Investigation of Corrosion Behavior for Copper-Based Shape Memory Alloys in different Media

Abstract- Copper based shape memory materials was interesting group of metal alloys that have a widespread potential in medical and industrial application due to their characteristics, the possibility of exhibiting shape memory behavior and lower cost. In this research the alloy (Cu-(15-40) wt%Zn-6wt.%Al) has been prepared by powder metallurgy technique Zn element (15, 20, 25, 30, 35, 40 wt%Zn) and fixed percentage of Al content which is 6 wt.%Al then aluminum replaced by (Si, Sn, Ni) element at fixed percentage of 6wt.%, in order to study the effect of these elements on SMA. After samples preparation examination were done by using XRD, SEM technique, DSC, Vickers hardness, Archimedes technique Zn element test can be show the alloy with 35wt% Zn have the higher corrosion resistance in all media (HCl, NaOH and sea water) and the addition of alloying elements in these percentages does not have effect on present phases. the hardness increased with zinc content because the formation of intermetallic compound of CuZn that responsible to hardness while The addition of Si, Sn and Ni leads to lower the hardness than aluminum. The bulk density increased with the alloys without addition alloying elements(Si, Ni and Sn ) while apparent porosity decreased with it the reason for this phenomenon due to the characterization of alloying elements that addition to the alloy. From the results of corrosion test can be show the alloy with 35wt% Zn have the higher corrosion resistance in all media (HCl, NaOH and sea water) and the addition of alloying element lead to improve the corrosion resistance. Finally, it is observed that the Copper base shape memory alloys with these types of additives are suitable for use in different application.

Keywords- Shape memory alloy, Smart materials, Corrosion behavior, Powder metallurgy, Transformation temperature.

1. Introduction

Shape memory alloys (SMAs) are metallic alloys, which can remember their shape when they are heated above a certain transformation temperature. This alloy also displayed drastic damping changes as a function of temperature. In another, define the materials that have the ability to change their shape, position, stiffness, natural frequency, and other mechanical characteristics when exposed to temperature or electromagnetic fields at a certain temperature. Copper-based shape memory alloys can be strained, and then convert to its primary shape [1]. The commercial Availability for the transformation temperature ranges between (-180 and +200 C) (copper-zinc-aluminum) alloy. This alloy was cheaper than Nickel-Titanium alloys, which can be melted in air very, ease, and have a shape-memory strain up to (4-5%). Hot work in air is well suitable; while cold work is suitable only for low aluminum-content alloys (<6%wt.) alloys [2]. The copper-based shape memory alloys are easy to fabricate mostly, their process are less expensive when compared to (Ni-Ti) shape memory alloys. However, in the polycrystalline state (Cu-Al-Ni) and (Cu-Zn-Al) shape memory alloys are brittle for this reason cannot be easily worked due to the high degree of order and high elastic anisotropy of the parent β-phase (austenitic) [2]. The derivation of Cu-based shape memory alloys are currently from three binary alloy systems i.e. Cu-Zn, Cu-Sn and Cu-Al [3], Cu-Zn based alloys which contained Al, Ga, Si, Sn, or Mn as ternary alloy and Cu-Al based ternary alloys with alloying elements such as Ni, Zn, Mn and Be [4,5]. Currently Cu–Zn-Al and Cu-Al-Ni shape memory alloys are the most available and uses in different useful practical applications. To obtain specific requirements the alloys can also be suitably modified by selectively alloying element such as quaternary and grain-refining additions [6]. The alloys (Cu-Zn-Al and Cu-Al-Ni) have been briefly studied and they are now more widely available. Due to thermal stability and higher operating temperatures for Cu-Al-Ni alloys than Cu-Zn-Al alloys, they may become one applicant for practical high-temperature shape-memory alloys if only their poor procedure ability can be enhanced by adding small amounts of alloying elements to the alloys [7], both marten site stabilization and parent-phase ageing effects were observed at temperatures greater than 120°C [8]. Cu-Zn-Al alloys Compositions usually fall in

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the range of (15-40 wt% Zn) and (6 wt.% Al). The martensitic transformation temperatures can be adjusted by varying chemical composition [9]. In different practical applications, when the alloys are exposed to different corrosive media for a longer time they are displayed to corrosion and pitting. Therefore, study of corrosion potential and pitting potential of the alloys are very necessary before they are put into biomedical and industrial applications. It was observed that corrosion rate of austenite was more than martensite in Cu-Al-Ni SMAs. It was detected that for the sample in the austenitic structure have current density is greater than for martensitic structure. This proves the corrosion resistance for the shape memory alloys have more than other tradition alloys because the hyperactive elastic behavior of polycrystalline structure [10]. The aim of this research is to prepare a set of Cu Zn Al shape memory alloys samples have a different percentage of zinc content by using powder metallurgy technique and study the corrosion rate in different solutions HCl, NaOH, and seawater. After that choose the sample that has the best corrosion resistance and prepared the second set of sample in same the percent of zinc content, by replaced aluminum content with (Si, Sn and Ni), finally study the hardness, porosity percentage, transformation temperature, and corrosion rate for two sets.

2. Experimental Work

The experimental work includes two main steps: The first step is the preparation of the first group of copper based shape memory alloys (Cu-Zn-Al) which have the different percent of zinc content (15, 20, 25, 30, 35, 40wt.%Zn) and aluminum content is (6%wt.Al) fixed by using powder metallurgy technique and then choosing the best alloy characterized and making it master alloy by addition the alloying element such as (Ni, Si and Sn) pure elements, the sample preparation includes many steps: Preparation and mixing of powders by ball mill for two hours, compacting of powders at 650 Mpa, All samples were sintered at (650 °C for 4 hours) under controlled atmosphere of argon. The second step is the characterization of samples including X-ray diffraction (XRD), Differential scanning calorimeter (DSC), microstructure test scanning electron microscope (SEM), micro hardness porosity measurement and corrosion rate test.

3. Results and Discussion

I. X-Ray Diffraction

X-ray diffraction tests were done for all samples after the sintering practices. Figure 1 & 2 shows the diffraction patterns, which result for the samples, were the phases that established because of sintering process could be distinguished. The phase analysis of (Cu-Zn-Al) alloys with and without additives was carried out by X-ray diffraction (XRD) using a Shimadzu X-ray diffract meter (type xrd- 6000/7000) operated at 40 kV and 30 mA with Cu Kα 1 radiation. The phases produced from the sintering process can be show in Figure 1. There are probably no pure metals presents that prove the sintering temperature and their time used in this work results in sintering reactions completely. It has been shown that most elemental powders (Cu, Zn and Al) form intermetallic compound [Cu Zn], X-ray diffraction showed that all samples alloys consist mainly of two phases (α + β) biphasic structure; the martensitic phase (α-phase) orthorhombic structure and the austenitic phase (β-phase) BCC structure, the centered cubic intermetallic phase β of binary alloy Cu-Zn exhibit a martensitic transformation but the transformation temperature that can be obtained by varying the composition are extremely low( practically lower than -50°C ) the addition third element such as (Al, Si, Sn) to the binary alloy (Cu-Zn) enables us to obtained the martensitic transformation, the temperature for which can be adjusted by the composition, over a wide range. The goal of quenching for Cu based shape memory alloys it is enough that the quenching process be sufficiently quick to prevent diffusion reactions. In certain cases, even air quenching may suffice. [11]

Table 1: The composition of alloys

| Sample symbols | Composition of alloy |
|----------------|---------------------|
| Alloy 1        | Cu-15wt.%Zn-6wt.% Al |
| Alloy 2        | Cu-20wt.%Zn-6wt.% Al |
| Alloy 3        | Cu-25wt.%Zn-6wt.% Al |
| Alloy 4        | Cu-30wt.%Zn-6wt.% Al |
| Alloy 5        | Cu-35wt.%Zn-6wt.% Al |
| Alloy 6        | Cu-40wt.%Zn-6wt.% Al |
| Alloy 1        | Cu-35wt.%Zn-6wt.% Si |
| Alloy 2        | Cu-35wt.%Zn-6wt.% Sn |
| Alloy 3        | Cu-35wt.%Zn-6wt.% Ni |

II. Transformation temperature investigation

The transformation temperature from an alpha-beta phase (or all-alpha phase) to all beta is known as the beta transition temperature. The beta transition is defined as the lowest equilibrium temperature at which the material is 100% beta. Below the beta transition temperature, (Cu-Zn) will be a mixture of α + β if the material contains some beta stabilizers or it will be all alpha phase if it contains no beta stabilizers. The beta transition is important, because the processing and heat treatment are often carried out with reference to some incremental temperature above or below the beta transition. DSC measurements have been employed, at constant rate of 10 °C/min of heating and cooling cycle for all samples. The measurements are carried out in the temperature range (-50°C to 400°C). Figure (3) shows the transformation temperature of the sample (Cu-15%Zn-6%Al). It can be seen that during the heating cycle we have more one peak (two stages) which refers to one phase transformation from (144.29°C to 182.44°C and 188.51°C to 214.36 °C). While during the cooling cycle of the alloy from austenite to martensite one peak will occur, at temperature (169.15°C to 130.81°C) for the first alloy (Cu-15wt. %Zn-6%wt.Al). for the alloy (Cu-35wt. %Zn-6%wt.Al) austenite start at 189.89°C and finished at 230.47°C while martensite transformation range 159.34°C - 129.51°C, when addition silicon element instead of aluminum to alloy (Cu-35%Zn-6%Al) lead to raise the transformation temperature, The silicon addition can also strengthen the austenite matrix, but it must be less than 6.5 wt. % because the weakening in fabric ability above that value [12, 13]. While Ni addition lead to decrease the transformation temperature.

Table 2 and Figures (9-11) show the alloy (Cu-35%Zn-6%Al) replaced aluminum with (Si, Sn and Ni) in same percentage of Aluminum. These addition percentages raise the transformation temperature of the alloy during both heating and cooling cycle.
Table 2: The transformation temperature for samples with additives

| Alloys                  | Heating (A s-A f)         | Cooling (Ms-Mf)         |
|-------------------------|----------------------------|-------------------------|
| 1 Cu-15wt.%Zn-6wt.Al   | 188.51°C-214.26°C          | 169.15°C-130.81°C       |
| 2 Cu-20wt.%Zn-6wt.Al   | 183.25°C-220.32°C          | 174.32°C-147.26°C       |
| 3 Cu-25wt.%Zn-6wt.Al   | 177.59°C-225.60°C          | 165.45°C-141.34°C       |
| 4 Cu-30wt.%Zn-6wt.Al   | 154.09°C-204.47°C          | 141.59°C-120.24°C       |
| 5 Cu-35wt.%Zn-6wt.Al   | 189.89°C-130.47°C          | 159.34°C-129.51°C       |
| 6 Cu-40wt.%Zn-6wt.Al   | 229.47°C-251.41°C          | 227.94°C-179.58°C       |
| 7 Cu-35wt.%Zn-6%wt.Si  | 313.78°C-361.22°C          | 280.10°C-239.13°C       |
| 8 Cu-35wt.%Zn-6%wt.Sn  | 225.82°C-229.20°C          | 221.66°C-217.52°C       |
| 9 Cu-35wt.%Zn-6%wt.Ni  | 317.16°C-350.63°C          | 133.19°C-61.47°C        |

Figure 3: Transformation temperature of alloy (Cu-15wt%Zn-6wt%Al)
Figure 4: Transformation temperature of alloy (Cu-20wt%Zn-6wt%Al)
Figure 5: Transformation temperature of alloy (Cu-25wt%Zn-6wt%Al)
Figure 6: Transformation temperature of alloy (Cu-30wt%Zn-6wt%Al)
Figure 7: Transformation temperature of alloy (Cu-35wt%Zn-6wt%Al)
Figure 8: Transformation temperature of alloy (Cu-40wt%Zn-6wt%Al)
Figures (9-11) show the transformation temperatures of the alloys. The transformation temperatures of the alloys (Cu-35wt%Zn-6wt%Si), (Cu-35wt%Zn-6wt%Sn), and (Cu-35wt%Zn-6wt%Ni) are presented in Figures 9, 10, and 11, respectively.

III. Scanning Electron Microscopic Investigation

Figures (12-16) show the microstructure results of all samples. The SEM and optical microscope micrographs are observed after the sample were ground by SiC emery paper with different grits starting from 600,800,1000 grit to get flat and scratch free surface. Finally, these samples were polished with smooth cloth. It insures the success of the manufacturing process and appearance of martensite phases in the form of layers and α alpha phase (bcc) it appear in the bright regions while dark regions it refers to the beta phase β. The microstructure includes some of pores, and the percent of these pores affect the alloy density as mentioned in section of porosity the specimens have been etched with (NH₄OH+H₂O₂+H₂O) etchant to reveal the grain boundaries in the microstructure.

Figure 9: Transformation temperature of alloy (Cu-35wt%Zn-6wt%Si)

Figure 10: Transformation temperature of alloy (Cu-35wt%Zn-6wt%Sn)

Figure 11: Transformation temperature of alloy (Cu-35wt%Zn-6wt%Ni)

Figure 12: SEM of sample (Cu-35%Zn-6%Al)

Figure 13: SEM of sample (Cu-40%Zn-6%Al alloy)

Figure 14: SEM of sample (Cu-35%Zn-6%Ni alloy)

Figure 15: SEM of sample (Cu-35%Zn-6%Si alloy)
IV. Vickers Micro hardness
The measurement of micro hardness has been done by taking the average of 3 readings; figures 17 & 18 show that the hardness increased with zinc content because the formation of intermetallic compound of CuZn that responsible to hardness, while the addition of alloying element decreased the hardness.

V. Apparent Porosity & Bulk Density
Archimedes role was applied to measure the bulk density and the apparent porosity for the alloys with and without additives, the bulk density increased with the alloys without addition alloying elements (Si, Ni and Sn) while apparent porosity decreased with it. Show the figure 19, the reason for this phenomenon due to the characterization of alloying elements that addition to the alloy. Apparent porosity depended on factors such as particles size and distribution, surface area, shape, etc. [14]
VI. Corrosion Test Result

Corrosion test is very important to display how a material will behave when exposed to a corrosive environment. The corrosion test was done by using the potentiodynamics polarization test in three different solutions (acid solution basic solution and seawater) for all samples with additives and without it, the test done at room temperature 25 ºC. in general the results show that the corrosion rate decreased with zinc content increased up to 35% that mean the best corrosion resistance was for the sample (Cu-35%Zn-6%Al) because the corrosion rate was (1.3871mpy) This is agreeing with the fact of the corrosion resistance of a pure metal or any alloy strongly depends on the exposed environment, velocity, temperature and the chemical composition. The data listed in Table 3, 4 and 5 show The Ecorr which is an indicator of the stability of surface Conditions. Thus, less variability in E corr values from different samples is indicative of more consistent surface processing. The Icorr and calculated CR are relative measures of corrosion and illustrate how much of a material will be lost during the corrosion process. Hence, the higher Icorr and calculated CR, cause more material lost. Figure 20 show the corrosion behavior and the corrosion rate of all samples in HCl media for all samples this figure demonstrate that the corrosion rate of samples decrease with increasing Zn concentration [10],while for a samples with additives [Si, Sn, Ni] the corrosion rate decreased with Si addition and have the best corrosion resistance ,while the corrosion rate increased with addition of (Ni, Sn, Al) in HCl media, the reason back to their positions in galvanic series.as seen in Figure 21.

| Alloy composition wt% | -Ecorr. mV | icorr. mA/cm² | Corrosion Rate (mpy) |
|------------------------|-----------|--------------|----------------------|
| Cu-15%Zn-6%Al         | 125.032   | 4.34         | 2.0832               |
| Cu-20%Zn-6%Al         | 114.707   | 3.98         | 2.0178               |
| Cu-25%Zn-6%Al         | 97.70     | 3.66         | 1.80072              |
| Cu-30%Zn-6%Al         | 93.52     | 3.251        | 1.618                |
| Cu-35%Zn-6%Al         | 79.1      | 2.75         | 1.3871               |
| Cu-40%Zn-6%Al         | 85.70     | 2.97         | 1.5158               |
| Cu-35%Zn-6%Al         | 79.1      | 2.75         | 1.3871               |
| Cu-35%Zn-6%Sn         | 70.89     | 2.53         | 1.369                |
| Cu-35%Zn-6%Ni         | 77.333    | 2.68         | 1.342                |
| Cu-35%Zn-6%Si         | 73.028    | 2.46         | 1.239                |

Table 4: Corrosion parameters of samples in NaOH media

Figure 20: Corrosion rate (mpy) of the Alloys in HCl

Figure 21: Corrosion rate (mpy) of the Alloys with additives elements in HCl media

Figure 22 show the corrosion behavior and the corrosion rate of all samples in NaOH media for all samples, as we say previously the alloy (Cu35%Zn6%Al) have the best corrosion resistance compared to other alloys in Figure 23 show the alloy with Sn addition have the excellent corrosion resistance, lower corrosion rate (1.1035mpy) because the formation of stable passive films on their surface during immersing in NaOH media. Figure 24 show the corrosion behavior and the corrosion rate of all samples in sea water media for all samples, as we say previously the alloy (Cu35%Zn6%Al) have the best corrosion resistance compared to other alloys, in Figure 25 show the alloy with Si addition have the excellent corrosion resistance, lower corrosion rate (0.9826 mpy) because the formation of stable passive films on their surface during immersing in NaOH media.
Table 5: Corrosion parameters of alloys in SEA WATER

| Alloy composition wt% | -Ecorr. mV | icorr. mA/cm² | Corrosion Rate (mpy) |
|-----------------------|------------|---------------|----------------------|
| 1 Cu-15%Zn-6%Al      | 77.031     | 2.67          | 1.289                |
| 2 Cu-20%Zn-6%Al      | 73.42      | 2.55          | 1.294                |
| 3 Cu-25%Zn-6%Al      | 69.76      | 2.42          | 1.1906               |
| 4 Cu-30%Zn-6%Al      | 67.30      | 2.33          | 1.1596               |
| 5 Cu-35%Zn-6%Al      | 61.050     | 2.12          | 1.0693               |
| 6 Cu-40%Zn-6%Al      | 66.072     | 2.29          | 1.1688               |
| 1 Cu-35%Zn-6%Al      | 61.050     | 2.12          | 1.0693               |
| 2 Cu-35%Zn-6%Sn      | 56.25      | 2.02          | 1.09383              |
| 3 Cu-35%Zn-6%Ni      | 58.071     | 2.01          | 1.0069               |
| 4 Cu-35%Zn-6%Si      | 58.32      | 1.95          | 0.9826               |
4. Conclusion
From studying the investigation of corrosion behavior of copper-based shape memory, alloy in different media the following conclusion can be drawn:
1. All the samples with and without additives consist of two main phases (β-phase) and (α-phase), this is obtained from XRD and microstructure observations.
2. The addition of 6% (Si, Ni and Sn) lead to raise the transformation temperature, but not too much different from other while when addition silicon element instead of aluminum to alloy (Cu-35%Zn-6%Al) lead to raise the transformation temperature, the martensite start at 280.10°C and finished at 239.13°C.
3. The transformation temperature increased with Silicon addition while it’s decreased with Ni addition.
4. The hardness increased with zinc content because the formation of intermetallic compound of CuZn that responsible to hardness whiles the addition of alloying element decrease hardness.
5. The apparent porosity decreased with addition of alloying elements (Si, Sn and Ni).
6. The corrosion rate decreases with increase in Zn percentage in all solutions (HCl, NaOH and SEA WATER) the perfect addition was silicon element because have lower corrosion rate in HCl and Seawater. While the alloy (Cu-35%Zn-6%Sn) have lower corrosion rate.

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