Microstructure, mechanical and corrosion properties of the 50%Ni-47%Ti-3%Cu shape memory alloy

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Abstract: In this study, the mechanical, microstructure and corrosion properties of Nickel-Titanium-Copper shape recovery alloys were investigated. The alloy was prepared by the powder metallurgy method, where powders of 50% Titanium, 47% Nickel and 3% Copper were mixed and cold compacted at (600,700 and 800) MPa to form cylindrical samples of (11mm diameter × 16.5mm length) and (11mm diameter × 5 mm length). After compaction process the specimens had more green strength for handling. The samples were subsequently sintered at a temperature of (850,900 and 950) °C for a period of 5 hours in an electric vacuum tube furnace. Multiple tests were conducted on the alloys including porosity measurements, scanning electron microscopy (SEM), compression strength, shape memory effect and corrosion rate test. The results indicate improvement in compression strength and shape memory effect with low sintering temperature and high compacting pressure as well as reduction in the corrosion rate.

Keywords: shape recovery alloys, compression strength, porosity, shape memory effect, corrosion rate, SEM.

1. Introduction
The shape memory alloys or the recovery alloys are metallic materials that can return to their previously defined shape and size when heated [1]. These alloys represent a highly important branch of smart or intelligence materials. SMAs consist of two important phases known as martensite and austenite; Austenite represent the high temperature or "parent" phase. Where the crystal structure of austenite appears as cubic structure. Martensite, on the other hand, represents the low-temperature phase. Martensite crystal structure appeared as tetragonal or monoclinic [2]. The temperatures at which martensite starts and finishes forming and austenite starts and finishes forming can be represent by the variables ; As, Af, Mf, Ms [3].SMAs consist of two important mechanical effects that are linked with phase changing: super elasticity and shape memory effect. Shape memory effect (SME) indicates the property of materials that can be deformed in their martensitic phase and return to their original shape when heated to austenite phase. Superelasticity is obtained when the transformation of martensite is stressed at a constant
temperature. Upon unloading the transformation described in a hysteresis, Ni-Ti alloy act as the most common SMA [4].

The excellent physical and mechanical nature of Ni-Ti SMAs allow to be used in many commercial applications including mechanical engineering, aerospace and the biomedical field [5]. Biological properties of Ni-Ti Shape memory alloys can be improved upon by surface modification or by the addition of a third element such as Cu [6].

Ni-Ti-Cu alloys can be obtained by the replacement of Nickel atom by Cupper in the equi-atomic Ni-Ti alloy. Cupper's addition as the third element increase the temperature of martensitic phase transformation in comparison with a binary Ni-Ti alloy. Furthermore, the addition of copper results in an effective stabilization of the characteristic temperatures of the SMA, improves its corrosion resistance, reduces hysteresis of transformation and inhibits Ni4Ti3 precipitation. The composition capability of martinsite start temperature can also be lowered by adding Cu. Unfortunately, increasing the Cu component above 10% destroys the alloy formability [7]. This was the main cause for using a non-melting technology. Recently, concentrated attempts has been made to use nonconventional manufacturing techniques such as the powder metallurgy technique, melt spinning (MS) and twin roll casting for manufacturing the Ni-Ti-based alloys. The main advantage of the powder metallurgy technique is that it allows the avoidance of thermo-mechanical treatment process needed after conventional casting [8].

The aim of this work is to prepare 50%Ni-47%Ti-3%Cu shape memory alloys by powder metallurgy technique and to study their different properties.

2. Experimental work

The preparation of 50Ni-47Ti-3Cu shape memory alloy samples was performed using the (PM) technique. Powder of 50% titanium was combined with powder of nickel by a percent of 47% and copper by a percent of 3% with a high purity (>99%) and placed in a container. This powder was subsequently mixed using an electrical mixer with a rotational speed fixed at 70rpm and a mixing time of 2 hours according to reference [9].

The powder mixture was subsequently compacted using single action tool steel mold in a press machine at 800, 700 and 600 MPa to obtain cylindrical specimens of (11mm diameter × 5 mm length) and (16.5mm length × 11mm diameter). The compaction displacement rate of the press machine was 2 mm/min. The time of holding of the machine was set at 4 minutes to assure that the desired dimensions were achieved. After finishing the compaction process the samples had enough green strength to be handled.

Sintering of the green specimens was conducted in an electric vacuum tube furnace at 950, 900 and 850 °C for a period of 5 hours.

Porosity percentage was measured based on the theoretical and actual density of the specimens [10].

\[
\text{Specimen porosity } \% = (1 - \frac{\text{actual density}}{\text{theoretical density}}) \times 100\% \quad (1)
\]

\[
\text{Actual density} = \frac{\text{weight}}{\text{volume}} \quad (2)
\]
The theoretical density was calculated from the equation below and found to be equal to 6.7 g/cm³.

\[ \rho_s = \sum_{i=1}^{n} W_t \times \rho_i \]  
\( \rho_s = \) "theoretical density" in (g/cm³),  
Wt = weight of powder in percent (%),  
n = number of powders,  
\( \rho_1,2,3 = \) powder density in (g/cm³).

The shape memory effect test was measured by compressing the (11mm diameter × 16.5mm length) specimens by nearly 0.06% of the main length with a displacement rate of 1mm/min and then applying heat at 110°C for 5 min. At last, slow cooling was carried out in furnace and the shape recovery was calculated by applying the equation below:

\[ \text{Shape memory effect} = \left( \frac{L_2-L_1}{L_0-L_1} \right) \times 100\% \]  
where:

L₀: (normal length of the samples)  
L₁: (length after compacting the samples by 0.06% )  
L₂: (length obtained after heating the samples to 110°C for a time of 5 min).

The samples compression strength was measured using a press machine.

Corrosion test were conducted using a three electrodes electrochemical corrosion cell. The working electrode (W.E) is the first electrode and it's referenced to the sample that is being examined. The platinum rod is the second electrode and it was used to provide the circuit current. The third electrode was the saturated calomel electrode (SCE) also known as a reference electrode which measure the value of voltage between the working electrode and the electrolyte.

The rate of corrosion (mm/yr) was measured in Hank's salt solution using the equation below:

\[ \text{Corrosion rate} = C \frac{M}{n\rho} \]  
where:

M: weight of the atom  
C: equal to 0.00327 and it's constant of mm/year.  
\( \rho \): density of the sample measured in g/cm³.  
i : density of the current measured in μ A/cm².  
n: transferred electrons numbers.
Using a water bath, the cell polarization temperature was set to 37±1˚C, similar to the temperature of the human body.

Scanning electron microscopy (SEM) was used to obtain the microstructure of the samples.

3. Results and discussion:
   - Compacting pressure effect the density of the samples. When the compacting pressure value increase the density increased [12] while the porosity decreased with an increasing of the compacting pressure as shown in table 1 (a). As the compacting operation starts powder particles are rearranged. Then by applying pressure a local distortion occurs at the powder contact area. When the pressure increase it causes an increase in the proportional volume of every particle subjected to deformation. Moreover, increases in the pressure lead to the removal of additional pores, the formation of new contacts, and the homogenous distortion of the total compact [13]. When the sintering temperature applied to the green samples it lead to decrease the porosity and the density will increase due to the shrinkage of original pores. When increasing the temperature of sintering further the porosity increases while the density decreases as seen in table 1 (b). Clear differences in pores size, porosity and pores distribution can be note for samples which were obtained by increasing sintering temperatures. Applying higher temperature of sintering of up to 950˚C in this study caused differences in shape and distribution of pores, as well as a more intense diffusion of alloying elements, as a result of small pores combine into large pores and forming unequal shapes, which agree with reference [14]. This can be seen clearly in SEM test results below, and it can be observed that the addition of copper causes a small increase in porosity when comparing the porosity percentage with the porous Ni-Ti alloy as seen in Emad's thesis[15].

Table 1. Porosity measurement test result (a-green samples, b- samples after sintering).

| No. | Density (g/cm³) | Pressure (MPa) | Porosity (%) |
|-----|-----------------|----------------|--------------|
| 1   | 4.97            | 600            | 25.7         |
| 2   | 5.1             | 700            | 23.82        |
| 3   | 5.13            | 800            | 23.43        |

| Temperature (˚C) | Pressure (MPa) | Density (g/cm³) | Porosity (%) |
|------------------|----------------|-----------------|--------------|
| 850              | 600            | 5.782           | 11.26        |
| 900              | 600            | 5.726           | 12.06        |
| 950              | 600            | 5.672           | 13.74        |
| 850              | 700            | 5.9134          | 10.89        |
| 900              | 700            | 5.889           | 11.06        |
| 950              | 700            | 5.789           | 11.32        |
| 850              | 800            | 5.994           | 8.16         |
| 900              | 800            | 5.953           | 8.62         |
| 950              | 800            | 5.937           | 9.65         |
- Scanning electron microscopy tests show the microstructure of the samples. The appearance of the pores and their distribution depends on the sintering temperature. ‘Figure 1’ shows the samples that were compacted at 800MPa. It can be seen that the porosity increased with an increase in sintering temperature and that irregular shapes were formed.

**Figure 1.** SEM test result at compacting pressure of 800 MPa and (a-850, b-900 and c-950˚C) temperature of sintering.

- Shape memory of the alloys improved with an increase in compaction pressure and decreasing the sintering temperature as shown in table 2. The optimum shape recovery was 88% at 850˚C temperature of sintering and 800MPa compacting pressure. This is due to the formation of austenite and martensite phase...
which are in charge of the shape recovery of the alloys as shown in differentials scanning calorimeter test results seen in ‘Figure 2’.

Table2. shape memory effect test results.

| No. | Pressure (MPa) | Temperature (°C) | Effect of shape (%) |
|-----|----------------|------------------|---------------------|
| 1   | 600            | 850              | 79.2                |
| 2   | 600            | 900              | 67                  |
| 3   | 600            | 950              | 64                  |
| 4   | 700            | 850              | 80                  |
| 5   | 700            | 900              | 71.4                |
| 6   | 700            | 950              | 67                  |
| 7   | 800            | 850              | 88.5                |
| 8   | 800            | 900              | 83.3                |
| 9   | 800            | 950              | 82                  |

Figure 2. Test results of DSC for samples at compacting pressure of 800 MPa and 850°C sintering temperature.

- Compression strength test results seen in table 3 showed improvement in strength of compression with increasing pressure of compacting and reducing the sintering temperature. The reason for the improvement can be attributed to the decreasing of the defects, including pores and micro-cracks that behave as a region for stress concentration and may lead to the early defeat of the alloys.
Corrosion rate was measured, though no clear relation was found between the corrosion rate and the sintering temperature. Nevertheless, it can be noted that reduction in corrosion rate with an increase in the compacting pressure at all the sintering temperature values as seen in ‘Figure 3’ below. This might be due to the reduction in the pore size which causes a reduction in the surface area of the sample exposed to Hank salt solution. The addition of copper increases the corrosion resistance when compared to porous Ni-Ti alloy as seen in reference [14].

| Temperature (˚C) | Pressure (MPa) | Compression strength |
|------------------|----------------|---------------------|
| 850              | 600            | 538.25              |
| 900              | 600            | 452.37              |
| 950              | 600            | 372.29              |
| 850              | 700            | 603.49              |
| 900              | 700            | 499.69              |
| 950              | 700            | 383.75              |
| 850              | 800            | 708.22              |
| 900              | 800            | 603.97              |
| 950              | 800            | 555.78              |

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4. Conclusions

1. Reduction in porosity percentage was observed when the compacting pressure increased, as well as lower sintering temperatures.

2. The optimum shape recovery percent was 88% at 800MPa compacting pressure and 850°C sintering temperature at the lowest porosity percentage.

3. Compression strength of the alloys can be improved when increasing compacting pressure (due to low porosity percent).

4. Scanning electron microscope tests show the samples microstructure with the appearance of the pores and their distribution.

5. Corrosion rate decreases with high compacting pressure at different sintering temperature due to decrease in porosity.

Nomenclature

\[ \rho \] The density in g/cm³

\[ A_S \] Austenite start temperature

\[ A_F \] Austenite finish temperature

\[ C \] Constant of mm/year

\[ i \] Current density μ A/cm²

\[ M \] Atomic weight

\[ PM \] Powder metallurgy

\[ SMA \] Shape memory alloy

\[ XRD \] X-ray diffraction
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