction, and other engineering fields (Alaba et al., 2018). All metals and alloys undergo a natural process of corrosion depending on the metal and the surrounding environment. Corrosion is the deterioration of materials by chemical interaction with their environment. For metals and their alloys, corrosion is the destructive result of electrochemical reaction between a metal or alloy and its surrounding or environment. The environment consists of the entire surrounding (air, water, acid, base, soil, etc.) in contact with the material.

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows (Nageh et al., 2007):

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack-like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to

carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion products.
9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

Corrosion of Copper in HCl

The cathodic reaction that occurs on the copper alloy surface in HCl is the oxygen reduction. Since Cu is nobler than H^+ in the electromotive series, and a cathodic reaction other than the displacement of H^+ must account for metal dissolution. This is readily available in terms of O_2 reduction from solution (Anees, 2013). Anodic dissolution of copper in chloride media has been studied extensively. The accepted anodic reaction is the dissolution of copper through oxidation of Cu to Cu^+ (Anees, 2013):

$$\mathrm{Cu} \rightarrow \mathrm{C}^+ + \mathrm{e}$$

Then Cu+ reacts with chloride ion from the solution to form CuCl:

$$\mathrm{Cu}^+ + \mathrm{Cl}^+ \rightarrow \mathrm{CuCl}$$

Insoluble CuCl precipitates on the copper surface. The CuCl species has poor adhesion, is unable to produce enough protection for the copper surface, and transforms to the sparingly soluble cuprous chloride complex, $CuCl_2$ (Kear et al., 2004).

$$\mathrm{CuCl} + \mathrm{Cl}^- \rightarrow \mathrm{CuCl}_2^-$$

It has also been reported that the $CuCl_2$ adsorbed on the surface dissolves by further oxidation (Kear et al., 2004).

$$\mathrm{CuCl}_{2.ads}^- \rightarrow \mathrm{Cu}^{++} + 2\mathrm{Cl}^- + \mathrm{e}$$

It is reported that the anodic dissolution of copper in the acidic chloride solution is controlled by both electro dissolution of copper and diffusion of CuCl_2^- to the solution bulk (Kear et al., 2004). The cathodic corrosion reaction in an aerated acidic chloride solution is:

$$4\mathrm{H}^- + \mathrm{O}_2 + 4\mathrm{e}^- \rightarrow 2\mathrm{H}_2\mathrm{O}$$

The total corrosion reaction of copper in acidic chloride solutions is as follows:

$$2Cu + 4H^{+} + 4Cl^{-} \rightarrow 2Cu^{2+} + 4Cl^{-} + 2H_2O$$

Corrosion of Copper in H_2SO_4

The reactions of copper with sulphuric acid may be divided into primary and secondary (Baeshov et al., 2014).

Primary:
1. $Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O$

This may be regarded as taking place in two steps:

(a) $Cu + H_2SO_4 \rightarrow CuSO_4 + H_2$
(b) $H_2 + H_2SO_4 \rightarrow SO_4 + 4H_2O$

2. $5Cu + 4H_2SO_4 \rightarrow Cu_4S + 3CuSO_4 + 4H_2O$

Secondary:
1. $Cu_2S + 2H_2SO_4 \rightarrow CuS + CuSO_4 + SO_2 + 2H_2O$
2. $CuS + 2H_2SO_4 \rightarrow CuSO_4 + S + SO_2 + 2H_2O$

Hence from the above reactions, copper reacts with sulfuric acid to produce copper sulfate, sulfur dioxide and water.

Several investigations have been carried out on corrosion influence on metal objects in different corrosive media. Most researchers use nanomaterial composites and alloys. In most cases, corrosion effects are analyzed using mechanical testing methods to investigate the influence of corrosion on the mechanical properties of metal. Mechanical properties here refer to the response of a metal to mechanical deformation (Nwigbo, 2017). Apostolopolous and Michaelopolous (2007) studied the influence of the degree of plastic strain, due to various levels of plastic deformation during bending, on the mechanical properties of class BSt 500_s tempcore steel, under various levels of salt spray corrosion. The results showed that even though an increase in plastic deformation resulted in an expected marginal increase in strength properties, it had a negative effect in ductility. The international community has not reached a consensus yet concerning the minimum required bending roll diameter, for stirrup production, which ranges between 4–10 times the diameter of the steel bar to be bent. It was also shown that this combination is crucial since strain fractures were recorded under the minimum required values set by the most current design guidelines and design oriented research. The results of this investigation are intended to offer an in-depth understanding of the impact of the underestimated factor of corrosion on the mechanical properties of steel undergoing plastic deformation in corrosive environments and to show the need of re-examination of existing codes.

The Impact of corrosion on mechanical properties of steel embedded in 27-year-old corroded reinforced concrete beams was investigated by Raoul et al. (2014), in which steel bars were extracted from a 27-year-old corroded reinforced concrete beam that had been exposed to a chloride environment. Bars with different degrees of corrosion and with different corrosion pit depths were tested in tension. A comparison was made between nominal and true stress for corroded and control steel specimens. It was noted that the degree of corrosion strongly affected the mechanical properties of the steel, particularly the ultimate stress and strain. Interestingly, the true yield strength of all the corroded steel bars remained almost constant while their true ultimate strength was considerably increased. A reduction of the ultimate elongation appeared to be the major effect of corrosion and affected the compliance with standards.

Wenjun Zhu (2014) investigated the mechanical properties of the corroded reinforcement using the tension tests. The yield strength and ultimate strength were studied based on the residual gravimetrical cross-section. The results found that the impact of corrosion on the ductility was more significant than that of the strength. The shape of residual cross-section was considered to be in deep relationships with the ductility of the reinforcement. The flexural performances of the beams were studied. The results showed that the corrosion deteriorated the capacity and the ductility of the corroded beams. The corrosion degree of reinforcement was found in linear with the residual yield capacity of the corroded beams. The short-span beams were formed from the corroded beams after bending tests. Mechanical tests were carried out directly to check the response of the corroded beams. The corroded short-span beams failed in bending mode with good ductility while the non-corroded beams performed a brittle shear failure mode, which showed that the corrosion of reinforcement could change the failure modes.

Daniela (2011) investigated the effects of corrosion on the static strength and fatigue life of 7075-T6 aluminum alloy using test specimens that were cut from flat sheets of aluminum and covered with masking material to restrict corrosion to a confined area. The corrosion process was accelerated by use of a galvanic corrosion cell. After corrosion, specimens were tested in tension and fatigue. The effect of corrosion on the tensile strength resulted in a large initial drop in strength, then a linear reduction in strength as mass loss increased. The tensile strength was observed to reduce significantly at low mass loss levels. The reduction of fatigue life due to corrosion tended to follow an inverse exponential reduction as mass loss increased. Even small amounts of corrosion reduced the fatigue life of the aluminum alloy drastically.

In this study, the effect of corrosion on selected mechanical properties of constantan rod (an alloy of copper and nickel) was studied in natural sea water, HCl and H_2SO_4.

Materials and Methods

The following materials were used during the experimental phase:

- Constantan wire, concentrated HCl, concentrated H_2SO_4, Sea water, etc.
- Tensile testing machine
- Brinell hardness testing machine
- Micrometer screw guage

Method

Preparation of Cu/Ni rods and the environment

Constantan rods (Cu55%/Ni45%), 2cm diameter (with composition given in Table 1), were cut into rods of length 10cm. The rods were then washed with acetone and dried to remove all traces of corrosion products that may serve as corrosion initiation sites. Concentrated HCl and H_2SO_4 were prepared in the Chemistry Laboratory at Ken Saro-Wiwa Polytechnic, Bori. Sea water collected from Kono River in Nigeria was used as one of the corrosive media. Two pieces of the constantan rods were first tested for mechanical properties – tensile strength, elastic modulus and hardness. Three pieces of the rods were then immersed separately in sea water, concentrated HCl and concentrated H_2SO_4 for a period of one month. The specimens were then taken out from the corrosive media after an immersion period of one month, cleaned, dried and tested for mechanical properties.

Table 1. 55/45 Copper -Nickel Chemical Composition

Element	**C**	**Si**	**Mn**	**Fe**	**Cu**	**Ni**
% Composition	**0.100**	**0.500**	**1.00**	**1.00**	**55.00**	**Bal.**

Mechanical Tests

Tensile test

Tensile test was carried out on both control and the immersed constantan specimens using universal tensile testing machine. The tensile test was carried out at room temperature using an Electron Control universal testing machine (Model WDW – 05) operated at a strain rate of 10^{-3}/s until fracture.

Before the test

Gage marks were made on the specimens. The initial gage length and diameter of each wire was then measured. Selected loads from the load scale of the machine were applied to the wire in tension to deform and fracture the specimen as shown in Figure 3.1 (b).

During the test

The different loads applied in tension and corresponding extension were recorded. The tests were conducted until fracture occurred in the specimen.

The various mechanical properties were calculated using the following relations;

Tensile strength, $= {P_{max}}./{CSA}$

Young's Modulus $= \frac{Stress}{Strain}$

Stress $= \frac{Force}{CSA}$

Strain$= \frac{Extension}{Original\ \ length}$

where, CSA = Cross sectional area

Rockwell Hardness Test

1. First, the indenter was pressed with the test pre-force (also referred to as pre-force or preload) to a penetration depth of h_0 in the specimen to be tested. h_0 defines the reference level (basis) for subsequent measurement of the residual indentation depth (h).
2. Next, the additional test force was applied for a dwell period defined in accordance with the standard (several seconds), whereby the indenter penetrates into the specimen to a maximum indentation depth of h_1. The test pre-force plus the additional test force gives the total test force (also referred to as total force or main load).
3. After the dwell period, the additional test force was removed and the indenter moves up by the elastic proportion of the penetration depth in the total test force and remains at the level of the residual indentation depth (h - expressed in units of 0.002 or 0.001 mm). This is also referred to as the depth differential (difference in indentation depth before and after application of the total test force).

Rockwell hardness (HR) was then calculated using the residual indentation depth (h) and a formula defined in the standard, taking account of the applied Rockwell scale.

Results and Discussion

This section gives the experimental results and compares it with the available results from other investigations on similar works. Table 2 gives the results from tensile and hardness tests on the various specimens before and after immersion in corrosive media. The interpretation and implications of the results are also presented and compared with standard results from similar investigations.

Test sample data

Gauge length = 100mm

Gauge diameter = 2mm

Table 2. Tensile test result

Load (kN)	Extension (mm)		
	Sample A (Control)	**Sample B (immersed in Sea water)**	**Sample C (immersed in HCl)**
0.0	0.00	0.00	0.00
10	0.20	0.20	0.35
30	0.40	0.75	1.00
50	1.00	1.20	1.60
80	1.60	1.90	2.60
100	2.00	2.40	3.20
120	2.30	3.00	3.90
130	2.70	3.30	4.70
140	3.10	4.00	-
143	3.50	4.50	-
150	4.50	-	-

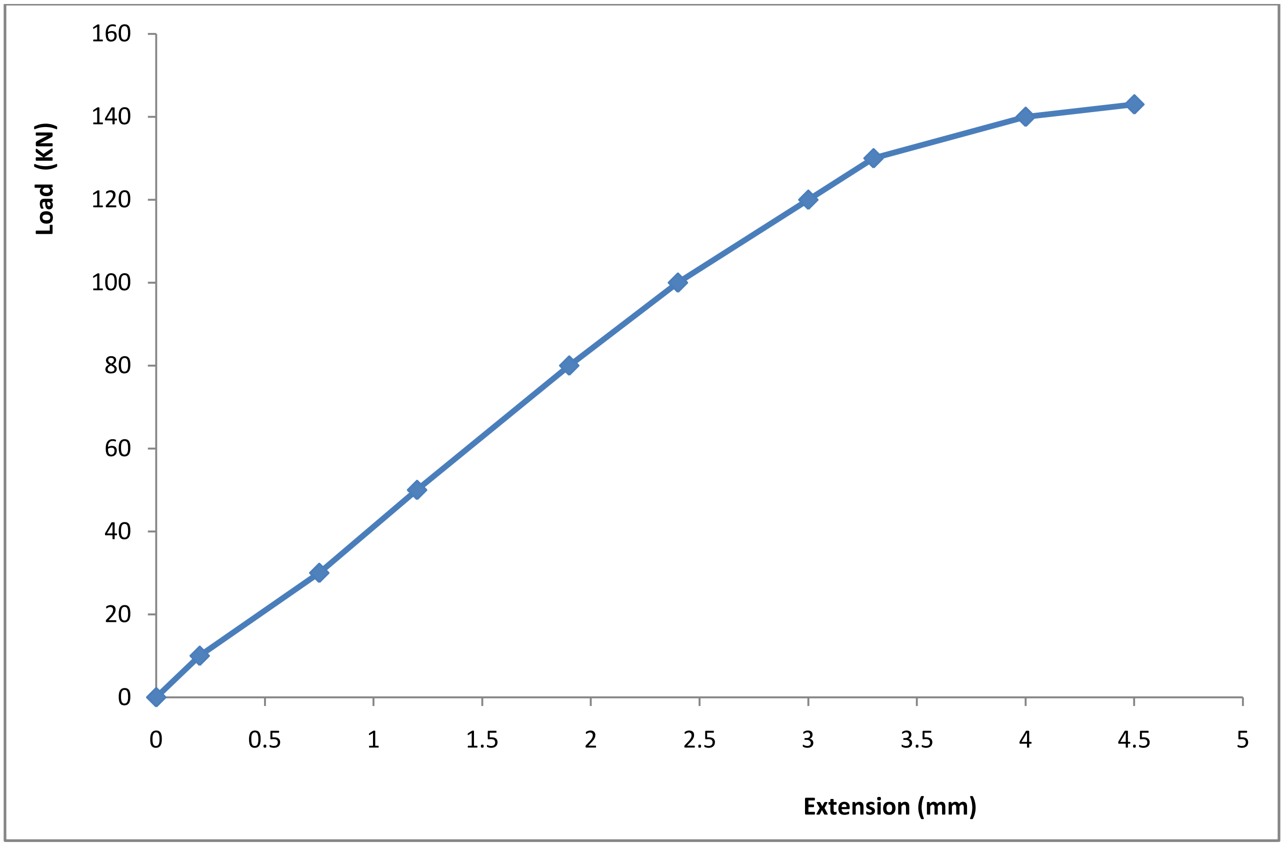

Figure 1: Load – Extension Diagram for Sample A (unsoaked specimen)

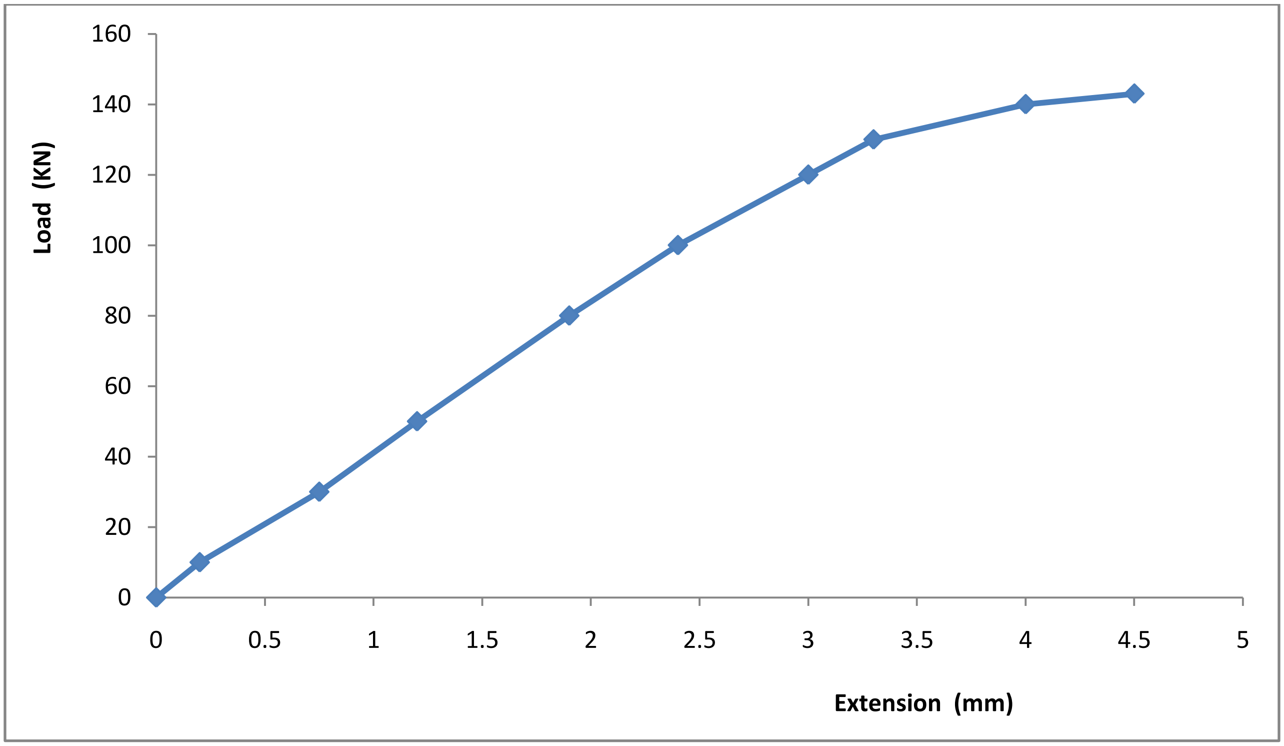

Figure 2: Load – Extension Diagram for Sample B (Specimen soaked in Seawater)

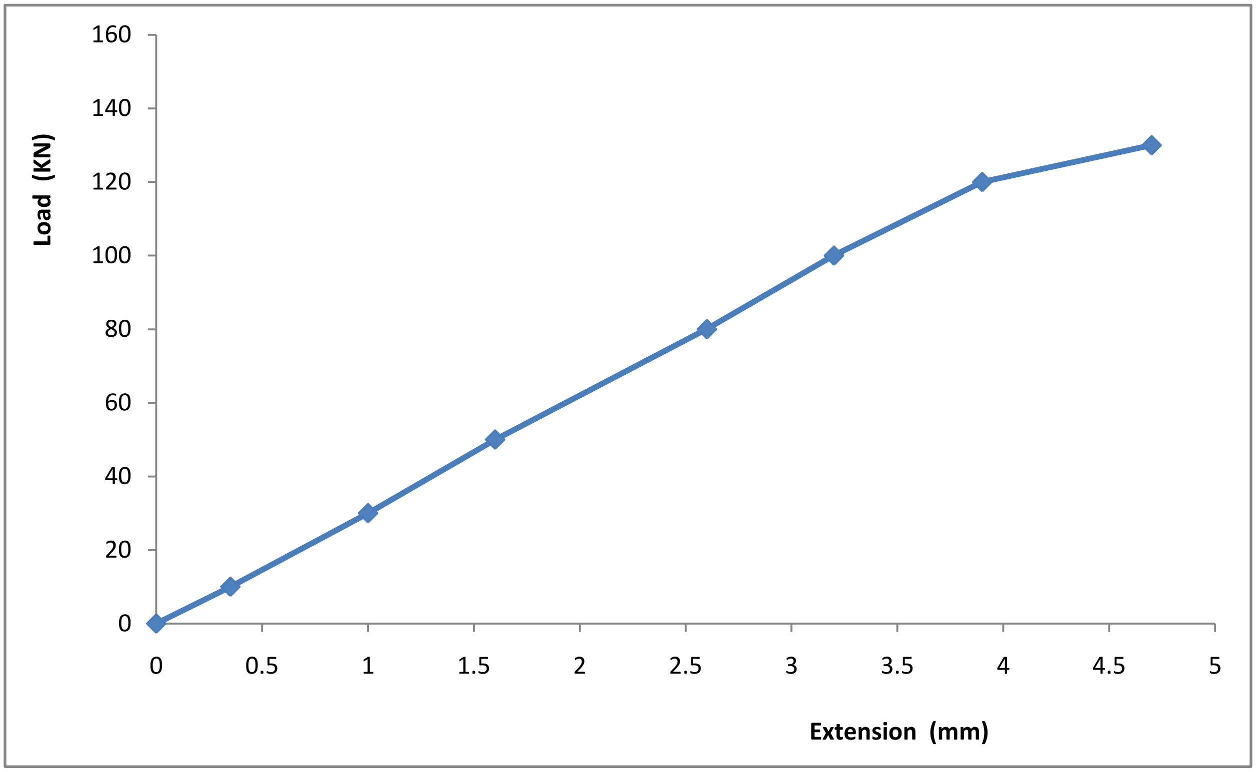

Figure 3: Load – Extension Diagram for Sample C (Specimen soaked in HCl)

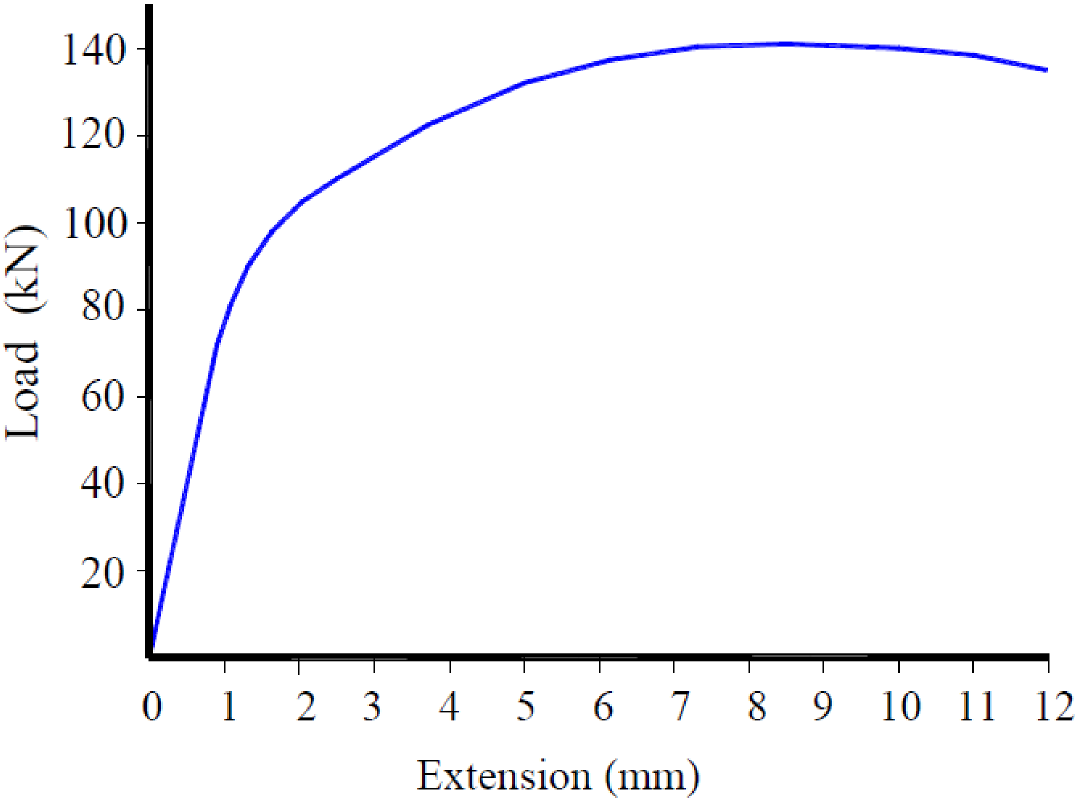

Figure 4: Load – Extension Diagram for unsoaked constantan wire by Ade (2014)

The tension test performed on the specimens shows that corrosion has drastic effect on the wire. Both Table 2 and Figure 1 show that the tensile strength of constantan wire decreases after immersion in corrosive media. For instance, after immersion in concentrated H_2SO_4, the wire dissolved completely and thus has no strength and other mechanical properties. This could be caused by the affinity of copper in constantan to sulphate forming cupper sulphate ($CuSO_4$) in the water formed. The tensile strength of the unsoaked constantan as evaluated from the Force – extension graph is 158 MPa, which differs from the result obtained by American Society of Materials Engineers (162 MPa) by about 2.5%. With immersion in HCl, the tensile strength decreases by 8% of that of the unsoaked. This might be caused by the decrease in diameter of wire due to the reaction between copper and HCl forming $CuCl_2$, leaving behind a small portion of wire with greater percentage of nickel.

Figure 1 actually shows a curvilinear graph of load – extension which agrees with the shape of graph obtained by Ade (2014) in similar investigation in which the maximum load is 140 kN (Figure 4). This disagrees with the value (152 kN) obtained in this work. The disparity might be as a result of the grade of alloy used by Ade (2014).

Also, the tensile strength, Young's modulus and hardness of the specimens decrease after immersion in HCl and sea water in that order.

The higher corrosion resistance of Cu-Ni alloy in sea water as compared with that in HCl indicates the formation of a protective barrier of Cu_2O layer on copper and Cu-Ni alloy. Ni segregates into the Cu_2O barrier layer via a solid state reaction and incorporates into the cation vacancies in the passive film, thus providing a decrease in the number of cavities, reducing the ionic conductivity, and as a result leading to an increase in the corrosion resistivity (Hosni et al., 2016). However the deterioration of the protective characters of Cu_2O may also be caused by the incorporation (doping) of the sulfide ions into the defective lattice structure of Cu_2O, which is known to be an ion deficient (Nageh et al., 2007).

Conclusion

Studies on the effect of corrosion on the mechanical properties of Cu55%/Ni45 alloy in H_2SO_4, HCl and natural sea-water environments were investigated at room temperature by testing the Cu-Ni alloy before and after immersion in the various corrosive environments. The results obtained, showed that the tensile strength, Young's modulus, stiffness and hardness of the specimens decrease after immersion in HCl and sea water with complete dissolution of the specimen in $H_2SO_{4.}$ The tensile strength of the unsoaked copper-nickel alloy as evaluated from the Force – extension graph is 158 MPa, which differs from the 162 MPa based on the American Society of Materials Engineers standard by about 2.5%. With immersion in HCl, the tensile strength decreases by 8% of that of the unsoaked. It is therefore concluded that the Cu-Ni alloys have higher corrosion resistance in sea water than in HCl solution, with practically little or no resistance to corrosion in concentrated H_2SO_4 solution.

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