Manufacture of shape memory alloys NiTi and NiTiCu by casting method and studying the effect of adding the copper element in different proportions to the binary alloy on the microstructure, phase transformations and conductivity

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Abstract. Thanks to unique properties, such as light weight, good biocompatibility, high strength, and relatively low cost, shape memory alloys are of interest to researchers. In this work alloys NiTi and NiTiCu with different weight percents were made from the copper element using the casting method by (VAR) furnace. Where the elements were melted at (1350°C) without a crucible to obtain best alloys of high purity, and after that the manufactured ingots were cooled with ice water to obtain the best homogeneity. The melting process was followed by the annealing process by an electric furnace at (750°C). After completing the manufacturing process, specimens were prepared for microscopic and mechanical tests, and wires were drawn for the purpose of electrical testing. Several tests and examinations were carried out to ensure that the alloys manufactured are SMAs. The microscopic examinations that were performed via OM showed that the copper element is uniformly distributed within a NiTi matrix. The results showed FESEM that the microstructure is symmetric and homogeneous, and also showed phase (Ti 002) and (Ti2Ni) and some defects. DSC examination showed the initial and final degrees of the austenite and martensite phase. In addition, the results of DSC showed that the best stable alloys are alloy NiTi and NiTiCu-3 and that the hysterical loop decreases with an increase in the percentage of copper. The results of the shape memory effect showed that the best SME was (88.98%) for alloy NiTiCu-3. As for the microhardness, it increased when the copper element was increased, so the maximum hardness of the specimen was at 2 wt.% Cu, and it seemed to decrease with the increase in the copper element. The electrical test that was performed using the 4T sensing method of wires showed that the conductivity value increases with the increase in ratio of Cu with the decrease in the resistivity. The best conductivity ratio was for alloy NiTiCu-3 where the conduction ratio was 24096.4 (Ω.Cm)-1 and it had the lowest resistivity 41.5 (Ω.Cm)10-6. Strain rate was tested and the resistivity, so the increase in the strain rate was observed with the increase in the copper element and the decrease in the resistivity.

1. INTRODUCTION

The Shape memory alloys are classified as a type of smart material that exhibits unique properties such as pseudo-elasticity and shape memory effect [1]. The most commonly used shape memory alloys are (Cu-base), (Fe-base) and (NiTi-base). The most commonly used alloy is nickel-based alloys
due to its good properties such as good workability, biocompatibility, pseudoelasticity and excellent corrosion resistance [2-4]. For this reason, smart alloys have been used in many applications such as biomedical fields, engineering and aerospace [5]. There are NiTi in two different forms depending on the temperature. The initial phase is called the martensite phase, where this phase is at a low temperature and high pressure, while the second phase is called the austenite phase and it is at high temperatures and low pressure [6].

The main problem for the manufacture of shape memory alloys NiTi is to choose the appropriate manufacturing method. In addition, the choice of the third element type that leads to improving the properties of the binary alloys. The process of manufacturing and forming smart alloys is of great importance to the homogeneity, microstructure and properties of the produced alloys. The manufacturing process includes two main methods, which are casting and powder metallurgy. The first method for manufacturing alloys is the casting method, which requires materials of high purity, which in turn affect the homogeneity and uniform distribution of materials. The method of casting includes several techniques Vacuum Arc Melting (VAM), Electron Beam Melting (EBM) and Vacuum Induction Melting (VIM) [7]. The technique of VAR was used in this way do not need a crucible, which is intended to produce alloys less contaminated with carbon (pure alloys). This method can be applied by using a consumable electrode which is consisted or by using a non-consumable electrode [8]. To adjust the phase transition degrees of binary alloys (lowering and raising the transition temperatures) is done by adding some elements such as Cu, Fe, Nb and Hf [9-11]. Some properties of (NiTi) have been developed by adding a third element. Copper is added as a third element, the addition of copper affects the martensitic transformation temperatures. The addition of copper leads to a narrowing of the hysterical loop, smaller temperature hysteresis, higher damping capacity and superior fatigue which leads to the use of alloy NiTiCu in several commercial applications [9, 12]. In this paper, four wires of different weight ratios (0, 2, 5 and 8 wt.% Cu) were manufactured from by means of a VAR furnace. The aim of the research is to study the microstructure, phase transformations, the effect of shape memory, in addition to studying the microhardness of bilateral and triple alloys and study the conductivity of the four wires and the strain rate with resistivity.

The paper contains the following sections: Related literature, the material and methods part (contains the manufacturing process, annealing, and preparing specimens for tests and examinations), the results and discussion part, and the last part include the most important conclusions of this work.

2. RELATED LITERATURE

In this section, a previous study similar or close to research has been added. An alloy (NiTi-1, NiTi-2) and (NiTiCu-1, NiTiCu-2) was made by means of a (VAR) furnace after the completion of the manufacturing process. The specimens were subjected to tests (Vickers hardness, SEM, DSC). The results showed that the microstructure is homogeneous and the hardness ratio increases with the increase in the percentage of copper and the initial and final temperatures of the austenite phase decrease significantly [13].

3. MATERIAL AND METHODS

3.1 Materials

Titanium metal at high purity (99.78 wt.%) and Nickel about (99.4 wt.%), while copper plates at high purity (99.7 wt.%) used as additive element at (2, 5 and 8 wt. %) to prepare shape memory alloys. Table 1 shows the different weight percentages of each the matrix element (NiTi) and copper element as additive material.
Table 1. Different weight percent of each (Ni, Ti, Cu)

| Alloys   | Ni (wt.%) | Ti (wt.%) | Cu(wt.%) |
|----------|-----------|-----------|----------|
| NiTi     | 55        | 45        | 0        |
| NiTiCu-1 | 54        | 44        | 2        |
| NiTiCu-2 | 53        | 42        | 5        |
| NiTiCu-3 | 52        | 40        | 8        |

3.2 Preparation of the specimen

The chosen elements with the different weight percents show in Table (1) were melted in (VAR) furnace type (ALD Vacuum Technologies AG) at 1350°C without graphite crucible.

In the present work, the elements (copper, titanium, and nickel) are fixed to a copper mold and then heated by irradiation using argon and tungsten electrode. Molten minerals have a similar shape to a grain of rice due to the surface tension. The melting process is followed by the cooling process with ice water, to obtain the best chemical consistency; the dissolution process was repeated several times. At 750°C and for a period of 24 hours, all the alloys were annealed by an electric furnace. After that, the ingots were cut using a metal cutting machine into specimens for the purpose of tests and examinations. In addition, a wire was cold drawn with a diameter (d = 0.15mm) and length (L = 10 cm) to prepare it for electrical testing. This wire could be used in several applications (actuator, sensor or controller).

3.3 Tests and examinations

3.3.1 Optical Microscopy (OM)

After cutting the specimens, the specimens were prepared by grinding and polishing in order to test the microstructure through the use of an Optical Microscopy (OM) with a magnifying force (40).

3.3.2 FESEM

Specimens were prepared by polishing and polishing to perform a test Field Emission Scanning Electron Microscopy of type cam scan Mv 2300 to verify the surface formation and chemical composition after thermal treatment of all specimens before and after adding the copper element.

3.3.3 Differential Scanning Calorimetry device (DSC)

Specimens were tested (NiTi, NiTiCu-1, NiTiCu-2, NiTiCu-3) by means of a differential calorimeter of type (SETARAM, model 131 Evo) to determine the starting and finishing of the transformations phase. The specimens, weighing (7 g), were placed inside an aluminium crucible that was heated inside a (DSC) device at a temperature ranging (-80 - +280) at a heating rate of about (10 ° C / min).
3.3.4 Shape Memory Effect (SME)

A test Shape Memory Effect was performed for the alloys specimens (NiTi, NiTiCu-1, NiTiCu-2, NiTiCu-3) through a pressure by about 0.06% of the real length, after which it was heated and the shape recovery percentage was calculated for each specimen as in the Equation (1) [13]:

\[
\text{SME\%} = \frac{L_2 - L_1}{L_0 - L_1} \times 100
\]  

Where:

Lo: Real length of specimen (mm).
L1: Length of specimen after pressing by (0.06%).
L2: the length of the specimen after heating.

3.3.5 Vickers Hardness (VH)

The microhardness test of the alloys made by the Vickers hardness test was carried out according to the (ASTM E384) standard. The dimensions of the specimens for this test (7 mm in length and 10 mm in diameter) were given as a load of 3 kg for a period of 15 seconds. Several readings were taken and the average indentation was calculated.

3.3.6 Resistivity and Conductivity

There are many methods used to measure the resistivity. Four-point probe resistivity test or known as four-terminal sensing or 4T sensing, the measurements of this method at high accuracy comparing with another methods. The resistivity and the conductivity calculated using the Equation (2) and (3) [14]:

\[
\rho = \frac{R A}{L} \quad (2)
\]

\[
\sigma = \frac{G L}{A} \quad (3)
\]

Where:

R: Resistance in (ohm).
\(\rho\): Resistivity (\(\Omega\).Cm).
A: Cross sectional area (cm2).
L: Length (cm).
\(\sigma\): Conductivity.
4. RESULTS AND DISCUSSION

4.1 OM results

Optical microscopy was performed after the thermal treatment. The results of the microscopic examination showed that the manufactured alloys are homogeneous and regular. In addition, the copper element is uniformly distributed within the matrix (NiTi). The following Figure 1 shows the alloy (NiTi) before and after adding the element copper. It also showed that there are some impurities as a result of the processes that followed the manufacturing process.

![NiTi 0 wt.% Cu](image)

![NiTiCu 2 wt.% Cu](image)

![NiTiCu 5 wt.% Cu](image)

![NiTiCu 8 wt.% Cu](image)

**Figure 1.** Images of Optical microscope results

4.2 FESME results

Figure 2 showed the results of the FESME examination of all specimens after the annealing process, as they showed that the microstructure is symmetrical and composed of a matrix in which sediments are distributed. In addition, it show the austenite phase (TiNi), the martensite phase (Ti 002), and the emergence of unwanted impurities as a result of the industrialization process and the processes that followed it.

![NiTi 0 wt.% Cu](image)
Figure 2. Images of Field Emission Scanning Electron Microscopy results

4.3 DSC results

To determine the beginning and end of the phase transitions DSC between (-80 - +280) was used, and the results of the analysis DSC were presented for each specimens.

Figure 3, 4, 5 and 6 shows an analysis of DSC for (NiTi) and (NiTiCu-3) the results show that the binary alloy is more stable. When copper is added, the hysteresis loop begins to decrease (the hysteresis loop is narrow) and this is important for some applications that need rapid phase transformations this is almost identical to research [13]. We notice in both figures the formation of two heat peaks (upon cooling) where the transition takes place from the austenite phase to the martensite phase. We also notice the formation of two exothermic peaks upon heating, as the transformation from the martensite phase to the phase of austenite in addition to the emergence of an unwanted phase (Ti2Ni)[16].

Table 2. Transformations phase for the four alloys

| Alloys         | Transformation Temperature (°C) |
|----------------|---------------------------------|
|                | As    | Af    | Ms   | Mf   |
| NiTi           | 92.8  | 150   | 80   | 30.2 |
| NiTiCu-1       | 99.9  | 140   | 50   | 13   |
| NiTiCu-2       | 10    | 40    | 10   | -30  |
| NiTiCu-3       | 0     | 30    | 0    | -20  |
Figure 3. DSC values for the binary (NiTi)

Figure 4. DSC values for the ternary (NiTiCu-1)

Figure 5. DSC values for the ternary (NiTiCu-2)
4.4 SME results

The most important characteristic of manufactured alloys is the shape memory effect. The results of this property improve with an increase in the percentage of the copper element within the alloy (NiTi). The effect of the shape memory effect of alloy (Ni55Ti45) 87.5%, while the shape memory effect reaches alloy (Ni54Ti44Cu2) 87.80%, while alloy (Ni53Ti42Cu5) improves by 88.44%, the best memory effect for alloy (Ni52Ti40Cu8) by 88.98%.

4.5 Microhardness results

The microhardness of all the alloys manufactured was studied before and after the heat treatment process at (750°C) temperature. Figure 8 show a slight increase in fine hardness is observed after heat treatment because the alloys become more homogeneous and more even. The graph shows that alloy (NiTiCu-1) has the best hardness among other alloys. As the copper element increases, the hardness value decreases [13].

Figure 6. DSC values for the ternary (NiTiCu-3).

Figure 7. Shape Memory Effect (SME).
Table 3. Hardness value before and after heat treatment.

| Alloys      | The hardness value before heat treatment | The hardness value after heat treatment |
|-------------|-----------------------------------------|----------------------------------------|
| NiTi        | 300                                     | 325.5                                  |
| NiTiCu-1    | 378                                     | 400.5                                  |
| NiTiCu-2    | 370                                     | 364.8                                  |
| NiTiCu-3    | 355                                     | 340.5                                  |

Figure 8. The microhardness results of the four alloys.

4.6 Conductivity and resistivity results

Conductivity and resistance tests were performed for all manufactured wires. Figure 9, 10 the results showed that the value of the conductivity increased with the increase of the copper element inside the (NiTi) matrix. Where it was observed that the best conductive wire is (NiTiCu-3) due to its high copper ratio (copper is known for its good conductivity) and less resistance. This feature is very important in many electrical applications, robots and sensors.

Table 4. The values of resistivity and conductivity for all manufactured wires.

| Alloys No. | Electrical Conductivity (σ) (Ω·Cm)$^{-1}$ | Electrical Resistivity (ρ) (Ω·Cm)$\times10^{-6}$ |
|------------|-------------------------------------------|-------------------------------------------------|
| wt.% Cu    |                                           |                                                 |
| 0          | 13192.6                                   | 75.8                                            |
| 2          | 16611.3                                   | 60.2                                            |
| 5          | 20048.12                                  | 49.88                                           |
| 8          | 24096.4                                   | 41.5                                            |
Figures 11, 12, 13 and 14 show the relationship between the strain value and the resistivity at room temperature and constant compressive pressure.

The four wires were tested through cooling and heating, and changes in the value of the strain and resistivity were observed. At the beginning the wire was heated up, gradually increasing the strain with a marked decrease in the resistance value. When the wire is cooled, the resistivity begins to increase with a decrease in the strain, the highest value of the resistivity is reached at a certain point, after which it decreases slightly until the wires are stabilize. The results also showed that the resistivity value in the austenite phase is less than the resistivity martensite (cooling has a direct effect on the resistivity value).

Through the graphs, it has been noticed that alloy (NiTiCu-3) has the best strain with the value of (0.0588%) and the best conductivity.
Figure 11. Resistivity vs strain at (0 wt.% Cu).

Figure 12. Resistivity vs strain at (2 wt.% Cu).

Figure 13. Resistivity vs strain at (5 wt.% Cu).

Figure 14. Resistivity vs strain at (8 wt.% Cu).
5. CONCLUSIONS

Four wires were successfully manufactured in different proportions using (VAR) furnace and the following results were concluded. Firstly, the results of the microscopic examination showed that the elements are homogeneously distributed within the manufactured alloys. Secondly, the results of FESEM examination showed austenite phase (Ti2Ni), martensite phase (Ti 002) and the defects of the manufacturing process. Thirdly, it showed the results of (DSC) the phase transformations represented by the austenite phase and the martensite phase. Fourth, the results of (SME) showed that the best alloy remembered for the shape is the alloy (Ni52Ti40Cu8). Fifth, the hardness improved at alloy (Ni54Ti44Cu2) and decreased with the increase of copper element. Finally the conductivity increases with the increase in the copper element and the increase in the strain rate, with the increase in the copper content inside the manufactured wires, and the decrease in resistivity.

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