The effect of different at.% Ag elements on the wear rate of nitinol alloys fabricated using the casting method

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Abstract. Shape memory alloys are considered smart alloys due to their properties, such as biocompatibility, superelasticity (SE) and shape memory effect (SME). These alloys are used in many applications (actuators, MEMS, biomedical and aerospace). In this work, the effect of adding the silver element to the NiTi alloy with different atomic percentages (zero, one, two and three at.% Ag) on mechanical properties, such as macrohardness and wear, was studied. The samples of this work were prepared by the casting method using a VAR furnace to obtain homogeneous shape memory alloys. The purity of the elements was Ni 99.2 %, Ti 99.7 % and Ag 99.99 %. In this work, many examinations were carried out to define the characteristics of the manufactured shape memory alloys, such as FESEM and OM, for microstructural analysis. Meanwhile, the mechanical properties were defined using macrohardness and wear tests. The results of the mechanical tests showed a slight impact in the percentage of the wear resistance and macrohardness at the point of increasing the silver element ratio to the binary alloy (NiTi). The photomicrographs of the OM and FESEM examinations showed that the Ag element is homogeneously distributed in the NiTi matrix. In addition, the FESEM examination showed the emergence of the martensite phase, austenite phase and some impurities. The results of the DSC test showed the degrees of the phase transformation for each alloy, and the SME recovery rate of 89.99% was achieved. Furthermore, the surface topography was analysed using an optical microscope for all the tested samples. The obtained results emphasised that the movement between the disc and the pins leads to a rise in the friction temperature and the formation of the layer of oxidation. These oxidation layers will be ploughed and uprooted to create many grooves at the surface of the samples. Hence, these grooves are similar for all samples and increased with increasing loads.

Keywords: Shape Memory Alloys, NiTiAg, Casting, VAR, Macrohardness, Wear.

1. Introduction

Smart alloys are considered a class of active materials (smart materials), which are used in applications requiring high precision. In particular, aerospace and medicine applications use the smart alloys widely, as these alloys possess the unique property of recovering their original shape after large deformation, which is known as the shape memory effect (SME) and pseudo elasticity (PE). Both of
these properties constitute a phase transformation from the low temperature and high pressure (martensite phase) to the high temperature and low pressure (austenite phase) [1]. When a certain stress is applied to all metal materials, this stress is removed. Most of the metals return to their original shape, but when the applied stress exceeds the force of carrying the material, a plastic deformation occurs, which leads to a permanent deformation. Most metallic materials have a recovery rate that does not exceed 0.1%, whereas shape memory alloys (SMAs) possess a seven%–eight% recovery rate [2].

The main problem is the manufacturing process of the SMAs as well as the type of alloy adopted, such as NiTi-based and the added element to this alloy of Cu, Ag, Pd or V. Each element has a certain effect on the mechanical and microstructure properties.

The main types of SMAs that have been used industrially are Ni-Ti-based, Fe-based and Cu-based. Among these three alloys, the NiTi-based alloys are the most widely used due to their excellent properties [3]. Nickel titanium binary alloys (nitinol) are probably the best-known materials in this class. However, these alloys are not always the most suitable for every purpose. One solution for improving this alloy is to add an element through the production process [4]. Each element has a specific impact on the properties of alloys; for example, adding Fe, V and Co causes the phase transformation temperatures to decrease, while elements, such as Hf, Zr, Au, Pd and Pt, have the opposite effect. Likewise, hysteresis decreases when adding the element Cu, whereas it increases when adding Nb and Fe [5]. Ag is one of the best electrically conductive materials that possesses high electrical conductivity and antibacterial effect biocompatibility and satisfactory stability. Therefore, it is predicted that the composite made with the NiTi and Ag component will have an excellent shape-memory effect, superelasticity, high electrical conductivity and good corrosion resistance [6–10].

The manufacturing process of SMAs is critical and has a significant impact on homogeneity, machinability, ductility, microstructure, biocompatibility and transformation temperatures. All of these properties are important in material applications. In general, there are two main methods of the manufacturing, as follows: powder metallurgy and casting methods, which are followed by several processes, such as cold and hot working, heat-treatments and surface treatments. Heat treatments have an important role in shaping the SMA [11]. The aim of this research is to manufacture an alloy (NiTiAg) using a VAR furnace with the addition of the silver element in atomic percentages (zero, one, two and three at.% Ag) to study its impact on macrohardness and wear resistance, as well as to examine the microstructure of the prepared alloy.

The rest of this paper consists of the following: Section 2 describes related works from previous studies; Section 3 focuses on experimental work, the manufacturing process, annealing, ingot cutting process and preparing samples for tests and examinations; Section 4 describes the results and discussion for all examinations and tests; and finally, Section 5 consists of the conclusions of this work.

2. Related Work

In this section, previous studies related to the NITI alloys-based casting techniques will be presented. Additionally, other relevant works concentrating on the impact of adding the silver element to the NITI alloys under different conditions and scenarios will be discussed.

The materials that were used for the casting method have important characteristics, such as high purity due to the presence of non-metallic elements. However, non-pure elements are greatly affected by the produced alloys. Non homogeneity leads to an irregular distribution and a change the properties of the products [11]. Vacuum induction melting (VIM) requires a graphite crucible. This method will contaminate the alloys with the carbon element. The carbon is considered a non-pure element; therefore, it will produce an alloy that does not have high purity [12]. On the other hand, the mechanism relies on the electron beam melting process, which produces high-purity alloys. The vacuum pressure rises during the melting process and leads to evaporation of some elements [13, 14]. Regarding the vacuum arc remelting (VAR), this method does not contain a graphite crucible and indicates a low percentage of the carbon element. Therefore, the alloy that is produced via this method
is considered high purity, high quality and homogeneous [15]. Adding the silver element to alloys that are NiTi-based is presented in [16]. This method was prepared by using the electron beam melting (EBM) technique. The results of this study showed that it is difficult to add silver to the binary alloy due to the high vapor pressure of silver. Another addition of the silver element to the binary NiTi alloy using arc melting has been proposed in [17]. The purpose of manufacturing this alloy was to use this alloy in the medical and orthodontic fields. The results showed that the silver solubility and silver recovery rate are low due to silver element evaporation. However, the wear resistance improved with the increasing silver percentage, and the range of phase transformation was also achieved. Manufacturing a thin film NiTiAg-based on the sputtering technique is presented in [18,19]. In this method, the thin films were manufactured from NiTiAg using the sputtering technique to increase the silver content (the silver component that was added is almost pure). The results showed that the high percentage of silver does not affect the phase transformations of alloy (NiTi). An Arc melting technique was used to introduce pure silver deposits into the matrix TiNi, which is proposed in [6]. The results of this technique showed that the melting process is quite difficult due to the evaporation of the silver element, and the silver element is distributed randomly inside the matrix TiNi. These alloys showed a good corrosion resistance, higher tensile strength and greater elongation than binary alloys. Adding the silver element to the binary alloys NiTi using the VAR method is presented in [20]. The results of this approach showed that the prepared alloys are homogeneous and stable. However, the silver element was lost with repeated melting due to the high steam pressure.

3. Experimental Work
3.1. Materials and Methods
The ternary TiNiAg ingot with an actual composition of Ni<sub>55</sub>Ti<sub>45</sub>Ag<sub>0</sub>, Ni<sub>55</sub>Ti<sub>44</sub>Ag<sub>1</sub>, Ni<sub>55</sub>Ti<sub>43</sub>Ag<sub>2</sub> and Ni<sub>55</sub>Ti<sub>42</sub>Ag<sub>3</sub> was prepared from 99.2% purity Ni, 99.7% purity Ti and 99.9% purity Ag through VAR at 1350 °C. There are two types of VAR technologies that are used to produce SMAs. The first method uses a non-consumable electrode, while the second method uses a consumable electrode. In this work, the VAR technique without a consumable electrode is preferred for many types of SMAs. Figure 1 illustrates the VAR furnace. At the beginning, the elements Ni, Ti and Ag were fixed on a copper mould and heated via radiation with the argon. After completing the melting process, the ingot was cooled with ice water. This process was repeated four times to obtain the best homogeneity. This process was followed by the annealing process at 660 °C for 24 hours. The process was followed by the cutting stage using a cutting machine to prepare the samples for the microstructural examination and mechanical tests.

3.2. Microstructural Examinations
The samples were examined by the field emission scanning electron microscopy (FESEM) before and after adding the silver element with different atomic proportions to the alloy (NiTi). Before starting the test, the samples were grinded using emery papers with particle sizes of 320, 500 and 1000 µm. After that, the samples were polished with a polishing cloth (chloride paste) and etched with etching solution.

Figure 1. Vacuum arc melting furnace.
(95 mL H2O + 3.5 mL HNO3 + 1.5 mL HF) for ten minutes [17]. After completing the preparation of the samples, the samples were coated with palladium and gold for two minutes. Finally, the examination was tested via using FESEM (cam scan Mv 2300), which is shown in Figure 2.

![FESEM examination device.](image)

Figure 2. FESEM examination device.

3.3. Phase Transformation
This first test was performed using the differential scanning calorimetry (DSC) device for the samples with different atomic percentages of the Ag element (zero, one, two and three a.t% Ag) to determine the degrees of phase transformation (As, Af, Ms and Mf). The second test was the SME. An examination was performed for the sample containing (zero, one, two and three a.t% of the silver element addition.

3.4. Mechanical Tests
3.4.1. Macrohardness Test
Vickers hardness apparatus was carried out for all the samples of SMAs before and after adding the Ag element, according to the ASTM E384 standards. Before the Vickers hardness testing, the samples (ten mm in diameter and seven mm in height) were prepared using the grinding process and emery papers (320, 500 and 1000 µm) and followed by the polishing process to obtain smooth surfaces. This test was performed via applying a load of three Kg for 15 sec. At least four readings were obtained, and then the average diameter of the indenter for all the samples was calculated. This test was performed using the Vickers macrohardness apparatus model (Universal Hardness Dia-Testor 722), as shown in Figure 3a. Figure 3b shows the macrohardness test samples.

![Hardness Dia-Testor, Hardness test samples.](image)

Figure 3. a: Hardness Dia-Testor, b: Hardness test samples.

3.4.2 Wear Test
In this work, the wear test was performed using the pin-on-disc technique for all SMAs before and after adding the Ag element, according to the ASTM-G99 standards. The samples of the wear test were two cm in height and one cm in diameter. Figure 4 shows the wear samples. Before the testing stage, the samples were prepared by grinding at 320, 500 and 1000 grit size and polishing using a suitable polishing cloth with chloride paste. After polishing, the samples were tested by the wear machine, changing the loads at five, ten, 15, 20 and 25 N at a constant time of 15 min and sliding speed of six cm / min. The wear rate was measured using the weighing method, and the weight loss for all shape memory samples was calculated using the sensitive electronic balance (the accuracy of the
balance is approximately 0.01 mg). The wear rate of the proposed method was calculated using the following formula [21]:

\[ \text{wear rate} = \frac{\Delta w}{S.D} \left( \frac{g}{cm} \right) \quad (1) \]

\[ \Delta w = w_1 - w_2 \quad (2) \]

Where:
\( \Delta w \) : change in the weight of the sample (g).
\( w_1, w_2 \) : weight of sample before and after the wear test (g).

\[ S.D = 2\pi r n t \quad (3) \]

S.D: sliding distance (cm).
\( r \): radius of the rotating disc (cm).
\( n \): number of rotations per min (rpm).
\( t \): sliding time (min).

Figure 4. Wear test samples.

4. Results and Discussion

4.1. FESEM Results

Figure 5 shows the micrographs of the FESEM examination and the photomicrographs of samples before and after adding the silver element (zero, one, two and three at.%) to the alloy NiTi. These photomicrographs show the appearance of the austenite phase (Ti2Ni) and martensite phase (Ti002) with some impurities because of the processes (casting, cutting and polishing).

Figure 5. Photomicrographs of the samples for different at.% Ag.
4.2. OM Results

Figure 6 shows the results of SMAs before and after heat treatment by annealing at 660 °C for 24 hr at one at.% Ag, two at.% Ag and three at.% Ag. These results revealed that the Ag element is distributed homogenously in the NiTi-based alloy, and all the grains are equiaxed. This is attributed to a uniform mixing of the components of manufactured shape memory alloys with different atomic percentages of the Ag element. As a result of the melting process, which is followed by annealing, the grains are smaller in size (refined grain size) as the amount of the Ag element increases.

![Photomicrographs of OM microstructures samples.](image)

A1: zero at.% Ag  A2: one at.% Ag  A3: two at.% Ag  A4: three at.% Ag

B1: zero at.% Ag  B2: one at.% Ag  B3: two at.% Ag  B4: three at.% Ag

Figure 6. Photomicrographs of OM microstructures samples.
A: Before annealing heat treatment with at.% Ag; B: After annealing heat treatment with at.% Ag.

4.3. DSC Results

The results of the differential scanning calorimeter examination showed that the degrees of thermal transformation (A_s, A_f, M_s, and M_f) explain the start and finish of both the austenite phase (B2) and the martensite phase (B19). The phase transformations were slightly affected by the increase in the silver element addition.

The results of the DSC examinations for (zero, one, two and three a.t%) is shown in Figure 7. The creation of two peaks during the cooling and heating process indicates the transition from the austenite phase to the martensite phase [22] with a shape memory effect of approximately 89.35%–89.99%.
4.4. Macrohardness Results
The macrohardness test was carried out for all samples before and after adding the Ag element at different atomic percentages. For each sample, at least four readings were taken, and then the average value was calculated. The obtained results of this test showed a slight increase in hardness with an increase of the atomic percentage of the Ag element. The slight increase in the macrohardness brought the grains close together and slightly refined the grains due to the heat treatment.

Figure 8 shows the effect of increasing the atomic percentage of the Ag element on Vickers macrohardness.

![Figure 8. Macrohardness vs at.% Ag.](image)

4.5. Wear Results
Figure 9 shows the wear behaviour of the samples before and after adding the Ag element when changing the applied load at a constant time of 20 minutes. The wear rate of the samples depends
strongly on the conditions of the casting process. During the casting process, many imperfections were created, which affected the properties of the manufactured ingots. An important imperfection is voids. These voids will fill the additive element and improve the wear resistance. Increasing the applied load leads to an increase in the wear rates for all specimens due to raising the temperature between the samples and rotating disc and then forming oxidation layers between them. Moreover, increasing the applied load will increase the plastic deformation of the samples and decrease the wear rate. The difference between the melting temperatures of Ni, Ti and Ag will encourage the formation of thermal stresses, increase the dislocations density and create a loop of dislocation to obstacle the fragment of the worn surface and decrease the wear rate. This is in agreement with [23]. There is a slight impact of adding Ag on the wear behaviour of the NiTi-based SMA because the NiTi alloy is harder than the Ag element. The dry sliding wear behaviour depends on the macrohardness of the sample. The added element will obstacle or pin the movement of the dislocations and increase the wear resistance (decreasing wear rate).

![Figure 9](image_url)  
**Figure 9.** Wear rate vs at.% Ag.

**Surface Topography**

The surface topography for all the samples before and after adding the Ag element in different atomic percentages was carried out. Surface topography is defined using an optical microscope for the samples, which are tested using the wear technique. Surface topography is a result of the changes to the loads at a constant sliding time and sliding speed. The relative motion between the rubbing disc (made of hardened steel at 60 HRC) and the pins (samples at different atomic percentages of the Ag element) causes a rise in the friction temperature and creates oxidation layers between the disc and pins. Afterwards, these oxidation layers will be ploughed and uprooted to create many grooves on the surface of the samples. These grooves are similar for the samples of different atomic percentages of the Ag element. Hence, increasing the applied loads causes more fragments of sample surfaces and creates deeper worn grooves. Regarding the increasing applied loads, it ploughs an additional oxidation layer at the surfaces of the samples, as shown in Figure 10.
5. Conclusion
SMAs (NiTiAg) have been successfully fabricated by the casting process using a VAR furnace with different atomic percentages of the silver element as zero, one, two and three at.%. This type of melting shows the production of the homogeneous alloy, and the silver element is uniformly distributed. The proposed method is evidenced by the examinations OM and FESEM. The results of FESEM showed the emergence of the martensite phase (Ti002) and austenite phase (Ti2Ni), in addition to some impurities as a result of the manufacturing process and the subsequent processes. The results showed that the macrohardness value increased slightly when the percentage of the silver element in the base alloy (NiTi) increased. The wear results showed a slight increase in the wear resistance (decreasing wear rate) with increasing silver due to the high hardness of the NiTi alloy (high hardness of Ti). The maximum value of the shape memory effect of 89.99 % at three at.% Ag was achieved. Meanwhile, the starting and finishing phases of austenite and martensite were defined by the DSC test. The proposed method emphasised that the width of the hysteresis loop was slightly affected by the increasing addition of the silver element. Moreover, the surface topography was analysed using an optical microscope for all tested specimens using the wear technique. The obtained results showed that increasing the applied loads directly produces more fragments of the sample surfaces and creates deeper eroded grooves.

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