Investigation of Wear Behaviour for NiTi Alloys with Yttrium and Tantalum Additions

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Abstract. A study of the effects of added Yttrium and Tantalum on the wear behaviours of NiTi shape memory alloys was completed to examine the effects of compacting pressure levels between 400 and 650 MPa and to investigate wear parameters such as load, sliding distance, and time to determine the wear rate for the prepared alloys. Several alloys were prepared using a powder metallurgical technique; the powder mixture had a basic chemical composition of 55% Nickel and 45% Titanium, and alloying elements of Yttrium and Tantalum were then added at weight percentages 1, 2, and 3 wt% of each element (at the expense of nickel) before the powders were mixed then compacted under a range of compacting pressures (400, 500, 600, and 650 MPa) to form cylindrical samples. Sintering was completed in two steps. The first step was done at a temperature of 500 °C for two hours, while the second step was done at 850 °C for six hours, both under vacuum conditions (6.7 E -02 Pa). The generated specimens were then left to cool. The wear behavior was then studied using pin-on-disk tests at variable loads and times (2, 5, 10, and 15 N and 5, 10, 15, and 20 min, respectively). XRD testing, apparent density and porosity, hardness, and surface roughness tests were also completed in this study. From the results, it is clear that the wear volume loss decreases with the addition of Tantalum by 0.52% with 3% Tantalum addition at 650 MPa compacting stress for a 15 N load; it also decreases by 0.48% with 2% Yttrium addition at 650 MPa for a 10 N load. The wear volume loss further decreases as the compacting stresses increase. In addition, the wear rate increased as the load and time increased for all tested specimens.

Keywords. Nickel Titanium (NiTi); Super-elasticity; volume wear loss.

1. Introduction
NiTi shape memory alloy properties, including strength, compatibility, and ductility, in conjunction with its unique shape memory effects and super-elasticity have made shape memory alloys particularly useful in medical applications [1]. Medical applications of NiTi include orthopaedics and orthodontics, and they are also used to make components of medical devices and instruments [2]. The excellent wear resistance of NiTi alloys is believed to be mainly ascribable to their pseudoelasticity, which results from a stress-induced martensitic phase transformation and the rearrangement of martensitic variants under
stress [3]. Hardness (H) and Young's modulus (E) are the key factors affecting wear behaviour [4]. Excessive surface wear and corrosion of NiTi increases health disadvantages because bodily fluids induce toxic and allergic reactions and Ni ions may be released into the blood stream [5]. Thus, it is very important to improve the surface properties of the NiTi shape memory alloys used in biomedical implants. A variety of surface treatment techniques, such as chemical passivation, anodic oxidation, electro polishing, thermal oxidation, and laser surface melting, have been used to enhance the biocompatibility of NiTi [6]. In particular, such efforts have been directed at improving the wear behaviours of biomedical devices. Liu et al (2007) modified the wear properties of NiTi by means of nitrogen plasma immersion ion implantation, while Yan and Liu (2015) studied the wear behaviours of austenitic NiTi shape memory alloys and Abedini et al (2009) studied the wear behaviours of both austenitic and martensitic states. Neupane and Farhat (2014) also studied the wear mechanisms of nitinol under reciprocating sliding contact.

The aim of the current research is to study powder metallurgy process variables such as compacting stress on wear behaviour as well as to study the effects of adding alloying elements such as Ta and Y on the wear behaviours of prepared NiTi SMAs. This also involves the study of wear parameters such as load, sliding distance and time on the wear rate for the prepared alloys.

2. Experimental details

The materials used in this study were 55%Ni-45%Ti mixed with tantalum and yttrium in percentages of 1, 2, and 3 wt% at the expense of nickel, as depicted in table 1. The samples were mixed for three hours then compacted under various compacting pressures using an electric hydraulic press to conduct uniaxial pressing into cylindrical shapes with average diameters 15.2 mm and heights of 6 mm prior to sintering inside a quartz tube vacuum furnace according to the heating cycle shown in figure (1).

![Figure 1. Sintering process cycle.](image-url)
The sintering process was accomplished in two steps. The first one was at a temperature of 500 °C for two hours and the second at 850 °C for six hours, both under vacuum conditions (6.7 E -02 Pa); the specimens were then cooled in the furnace. This two-step process was done to eliminate impurities in the green samples. After sintering, all surfaces were ground with 180, 220, 320, 400, 600, 800, 1,000, 1,200, and 2,000 grit silicon carbide papers before being polished with alumina solution and 3 μm diamond paste to obtain a mirror finish. Samples were then washed with distilled water. A manual dryer was used to dry the samples, which were then kept with silica gel in well-sealed containers to keep them completely dry. Before the wear tests, the samples were further dried using the same dryer.

The dry sliding wear was studied using a pin on disk method, as shown in figure (2), at 200 rpm and a constant radius of 5 mm with varying sliding distances and loads of 2 N, 5 N, 10 N, and 15 N. The ball of the pin, made from carbide steel, was 6 mm in radius. Each sample was weighed before testing using a 0.0001-accuracy sensitive balance. After certain periods of time (5, 10, 15, and 20 min), the sample test was weighed, and the dry sliding wear rate determined according to equation (1). The instrument also measured the coefficient of friction between the sample and pin. This test method complies with ASTM G 99 [7].

Wear volume loss (cm³) = \( \frac{\text{weight loss (g)}}{\rho \text{ theoretical density}} \) ...... (1)

where

Weight loss (g) = quantity loss after 5, 10, 15, or 20 min and

\( \rho \) (g/cm³) = theoretical density of the element for the specimen (g/cm³).

| Table 1. Alloy codes and compositions for this study. |
|---------------------------------|---------------------------------|
| Alloys code | Chemical compositions (Wt. %) |
|----------|-------------------------------|
| 1        | A 55 Ni - 45Ti                |
| 2        | B1 54 Ni – 45Ti – 1 Y        |
| 3        | B2 53 Ni – 45Ti – 2 Y        |
| 4        | B3 52 Ni – 45Ti – 3 Y        |
| 5        | C1 54 Ni – 45Ti – 1 Ta       |
| 6        | C2 53 Ni – 45Ti – 2 Ta       |
| 7        | C3 52 Ni – 45Ti – 3 Ta       |
The porosity and density of the sintered samples were determined per ASTM B-328 using the following procedure:

1. Drying the samples and then using the sensitive balance to measure the mass, A
2. Using a suitable evacuating pump manufactured for the purpose at room temperature to immerse the specimen in oil with a density of 0.8 g/cm³ for 30 min under the effect of reduced pressure.
3. Measuring the mass of the fully impregnated samples in air, B.
4. Measuring the mass of the fully impregnated samples in water, F.
5. Calculating the porosity and the density using the following equations [8]:

\[
P = \left( \frac{B - A}{(B - F)D'} \times 100 \right) D_w \quad \text{.......................... (2)}
\]

\[
D = \left( \frac{A}{B - F} \right) D_w \quad \text{.......................... (3)}
\]

where

\[D' = \text{the density of the oil, and}\]

\[D_w = \text{the density of water.}\]

3. Result and discussion

Several physical tests such as X-ray diffraction, porosity, and apparent density, as well as mechanical tests such as microhardness, surface roughness, and wear testing were performed. The wear test was the most important test for this study, and various wear parameters were used such as load, sliding
distance, and powder metallurgy process variables such as compacting pressure. This was done to study their effects on wear rates.

3.1. X-Ray Diffraction test

The XRD test allows identification of the phases of a crystalline structure. The test was done for the elemental powder base samples, base alloys after sintering, and B3 and C3 alloys after the sintering process. Figure (3) depicts the XRD pattern for NiTi powder; this pattern shows only Ni and Ti phases, as no phase transformation occurs during the mixing or compacting process due to the lack of sufficient heat. These patterns match the standard patterns for Ni and Ti powders. Figure (4) illustrates the XRD patterns for the base alloy after sintering in accordance with the heating cycle mentioned in the previous chapter. In this pattern, all Ni and Ti have been transformed to the monoclinic NiTi phase and hexagonal Ni3Ti phase. Figures (5) and (6) depict the XRD patterns for B3 and C3 alloys after the sintering process, showing the same pattern as for the base alloy after sintering process; this means that the additives have not led to the occurrence of additional compounds, as desired.

![Figure 3. XRD pattern for NiTi powder](image-url)
Figure 4. XRD pattern for base alloys after sintering process.

Figure 5. XRD pattern for B3 alloys.

Figure 6. XRD pattern for C3 alloys.
3.2. Porosity and apparent density after sintering

The density and porosity of the sintered samples are shown below in figures (7) to (10). The density increases as the compacting stress increases, while the porosity decreases as the compacting stress increases.

**Figure 7.** Density of sintered sample vs compacting stress.

**Figure 8.** Density of sintered sample vs compacting stress.

**Figure 9.** Porosity of sintered sample vs. compacting stress.
3.3. Hardness test results

The hardness of the samples was measured by using a Vickers's Microhardness tester. The applied weight was 200 g and the incubation time was 10 secs under applied weight as seen in figures (11) and (12), the hardness value of all sintered samples increased as the compacting stress increased. Figure (11) shows that the hardness values for NiTi alloys with yttrium additives are higher than those for NiTi alloy in this work, Figure (12) also shows that the sample with the highest percentage of tantalum additives and compacting stress showed the highest hardness values.
3.4. Surface roughness test results

A roughness tester model TR200 with cut off equal to 1.2 µm was used to quickly and accurately determine the surface texture or surface roughness of all samples. A roughness tester shows the mean roughness value (Ra) in micrometres or microns (µm). Surface roughness is a very important property affecting the behaviours of mating contact surfaces. Rougher surfaces tend to wear more rapidly and have higher coefficients of friction compared to smooth ones [9]. Figure (13) shows the effect of yttrium additives on surface roughness values, suggesting that incrementing yttrium percentages reduces surface roughness values; the same effect applies to tantalum additives, as seen in figure (14), and it is clear from both figures that the surface roughness is reduced as the compacting stress increases. This is natural because the pores are reduced in such circumstances.

![Figure 13. Surface roughness vs compacting stress.](image)

3.5. Effect of sliding distance

Samples with 15.2 mm diameters were subjected to wear tests under various loads (2, 5, 10, and 15 N) and for different times (5, 10, 15, and 20 min) at room temperature. The results are presented and shown in figures (15) to (29).
Figure 15. Wear volume loss vs time for A base alloy of 400 MPa.

Figure 16. Wear volume loss vs time for A base alloy of 650 MPa.

Figure 17. Wear volume loss vs time for B1 alloy of 400 MPa.
Figure 18. Wear volume loss vs time for B1 alloy of 650 MPa.

Figure 19. Wear volume loss vs. time for B1 alloys at varying compacting stress at 15 N load.

Figure 20. Wear volume loss vs time for B2 alloy of 400 MPa.
Figure 21. Wear volume loss vs time for B2 alloy of 650 MPa.

Figure 22. Wear volume loss vs time for B3 alloy of 400 MPa.

Figure 23. Wear volume loss vs time for B3 alloy of 650 MPa.
Figure 24. Wear volume loss vs time for C1 alloy of 400 MPa.

Figure 25. Wear volume loss vs time for C1 alloy of 650 MPa.

Figure 26. Wear volume loss vs time for C2 alloy of 400 MPa.
Figure 27. Wear volume loss vs time for C2 alloy of 650 MPa.

Figure 28. Wear volume loss vs time for C3 alloy of 400 MPa.

Figure 29. Wear volume loss vs time for C3 alloy of 650 MPa.
Figures (15) to (28) show that the wear volume loss of all tested samples under a 15 N load was higher than under 10 N, 5 N, and 2 N loads, while being similarly higher for 10 N than for 5 N and so on. This is attributed to increase in friction at the surface as the load on the material increases [10].

In addition, the wear rate increased as the time increased for all tested specimens, almost certainly because more time under friction tends to remove more material from a surface, increasing the wear rate attributed to increased plastic deformation of the material's surface as particles of the material are pulled out [11]. Figure (19) illustrates the wear testing results for the B1 alloys, which lost a lot of weight at 15 N loads only.

It is clear that the base alloys undergo more wear volume loss with increasing time and loads than the alloys with additives; this can be attributed to the effect of these additives on the hardness and surface roughness of the alloys. Thus, whenever hardness increases, the surface roughness decreases, and the wear volume loss also decreases. As seen in previous figures, the wear volume losses of base alloys at 400, 500, 600, and 650 MPa were higher than the wear volume loss of C1, C2, and C3 under 400, 500, 600, 650 MPa; the wear volume losses for B1 at 400, 500, 600, and 650 MPa were higher than for base alloys only, while B2, B3 at the same compacting stresses had lower wear volume losses than the base alloys. Interpreting these results, the B2 and C3 alloys at 650 MPa and 15 N load showed the best results, with wear volume losses decreasing at a rate of 0.489 and 0.52, respectively; the B3 alloy at 650 MPa and 15 N decreased at a rate of 0.23.

3.6. Effect of compacting pressure

The figures below illustrate that the wear volume loss decreased as the compacting stress increased. This is clearly because the number of pores decreases; the surface friction also decreases as the hardness increases and the surface roughness decreases.

![Figure 30. Wear volume loss vs time for B2 alloys at 15 N Load.](image)
**Figure 31.** Wear volume loss vs time for B3 alloys at 15 N Load.

**Figure 32.** Wear volume loss vs time for C2 alloys at 15 N Load.

**Figure 33.** Wear volume loss vs time for C3 alloys at 10 N Load.
3.7. Effects of adding alloying elements

Figure (22) shows the effects of adding Y on wear volume loss; it can be seen that adding 2% Y decreased the wear volume loss, while adding 1 and 3% increased the wear rate. No more than 3% was added because this would create different compounds with NiTi. Figure (23) shows the effects of adding Ta on wear volume loss; it is clear that increasing this addition from 1% to 3% Ta decreased the wear volume loss. The reason for this reduction in wear volume loss may by simply that increased Ta addition reduces the porosity and surface roughness and increases the hardness gradually, thus reducing the wear rate.

![Figure 34](image1.png)

**Figure 34.** Wear volume loss vs time for A, B1, B2, and B3 at 10 N load and 650 MPa.

![Figure 35](image2.png)

**Figure 35.** Wear volume loss vs time for A, C1, C2, and C3 at 15 N load and 650 MPa.
4. Conclusion

- Sintering at 500 °C for 2 hours and at 850 °C for 6 hours under vacuum conditions (6.7*10^-2 MPa) is sufficient to complete the transformation process of Ni, Ti, Ta, and Y into an alloyed structure.
- A two-phase structure appeared in all alloys, composed of monoclinic NiTi and hexagonal Ni3Ti.
- Two alloys with Y additives (1 and 3 wt%) had hardness values lower than the NiTi alloy with 2% additives, while, the addition of Ta consistently increased the hardness values as the percentage of additive increased.
- The addition of Ta decreased the surface roughness as the percentage increased, while alloys with Y additives at 1 and 3 wt% had surface roughness that was higher than alloys with 2% additive.
- The addition of Y at 1 and 3 wt% to NiTi alloys reduced the wear resistance of these alloys, while the wear resistance increased at 2% Y content. The addition of Ta at the same percentages increased the wear resistance gradually as the additive increased from 1 to 3%.
- The wear volume loss decreased as the compacting stress increased.

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