Effect of low temperature annealing on the wear properties of NITINOL

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Abstract. NiTi shape memory alloy is a wonder material that is a solution looking for problems. The material finds wide biomedical applications like endodontic files for root canal treatment and cardiovascular stents. This material has rendered the surgical procedure simple compared to that with the existing Stainless Steel (SS) or titanium ones. NiTi as an endodontic file would cause less discomfort to the patients in comparison to that with far stiffer SS or titanium ones. Here nearly equi-atomic 50:50 commercial NiTi rods were subjected to low temperature aging at 300 to 450°C. The wear resistance of the as-received and the heat-treated samples was studied using adhesive wear tests on hardened steel counter face. Abrasive wear tests were run against Alumina disc to simulate the working of endodontic drills and files against dental hard and soft tissues. The abrasive wear resistance is expected to be proportional to the Vickers Hardness of the material and is high for the 450°C heat-treated sample. A correlation between the mechanical properties and microstructures of this material is attempted.

1. Introduction

The Nickel-Titanium alloy also known as NITINOL was developed in the 1960s. The alloy is called NITINOL as it is an equi-atomic combination of two elements nickel and titanium and developed at the Naval Ordinance Laboratory. This Nickel-Titanium alloy can exhibit shape memory effect and superelasticity (Bradley et al., 1996). These two special properties are found in them due to the martensitic transformation in it (Brantley, 2001). The three phases are known reported in this alloy are austenite B2, martensite B’19 and the R-phase B19. The austenitic phase is a high temperature phase that possesses an ordered BCC structure (like CsCl) whereas the martensitic phase is a low temperature phase with an ordered monoclinic structure. The R-phase is an intermediate phase that is seen to form either during the forward or the reverse transformation of martensite from austenite in some cases.

NITINOL has proved to be the workhorse in many of the bio-medical applications such as the endodontic files used for root canal treatment, cardiovascular stents, as filters in the blood stream, as orthodontic arch wires and so on. This endodontic treatment by the dentists concerns the removal of the dead cells and tissues from the tooth cavity and filling the cavity with cementing materials (Cohen et al., 2002). The dentists need to go through a lot of challenges concerning the root canal profile. The tools used were martensitic stainless steels. These NiTi instruments were brought into this field considering their low modulus of elasticity as compared to that of Steel and wide “elastic” working ranges (8% elastic strain) and the huge difference between the moduli of elasticity of the austenite and...
the martensite in the thermoelastic ones (Walia et al., 1988). The other important property that has made NiTi alloy popular in the field of endodontic is its superior flexibility compared to that of stainless tools, which enables the root canal preparation preserving the tooth structure (Tepel et al., 1997) at minimum discomforts to the patient.

The two remarkable properties namely the shape memory effect and superelasticity of the alloy are largely governed by the chemical composition, the thermal and mechanical history of the alloy including the final cold finishing operation. The NiTi ingot is hot worked to reduce the dimensions and breakdown the cast structure. This is followed by a set of cold work and process annealing to engineer microstructure with improved shape memory property (Fuentes et al., 2002). The process of final cold working the material is to improve the dimensional control to close tolerance and improve the yield and ultimate strengths whereas any heat-treatment to follow makes the alloy soft and ductile strong (Kou. S, 2003).

The aim of this paper is to investigate the effect of annealing on the microstructure and abrasive wear properties of the cold worked and heat treated alloys. The abrasive wear is an important property to be evaluated for the endodontic tools used in root canal treatment. For this the tool materials have to be tested against an abrasive material similar to the tooth tissues. The changes in the microstructure of the alloy and its influence on the mechanical properties of the alloy are also studied.

2. Experimental Procedure
A commercial Ni49.8 at% Ti 50.2 at% alloy is investigated. The alloy was procured from a supplier Baoji Sunhope Titanium Industries Ltd in China in the form of rods of 3.04 mm diameter and 16 cm length. The alloy was made by the standard procedure of vacuum induction melting (VIM) followed by vacuum arc Remelting (VAR). The final cast material was hot rolled, hot drawn and finally finish drawn by a 40% cold work to achieve chemical homogeneity and also have control over the dimension. The manufacturers reported their material was nearly equiatomic and was a shape memory alloy.

First the chemical composition of the alloy was ascertained by the Energy Dispersive X-ray analysis (EDAX) using Neon-40 FESEM/FIB set-up. Then the alloy samples were annealed at temperatures of 300, 350, 400 and 450°C for duration of one hour using SIGMA box furnace in a controlled Argon atmosphere at a heating rate of 10°C/minute and were air quenched after the soaking. Adhesive wear was carried out on the as-received and 450-HT NiTi samples using pin-on-disc tribometer according to ASTM-G99a. Small samples of approximately 5cm long were sliced from all test rods using an isomet diamond slicer. The tests were conducted for 1Kg and 2Kg loads keeping the wear track diameter and disc speed constant at 100mm and 400 rpm respectively.

The as-received as well as the annealed samples were subjected to abrasive wear test using pin-on-disc DUCOM machine as per ASTM G-132a. The abrasive wear tests were carried out with loads of 0.5 and 1Kg keeping wear track diameter and the disc speed constant at 100mm and 100rpm respectively and the corresponding readings of wear and coefficient of friction were noted. An AA60 K5 V8 abrasive wheel of 60 microns (alumina) was chosen for the test keeping in mind the working conditions that would be met by the endodontic files and drills. The abrasive disc size had 150mm outer diameter, 31.75mm inner diameter and was 6mm thick. The test conditions will approximately simulate the conditions met by endodontic tools when they run against tooth and the associated tissues. We know the hardness of Dentin and synthetic alumina are 3 to 4 on the Mhos scale.

The worn surfaces of the samples were examined using a Neon-40 FESEM/FIB Scanning microscope. The worn surfaces were studied at different magnifications to understand the nature of wear. The Vickers macro-hardness of the samples was determined. The samples of approximately 10 mm long were sliced from all the rods using an isomet and the cut surfaces were polished to obtain a mirror finish to see clearly and measure the Vickers indentation. The tests were carried using 5Kg load on polished surface of the 3mm rod held in a fixture.

The micro-structures of the samples were investigated with Dewinters optical microscope. Samples of approximately 10 mm long were cut from the rods using isomet. The sample surfaces were prepared by the usual metallographic procedures and finish polished using 1 micron diamond
paste. The polished samples were then etched using a solution of 10HF: 40 HNO₃: 50 H₂O and the representative micro structures were captured at suitable magnifications.

3. Results and discussion

3.1 EDAX

The elemental composition of the alloy determined by EDAX is shown in table 1

| Element | Weight% | Atomic% |
|---------|---------|---------|
| Ti K    | 32.79   | 50.10   |
| Ni K    | 40.03   | 49.90   |

It is observed that the alloy is a slightly titanium-rich above the equiatomic one with 50.1% Titanium and 49.9% Nickel.

3.2 Wear

3.2.1 Adhesive Wear

The curves below depict the trend of the adhesive wear test carried out for the samples at 1 and 2 Kg loads.

![Fig 1 Adhesive wear curve of as-received NiTi alloy at 1Kg load](image)

It is clearly seen from the above figures 1 and 2 that the samples have not worn significantly. A very similar trend was seen for both the samples run at 2 Kg load also. Hence adhesive wear in spite
of a reasonable frictional coefficient is woefully small (not significantly larger than the wear machine tolerances) to draw any meaningful conclusions. The excellent adhesive wear resistance of this material is yet to be clearly understood.

Further, wear is not an intrinsic material property but is a function of the tribo-system comprising of the material, its surface conditions, the counter face, load on the wear pair, atmosphere, temperature, speed of testing and lubricant to name a few variables. Wear tests somewhat similar to the service conditions would be more meaningful.

3.2.2 Abrasive Wear

The wear curves for the samples subjected to abrasive wear test are shown in figures 3 and 4. The test conditions chosen are approximately similar to the working conditions for the endodontic drills.
Fig. 3 Wear curves for the samples at 0.5 Kg load

Fig. 4 Wear curves for the samples at 1 Kg load
The results of the abrasive wear test for the two loads are shown in table 2.

| Sample  | 0.5Kg | 1Kg  |
|---------|-------|------|
| As-received | 125µm | 225µm |
| 300     | 85µm  | 176µm |
| 350     | 65µm  | 142µm |
| 400     | 84µm  | 178µm |
| 450     | 81µm  | 150µm |

It is observed from the above table that the wear of the as received sample for 0.5kg load is seen to be high (125µm) and it is decreasing for samples aged upto 350°C (65µm). Then it is increasing with increase in aging temperature till 450°C (81µm). The reduction in wear in the cold worked samples aged upto 350°C must be from the stress-relief toughening that is noticed during low temperature annealing of cold worked materials. This is similar to the variations of hardness on annealing for one hour of cold worked alloys within the recovery range (R. M. Brick et al., 1949).

Fig. 5 Wear data showing the coefficient of friction data for as-recd NiTi at 0.5Kg load

The wear results for 1 Kg load are similar in nature to that of 0.5Kg as seen in figure 5 above and the wear is nearly double those of 0.5Kg ones.

The wear for 0.5 and 1 kg loads for the samples is shown in the figure 6.
The abrasive wear resistance is clearly improving with one hour stress relieving till temperature of 350°C due to recovery process in the cold worked ordered intermetallic NiTi. However at temperature of annealing above 350°C softening of the cold-worked material seems to be taking place.

The figure 7 is the SEM image of the worn surface of the as-received material.

The figure 7 shows narrow and deep plough wear tracks on the surface associated with lot of debris confirming the high wear of the as-received sample. The black regions show the debris that has come out of the test sample during the test. Large amount debris seen the micrograph also concur with extent of damage suffered by the sample as seen in figure 7. The figures 8 - 11 are the SEM photos the worn surfaces for the aged samples.
Fig. 8 SEM image of worn 300-HT sample

Fig. 9 SEM image of worn 350-HT sample
It is clearly seen from the figures 8 - 11 that the plough marks are shallow in the 300°C sample confirming a reduction in the wear of this sample. Very little debris is seen. Also very light-colored debris is seen in the image possibly due to the increase in the hardness and ductility of the material on account of the heat-treatment. The wear marks are seen to become still shallow for the 350°C annealed one with further reduction in the amount of debris. Furrows seem to deepen in the 400°C annealed sample with the fewer wear tracks as compared to that in the as-received sample. Surprisingly the wear plough marks are seen to be very deep and closely spaced for the 450°C annealed one. Higher wear seems to go well with the reduction in the hardness of the sample to a low value as seen in figure 12. This reduction in the hardness could be the result of annealing at 450°C.

3.3 Vickers hardness
The variation of the Vickers hardness for the samples is as shown in the figure 12.
Fig 12 Variation of Vickers Hardness for the as-received and aged samples

It is clearly seen from figure 12 that there is no one to one correspondence between wear and hardness of the material. Wear is very complex in nature to be correlated with any one mechanical property. As per the above graph the hardness is high in the as-received condition from the 40% final cold-working done by the manufacturer on the material. The hardness looks to increase with aging at 300°C temperature and reach a peak value at the 350°C aged condition but is lower in the 400 or 450°C aged ones. This variation of the hardness is not directly related to the variation of the abrasive wear phenomenon.

3.3 Optical Microstructure

The figure 13 shows the micro-structure of the as-received cold-worked sample.

Fig. 13 As-received micro-structure
As per figure 13, the structure shows very fine grains as a result of lot of hot as well as cold working operations undergone by the sample. The structures of the aged samples are shown in the figures 14 - 17 shown below.

![300-HT micro-structure](image)

**Fig. 14** 300-HT micro-structure

![350-HT micro-structure](image)

**Fig. 15** 350-HT micro-structure
As observed from figures 13 - 17, the grain size appears to be too small to be resolved under the optical microscope. These small sized grains have resulted from the multistep manufacturing of the samples from the casting stage. Polishing as well as etching of this sample posed a lot of challenges possibly due to its very fine grains in the structure. The microstructures of all the samples were obtained only after repeated polishing and etching. All the structures seem to be similar possibly due to their submicroscopic nature and what are seen may be artifacts generated due to specimen preparation procedures. Small variations in the hardness values seen are similar to those observed during initial stages of annealing of cold worked alloys. The same specimen when etched with Acetic acid Keller’s reagent gives the following micro-structure as seen in figure 18.
Fig. 18 As-cast microstructure

As seen in Fig. 18, the micro-structure shows fine needle-like structures. Hence optical microscopy in case of this alloy is grossly inadequate in concluding about its behavior. Transmission Electron Microscopic studies are on to ascertain the structure and grain size of the samples in the as received and heat treated conditions to better our understanding of this alloy.

4. Conclusions

- The wear of the as-received sample is the high but it comes down to a minimum at the 350°C aged condition.
- The wear again increases somewhat for the 400°C and 450°C aged condition.
- The scanning micrographs of worn specimens show deep ploughing marks in the as-received sample depicting maximum wear but the wear marks are seen to become less sharp at the 350°C aged sample and they become somewhat prominent for the 400 and 450°C annealed ones.
- Vickers hardness is high for the as-received sample but increases further to a maximum at the 350°C aged condition and reduces somewhat on annealing at 400 and 450°C. This is the usual way the hardness of a cold worked sample vary on annealing upto their recovery state and beyond.
- Microstructure of the as-received sample has very fine grains Aging does not have any significant effect on the optical microstructures on aging upto 450°C.

5. References

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