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Investigation the effect of Al and Ce on microstructure, corrosion, and wear behavior of α-brass alloy

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Abstract:
The Al-brass alloy including Ce was developed in this work as an alternative to the As-Al-brass, as the latter causes environmental and health issues. This research is devoted to study the effect of different percentages of Ce addition (2, 3, 4) wt.% and Al (4 wt.%) to α-brass alloy (CuZn30%) produced by die casting on mechanical and electrochemical properties. The morphology and compositional changes of Ce Al alloys, X-Ray Diffraction tests, corrosion behavior in 3.5%NaCl solution, hardness test, and dry wear performance has been investigated. Comparing with α- brass alloy, Brinell hardness was increased by (161%) while corrosion and dry wear rate decreased by (79%) and (93%) respectively for the best specimen which contained (4%wt Ce + 4wt% Al). The phases are presented after corrosion test conditions as revealed by XRD analysis are (Al_2O_3, ZnO, CuO).

Keywords: *Brass alloys, Cerium, Corrosion behavior, Wear resistance, Aluminum*

I. INTRODUCTION

Owing to their superior thermal and electrical conductivity, great resistance against corrosion and production ease, copper-based alloys are commonly employed in the marine environment. Brass alloys are broadly utilized in industrial applications especially heat exchangers and condensers that working in saline water [1]. Dezincification [2,3], pitting corrosion [4], and cracking by stress corrosion [5,6] of brass in the water have been broadly investigated. Brass De-alloying or dezincification could be easily detected by naked eyes as the alloy creates a reddish color having a clear disparity with the original yellowish color. In general, there are two de-alloying types. The uniform or layer de-alloying frequently happens in alloys having high zinc content; the external layer is de-alloyed and being dark, meanwhile, the internal part does not influence. Plug de-alloying can be characterized by the existence of the dark de-alloyed plugs in the non-affected low Zn alloys matrix [7–11]. Two theories were suggested for brass de-alloying. The first theory refers to the anodic dissolution occurrence in the brass (both Cu and Zn); however, the Cu ions plate comes from the solution into the remaining surface of brass forming a porous layer. The second theory refers that fewer noble alloying elements are dissolved in a selective manner, leaving gaps or spaces within the lattice structure of the brass that lead to produce a skeletal copper having weak mechanical reliability [12]. During the past decade, a variety of alloy components were used to mitigate brass alloys' dezincification and corrosion. Arsenic (As) was particularly included into many conventional alloys of brass, such as HSn70-1, HAl77-2, and H68 due to their effective ability in inhibiting the dezincification of brass [13,14]. However, because As can cause environmental and health issues, suitable alternatives need to be developed for improving the brass alloys resistance against corrosion. Rare-earth elements are possible alternatives to As [15].

In this study, the hardness, corrosion, and wear tests were conducted utilizing brass alloys with Cerium and Aluminum. The influence of Cerium and Aluminum on the microstructure's grain refinement and properties (hardness, corrosion resistance and wear resistance) of alpha brass alloy were investigated.

II. Experimental Work

Ingots of Cu and Zn were put inside a gas furnace to prepare α-brass alloy (CuZn30%). The Cu melting temperature was 1083 ℃ and for Zn was equal to 419.6 °C. The temperature required for melting the α- brass alloy (CuZn30%) was 965°C. Consequently, a compensative 5wt% Zn were added prior the casting step to prevent losing of Zn according to [16] procedure. The molten alloy was well mixed using a ceramic rod to homogenize the molten alloy using Argon gas throughout the process of melting to reduce the oxidation.

For Al brass alloy with Ce specimens preparation, aluminum pieces with cerium powder was warped by aluminum foils and added to the melted α-brass (CuZn30%) alloy. To reduce the inclusions formation, the borax was added to the molten metals. A rod of graphite was used for melt stirring process in order to achieve a homogenous melt. After this process, a cylindrical die manufactured from steel was used for the casting process of the molten alloys. The casting processes has done from one side mold (with outer diameter 31.78mm, inner diameter 20 mm and height 120mm). Prior to casting process, the die was pre-heated and lubricated by using a graphite in order to make the ejection of specimen from the die much more easier.

An electrical furnace at 500 °C lasted for 10 hr. in order to homogenize the composition. To acquire the nominal compositions of alloys (as-homogenized), an x-ray fluorescence (XRF) is used and the composition is listed in Table 1.

Table 1
Chemical composition of brass alloys

specimen	α-Brass	Cerium	Aluminum
A1	100%	0 %	0%
A2	94 %	2%	4%
A3	93 %	3 %	4%
A4	92 %	4 %	4%

The resulting ingot was machined by turning to obtain favorable dimensions of the test specimens. The specimens were 14 mm and thickness 3 mm to examine the hardness, XRD, microstructure observation, and corrosion test , while for wear testing the specimens were 14 mm in diameter and 5 mm thickness.

Specimens' microstructure was detected using light optical microscope (LOM) at 100x and 400x magnification. According to ASM E3-11, standard metallographic preparation was performed using 10 gr FeCl3 + 100 ml distilled water as an etchant [17]. X-ray diffraction analysis has been conducted for the alloys using XRD instrument (Mini flex2). It has been regulated to the speed of scanning diffract meter 6^0 per minute, and it was a group of diffraction angle ($2\theta^0$) (5^0-80^0) and a step time of 0.2 seconds. The system works X-ray diffraction image plate with the (target: copper) radiation is working on a 40.0 kV and 30 mA.

Microhardness test was used to measure hardness values by microhardness Vickers (HV) device (HVS-1000) using a load of (500 g for 10 sec), the hardness was recorded as an average of three hardness readings for each specimen accordance to ASTM E 18.[18]

Electro-chemical examination is one of corrosion measurement techniques performed to detect the cathodic and anodic performances (i.e. watching the reactions of corrosion on specimen of wanted metal). Polarization tests were done by Potentio-static tester type (winking M lab 200, Germany). Consuming standard electro-chemical cell with open necks for working electrode (brass alloys), saturated calomel electrode SEC reference electrode, and auxiliary electrode (Pt. electrode). The resistance of corrosion of the specimens (A1, A2, A3 and A4) were performed in 3.5% NaCl solution at room temperature. Corrosion rate measurement is got by using the following equation [19].

$$\textit{Corrosion rate} = \frac{0.13\, Icorr(Ew)}{\rho} \quad \ldots\ldots\ldots 1$$

Where:

E.W= equivalent weight (g/eq.)

ρ= density (g/cm³)

0.13 = metric and time conversion factor

icorr.= current density (μA/cm²).

mpy = rate of corrosion (mils per year).

The dry sliding wear test was examined by using pin-on-disc concept using (300 rpm) and constant radius of 7 mm and the loads (5,10 , and 15)N. The weight of the specimen was measured before the test using (0.0001) accuracy electric balance. test specimen was weight again for several periods of time (10, 20, 30, and 40 min) according to ref [20] procedure. The wear tester that was used in this research is revealed in **Figure 1** [**21**] displays a drawing of a pin on disk device.

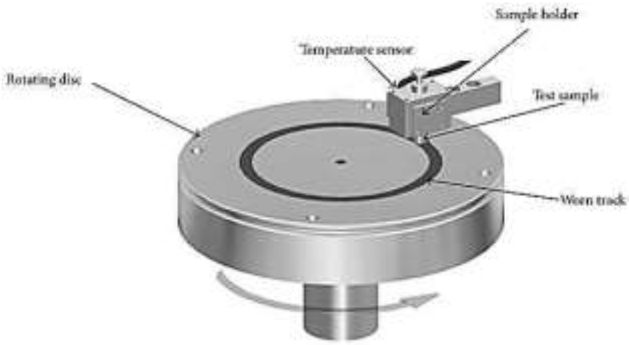

Fig. 1. Diagram of pin-on-disk (POD)[21]

III. Results and Discussion

3.0 Chemical Composition

Table 2 Detected chemical composition of α- brass alloy without & with addition (2, 3 and 4) wt.% Ce and 4wt.% Al cast plates using a X-Ray Fluorescent Analysis (XRF).

Table 2

Chemical composition of α- brass alloy without & with addition (2, 3 and 4) wt.% Ce and 4wt.% Al cast plates

Specimen code	Specimen	Chemical Composition								
		Zn	Fe	Ni	Pb	Sn	Ce	Mn	Al	Cu
A1	α -brass	28.79	0.35	0.31	2.15	0.0006	-	0.007	-	Bal

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A2	2wt% Ce	29.95	0.34	0.33	1.84	0.0005	1.42	0.09	3.02	Bal
A3	3wt% Ce	29.80	0.43	0.32	1.92	0.0005	2.24	0.08	3.09	Bal
A4	4wt% Ce	28.85	0.84	0.42	0.92	0.0004	3.02	0.11	3.15	Bal

3.2. Microstructure

Optical microscope was used to investigate the microstructure of etched specimens. Optical images with (200X,400X) showed that refined microstructure has occurred in the α-brass alloy after addition of (2,3 and 4wt %) cerium and 4wt % Aluminum. This change in grain size affects the properties of α- brass alloy . Figures (2-3) shows the microstructures of specimens without & with (4wt %) Ce and (4wt %) Al. From these figures it was showed that the addition of Ce will enhance the grains refinement and strength of the grain boundaries [22].

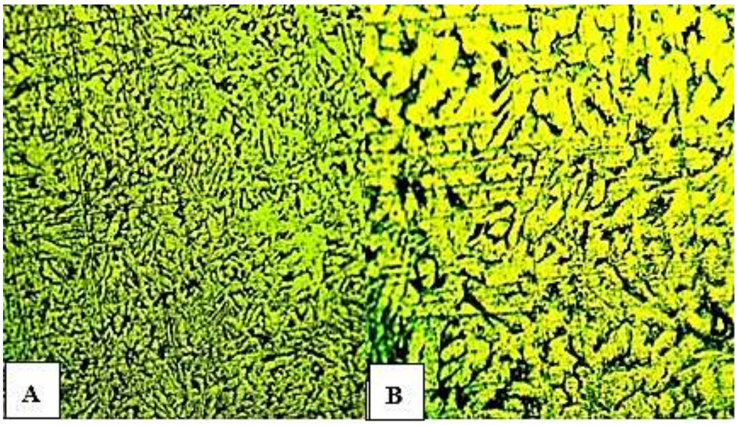

Figure 2. Microstructure of α- brass after heat treatment (A 20X, B 40X)

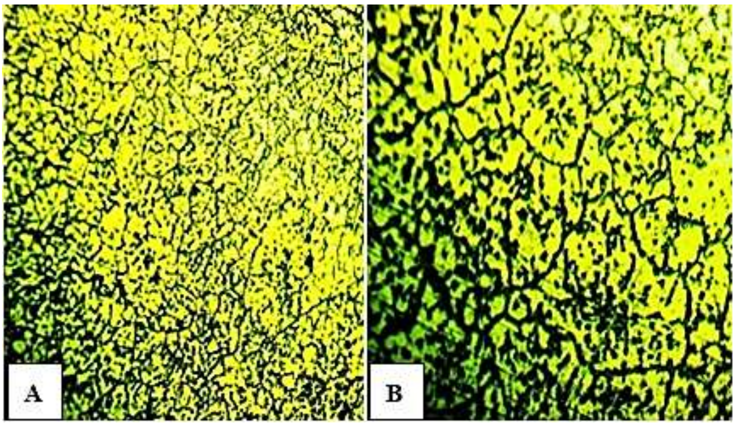

Figure 3. Microstructure of (α- brass +4wt %Ce +4 wt% Al) after heat treatment (A 20X, B 40X)

3.1 X-Ray Diffraction Test

The technique of XRD is important to identify the phases of crystalline structure. Figures 4 and 5 show the XRD patterns for specimens of **α- brass alloys with** (4%Ce and 4% Al) before and after corrosion test respectively. It can be observed that before corrosion only α-phase presented , since the amounts of additives was less than 5wt% while the device senses limits to be overhead 10%, and after corrosion test for the same specimen it can be observed in the XRD pattern there are (CuO , Al_2O_3 , ZnO) .

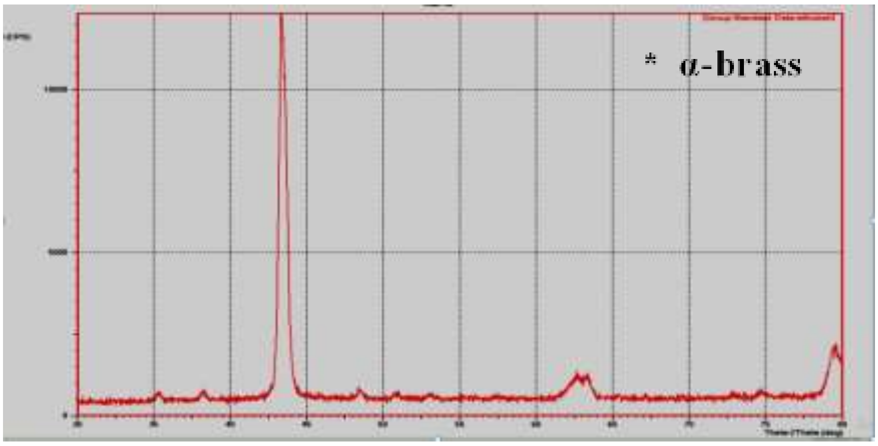

Fig. 4. XRD for specimen of (α-brass with 4%Ce and 4% Al) before corrosion test

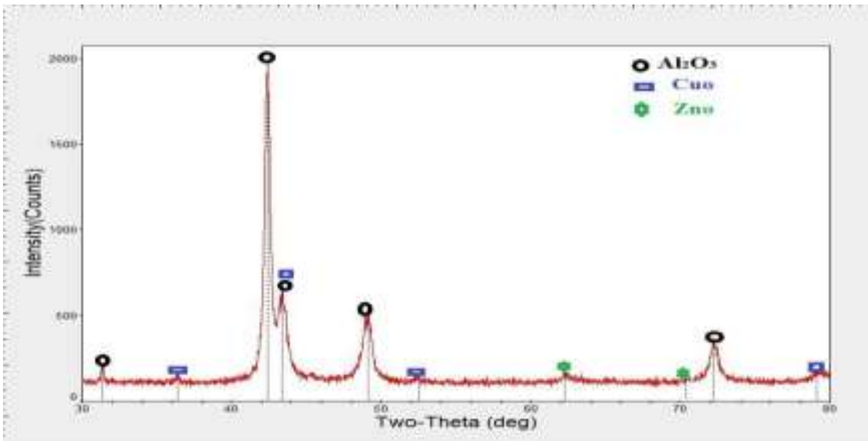

Fig. 5. XRD for specimen (α-brass with 4%Ce and 4% Al) after corrosion test

3.2 Electrochemical Test

Polarization curvatures for specimens A1, A2, A3 and A4 are showed in Figure 6 . Tests were accompanied with and without cerium and aluminum accompaniments to recognize the corrosion behavior in such surroundings. Table 3 shows the characteristic parameters of the electrochemical test. Icorr is corrosion current density and Ecorr is corrosion potential. The last of the Ce Al brass is smaller than that of the α-brass alloy. The corrosion rate for specimen A1 (without additive) was ($4.024*10^{-7}$mpy), though after adding 4 wt.% aluminum with dissimilar addition of cerium (2, 3, 4) wt.%. The corrosion rate gave ($2.8496*10^{-7}$, $2.5832*10^{-7}$, $0.84067*10^{-7}$) mpy for A2, A3, A4 respectively. The adding of Al to copper increase its resistance for corrosion in salt solutions. The resistance for the corrosion of brass with Al contented up to 4% has been qualified to maintainable defensive deposit of alumina that creates rapidly on the surface of the alloy post disclosure to the environment of corrosion **[22].** In NaCl solution, the Ce Al brass is uncovered to have higher resistance of corrosion than that corresponding in the brass. The adding of Ce consequences in a noteworthy increasing of polarization resistance, corrosion formed layer is thick and has a considerable enhanced bonding with the matrix. It is probable that this dense layer withdrawn the diffusion of Zn ions from matrix to the solution and thus enhance the corrosion resistance **[20].**

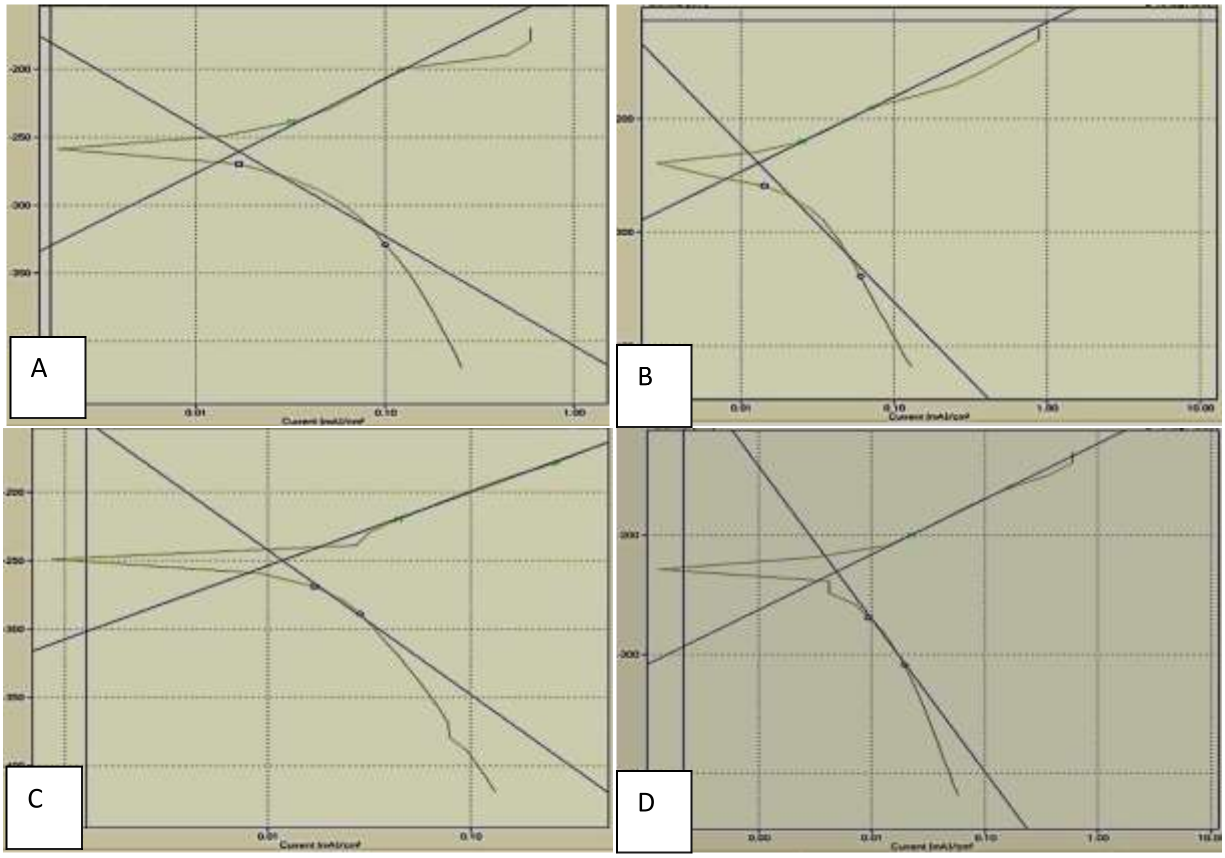

Fig. 6. Potentiostatic Polarization curve for : A)A1 reference , B) A2 , C) A3 , and D)A4 specimens in 3.5 % NaCl.

Table 3
corrosion parameters (E corr., I corr., and Corrosion rate (mpy))

Specimen code	**specimen**	**Icorr.(μA/)/cm^2**	**E corr. (mV)**	**Corrosion rate (mpy)**	**IE%**
A1	Without Ce &Al	16.86	-260.8	$4.024 * 10^{-7}$	-
A2	2 wt.% Ce+4%Al	12.95	-239.0	$2.8496*10^{-7}$	29.18
A3	3 wt.% Ce+4%Al	11.75	-249.8	$2.5832*10^{-7}$	35.80
A4	4 wt.% Ce+4%Al	4.92	-230.7	$0.84067*10^{-7}$	79.10

3.3 Hardness Results

The alloys hardness values increase as the content of cerium increases. In the hardness assessment, extreme plastic flow has been attentive in the controlled area conventional underneath the indentation, external where the material stays accomplish elastically. Straight below the indentation, the density of the particulates increased neighboring, related to the areas away from the depression. Meanwhile the crystals plastic deformation is instigated by the dislocations wave, any difficulty to dislocation wave will encumber deformation resulting in crystal strengthening. Consequently, increasing of hardness as cerium content increase is attributed to the solute hardening that produced by the atoms of the cerium solute **[23].**

Table 4
The hardness of the examined specimens

Specimen Code	Alloy specimens	**Vickers hardness(HV) gm/mm^2**
A1	Without Ce and Al	102.09
A2	2 wt.% Ce + 4wt%Al	222.29
A3	3 wt.% Ce + 4wt%Al	257.29
A4	4 wt.% Ce +4wt%Al	265.88

3.4 Dry Wear Test

Figures 7. Show the relationship between weight loss of α- brass without & with (2, 3, and 4wt.% Ce) and period underneath different load (5, 10 and 15)N. Form these figures, it's clear that the weight loss increased with increasing applied loads. The reason for this is due to the increase in friction at the surface as the load on the material increase **[24]** .In addition , the wear rate increase as the period upsurge for all verified specimen , this is certainly because extra friction time inclines to eliminate extra material from the exterior , this increase in the weight loss ascribed to upsurge the material plastic deformation on the external , particulates of the material pullout **[25].** The addition of cerium to α- brass with different percentages (2, 3, 4) wt.% led to increase the hardness, then the wear resistance increases as the hardness increase.

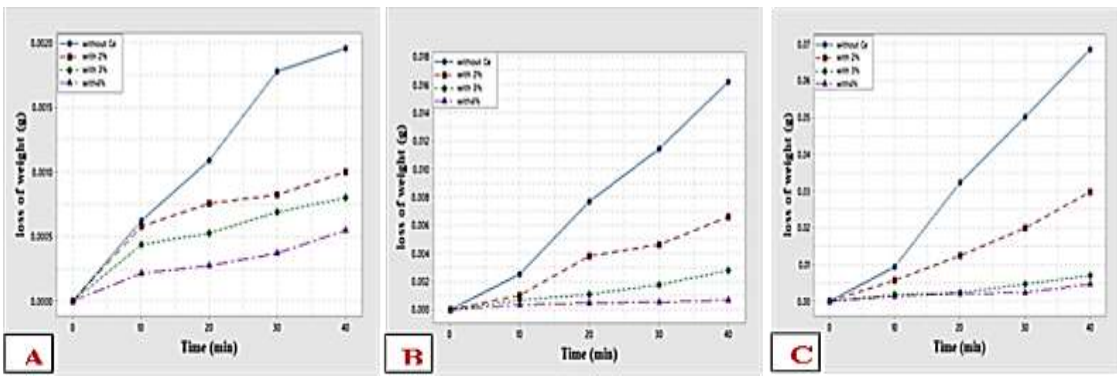

Fig. 7. Weight loose vs time under load a) 5N, b) 10 N, and c) 15 N

IV. CONCLUSIONS

Results of experiments counting the prepared α-brass alloys analysis to evaluate and study Ce and Al alloying elements effect of on the mechanical , microstructure, and corrosion properties of α-brass alloy as:

1. Cerium and Aluminum has a substantial effect on microstructure properties. They provide finer grains and increase the strength the boundaries of the grains.
2. Vickers hardness(HV) of α-brass alloy is increased with addition of Ce and Al by (118%), (152%), and (161%), for specimens of 4wt.% Al with (2, 3 4 wt.%) Ce, respectively.
3. Corrosion rate of α-brass alloy is decreased with addition of Ce and Al by (29.18 %), (35.80%),and (79.10%), for specimens of 4wt.% Al with (2, 3, and 4 wt.%) Ce respectively
4. Dry wear rate of α-brass alloy is decreased with addition of Ce and Al by (59%), (89%),and (93%), for specimens of 4wt.% Al with (2, 3, and 4 wt.%) Ce respectively at applied load 15 KN for 40 min.

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