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Effect of Heat treatment, Mechanical Properties studies and corrosion response on Manganese bronze

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Abstract

The main aim of the work is to study the changes in mechanical, metallographic and corrosion behavior of the Manganese bronze specimens before and after the heat treatment processes with varying temperatures and at a constant time. The Manganese bronze specimens were subjected to various heat treatment processes such as annealing, normalizing and quenching in water media at 250^{0}C, 350^{0}C, 400^{0}C and 600^{0}C for a 60 minute soaking time .Weight loss experiments showed that the heat treatment in the range of 250^{0}C to 350^{0}C is optimum for corrosive environments. The electrochemical (Corrosion) response of the specimens exhibiting the low corrosive rates at 350^{0}C annealed temperature.

Keywords: Manganese bronze; heat treatment; hardness; corrosion tests; microstructures.

Introduction

COPPER and copper alloys constitute one of the major groups of commercial metals. They are widely used because of their outstanding ability to resist corrosion, some bronzes, are used for pipes, valves, and fittings in systems carrying potable water, process water, or other aqueous fluids. Typical chemistry of manganese bronze is 60 to 68% Cu, 3 to 4% Fe, 3 to 7.5% Al, 2.5 to 5% Mn, and a balance of zinc [1]. However, the bronze used in the present work contains about Cu-65%, Zn-26%, Al-4%, Mn-2%, Fe-3%. Manganese bronzes are specified for marine propellers and fittings, pinions, ball bearing races, worm wheels, gear shift forks, and architectural work. Manganese bronzes are also used for rolling mill screw down nuts and slippers, gears, and bearings, all of which require high strength and hardness. Most of the higher-strength alloys have better-than-average resistance to corrosion and wear properties. High-strength brasses also called manganese bronzes and high-tensile brasses, these Cu-Zn-Fe-Al-Mn alloys (C86100 to C86800) are among the strongest (as cast) copper-base materials [2]. Manganese contributes to strength, but its principal functions may have more to do with castability. The high-zinc, low-aluminum alloys C86400 and C86500 have duplex (alpha + beta) structures [2]. Stresses can be relieved at 175 to 200 °C (350 to 400

°F). However, till date as per the author's knowledge no investigation was observed on Manganese bronze (Cu-65%, Zn-26%, Al-4%, Mn-2%, Fe-3%). In the present work an attempt has been made to study the effect of heat treatment on mechanical, microstructural and electrochemical properties of Manganese bronzes using potentiodynamic polarization techniques.

Experimental procedure

The Manganese bronze specimens were supplied in the cylindrical shape with diameter of 25 mm and a thickness of 20 mm. The composition of this alloy is mentioned in the Table 1. The specimens were prepared by casting technique. The specimens were annealed, quenched and normalized at 250^0C, 350^0C, 400^0C and 600^0C in the high temperature tubular (supplier: VB ceramic consultants, Chennai, India.) and oxidation furnaces (supplier: VB ceramic consultants, Chennai, India.) for a 60 minute soaking time at that temperatures with a heating rate of 5^0C/min. The quenched samples were cooled in a water media. The un-heat treated and heat treated specimens were metallographically polished for optical microscopic examination using belt grinder, emery papers and Aluminium paste sequentially. They were chemically etched in a solution of 5g of Potassium-dichromate ($K_2Cr_2O_7$) and 10 ml Hydrochloric acid (HCl) in 100 ml of distilled water. The microstructural analysis of the samples were carried out through optical microscope (model: T1600, supplier: Metasonic Engineers, Secundrabad, India.). The area of different phases present in the alloy microstructure was determined by Image analyzer. The Brinell hardness tests were carried out for each specimen using a 500 kg load Brinell hardness tester and diameters of the indentations were found by using microscope. The Brinell hardness values of all specimens were calculated using the formula given below.

$$BHN = \frac{2P}{\pi D\left(D - \sqrt{D^2 - d^2}\right)}$$

Where, BHN is the Brinell hardness number, P is the applied load, D is the diameter of the indenter and d is the diameter of the indentation[5].

Before the heat treated Manganese bronze samples were cleaned with acetone, the samples were weighed by using electronic balance (Wenser, MAB 220 model, max. weight = 200 gm. and d=0.1 mg) and subjected to 0.1N H_2SO_4 for 2 hour time period. The samples were removed from the solution, dried in hot air oven and weighed in electrical balance to obtain loss in weight. Corrosion rates were calculated using the formula below [6].

$$Corrosion\ rate\ (mpy) = \frac{534\, w}{\rho A T}$$

Where, w is the weight loss of the sample (mg), ρ is the density (gcm^{-3}), A is the surface area of the sample (in^2) and T is the time (hour).

To study the electrochemical behavior of annealed Manganese bronze, all samples were polished with 120 grit SiC papers for obtained a smooth surface and exposed area of the sample was 1 square centimeter. A typical three-electrode electrochemical corrosion cell was used in all the experiments. A saturated calomel electrode (SCE) was used as reference. All measured potentials were referred to this electrode. A platinum foil was used as the counter electrode. The Manganese bronze samples were used as working electrodes. A potentiostat (IVIUM), controlled by a personal computer, and the commercial software was employed to obtain the potentiodynamic polarization curves. Before each experiment, the open circuits potential (OCP) was recorded for 60 min. Polarization curves were obtained potentiodinamically. Potentiodynamic polarization tests were carried out from -0.9250 V versus OCP to +1.8000 V versus reference electrode at a scan rate of 1 mV/s. The corrosion potential (E_{corr}) and corrosion current (I_{corr}) corrosion rate were determined from the polarization curves. The corrosion rate can be determined using the formula expressed as follows [7].

$$Corrosion\ rate\ (mpy) = K_1 \frac{i_{corr}}{\rho} EW$$

Where, K_1 = 0.1288 (mpy), EW is the equivalent weight, ρ is the density of the material (gcm^{-3}), I_{corr} is the corrosion current ($\mu A/cm^2$).

3. RESULTS AND DISCUSSION

Hardness

The graphical representation of the average Brinell hardness of the samples showed in the Figure 1: and values were listed in the Table 2. The mechanical property of an alloy mainly depends upon the heat treatment processes. Therefore, the requirement of the properties decides the type and temperature of heat treatment to be adopted. In quenching process the hardness values are increased due to decrease in grain growth at high temperatures. Whereas, in the case of annealing BHN values drastically decreased with increment in temperature. The Manganese bronzes are not responding to Normalizing process.

Microstructure results

The microstructure of the un-heat treated and annealed Manganese bronze alloy is shown in the Figure 2: and Figure 3: respectively. The microstructure shows bright area of α-phase in a darker matrix of β-phase. The Manganese bronze alloy heated in the recrystallization temperature range of 250 to 600 ^{0}C. The variation in area fractions of α and β-phases in the annealed alloy at 250^{0}C, 350^{0}C, 400^{0}C and 600^{0}C as determined by Image analyzer were listed in the Table 3. The area fractions of α and β-phases in the heat treated alloy showing increase in α-phase from 24.393 to 81.442 percentage which was proved to increase the corrosion resistance of the copper alloys. The increase in α phase vs. annealing temperature graphically showed in the Figure 4.

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Weight loss measurements

The corrosion performance of Manganese bronze was studied by using weight loss method. As seen from Table 4. The percentage of weight loss of Mn bronze in 0.1 N of H_2 SO_4 solution increases with respect to temperature. As the temperature increases the percentage of weight loss also increases. The percentage of weight loss for not heat treated specimen is higher than the Annealed specimen (250^0C). We can confirm that the heat treatment of alloy below the recrystallization temperature is optimum for corrosive environment.

Electrochemical study

To investigate the effect heat treatment on the corrosion behavior, electrochemical tests were conducted on the annealed Manganese bronze samples in 0.1N H_2SO_4. Figure 5: shows a set of potential, E, vs. logarithm plots of the absolute value of the current density, I_{corr}, for annealed ($250^{0,}$ 350^0, 400^0, 600^0 C) manganese bronze specimens. Values of corrosion potential (Ecorr), corrosion current density (I_{corr}) and corrosion rate (CR) were estimated and listed in Table 5. The I_{corr} and E_{corr} were calculated from the potentiodynamic plots by using the Tafel extrapolation method. Corrosion current density (I_{corr}) was observed, that I_{corr} value increases at 400^0C and decreases at 350^0C among all the temperatures including un heat treated sample and Corrosion Rates also. As increase the temperatures the corrosion rates were initially increases then decreases, again its increases and then decreases with respect to the annealed temperatures. The nature of anodic branches was nearly the same for annealed 250^0 and 600^0 temperatures and un-heat treated sample, but the cathodic branches was not same for these temperatures. At 350^0 and 400^0 C the behavior of polarization curves showed that the natures of anodic curves were exactly same, the potential has drastically got down from 1.6 V to 0.5 V with respect to Log I (0.67) then gradually decreases up to 0 V but the cathodic curves showed more negative for 400^0 and less negative for 350^0 corresponding to Log I. However the results were not comparable with corrosion rate of weight loss. Both weight loss corrosion rate as well as potentiodynamic corrosion rates, we can conclude that the range of annealed temperatures 250^0 is optimum for weight loss CR and 350^0C is optimum for potentiodynamic tests.

Conclusions

- Annealed specimens showed a decrease in BHN values as the heat treating temperatures raises.
- Quenched samples showed an increment in the hardness with the raise in heat treating temperatures.
- Normalized samples showed a sudden increment and decrement hardness results.
- Increase in α-phase content was observed with increasing annealed temperatures.
- Weight loss results showed that annealing at 250^0C is optimum for corrosive service conditions.
- Heat treatment at 350^0C results in decreased corrosion rate of the alloy observed from the potentiodynamic tests.

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Table 1: ***Composition of the Manganese bronze specimens used in the present study***

Alloy*	Composition, wt.%
Manganese bronze	Cu-4Al-2Mn-29Zn-3Fe

*Supplier: Krish Met Tech Pvt. Ltd., Chennai, India.

Table 2: ***Average Brinell hardness of the heat treated Manganese bronze samples at 500kg load.***

Alloy	Heat treatment process	Temperature			
		250 ^{0}C	350 ^{0}C	400 ^{0}C	600 ^{0}C
Manganese bronze	Normalizing	80	100	93	74
	Quenching	80	86	86	100
	Annealing	86	86	74	38

Table 3: ***Area phase variations of the optical microstructures with the heat treated temperatures.***

Alloy	Phases	Temperature			
		250 ^{0}C	350 ^{0}C	400 ^{0}C	600 ^{0}C
Manganese bronze	α	24.393	25.849	51.406	81.442
	β	75.607	74.151	48.594	18.558

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Table 4: ***Effect of annealing heat treatment at different temperatures on Manganese bronze samples dipped in H_2SO_4 solution for 2 hour time.***

Alloy	Heat treatment process	Heat treatment temperature (^{0}C)	Weight loss (mg)	Surface area (in^2)	Corrosion rate (mpy)
Manganese bronze	Annealing	250	0.1	1.931393724	1.765544562
		350	2.2	1.985247187	37.78832056
		400	3.2	1.930831584	57.92672142
		600	8.3	1.933598479	142.83045
	No heat treatment	-	0.2	1.948621965	3.499869905

Table 5: ***Effect of annealing heat treatment at different temperatures on Manganese bronze samples obtained from the potentiodynamic polarization investigation.***

Alloy	Heat treatment process	Temperature	$I_{corr\ (mA/cm^2)}$	$E_{corr\ (mV)}$	Corrosion rate (mpy)
Manganese bronze	Annealing	250	1.104	-620.00	516.0387
		350	1.063	-433.33	496.5397
		400	1.239	-490.00	579.0052
		600	1.130	-443.33	528.0604
	No heat treatment	-	1.211	-630.00	565.8291

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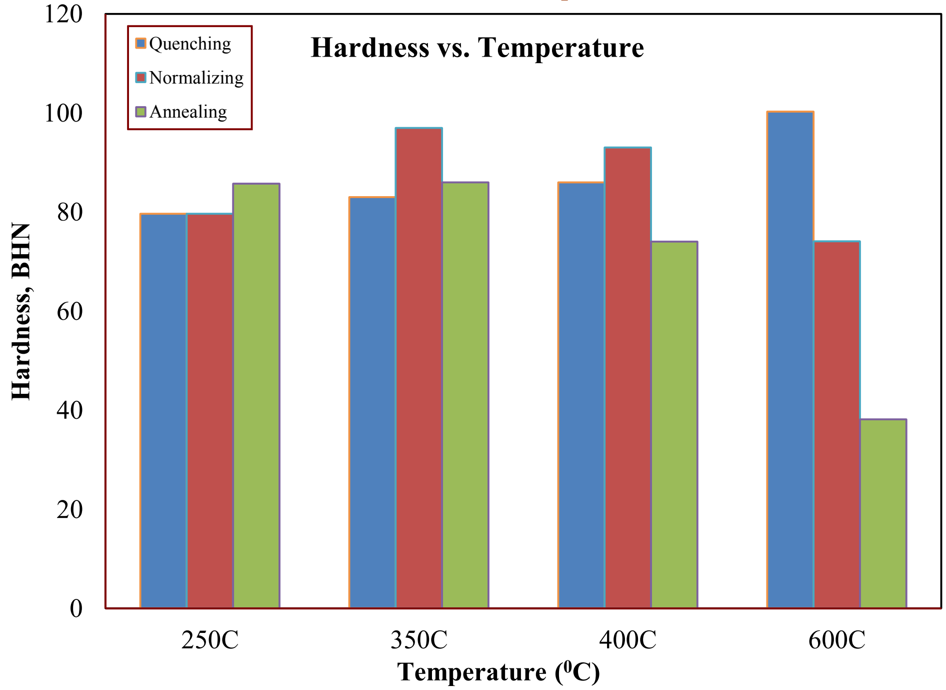

Figure 1: ***Effect of heat treatment process on average hardness of Manganese bronze at 500kg load.***

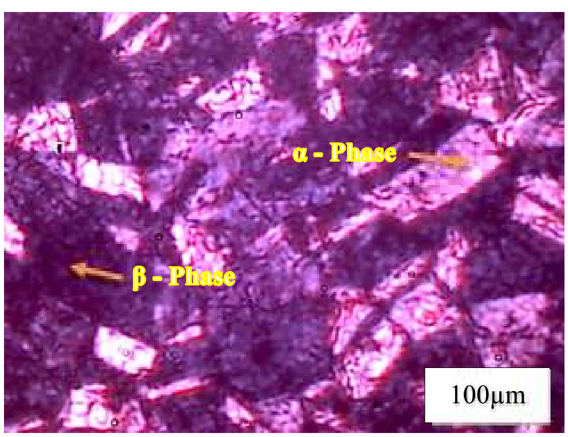

Figure 2: ***Optical micrographs of un-heat treated Manganese bronze specimen.***

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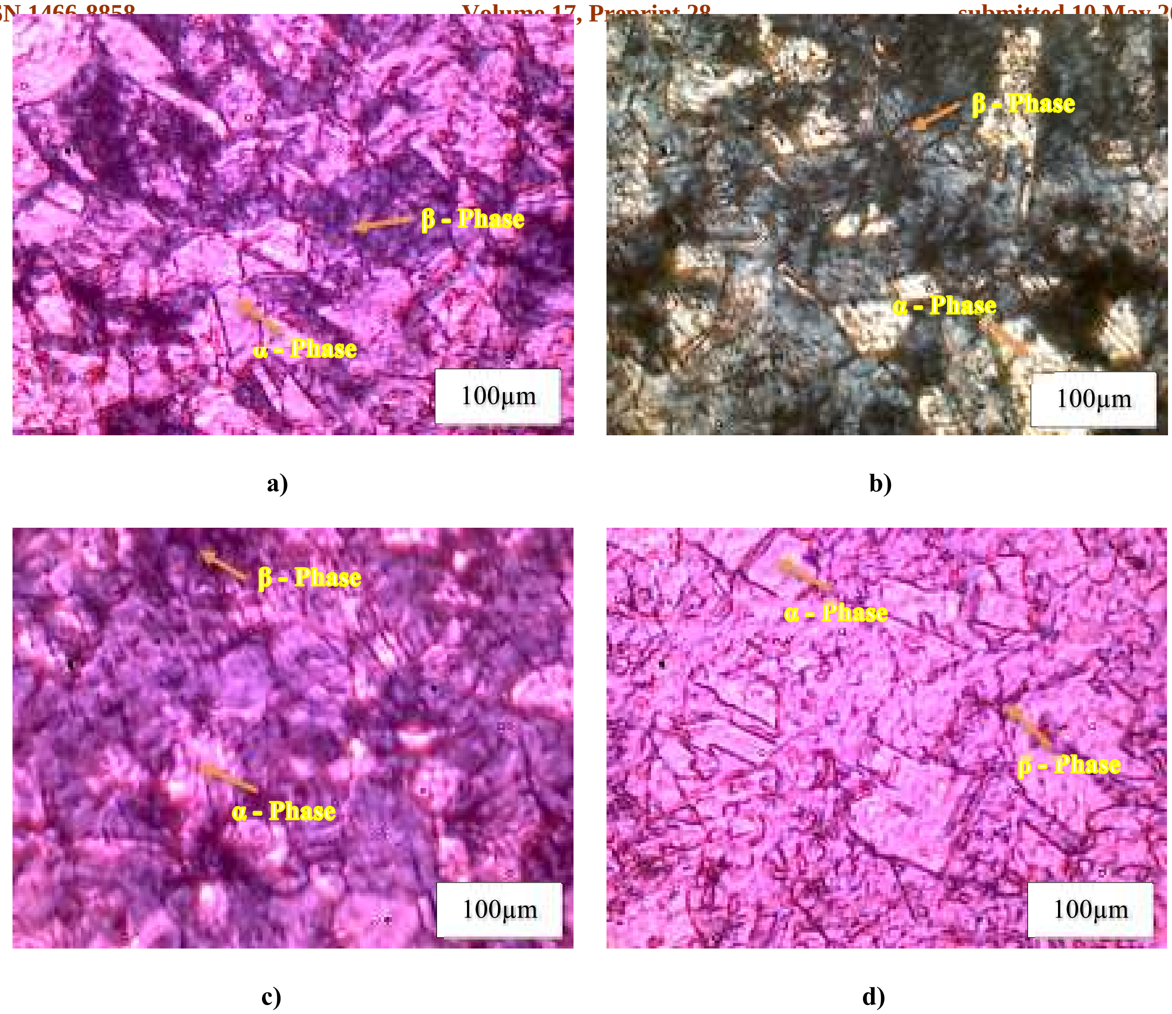

Figure 3: *Optical micrographs of annealed Manganese bronze specimens at a) 250^{0}C, b) 350^{0}C, c) 400^{0}C and d) 600^{0}C.*

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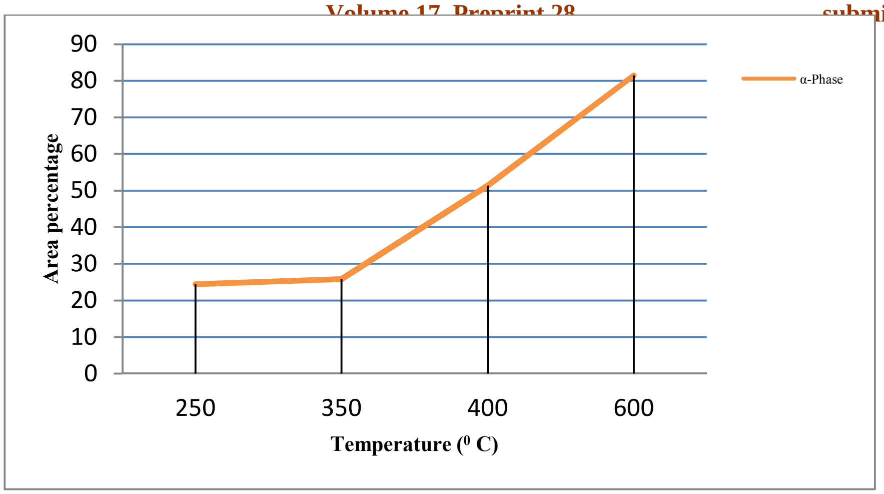

Figure 4: ***Area percentage of α-phase variation with the annealing temperature.***

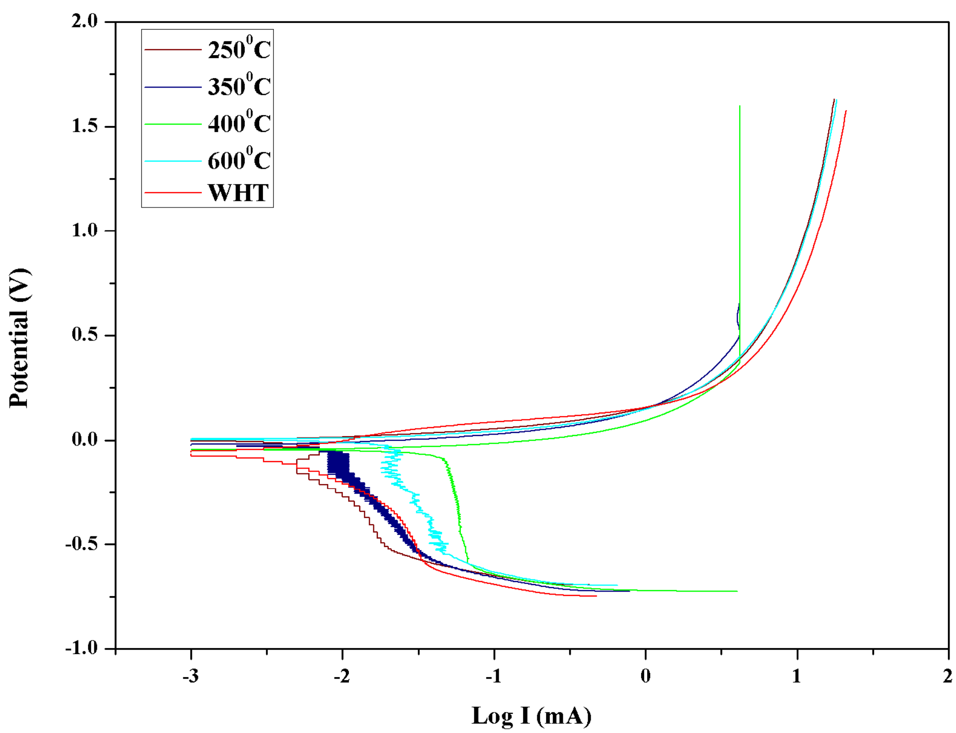

Figure 5: ***Potentiodynamic polarization curves of annealed samples at 250^{0}C, 350^{0}C, 400^{0}C, 600^{0}C and without heat treatment respectively.***