ABSTRACT

Brass alloys with a zinc content of 35 % and more have a mixture of the alpha (FCC) and beta (BCC) phases, that causes an increasing in hardness significantly. Further, this alloy can be formed only by hot-working. Therefore, it appears problematic of oxidation at high temperature. This leads to create an idea of improving oxidation behavior of the \( \alpha + \beta \) (Cu-Zn40) brass alloy by adding different amounts of aluminum (1, 3 and 5) wt %. Cyclic oxidation tests were conducted on the \( \alpha + \beta \) (Cu-Zn40) brass with and without aluminum in the air at temperatures range between 500-700°C for 18 hours at 6 hours cycle. All specimens exhibited parabolic oxidation rate dependence and the value of \( K_p \) for \( \alpha + \beta \) (Cu-Zn40) brass alloy with aluminum is nearly lower than that for \( \alpha + \beta \) (Cu-Zn40) brass alloy under the same condition. The phases appear in the cyclic oxidation of \( \alpha + \beta \) (Cu-Zn40) brass surface after addition of aluminum under further most test situations as exposed by XRD examination are (Al\(_2\)O\(_3\), ZnO, CuO).

KEYWORDS: Brass Alloys, Brass Oxidation, High Temperature Oxidation, Copper Base Alloys, Brass (Cu-Zn40)
oxides, sulfides, carbides. The utmost usually construction is the exterior oxide layer that is created afterward growth of oxide nuclei which leads to the creation of an oxide layer which is totally envelop the metallic surface. The further growth of the oxide layer formerly occurred by transmission of oxygen anions and/or metallic cations through the scale layer as illustrated in Figure 1, for both models of limited anionic diffusion (Figure 1a) and limited cationic diffusion (Figure 1b) [5]

**Figure 1: Two Models of the Oxide Scale Growth by Diffusion Through the Scale Layer. The Black Dot Contour Illustrates the Positions of the Scale Growth [5]**

The kinetics of oxidation laws were sequentially illustrated by drawing the difference of the gains in weight vs. test time [6]. The gain in weight statistics is suitable for measuring the kinetics of oxidation through a cyclic test. A computer program is usually used to calculate the best fit to the equation \( \Delta W/A = Kt^n \) where, \( \Delta W/A \) is the gain of weight per unit area, \( K \) and \( n \) are constant and \( t \) is the time of oxidation [7]. Oxidation rates can be reported in several different but equivalent ways, including weight gain or loss per unit time and change in the thickness of the oxide per unit time \( (\frac{dy}{dt}) \) [8]. The rates of thickening have been found to fall mostly into four categories, examples of which are shown in Figure 2 [9]. In the equations which follow, \( y = \) Oxide thickness, \( t = \) Oxidation time, and \( C_1 \) to \( C_7 \) are constant [8].

The rates of thickening have been found to fall mostly into four categories, examples of which are shown in Figure 2 [9].

Ali H. Haleem et. al. [10] performed repeated oxidation tests on the alpha brass alloy with and without aluminum adding at a extensive variety of temperatures (500-900 °C) in static air for 52 hrs at 4 hrs cycle. The oxidation kinetics exhibits breakaway concert for alpha brass alloy at 800 and 900 °C. These illustrations that the oxidation concert of this alloy is non-protecting. The appeared phases on the repeated oxidation of alpha brass alloy without aluminum adding as exposed by XRD examination are: ZnO, CuO and Cu₂O. **alpha** brass alloys including aluminum exhibitions sufficient oxidation resistance. This is due to the creation of protecting alumina.
Improving Oxidation Behavior of (Alpha- Beta) (Cu-Zn40) Brass by Aluminum Addition

Hardik and Chaudhri[11] inspected the effect of the perpendicular centrifugal casting procedure on the wear of brass alloy (CuZn40Pb2) on variable mold revolution speeds and pouring temperature. In this work hollow tubular bush was arranged at different mold rotation speeds as 950, 1050 and 1150 rpm at 1000°C & 1050°C pouring temperatures. This work includes the chemical structure of brass alloy (CuZn40Pb2) and the valuation of their tribological reply when exposed to Pin-on-disc wear test.

S. R. Hussein [12] mentioned that the adding of (2, 3 and 4) wt % cerium and 4wt% aluminum to α-brass alloy reduces the corrosion rate in saline solution (3.5% NaCl). Additional the(α- brass+4 wt% Ce+4wt% Al ) alloy exhibit less wear rate than α- brass alloys.

This research aimed to improve oxidation resistance of α+β (Cu-Zn40) brass alloy by adding of a different percentage (1, 3 and 5) wt % of the aluminum, and find optimal fraction of the aluminum in order to get the greatest oxidation resistance.

EXPERIMENTAL WORK

Three types of metals (copper, zinc and aluminum) had been used to obtain the required forms through the plumbing in the metal mold and using appliances and equipment to end. Table 1 detect chemical composition of α+β (Cu-Zn40) brass alloy without & with additions of (1, 3 and 5) wt.% Al. Current examination has been done by overwhelming a computerized spectrometer.

| Specimens          | Chemical Composition [%] |
|--------------------|--------------------------|
|                    | Zn | Pb | Sn | P  | Al | Fe | S  | Sb | As | Cu   |
| α+β brass          |    |    |    |    |    |    |    |    |    | Bal. |
| 1wt% Al            | 41.01 | 0.06 | 0.06 | 0.017 |    | 0.016 | 0.081 | 0.21 | 0.031 | 0.071 |
| 3wt% Al            | 38.67 | 0.05 | 0.04 | 0.019 | 1.03 | 0.027 | 0.077 | 0.24 | 0.027 | 0.079 |
| 5wt% Al            | 42.55 | 0.09 | 0.09 | 0.015 | 2.91 | 0.029 | 0.072 | 0.19 | 0.031 | 0.091 |

Melting and casting completed by adding (1, 3 and 5 wt.%) of aluminum to the α+β (Cu-Zn40) brass alloy, this alloy melting in 965˚C Whereas the melting point of Zn is (419.6˚C). Consequently additional 5 wt % from zinc to recompense with missing zinc ratio during melting. Melted was stirred with ceramic bar.

The metal is discharged into the cylinder-shaped metal mold (with outer diameter 30mm, inner diameter 20mm and height 100mm). Hollow surface was covered by a smooth coating of hotness resistant graphite to relaxed removal the injected metal rod. Rod specimens of α+β (Cu-Zn40) brass alloy without & with (1, 3, and 5 wt % Al) after casting process were machined for getting of disk specimens with dimensions 16mm diameter besides 4 mm thickness.

Heat Treatments

Heat treatment was conducted at a temperature (500˚C) for (10) hr. in order to homogenize the composition, to eliminate the semi-soluble phases and to ensure that the casting elements and were regularly distributed in the alloy, giving the alloy homogeneous properties.

Cyclic Oxidation in Air

Cylindrical specimens with 16mm as diameter and 4 mm as thickness of α+β (Cu-Zn40) brass alloys without &
with (1, 3, and 5 wt % Al) have been precisely weight recorded there after mounted into ceramic pots. Cyclic oxidation checks were performed in a chamber holding furnace in the temperature 500–600 and 700 °C for 18 hours at 6 hour for each cycle in still air at pressure of one atmosphere.

Weight changes of all specimens before and after each oxidation cycle were recorded. Usually, at least 3 weight measurements were occupied.

RESULTS AND DISCUSSIONS

Microstructure Test

The light optical microscope used to get the microstructure of etched specimens. Figure 3b appeared that softened microstructure has happened in the α+β (Cu-Zn40) brass alloy after addition 5wt % aluminum compared to α+β (Cu-Zn40) brass alloys Figure 3a. It appeared two phases. The light phase is (α) and the dark phase is (β).

Cyclic Oxidation in Air

Oxidation kinetic studies offer value devidence about the oxidation kinetic and the rate-restrictive step of the entire interaction. Rate of oxidation evaluated likewise usually aids as a foundation for a quantitative arithmetical explanation of the behavior of oxidation. The specified weight change information of the α+β (Cu-Zn40) brass alloys without and with aluminum (1, 3, and 5 wt.% for every test temperature are plotted in Figures 4, 5 and 6 as a function of time. The early kinetic is fast, but the rate of specific weight change slowly reductions at lengthier times. The kinetic of oxidation can defined the growth rate time constant or n value, which is institute as the exponent the rate equation [13]:

\[ \Delta W/A = Kt^n \]

Whereas \( \Delta W \) is the weight change, \( A \) is the surface area of specimen, \( K \) is the rate constant, \( n \) is the growth-rate time constant, and \( t \) is the time of oxidation. The exponential constant \( n \) describes the oxidation rate as shadows: if \( n=1 \), the oxidation rate is linear, and if \( n=0.5 \) the oxidation rate is hypothetically parabolic, but if \( n=0.33 \), formerly the oxidation rate is cubic. Whereas the worth of \( n \) is larger or lesser than 0.5 formerly oxidation kinetic does not occurs the simple parabolic behavior and this suggests a slower or faster oxidation rate. For instance, for \( n>0.5 \) it is an “over parabolic”, whereas formula \( n <0.5 \) the rate is “under parabolic” (sub-parabolic). The outcomes displayed that sub parabolic may be found due to the effect of grain boundaries (short circuits).
For the parabolic kinetics, the rate equation takes the form [13]:

\[ \Delta W/A = Kt^{0.5} \]  

(2)
where \( k \) now refers to the parabolic rate constant. A plot of specific weight change vs. square root of time gives a line as in Figures (7, 8, and 9) the slope is the parabolic rate constant in units of (mg/cm\(^2\))/hr.1/2. The \( K_p \) value is then squared to give \( K_p \) in units of (mg^2/cm^4)/hr., as in the following expression:

\[
(\Delta W /A)^2 = K_p t
\]

(3)

The parabolic oxidation rate constants for all of experiments are calculated and the linear lines represent the least squares curve fits to the data in Figures (7, 8, and 9), the parabolic oxidation rate constants (\( K_p \)) for the set of experiments are listed in Tables (2, 3, and 4).

![Figure 7: Linear Fitted Outcomes of Specific Weight Change vs. \( t^{1/2} \) Plot for \( \alpha + \beta \) (Cu-Zn40) Brass Alloys Without & With ( 1, 3, and 5 wt % Al) at Temperatures 500 °C for 18 hr at 6 hr Cycle](image1)

![Figure 8: Linear Fitted Results of Weight Gain vs. \( t^{1/2} \) Plot for \( \alpha + \beta \) (Cu-Zn40) Brass Alloys Without & With ( 1, 3, and 5 wt % Al) at Temperatures 600 °C for 18 hr at 6 hr Cycle](image2)
From the experiment work, data revealed that a parabolic oxidation rate ($K_P$) obeys an Arrhenius-type equation of form[14]:

$$K_P = K_0 \exp(-Q/RT)$$

Where $K_P$ is the parabolic oxidation rate, $K_0$ is the pre-exponential factor, $Q$ is the activation energy, $T$ is the temperature (K), and $R$ is the universal gas constant (8.314 J/mol.K) [14]. Plot of $\ln(K_P)$ vs. $(1/T)$, the effective energy is calculated from the least square fitting (using Microsoft Excel 2010) of the observed data in the temperature range (500-700°C) is to 11.50 KJ/mol, 6.591KJ/mol, 1.760 KJ/mol, and 4.031 KJ/mol, for $\alpha+\beta$ brass without & with (1, 3, and 5 wt % AL) respectively, as shown in Figures(9-12)

Table 2: n Values and Parabolic Oxidation Rate Constants $K_P$ for Cyclic Oxidation at 500°C for 18 hr at 6 hr Cycle

| Al wt.% | n values | $K_P$ (mg²/cm⁴)/sec. |
|---------|----------|----------------------|
| 0       | 0.65     | 2.280*10⁻⁶           |
| 1       | 0.37     | 1.537*10⁻⁶           |
| 3       | 0.59     | 9.409*10⁻⁷           |
| 5       | 0.53     | 4.669*10⁻⁷           |

Table 3: n Values and Parabolic Oxidation Rate Constants $K_P$ for Cyclic Oxidation at 600°C for 18 hr at 6 hr Cycle

| Al wt.% | n values | $K_P$ (mg²/cm⁴)/sec. |
|---------|----------|----------------------|
| 0       | 0.60     | 1.276*10⁻⁶           |
| 1       | 0.53     | 9.473*10⁻⁷           |
| 3       | 0.56     | 7.396*10⁻⁷           |
| 5       | 0.54     | 4.993*10⁻⁷           |

Table 4: n Values and Parabolic Oxidation Rate Constants $K_P$ for Cyclic Oxidation at 700°C for 18 hr at 6 hr Cycle

| Al wt.% | n values | $K_P$ (mg²/cm⁴)/sec. |
|---------|----------|----------------------|
| 0       | 0.625    | 1.629*10⁻⁶           |
| 1       | 0.60     | 1.284*10⁻⁶           |
| 2       | 0.583    | 9.025*10⁻⁷           |
| 3       | 0.544    | 5.304*10⁻⁷           |

Improving Oxidation Behavior of (Alpha-Beta) (Cu-Zn40) Brass by Aluminum Addition

Figure 9: Linear Fitted Results of Weight Change vs. $t^{1/2}$ Plot for $\alpha+\beta$ (Cu-Zn40) Brass Alloys Without & With (1, 3, and 5 wt % Al) at Temperatures 700°C for 18 hr at 6 hr Cycle
Figure 9: Plot of $K_p$ vs. $1/T$ for $(\alpha+\beta)$ (Cu-Zn40) Brass cyclic oxidized in Air for 18 hrs at 6 hr Cycle

Figure 10: Plot of $K_p$ vs. $1/T$ for $(\alpha+\beta)$ (Cu-Zn40) Brass with 1% Al cyclic oxidized in Air for 18 hrs at 6 hr Cycle

Figure 11: Plot of $K_p$ vs. $1/T$ for $(\alpha+\beta)$ (Cu-Zn40) Brass with 3% Al cyclic oxidized in Air for 18 hrs at 6 hr Cycle
Improving Oxidation Behavior of (Alpha- Beta) (Cu-Zn40) Brass by Aluminum Addition

From the outcomes above it’s obvious that the adding(3%Al) is the finest addition for creates protective oxide layer from aluminum oxide since it has less of activation energy(1.760Kg/mol).

X-ray Diffraction Test

Figure 13 illustrate the major phases formed on the surface of α+β (Cu-Zn40) with 5%Al brass alloys cyclic oxidized in air for 18 hrs at 6 hr cycle. These phases which are present in sufficient amounts are Al₂O₃ and small amounts of CuO and ZnO.

CONCLUSIONS

From the cyclic oxidation tests of (α+β) (Cu-Zn40) brass alloys without & with (1,3, and 5 wt.% Al) at temperatures between 500-700 °C for 18 hr at 6 hr cycle the following results can be concluded:

- Over the temperature range between 500-700°C, the parabolic rate constant (K_p) for (α+β) (Cu-Zn40) brass alloys varies from K_p =0.280*10⁻⁶ at 500 °C to K_p = 1.629*10⁻⁶ at 700 °C.
- The activation energy of (α+β) (Cu-Zn40) brass alloys is 11.5 KJ/mol.
- All (α+β) (Cu-Zn40) brass alloys with Al addition (1, 3, and 5wt %) revealed good cyclic oxidation resistance compared with(α+β)(Cu-Zn40) brass alloys and the value of K_p is nearly lower than that for(α+β) (Cu-Zn40)
brass alloy under the same condition. the parabolic rate constant \( (K_p) \) for \((\alpha+\beta)\) (Cu-Zn40) alloy with 5% Al varies from \( K_p = 4.669 \times 10^{-7} \) at 500 °C to \( K_p = 5.304 \times 10^{-7} \) at 700°C.

- The activation energy is 1.760 KJ/mol for \((\alpha+\beta)\) (Cu-Zn40) brass alloy with 3wt %Al.
- The scale formed on the surface of 5wt%Al consist of \( \text{Al}_2\text{O}_3 \), and small amounts of \( \text{ZnO} \) and \( \text{CuO} \).

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