Fabrication of Porous NiTi Shape Memory Alloy Objects by Powder Metallurgy for Biomedical Applications

IOP Conf. Series: Materials Science and Engineering **518** (2019) 032056 doi:10.1088/1757-899X/518/3/032056

Fabrication of Porous NiTi Shape Memory Alloy Objects by Powder Metallurgy for Biomedical Applications.

Nawal Mohammed Dawood[1], Abdul-Raheem Kadhum Abid Ali[1] and Alaa Abdulhasan Atiyah[2]

[1]University of Babylon, Babylon, Iraq
[2]University of Technology, Baghdad, Iraq

Abstract. This research, studied the effects of compacting pressure (150-450) MPa and Copper additions (2.5, 5, 7.5 and10) wt% on the mechanical properties of NiTi based shape memory alloys prepared by powder metallurgy. Several mechanical tests such as Rockwall macro hardness measurements, compression test and shape memory properties of the prepared alloys were achieved. The results showed that the addition of Copper with (2.5-10) wt. % to NiTi prepared alloy resulted decreasing the hardness relatively with comparison to master alloy without copper also, there is a distinguished increase in SME properties obtained from hardness test for the NiTi alloys with addition of copper. The result showed that the increasing in compacting pressure and Cu additives have an essential effect by improvement the mechanical properties of the prepared alloys.

1. Introduction

Porous Ni-Ti shape memory alloys have recently become a central item of attention. It is usually used as hard tissue implants (such as artificial bone) because of its porous structure, good mechanical properties, high biocompatibility, shape memory effect (SME) and excellent pseudo elasticity [1]. The porous structure and related compressibility allow the transport of body fluids, and they are beneficial for the ingrowth of newborn bone tissue, making the fixation of implant more natural and reliable. Similar to other metals, unsatisfactory surgical outcome has been found from materials with higher elastic modulus mismatch with human bones. Uneven distribution of stress of high elastic modulus material carries most of the load giving the risk of loosening the implant [1, 2]. In this connection, the appropriate elastic modulus can be obtained from porous NiTi through adjustment of the synthesis process. These porous materials provide a combination of high strength, high toughness and relatively low stiffness. High strength is an important parameter for preventing deformation, fracture, high toughness is essential to avoid brittle failure and low stiffness, or low modulus is useful to minimize stress-shielding effects. Shape - recovery behavior can make good mechanical stability within the host tissue. Meanwhile it has been obtained that an appropriate range of pore sizes and interconnectivity enable morphology similar to that of bone [3, 4]. The addition of Copper, as a third major alloying element, results in increasing the characteristic temperatures of the martensitic transformation, in comparison to a binary NiTi alloy. Further, copper causes good stability of characteristic temperatures and good corrosion resistance, narrow transformation hysteresis and prevention of Ti_3Ni_4 precipitation. Currently, many researches has been done the non-traditional production techniques such as powder metallurgy (PM), melt-spinning (MS) or twin roll casting (TRC) for manufacturing the NiTi-based alloys [5]. The main advantage of the powder metallurgy is avoiding typical thermo mechanical treatment needed after traditional casting.

However, powder metallurgy produces pore that diminishes mechanical properties. This research aims to study of the effect of compacting pressure and the Copper additives on the mechanical properties of Ni-Ti shape memory alloys prepared by powder metallurgy.

2. Experimental procedures

The samples are prepared using powder metallurgy process. Elemental Ti , Ni and Cu powders, with commercial purity (99.5%) and average size of 127.188 µm for Ti, 141.0-216.0 µm and 50.273 µm for Ni and Cu alternatively, were used in the present study as a starting material for producing NiTi and NiTiCu shape memory alloys. Powders were weighted in proper proportions as shown in Table. 1 and mixed in electric rolling mixer for 6 hours. Electric hydraulic press with one directional pressing is used to press green samples. Compacts were prepared, at room temperature, in a form of disc with dimension (14 diameter and 4 mm thickness) and cylinder with(10 diameter and 20 mm height) under a different pressure of 150, 250, 350 and 450 MPa as shown in table.1 Sintering was performed under protective atmosphere of argon in the tube furnace attached with tube of quartz at 850 °C for 9 h. Rockwell hardness was used to measure the hardness of the sintered samples with 1.5875 mm ball diameter as indentation ball. The value of hardness has been taken for 3 times in different places along the surface of each sample and the average of three reading has been taken to get the hardness value.

Table 1. Detail description of prepared sample

ALLOYS	SAMPLE CODE	COMPACTED PRESSURE(MPa)	DESCRIPTIONS (WT. %)
A	A1	150	55% Ni + 45 % Ti
	A2	250	
	A3	350	
	A4	450	
B	B1	150	52.5 % Ni + 45% Ti + 2.5% Cu
	B2	250	
	B3	350	
	B4	450	
C	C1	150	50 % Ni + 45 % Ti + 5 % Cu
	C2	250	
	C3	350	
	C4	450	
D	D1	150	47.5 % Ni + 45% Ti + 7.5 % Cu
	D2	250	
	D3	350	
	D4	450	
E	E1	150	45% Ni + 45% Ti + 10 % Cu
	E2	250	
	E3	350	
	E4	450	

The shape memory effect is calculated from Rockwell indentation as follows [6].

$$\text{Shape memory effect (SME\%)} = \frac{d_b - d_a}{d_b} \times 100 \tag{1}$$

Where: d_b = average impression diameter in (µm) just before heating. d_a = average impression diameter in (µm) just after heating

Compression test was used to determine the SME of sintered porous Ni–Ti alloys. The Shape memory effect determined from compression test as follows [6, 7].

IOP Conf. Series: Materials Science and Engineering **518** (2019) 032056 doi:10.1088/1757-899X/518/3/032056

$$\text{Shape memory effect (SME\%)} = \frac{L2 - L1}{L\circ - L1} \times 100 \qquad (2)$$

Where: L◦ = initial distance between two indentation reference marks on the surface of a specimen parallel to the compression direction., L1 = is the distance between the indentation marks after compression and direction., L2 = is the distance between the indentation marks after recovery heating.

The reported values are the average of three measurements. Furthermore, strain recovery percentage during shape memory effect is also calculated as follows [6, 7].

$$\text{Strain recovery } (\in r\,\%) = \frac{L2 - L1}{L\circ} \times 100 \qquad (3)$$

Where: ϵr = recovery of strain percentage (%) .

During compression test, the sintered cylindrical specimens with (10mm diameter and 20 mm in height) dimension were compacted along the axial at a constant strain rate of (0.1mm/min) at ambient temperature. The diagrams of stress–strain for each case were recorded with the aid of computer control electronic universal testing machine. The slope of the linear deformation stage during compression was used to present qualitatively the Young's moduli of the materials. The microstructure and chemical composition of the prepared alloys was determined by using scanning electron microscope attached to an energy-dispersive system (EDS).Transformation temperatures and the phase identification of the sintered samples were determined by differential scanning calorimeter test and X - Ray diffraction test respectively. All these tests have been done in Al-Razi metallurgy research center/ Iran. The results and details of these tests were mentioned in Ref [8].

3. Results and discussion

Mechanical tests included hardness measurements, compression test results and shape memory effect properties. The mechanical tests are achieved with respect to several parameters such as compacting pressure and copper content in the prepared samples.

3.1 Rockwell B macro hardness

In the current study macro hardness of the samples was determined by using Rockwell method HRB. Hardness measurements were carried out for the prepared samples (master alloy and the master alloy with different additives of copper).As can be observed in Figure.1 when the compacting pressure is increased from (150 to 450) MPa, the hardness value for all samples (without and with copper additions) have been increased. This is in good agreement with the fact that as the compacting pressure is increased, the bonding between the particles is increased (i.e. Better inter diffusion). Further, this leads to more pores elimination, these results are in agreement with other investigator [7].

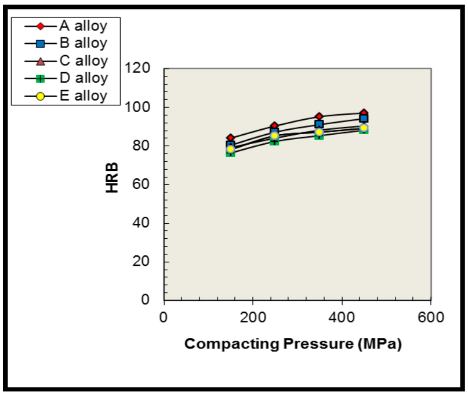

Figure 1. Effect of compacting pressure on the HRB values for alloy A, B, C, D and E sintered at 850°C for 9 hours.

In the comparison with the master sample, we can find that the values of hardness are decreased with increasing Cu additions as shown in Figure 2 at different compacting pressure (150, 250, 350 and 450)

MPa. The hardness values for A4, B4, C4, D4 and E4 samples at 450 MPa compacting pressure are 97.1, 94. 2, 90. 4, 88.2 and 89.2 respectively, these results illustrated that the master sample A4 has the higher values of hardness and the increasment of copper additives decrease the values of hardness. These results are in agreement with [9] .It can also be notice that E4 sample which has 10 wt. % of copper appears a slightly increase of hardness values compared with D4 samples which has 7.5 wt. % of copper addition. This reduction of hardness for Ni - Ti - Cu relation to Ni - Ti alloy can be associated to the change of microstructure morphology induces by copper addition. In fact, the lower level of hardness in Ni - Ti - Cu when addition of copper until 10 at % makes the material more ductile by reducing the stress to induce or reorient variants of martensite. While the addition of copper beyond at % ≥ 10 causes the material to become brittle. These results are in agreement with several researchers [5,9].

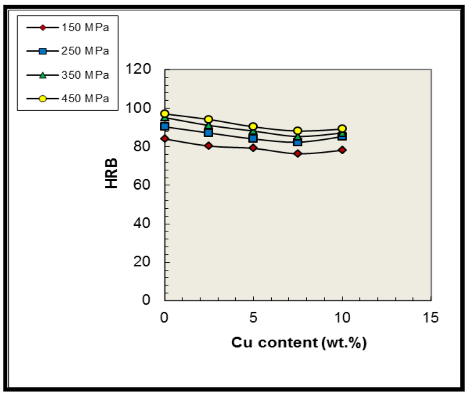

Figure 2. HRB Vs copper content for alloy A, B, C, D and E compacted at different compacting stress**.**

3.2 Compression test

In the test the samples divided into two groups, Figure 3 showed the compression stress- strain curves of the first group. This group includes A3 (without copper) sample and B3, C3, D3and E3 samples which contain (2.5 , 5 , 7.5 and 10) wt. % Cu alternatively.

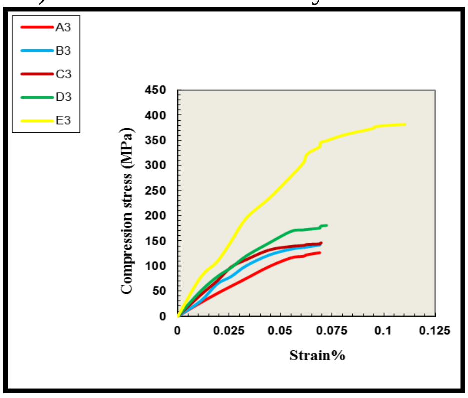

Figure 3. Compression stress-strain curve for alloys A3, B3, C3, D3 and E3 which compacted at 350 MPa and sintered at 850°C for 9hours.

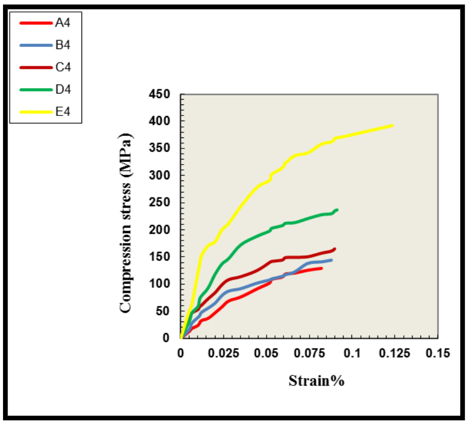

Figure 4. Compression stress-strain curve for alloys A4, B4, C4, D4 and E4 which compacted at 450 MPa and sintered at 850°C for 9hours.

Figure 4 showed the compression stress- strain curves of the second group. This group include A4 (without copper) sample and B4 , C4 , D4 and E4 samples which contain (2.5 , 5 , 7.5 and 10) wt. % Cu respectively. It is obvious from Figure 3 and Table .2 that the compressive strength, yield strength and modulus of elasticity(E is determine as the pest - fit slope of the linear part of the compression stress-strain curve) are increased with increasing copper addition from (2.5 to 10) wt. %. The values of σy com, σy and E are increased by 12%, 11% and 11 % respectively for B3 samples and by 15 %, 18 % and 152 % respectively for C3sample in comparisons to A3 sample without copper addition .As can be observed from Figure 4 and Table.3 that the addition of copper increases the values of σ com, σy and E of the alloys with different content of copper with respect to master samples. It is obvious that the E4 sample have the highest increasing percentage reaches to 203 % for σ com (compression strength) and 103 % , 244% for σy (yield strength) and E (modulus of elasticity) with comparison to A4 sample without addition of copper .

Table. 2. Compression Properties (Compressive Strength, Modulus of elasticity and Maximum Strain) for first group of samples.

Sample	Compressive strength σcom (MPa)	Yield Strength σy (MPa)	Modulus of elasticity E (GPa)	Maximum Strain Ɛ (%)
A4	129. 213	118.194	2. 572	8. 21
B4	144. 327	128.936	3. 354	8. 79
C4	165. 19	134.243	5. 412	8. 98
D4	236. 922	153.226	7. 561	9. 12
E4	392. 256	240.169	8. 877	12.34

IOP Conf. Series: Materials Science and Engineering **518** (2019) 032056 doi:10.1088/1757-899X/518/3/032056

Table. 3: Compression Properties (Compressive Strength, Modulus of elasticity and Maximum Strain) for second group of samples

Sample	Compressive strength σcom (MPa)	Yield Strength σy (MPa)	Modulus of elasticity E (GPa)	Maximum Strain Ɛ (%)
A3	126. 532	110. 213	2. 374	6. 89
B3	142.755	123.241	2.643	6. 91
C3	146. 185	130.421	5. 998	6. 96
D3	180. 768	141.920	6. 138	7. 22
E3	381. 601	225.634	7. 013	11. 02

The compressive strength, yield strength and modulus of elasticity for samples in the first and second groups as a function of copper concentration are shown in Figs. 5, 6 and 7 respectively. From Figurs 5 to 7 and Tables. 2, 3 can be verified that the addition of copper to NiTi alloys increase the compressive strength, yield strength and modulus of elasticity for the first and second groups of samples, it has been reported that the copper addition to binary NiTi alloy improved the mechanical properties of the alloy. This is may be ascribed to the ability of copper to strength the parent phase. The strengthing of the parent phase increased by increasing Cu content as experimentally observed by [10].

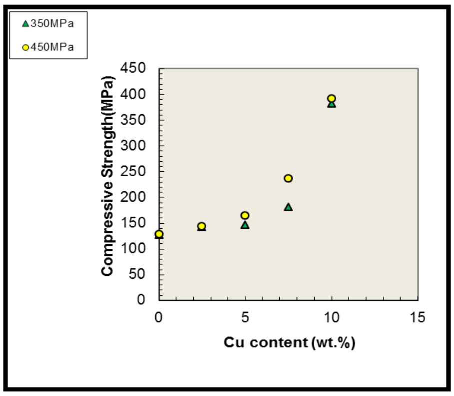

Figure 5. Compressive strength as a function of Cu content for A, B, C,D and E alloys which compacted at 350 MPa and 450 MPa and sintered at 850°C for 9 hours.

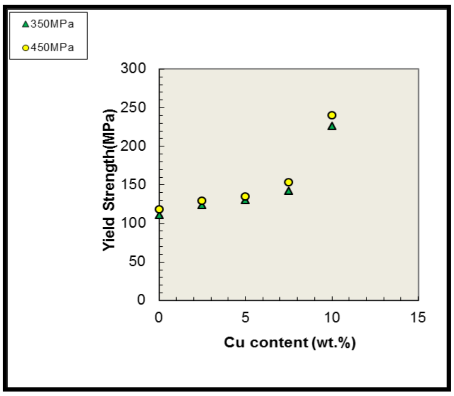

Figure 6. Yield strength as a function of Cu content for A, B, C, D and E alloys that compacted at 350 MPa and 450 MPa and sintered at 850°C for 9 hours.

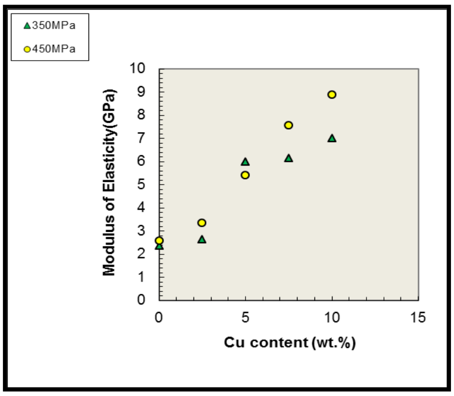

Figure 7. Modulus of elasticity as a function of Cu content for A, B, C,D and E alloys which compacted at 350 MPa and 450 MPa and sintered at 850°C for 9 hours.

In addition, the addition of copper to binary NiTi alloy reduced slightly the hardness of the alloy and makes the material more ductile by reducing the stress to induce or reorient variants of martensite [9, 10]. It is known that the increase of stress with strain caused of increasing the area under stress - strain curves that mean that the toughness of the alloy was increased also, as a result the addition of copper increased the area under the curve that mean the increasing of alloy toughness. Compressive strain as a function of copper concentration for first group and second group of samples is shown in Figure 8.

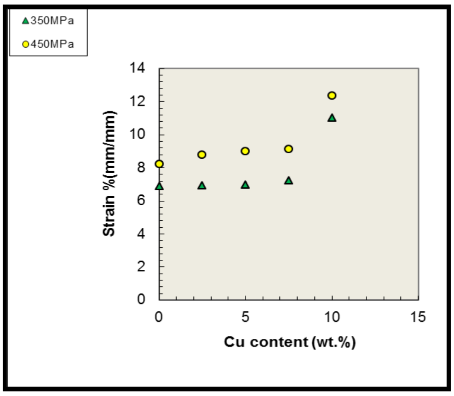

Figure 8. Strain as a function of Cu content for A, B, C, D and E alloys that compacted at 350 MPa and 450 MPa and sintered at 850°C for 9 hours.

Figures 5and 8 illustrates the presence of another factor beside copper concentration affecting the mechanical properties of the prepared samples. The compacting pressure of these samples can be considered as this factor. The mechanical properties σcom, σy, E and maximum Ɛ increase with increasing the compacting pressure from 350 to 450 MPa because the total porosity in the mass decrease. It is better to describe stiffness of implants by the apparent young's modulus of the samples. The apparent young's moduli of the NiTi SMA sample in the present research are reaches to 8. 87 GPa similar to the young's modulus of bone (10- 30) GPa reported in bio reference **[11].** In Table.4 mechanical properties of the NiTi SMA samples of this research were compared with bulk NiTi and cortical bone.

Table. 4: Mechanical properties of cortical bone [11] and Porous NiTi of the current study and dense NiTi [12].

Materials	Young's modulus (GPa)	Strength (MPa)
Cortical bone	10 - 30	70 -150
Dense NiTi	28 - 75	745 - 960
Porous NiTi	2. 3 – 8. 87	126 - 392

Young's modulus of porous NiTi is near to that of the cortical bone. A big stiffness difference implant and cortical bone causes a load transformation failure with the reduction of the mechanical stress. This is the so- called stress - shielding phenomenon [12]. Low rigidity porous NiTi is expected to prevent stress - shielding and improve the reduction of the mechanical stress and promote bone formation and bone remodeling in the implant surgery such as internal fracture fixation [11, 12].

3. 3 Shape memory effect properties

3.3.1 Shape memory effect from hardness test

The values of SME obtained from Rockwell hardness test for master samples A1, A2 , A3 and A4 are 3.41 % , 3.62 % , 3.89 % and 3.91 % at different compaction pressure 150,250,350 and 450 MPa respectively. Figure 9 showed the SME values related to compacting pressure for all prepared alloys. It is clear from this figure that the SME for master samples increased by increasing compacting pressure because of elimination of porosity and the SME values for master alloys showed smaller values than the values of dense form which up to 8- 10 % [**10,13**]. This behavior because there is only martensite phase for dense NiTi SMA while for the porous state there is martensite , austenite and other phases at the same time [**7**]. The SME values for prepared master samples with 2.5wt.% of copper additives are 3.86 % , 3.98 % , 4.43 % and 4.97 % for B1, B2, B3 and B4 samples at 150 , 250 , 350 , and 450 respectively (see Table.5).These results indicated that the increase of compaction pressure at 2.5 wt. % of copper additives increase the SME properties for the Ni -Ti - Cu alloys as shown in Figure 9.

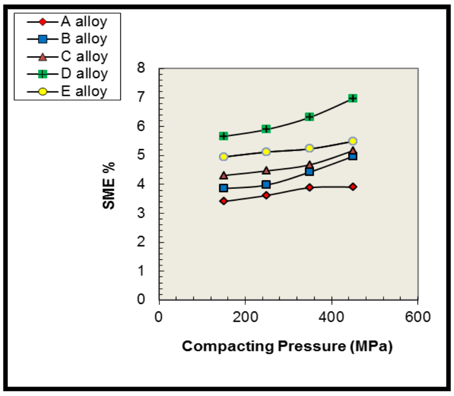

Figure 9. Effect of compacting pressure on SME properties obtained from Hardness test.

Also, by comparing the SME values for master samples A1 , A2 , A3 and A4 which compacted at 150, 250, 350 and 450 MPa respectively with B1 , B2 , B3 and B4 Which compacted at the same pressure . It can be noted that the copper addition in substitution of nickel cause a significant increase in the SME properties of NiTi alloys. SME for NiTi samples increased with increasing copper addition from (2.5 wt. % to 10 wt. %) as shown in Figure 10 and Table.5. The addition of copper element to NiTi binary alloy makes the flow stress or the critical stress in the martensitic state (i.e. the stress to move twin boundaries in martensitic) is very low which mean that Ni-Ti -Cu alloys are much easily deformed in the martensitic state compared with binary NiTi alloy [10] .

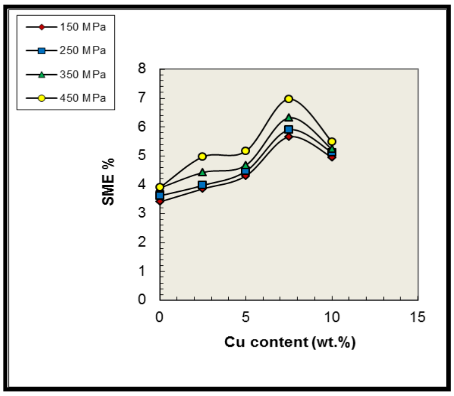

Figure 10. Effect of copper content on SME properties obtained from Hardness test**.**

3. 3.2 Shape memory effect from compression test

Shape memory effect and shape recovery are calculated from compression test. The values of shape memory effect and strain recovery for all prepared samples are shown in Table. 5 .

Table. 5: Shape memory alloy from hardness Rockwell (HRB), Shape memory alloy and Shape recovery under Compression for all prepared alloy at RT.

ALLOY	*Sample Code*	*HRB Test*	*Compression Test at RT*	
		SME %	*SME %*	*S. R %*
A	A1	3.419	3.125	0.112
	A2	3.626	4.339	0.256
	A3	3.894	5.486	0.352
	A4	3.916	5.850	0.029
B	B1	3.860	4.945	0.573
	B2	3.982	5.194	0.458
	B3	4.434	5.206	0.871
	B4	4.975	5.982	0.853
C	C1	4.318	6.030	0.805
	C2	4.474	6.456	1.369
	C3	4.683	6.513	0.514
	C4	5.170	7.338	0.262
D	D1	5.662	6.230	0.390
	D2	5.908	6.712	0.476
	D3	6.300	7.236	0.725
	D4	6.978	8.061	0.214
E	E1	4.952	6.420	0.819
	E2	5.121	6.812	0.873
	E3	5.239	7.335	0.231
	E4	5.492	8.213	1.235

It is clear from the Table, that the SME for master samples A1 , A2 , A3 and A4 are 3.125%, 4.339% , 5.486% and 5.852% respectively at different compacting pressure (150 , 250 , 350 and 450) .These results illustrate that the SME properties for master samples increased with increasing the compaction pressure as shown in Figure 11 this attributed to elimination of porosity by increasing the compaction pressure. Figures 12 and 13 illustrate the strain recovery as a function of compacting pressure and Cu content respectively. The SME properties for master samples also increase with addition of copper at different additives, for example the SME for A4 sample at 450 MPa is 5.85 % while the SME for D4 with 7.5 wt. % Cu at 450 MPa is 8.061 which mean that the improvement percentage of SME properties are 37 % with 7.5 wt. % of Cu at 450 MPa compacting pressure.

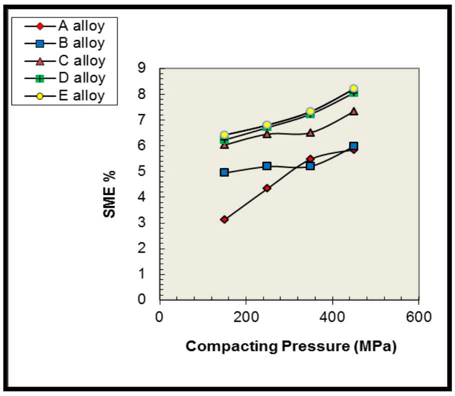

Figure 11. Effect of compacting pressure on SME properties obtained from compression test at RT (room temperature).

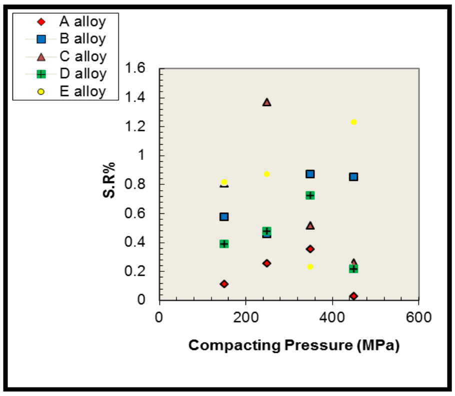

Figure 12. Effect of compacting pressure on strain recovery properties obtained from compression test at RT.

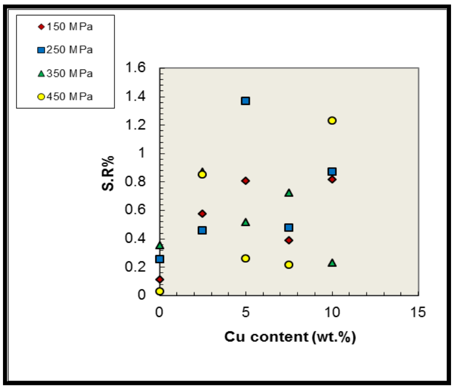

Figure 13. Effect of copper content on strain recovery properties obtained from compression test at RT.

Figure 14 illustrates the values of SME as a function to copper content in the prepared samples. This improvement in SME properties of Ni-Ti-Cu alloys are ascribed to NiTi phase and ($CuNi_2Ti$) intermetallic compounds. These phases that formed in Ni- Ti-Cu alloys strongly improvement SME properties of the alloys. Similar results are found in [14].

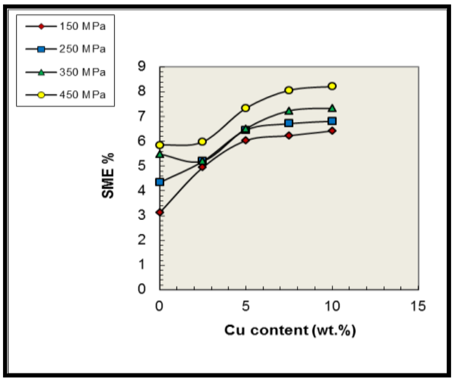

Figure 14. Effect of copper content on SME properties obtained from compression test at RT.

4. Conclusions

Porous NiTi-SMAs can be prepared by conventional sintering or (vacuum sintering at atmospheric pressure) method from elemental Ni and Ti powders. Conventional sintering has proven to be a viable method of producing porous NiTi SMA from powders. It has been used to produce homogenous NiTi with densities of up to 96% of theoretical density. The results can be summarized as follows:

1. The addition of Copper with (2.5-10) wt. % to NiTi prepared alloy resulted in decreasing the hardness relatively with compared to master samples without copper. There is distinguished increase in SME properties obtained from hardness test for the prepared NiTi alloy with the addition of copper.
2. The compressive strength (σcom), yield strength (σy) and young modulus of elasticity (E) have increased with increased copper addition to NiTi alloys.
3. The value of young modulus E of the porous NiTi in the present study is ranged from (2. 5 – 8. 8) GPa for samples compacted at 450 MPa which is near to that of the cortical bone (10-30) GPa and thus reduce the danger of stress shielding after implantation in human bodies.

References

[1] Iijima M, Oh H and Kawashima I 2002 Micro X - Ray Diffraction Study Of Super Elastic Nickel - Titanium Orthodontic Wires At Different Temperature And Stress *Bio material* **23** 1769 - 1774.
[2] Yun B, Jian L and Yili Y 2000 Stress - strain behavior of porous Ni - Ti shape memory inter metallic synthesized from powder sintering *inter metallic* **8** 643 - 646.
[3] Cismasiu C 2010 shape memory alloys, Janeza Trdine, Croatia.
[4] Gur A K, Orhan N and unsaldi E 2010 Production of porous Ni - Ti alloy and test of its biocompatibility under in - vivo conditions *j. Biomedical science and engineering* **3** 1161-1168.
[5] Goryszka T and Humbeck J V 2008 *NiTi Cu shape memory alloy produced by powder technology* Journal of alloys and compounds **456** 194 - 200.
[6] Aria pour A 1998 Effect of Nitrogen on Fe - Mn - based shape memory alloys *Ph. D .Thesis*, university of Toronto, Canada.
[7] Mohammed M A 2013 corrosion behavior of biocompatible coatings of porous NiTi shape memory alloy *Ph.D. Thesis*, production engineering and metallurgy department, university of technology.

IOP Conf. Series: Materials Science and Engineering **518** (2019) 032056 doi:10.1088/1757-899X/518/3/032056

[8] Dawood N M, Ali A K A , Atiyah A A 2015 Characterization of (NiTi) and (NiTiCu) Porous Shape Memory Alloys Prepared by Powder Metallurgy *Arabian journal for science and engineering* **40** 901-913.
[9] Deaujo C J, Dasilva N J and dasilva M M A comparative study of Ni - Ti and Ni - Ti - Cu shape memory alloy processed by plasma melting and injection molding *Material and design* **32** 4925-4930.
[10] Otsuka K and Rin X 2005 physical metallurgy of Ti-Ni based shape memory alloys *progress in materials science* **50** 511-678.
[11] Wong J Yand Bronzing J D 2007 *Biomaterial* Tylor Francis Group, LLC, New York.
[12] Sad vnezhaad S and Hosseini S 2009 Fabrication of porous NiTi - shape memory alloy objects by partially hydride titanium powder for biomedical applications Materials and design **30** 4483 - 4487.
[13] Yasze mski M, Trantolo D and Lew K and rowski 2004 Biomaterials in orthopedics Marcel Dekker, INC, New York BASEL.
[14] Fukuda T, Kakeshita T and Houjoh H 1999 Electronic structure and stability of intermetallic compounds in the Ti – Ni system *materials science and engineering* **A.27** 166–169.