Characterization of Ni-Ti-Ag Shape Memory Alloy

Khansaa D. Salman

Laith J. saud

Suad A. Shihab

1Electromechanical Engineering Department, University of Technology, Baghdad, Iraq
2Control and Systems Engineering Department, University of Technology, Baghdad, Iraq

corresponding author’s e-mail : soad.ahmdshehab@gmail.com@uotechnology.edu.iq

Abstract. In this paper, specimens of Ni-Ti shape memory alloy incorporating different percentages of Ag nanoparticles are constructed and three of its properties are studied which are density, porosity, and electrical conductivity. The specimens are constructed using powder technology. The construction process involved three main steps; mixing, compacting, and sintering. Before conducting the tests necessary to reveal the alloy properties mentioned above which represent the focus of this work, the constructed ternary Ni-Ti-Ag alloy specimens were first tested to check some of its characteristics and prove that the constructed alloy is a shape memory alloy. These tests included the Differential Scanning Calorimeter (DSC) test, the X-Ray Diffraction (XRD) test, the Scanning Electro-Microscopy (SEM) test, and the Shape Memory Effect (SME) test. The results of these tests reflected the homogeneous distribution of the Ag nanoparticles in the Ni-Ti matrix and indicated the formation of the austenite (Ti$_2$Ni) and martensitie (Ti 002) phases, and that the alloy has a very good SME (89.9% for the 10 wt.% percentage of Ag nanoparticles). Next to this step, porosity test and electrical resistance test were carried out. The results and related calculations for these tests showed that increasing the weight percentage of Ag nanoparticles decreases the porosity and increases the density as well as the electrical conductivity..

Keywords: Shape memory alloy, Ni-Ti matrix, Ag nanoparticles, microstructure, physical properties.

1. Introduction

Nickel–Titanium alloy has been considered for many decades as an important alloy in many industrial applications because of its shape memory effect (SME) [1]. A smart alloy is an important intelligent material (smart material) which can remember its original shape. The technical name of smart alloys is “Shape Memory Alloys (SMAs)”. A SMA is defined as an alloy that exhibits special properties of pseudo elasticity and shape memory effect (SME) [2]. The Nickel–Titanium (Ni-Ti) alloy was first developed in the1960s. This alloy was named Nitinol as an acronym for the composing
elements and the location of commencing research [3]. Many methods exist for preparing shape memory alloys such as: melting, heat treating, powder metallurgy, thermal spray, and thin film fabrication [4]. Powder metallurgy is considered as a new technique used to fabricate shape memory alloys. The work done so far using this technique is limited as it is new, but, there is an increasing interest in it due to its advantages [5]. Powder metallurgy is used to produce a near net shape memory alloy. There are two types of powder metallurgy to manufacture Ni-Ti SMAs. The first is raw powder sintering, while the second is alloying powder sintering. Raw powder sintering improves the homogeneity of Ni-Ti SMAs [6]. The Ni-Ti matrix got high attention in engineering applications. The addition of ternary or even quaternary elements to the binary Ni-Ti alloy is used to alter specific properties. Ag element is considered as an important element to obtain new ternary functional material for industry. Ag is to replace either Ti or Ni atoms in the Ni-Ti matrix [7]. The aim of this work is to prepare an Ni-Ti-(Ag nanoparticles) shape memory alloy with improved characteristics and properties.

2. Experimental procedures

2.1 Materials Used

In the present work, Ni and Ti powders (manufactured by Sky Spring Nano Materials - USA) are used with grain size of 40 μm for Ni and 50 μm for Ti. Ag nanoparticles with grain size of 25nm is used as an alloying element to produce the ternary Ni-Ti-Ag alloy. The weigh percentages of Ag nanoparticles as well as for Ni and Ti are summarized in Table 1 for the five specimens made in this work.

| Specimen | Ag (nm) | Ni(μm) | Ti (μm) |
|----------|---------|--------|---------|
| 1        | 0       | 50     | 50      |
| 2        | 3       | 50     | 47      |
| 3        | 5       | 50     | 45      |
| 4        | 7       | 50     | 43      |
| 5        | 10      | 50     | 40      |

2.2 Preparation of the specimens

The powder mixture consists specific portions of Ni, Ti and Ag nanoparticles with 1% volume fraction of acetone. Acetone plays the role useful as a lubricant [8]. The powders were mixed by an electrical mixer with a rotating speed of about 350 rpm for 2 hrs. After the mixing process, the powder mixture was cold pressed (compacted) by uniaxial direction pressure at 600 MPa to obtain a green compact in the form of a cylindrical specimen with 10mm height and 10mm diameter. Afterwards, the green compacts were sintered at 600°C for 6 hrs. With a heating rate of 1.666°C/min. in an electrical furnace provided with argon.

2.3 Microstructure and Phases Formation Tests

After preparation of the specimens, a microstructure test for all of the specimens was carried out using Scanning Electron Microscopy (SEM). This test aimed at determining the effect of compacting pressure and sintering temperature on the microstructure of the constructed shape
memory alloy. The second test carried out was the X-Ray Diffraction test. The purpose of this test was revealing phases’ formation before and after adding Ag nanoparticles. The Differential Scanning Calorimeter (DSC) test was done to obtain the starting and finishing temperatures for phases transformation. The weight of the specimens used ranges between 5 and 10 mg, and are put in aluminum crucibles. The specimens are heated between -50°C and + 200 °C with scan rate of 5°C/min. Cooling the specimens was done through pumping liquid nitrogen.

2.4 Shape Memory Effect Test
The shape memory effect for the specimens was determined by compressing the specimen by 0.06 % of its original length [9] with a compression rate of 1mm/min. This step was followed by heating the specimen in a furnace at 120 °C for 5 Mins and then cooling it in the air. The shape memory effect was calculated using the following equation [10].

\[
\text{SME\%} = \frac{(L_2 - L_1)}{(L_0 - L_1)} \times 10
\]

Where:
L_0: the original length of the specimen (mm).
L_1: the length of the specimen after compression (mm).
L_2: the length of the specimen after heating and cooling (mm).

2.5 Physical Properties Tests
The specimens’ physical properties tests done in this work included porosity test and four-point probe resistance test. The porosity was found using the following equation [11].

\[
\text{Porosity\%} = \left(1 - \frac{\text{actual density}}{\text{theoretical density}}\right) \times 100
\]

The actual density for each of the samples was obtained by dividing its weight by its volume, and the theoretical density was obtained using the equation 2:

\[
\rho_{th} = \sum_{i=1}^{n} \text{wt}_i \times \rho_1 + \text{wt}_2 \times \rho_2 + \text{wt}_3 \times \rho_3 + \cdots + \text{wt}_n \times \rho_n
\]

Where:
\(\rho_{th}\): Theoretical density of specimen (g/cm3).
\(\text{wt}.\): weight percentage (%).
\(\rho_1, 2, 3, \ldots, n\): density of elemental powders (g/cm3).

\[
\rho_e = \frac{R \times A}{L}
\]

\[
\sigma = \frac{1}{\rho_e}
\]

Where:
e: electrical resistivity.
R: Specimen electrical resistance.
A, L: Area and length parameters for the cylindrical specimen.
\( \sigma \): Specimen electrical conductivity.

3. Results and Discussion

3.1 Microstructural analysis

The microstructure of the constructed alloy specimens, that contain different percentages of Ag nanoparticles, was achieved using SEM test. The images obtained through this test are given in figure 1. The images depict the homogeneous distribution of Ag nanoparticles in the Ni-Ti matrix with little amount of pores. Due to their low melting temperature, the Ag nanoparticle melted and filled the interstitial voids between the particles of the Ni-Ti matrix. It could be observed that Ag particles surrounded those of the Ni-Ti matrix and that there is no inter diffusion between them. This agrees with ref. [12]. The shape and distribution of the created pores depend extremely on the sintering temperature, and the coalesce goodness of Ag nanoparticles with those of Ni-Ti depends on this temperature.

![Figure 1: Images obtained with SEM test for the tested specimens.](image_url)

3.2 X-Ray Diffraction (XRD) analysis

The results of the XRD analysis are shown in figure 2. The results indicated the existence of austenite (Ti2Ni) and martensite (Ti 002) phases using JCPDS – Card file as shown for Ti (96-900-8518), Ag(96-9008694), Ni (96-2100647), Ti 002(96-900-8518).
3.3 Differential Scanning Calorimeter (DSC) test results

The DSC test was done for all of the specimens to obtain the phases transformation temperatures using DSC device (TA-1A) made in Iran. The test was conducted at Polymer Engineering Department, (Amirkabir University of Technology/ Tehran, Iran). These temperatures represent the starting and the finishing temperatures of the austenite phase (As, Af) and the starting and the finishing temperatures of the martensite phase (Ms, Mf). The outcome of this test is given in figure 3. The results indicate the presence of peak temperatures for heating as well as cooling cases. This emphasis the transformation between austenite martensite phases. The results obtained here revealed that the constructed Ni-Ti-Ag alloy is a shape memory alloy.

3-4 Shape Memory Effect

The value of SME for the specimen with 10 wt.% Ag nanoparticles was calculated according to procedure of section 2.4 and it was found to be 89.9%.

3-5 Density and porosity results

Regarding density and porosity test, the results obtained indicated that the density increases and porosity decreases with the increase of Ag percentage. The added Ag particles fill the voids between the other particles, and during compression, the applied pressure arranges the powder particles and gets them close together, and causes more contact points between them. This leads to forming
localized plastic deformation and then the density increases and porosity decreases [13]. The effect of increasing Ag nanoparticles on density and porosity is depicted in the graphs of figures 4 and 5.

![Figure 4: Density verses Ag percentage.](image1)

![Figure 5: Porosity verses Ag percentage.](image2)

Also, after sintering necks are created between particles of the powders and afterward these necks coalesced together causing an increase in the density and a decrease in the porosity.

3-6 Electrical conductivity

The electrical conductivity for each specimen was found depending on its measured resistance using the procedure stated in section 2.4. The measurements results obtained with the values of the calculated conductivity are listed in table 2, with two charts in figures 6 and 7 being given for depicting the effect of adding the Ag part and for comparison purposes. The results indicate that the resistivity decreases, and so the conductivity increases, as the percentage of Ag in the alloy increases.

![Figure 6: Resistivity versus Ag percentage chart.](image3)

![Figure 7: Conductivity versus Ag percentage chart.](image4)

| Ag percentage | Electrical Resistivity \((\times 10^{-6} \Omega \text{Cm})\) | Electrical Conductivity \((\Omega \text{Cm})^{-1}\) |
|---------------|-------------------------------------------------|---------------------------------|
| 0 wt.%        | 80.7                                            | 12391                           |
| 3 wt.%        | 73                                              | 15872                           |
| 5 wt.%        | 50.7                                            | 19723                           |
| 7 wt.%        | 43.2                                            | 22355                           |
| 10 wt.%       | 40.5                                            | 24691                           |
Conclusions

This paper was about composing and analyzing a ternary alloy with Ni-Ti matrix as the base and Ag nanoparticles as the addend. The results of this work showed that the density and electrical conductivity increases with increasing the amount of Ag in the alloy, while the porosity decreases. The 10 wt.% percentage of Ag gave the best value for the shape memory effect which was about 89.95%. The results of scanning electron microscopy revealed the homogenous distribution of Ag nanoparticles in the Ni-Ti matrix with little amount of pores. While the X-ray diffraction results depicted the creation of Austenite phase ($\text{Ti}_2\text{Ni}$) and martensite phase (Ti 002). These phases are responsible for the shape memory effect.

The main contribution of this work relies in using nanoparticles of Ag powder as well as trying different Ti percentages with keeping fixed percentage of Ni. The outcomes of this study are hoped to be a contribution to the related literature and the world of SMA applications considering that the study used powder technology in construction and used nanoparticles of Ag, as well as taking into account samples with different percentages of Ag.

References

[1] K. Otsuka, X-Reu, "Physical metallurgy of Ti-Ni based shape memory alloy", Prog. Material Sci-50 Pf., pp. 511-678, 2005.

[2] Raul B. Perez Socz, Vicente Recart, Maria Lino, Oscar A. Ruano and Tose San Juan, "Advanced shape memory Alloys Processed by power Metallurgy", Advanced engineering materials, vol.2, no.1-2,2000, pp.49-53, 2000.

[3] N. M. Dawood, M. Juber, "Studied the Effect of Cooling Rate on The Phase Transformation Behavior and Hardness of Ni-Ti Shape Memory Alloy", No.(2)/Vol. 23,No.2, 2015.

[4] CN aresh, PSC Bose, CSP Rao," Shape Memory alloys: a state of art review", IOP Conf. Series: Materials Science and Engineering 012054, 149 (2016).

[5] R. M. GERMAN and K.S. CHURN, " Sintering Atmosphere Effects on the Ductility of W-Ni-Fe Heavy Metals", Metallurgical Transactions A, Vol. 15A, 1984-747.

[6] M. Bram, A. Ahmed – Khanlou, A. Heckmann, B. Fuchs, "Powder metallurgical Fabrication processes for Ni-Ti shape memory alloy parts", Article in materials science and Engineering A 337 (1-2): 254-263, 2002.

[7] Giberto H. T. Alvares da Silva, Jorge Otubo," Desiging Ni-Ti Ag Shape Memory Alloy by Vacuum Arc Rcmelting: First practical Insights on Melting and Casting", Shape Memory. Super elasticity, ASM International 2018.

[8] Bozzone S., "Solid Oral Dosage Forms Powder Blending", Ikey Meeting, 2001.
[9] Marek Novoltny, "Shape memory alloys (SMAs)" , 2008

[10] Jianfeng Wan and Xing Huang ,"Effect of Nitrogen Addition on Shape Memory Characteristics of Fe-Mn-Si-Cr alloy", Material Transaction, Vol.43, pp. 920-925, 2002.

[11] J.T. Al- Haidary and Shadi Al-Khatib, "Manufacturing and characterization of dental shape memory alloy", Materials Science

[12] M. Bitzer, M.Bram, H. P. Buchxemer and D. Stover "Phase Transformation Behavior of Hot Isostatically Pressed NiTi", Journal of Materials and Engineering A,Vol. 419, pp. 45-49. 2006.

[13] Bolton W., 1988, Engineering Materials Technology, Butter worth Heinemann Oxford