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Effects of Ag and Cu Nanopowders on Mechanical and Physical Properties of Niti Shape Memory Alloy

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Abstract:
Nickel Titanium shape memory alloy reinforced with nano particles have different and many uses in multi implant applications due to their excellent characteristics. The present work is aimed at studying the preparation of nitinol reinforced with nano particles of copper and silver. A base alloy of (55% Ni + 45%Ti) has been prepared by using powder metallurgy technique with a determined suitable compacting pressure of 650 MPa and sintering for 5 hours at 850° C in argon gas furnace. Samples with 0.5wt% of Cu or/and 0.5wt% of Ag nanoparticles were prepared. Mechanical and physical characterization included microhardness, porosity, shape memory effect, microstructure, x-ray diffraction and particle size analysis. The results showed that the hardness value increase at 0.5 wt% of Cu and 0.5wt% of Ag together to 287 Hv and to 5.3 in shape memory effectwhile the porosity decreased to (23.1) for alloy with the same percent.

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List of Abbreviation

Abbreviation	Definition
NiTi	Nickel-Titanium
Cu	Copper
Ag	Silver
SMAs	Shape Memory Alloys
VIM	Vacuum Induction Melting
VAR	Vacuum Arc re-melting
XRD	X-ray Diffraction
SME	Shape Memory Effect

I. INTRODUCTION

Nickel rich nitinol alloy are the most commonly used shape memory alloys and they have been widely used for biomedical, electrical and mechanical application due to their high strength, good corrosion resistance, good ductility,which is related to the martensitic transformation with different deformation modes, low anisotropy relatively small grain size and smooth surface properties as compared to equiatomic NiTi SMAs. Recently, high nickel rich NiTi SMAs are coming into prominence owing to their distinct super elasticity and shape memory properties[1,2].A lot of techniques are used to produce nitinol alloys.

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Vacuum induction melting (VIM) and vacuum arc re-melting (VAR) are most commonly technique used because of using a graphite crucible, carbon will be originated during VIM process and the melt could be contaminated. For the VAR process, the melt exists only for a short time and this mean that there will be no contamination. Hence, a combination of (VIM/VAR) can be used. Such processes have to be repeated for several times to overcome the inhomogenity of ingots and the cost of the production will be higher [3]. An alternative technique to produce nitinol alloys is the powder metallurgical processes. Many methods can be used for sintering like solid or liquid phase sintering, hot or cold isostatic pressing and plasma sintering. Many alloying elements can be used during sintering to improve the mechanical properties of alloys.There are a lot of researches that focused on enhancing the mechanical properties of the produced nitinol. Some of these researches studied the effect of many alloying elements on the overall properties of nitinol. Among many alloying elements, copper was reported as an important element since it plays a significant role in improving the hardness for nitinol alloys, adding of copper as an alloying element 2.5 % to replace Ni content will increase the hardness to its maximum value [4]. Also some of researches have been shown that silver addition to nitinol increases the transformation temperatures and improves corrosion resistance and mechanical properties [5].Other research have been described the antibacterial function into biomedical TiNi shape memory alloyby the addition of element Ag, the antibacterial effect is attributed to the release of Ag ions from the tiny Ag precipitates. Therefore, TiNiAg

alloy is believed to be a functional biomaterial which combines antibacterial activity and shape memory effect [6].The objective of the current work is to investigate the main parameters of powder metallurgical process to produce nitinol alloys, the best weight percentage of copper or/and silver additive to improve nitinol properties.

II. POWDERS USED IN THE PRESENT STUDY

The materials used to prepare NiTi alloys in this study are shown in Table1.

Table 1: Purity and Particle Size of the Powders

Metal powder	Average of Particles Size	Purity (%)	Source
Ni	44.93 µm	99.5	Gentral Drug House (p) Ltd.India
Ti	99.17 µm	99.9	BDH chemicals Ltd poole England
Ag	80 nm	99.9	Nanjing Nano Technology
Cu	10-30 nm	99	Nanjing Nano Technology

X-Ray diffraction (XRD) was used in order to define the phases of all samples. The X-ray is generated by general electrical diffractometer type (Equino X3000-France made) operating at a voltage of about 40 kV, a current of about 30 mA., and Cu target, wave length of 1.54060 A°. The detector was moved through an angle of $2\theta = 0$ to 100 degrees.

III. SAMPLES PREPARATION

To study the effect of Cu and Ag nanoparticles on some physical and mechanical properties of the base alloy (55%Ni+45%Ti),samples coded in Table 2 were prepared .Wet mixing for 1 hour was carried out in the presence of (5 ml) ethanol solution with a purity of 99.95% using ultrasonic mixer. Then the mixture was dried at 80 °C for 30 min. Uniaxial compacting via double action steel die was carried out on electro hydraulic press to prepare cylindrical samples with (13 mm) in diameter and (5mm) in height. Suitable compacting pressure was determined

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experimentally basing on the constancy of the green density.

Table 2: Prepared Samples in This Study

Samples Code	Weight Percentage (%)			
	Ni	Ti	Cu	Ag
A_1	55	45	-----	-----
A_2	54.5	45	0.5	-----
A_3	54.5	45	-----	0.5
A_4	54	45	0.5	0.5

A pressure of 650MPa was determined with duration of 4 min. and used to prepare all samples. Figure 1 shows the effect of compacting pressure on the green density.

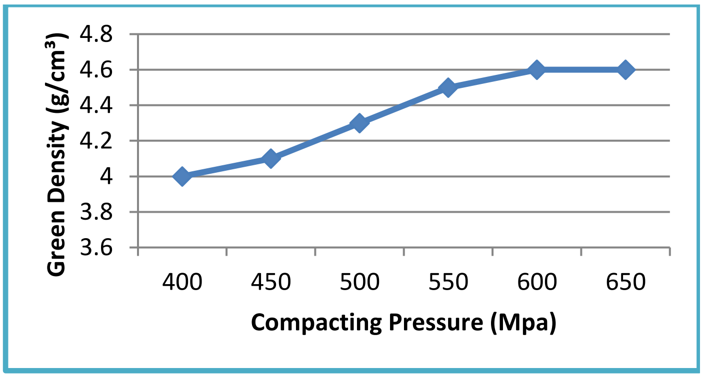

Figure 1: Effect of Compacting Pressure on Green Density.

The sintering process of the green compacts was achieved in quartz tube inside a tube furnace with a continued stream of inert gas (Argon) from initial to final stage of sintering. The heating rate used was 10∘ C/min. The sintering process of all samples includes the followed heating cycles:

a. Heating green compacts from room temperature to 550∘C and soaking at 550∘C for 1 hour and then heating to 850∘C.

b. Soaking time for 5 hours at 850∘C.

c. Slow cooling in the furnace with a continuous flow of argon to room temperature.

IV. Samples Tests/Results and Discussion

A. Microscopic Analysis

Appropriate grinding and polishing were carried out for the sintered samples of (13mm diameter×5 mm height) by using paper grits as (220,400,600,800,1000,1200,2000, and 2500) and polished by using diamond solution, via a grinding and polishing machine, then etching solution consist of (16%HNO3, 9%HF, 75%H2O) at room temperature was used [7]. All samples were washed by distilled water and dried using electric drier. Optical microscope was used to capture the microstructure of the surface sample.The microstructures of the prepared samples are shown in Figure (2).The figure illustrates the

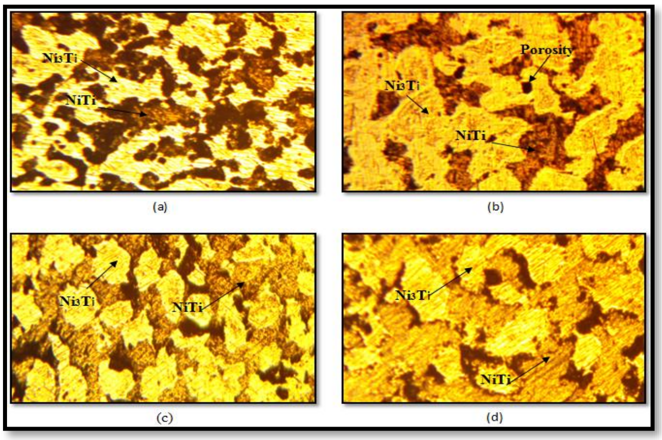

Figure 2: Microstructure for sintered alloys (400x): a) base alloy, b) NiTi 0.5 %Cu alloy,c) NiTi0.5% Ag alloy, d) NiTi 0.5%Cu 0.5% Ag alloy

microstructure of etched alloys after sintering process.The microstucture for alloys showed the grain boundaries, pores in different sizes and the present phases. Many pores with different sizes can be seen on the surface, since the samples were prepared by powder metallurgy technique.

B. X-Ray Diffraction Analysis

The X-ray Diffraction test (XRD) was carried out for all samples. It is seen from Figures 3,4,5 and6that the (Ni,Ti,Ag & Cu) powder are pure.

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Figures 7,8,9,10 show that there are probably no pure metals present and contained two phases; the martensitic phase (monoclinic) and the austenitic phase (cubic), in addition to Ni3Ti which proves that the sintering time and temperature used in this work result in complete sintering reaction. The suggested reactions during the process are as follows [8]

Ni+Ti NiTi ΔG:-67 KJ/mol……………(3)

Ni+Ti Ni3Ti ΔG:-140 KJ/mol ………....(4)

According to the binary phase diagram of NiTi system. NiTi and Ni3Ti are stable compounds and reaction (4) is more thermodynamically favored than reaction (3). It is also found from Figures 7,8,9&10 the absence of any oxides that is attributed to the controlled argon atmosphere used during the sintering process.Figures (3-10) conform to standard chart [4&9]

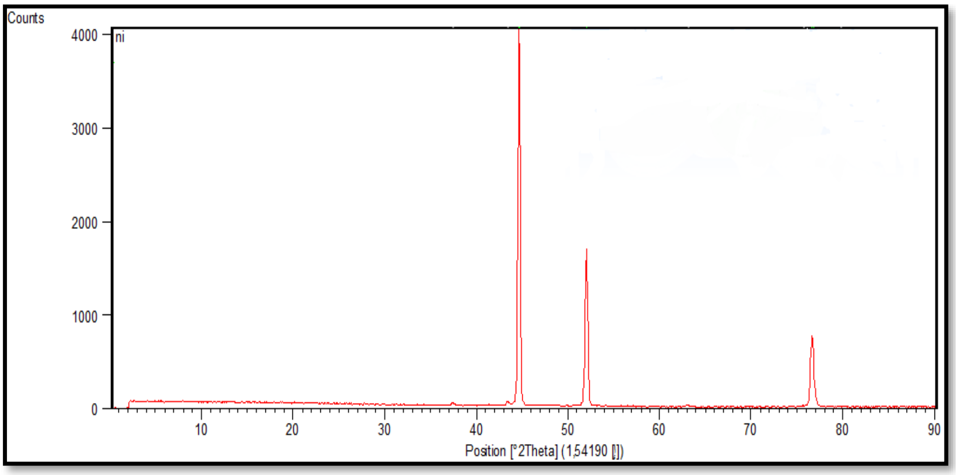

Figure 3: XRD pattern of Ni powder.

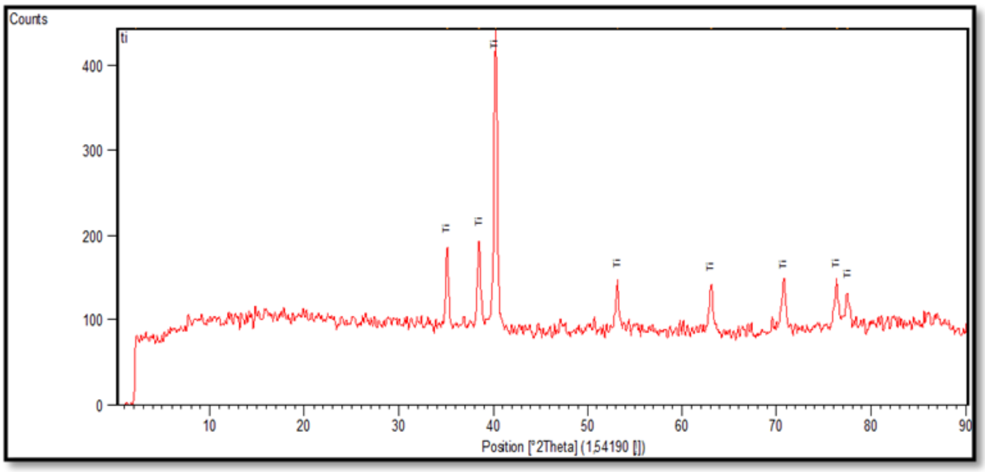

Figure 4: XRD pattern of Ti powder

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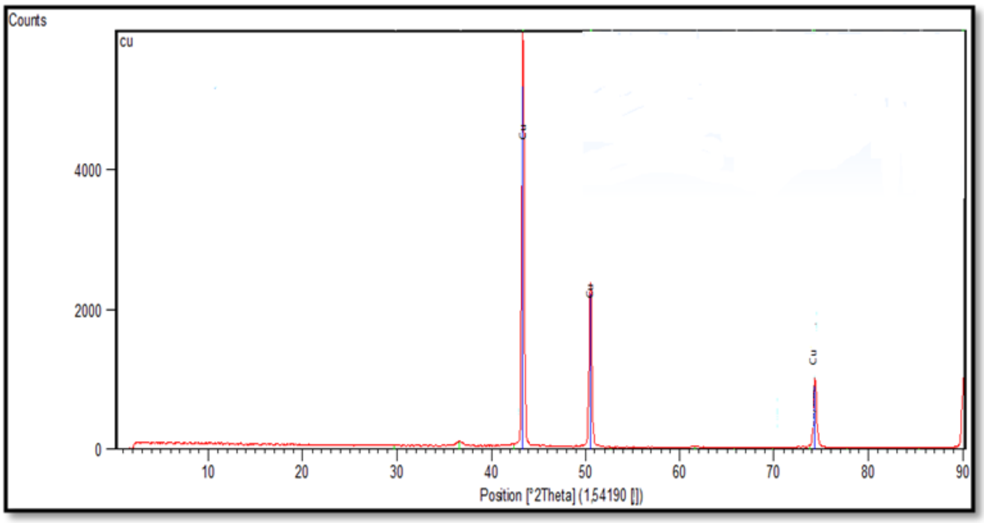


Figure 5: XRD pattern of Cu powder.

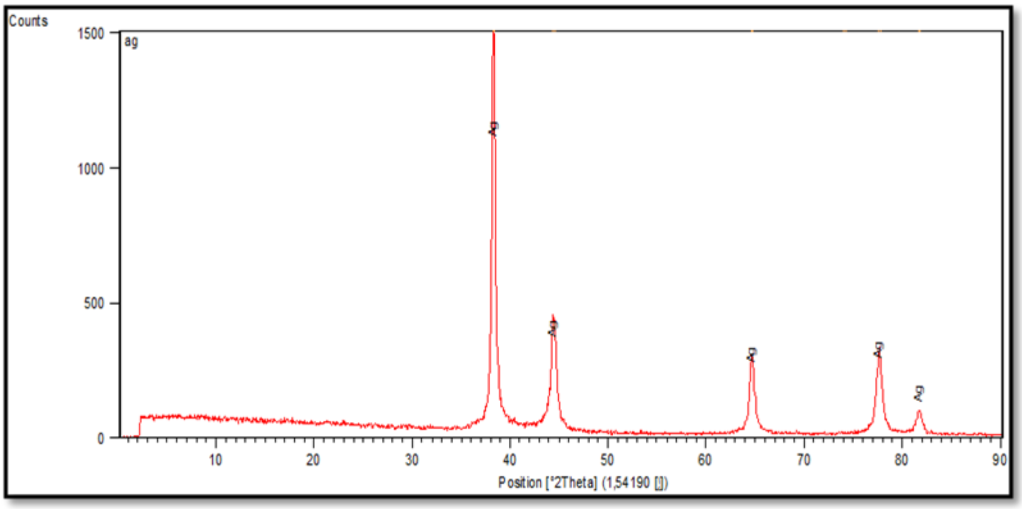


Figure 6: XRD pattern of Ag powder

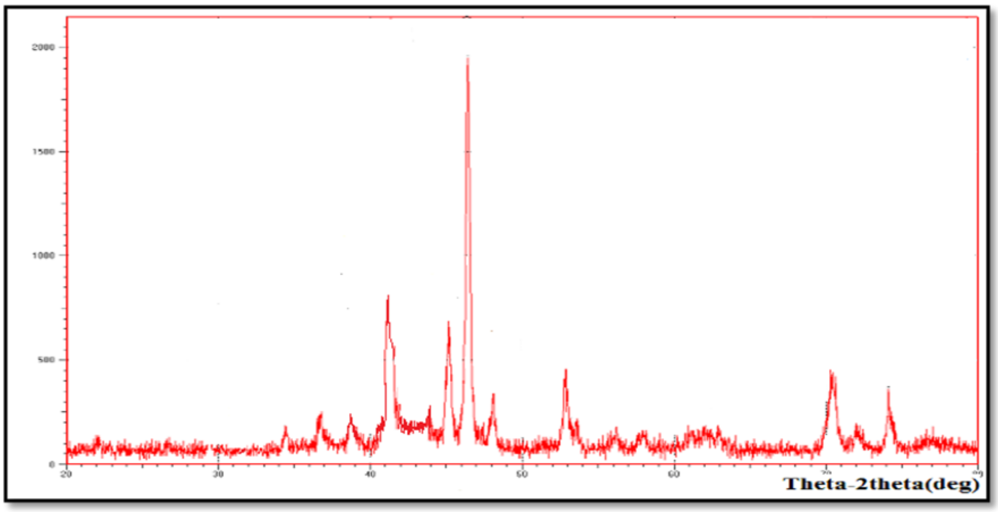
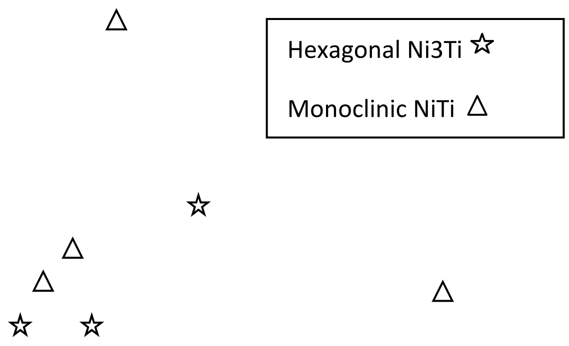


Figure 7: XRD pattern of A1alloy after sintering.



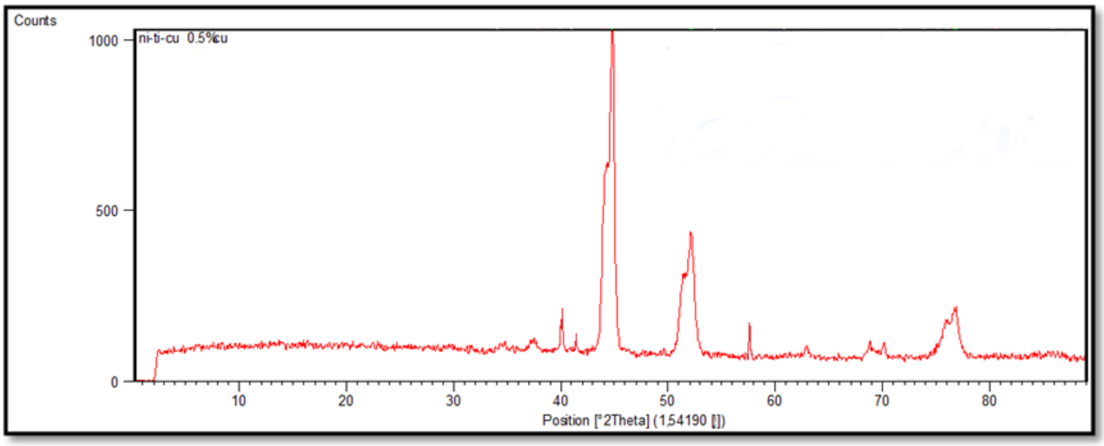


Figure 8: XRD pattern of A2alloy

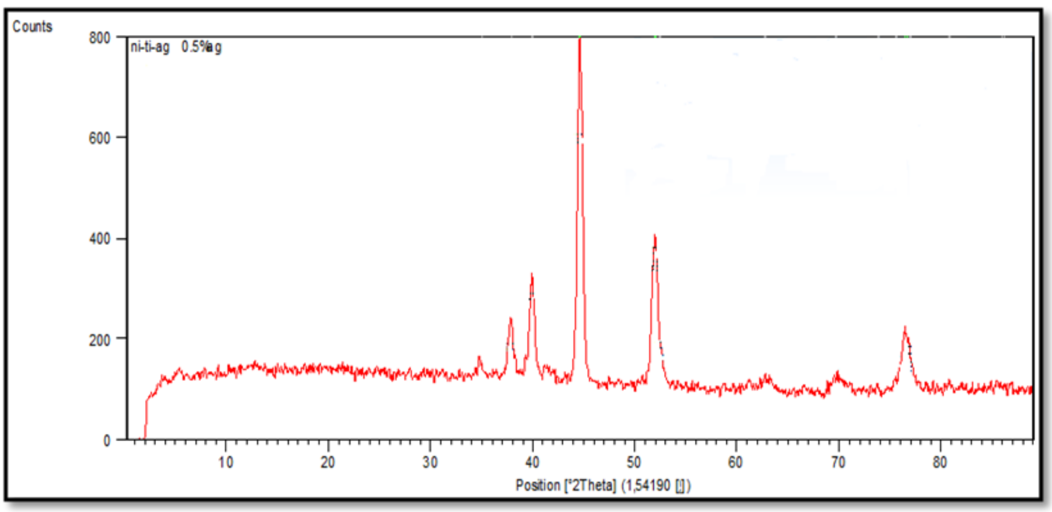


Figure 9: XRD pattern of A3alloy.

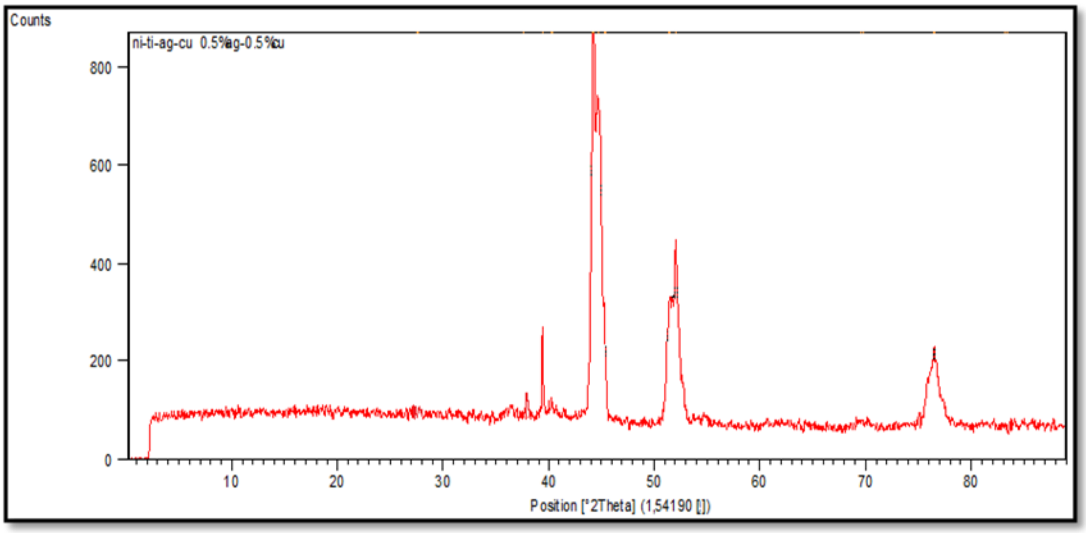


Figure 10: XRD pattern of A4alloy.

C. Hardness Test

Vickers hardness test was used to measure the hardness of the sintered samples at loading 500 g held for 10 seconds, and the value of hardness has been recorded as an average of three reading in different places at the surface of each sample. This test is achieved by using Vickers hardness testing machine type (HVS-1000). Figure (11) shows the results of this test.

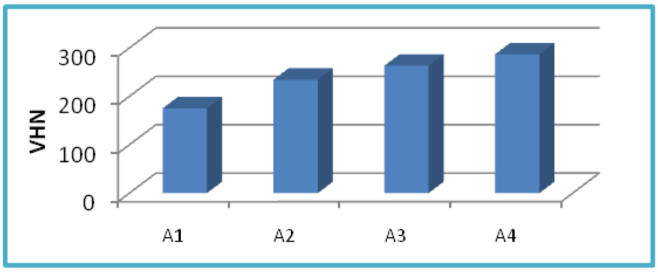


Figure 11: Vickers Micro Hardness for Samples.

The results indicate that the hardness of the A4 alloy is higher than that of others and the hardness of A3 alloy is higher than that ofA2 alloy due to the addition of Cu which makes the material more ductile by reducing the stress to induce or reorient variants of martensite. These finding agree with Dawood and Araujo [9,10].

D. Porosity Measurements

Porosity was measured by using Archimedes method depending on weighing of sintered samples as follows [11]:

1. The weight of dry sample was measured.

2. The sample was immersed in distilled water for 24 hours. The weight of wet sample was measured.

3. After impregnation of the tested sample, suspended mass was measured when the sample is suspended in water.

4. The sample was cleaned with cotton cloth to remove all excess water from its surface. Immediately the sample was weighted to determine the saturated mass.

5. Porosity was measured by the following equation:

Porosity % = (Ws-Wd/Ws-Wn) x 100 ………………………………. (5)

Where:

Ws = weight of sample after immersing it in the distilled water for 24 hours.

Wd = weight of the dry sample after sintering.

Wn = weight of immersed sample in the distilled water and suspended in air.

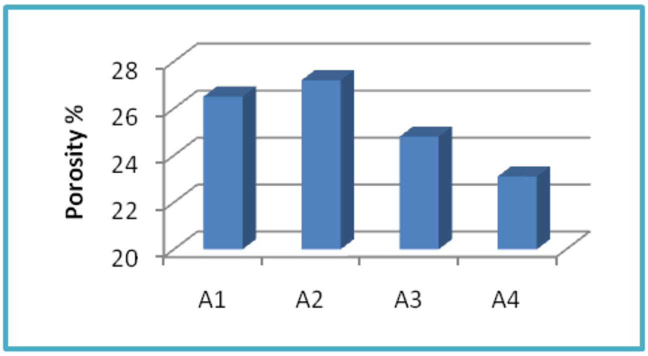


Figure 12: Porosity Percentages for the Samples.

Figure (12) shows the results of this test. From the figure it can be seen that the porosity of sintering sample (A2) increase this result has been agree with Dawood [8]. This increasing can be explained as following: the diffusion of Cu atoms in titanium is several times higher than diffusion of nickel atoms in titanium. Also, the diffusion ratio of Cu and nickel atoms in titanium is higher than titanium in copper or nickel. As a consequence, titanium particles create a base for alloy, where first copper atoms diffuse in Ti and then nickel is diffuse. In this manner, the volume of the pores increases. Using this mechanism, pores with smaller size can be created at the border between titanium particles and copper/nickel [12].

E. Shape Memory Effect

The shape memory effect (SME) was found out after the Brinell hardness test at room temperature. Brinell hardness tester was used to measure the hardness of the sintered samples with 2.5 mm ball diameter as indentation ball and (187.5 kPs.) as applied load for 10 sec. An average of three readings has been recorded in this test. Subsequently the sample was heated to 80°C for one hour in a vacuum furnace and cooled in vacuum. SME was determined according to the following equation [11]:

$$SME\ \% = d_b - d_a / d_b \times 100 \ldots\ldots\ldots\ldots\ldots.. (6)$$

Where:

d_b = average impression diameter in (μm) before heating to 80°C.

d_a = average impression diameter in (μm) after heating to 80°C.

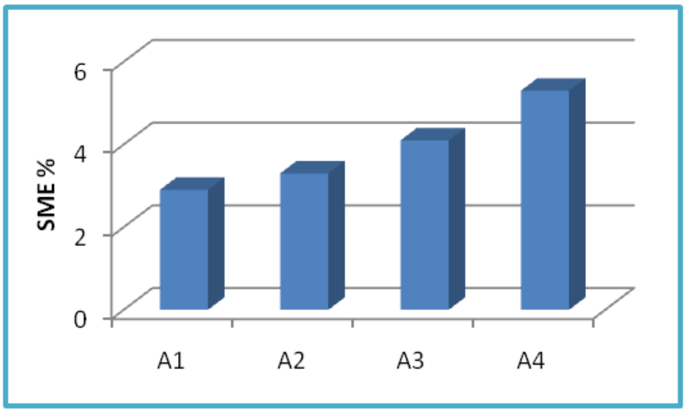


Figure 13: SME properties for all samples.

SME values for nitinol alloy showed smaller values than the values of other alloys.

V. CONCLUSIONS

Based on the obtained results, the following conclusions are made:

1. Sintering at 550° C for 1h, then 5 hrs. soaking samples at 850°C under argon condition is sufficient to complete the transformation process of Ni, Ti, Cu and Ag to alloy structure.

2. Two phases structure is appear in all alloys monoclinic NiTi and hexagonal Ni3Ti.

3. Adding of 0.5 wt% Cu together with 0.5 wt% Ag increases the hardness of NiTi SMA by 287% while such addition reduces the porosity by 23.1%.

4. The addition of Cu & Ag increase the shape memory effect for the base alloy by 5.3%.

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