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Investigating the effect of the addition of WC into NiTi for stent application

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Abstract. Nitinol is used for self-expandable stents used in biomedical applications considering their excellent properties of being superelastic and biocompatible. Minimally invasive implants need to be securely positioned in the human body with the property of being visible with the help of X-rays. Limited radiopacity of nitinol implants requires additional markers on the implants to facilitate accurate placement of the implant. This study explores the path of adding different concentrations of tungsten carbide (WC) to nickel-rich nitinol powder. Tests were conducted by compacting the mixed powders with a hydraulic press and then furnace sintering the green samples, with varying pressures and temperatures, to produce the solid parts. The mechanical properties of density and hardness of the sintered samples were measured and compared. An increase in hardness from 76 HV to 150 HV indicated that better mechanical properties could be achieved. Fully dense samples without any pores were obtained. These results show potential for the introduction of WC to nitinol for additively manufactured parts.

Introduction

Nitinol is a shape-memory alloy made of nickel and titanium, both of which are present in near-equal amounts. Recent advances in biomedical applications have been seen to be utilized as catheter tubes, guide wires, stone retrieval baskets, filters, needles, and stents [1]–[4]. Due to its excellent properties of shape memory alloy effect, superelasticity, high corrosion resistance, good biocompatibility, and good ductility, it is a desirable choice for implant applications [5]–[7]. However, nitinol poses the challenge of being radiolucent, which induces the challenge of the precise placement of the device in the human body. To combat this challenge and enhance other properties, the alloying of nitinol was evaluated. Among many other options erbium (Er) [8], tantalum (Ta) [9], and tungsten carbide (WC) [10] are often combined with other metals to enhance the mechanical properties of the primary material. WC possesses many important features that make it desirable for use in stents such as its high hardness, resistance to corrosion, high density (when compared to NiTi), and biocompatibility. As reported by Mussatto [11], adding WC into stainless steel during the laser bed fusion process resulted in increased strength of the parts produced with a stronger crystallographic texture.

In this present study, we evaluate the possibility of the addition of WC in nickel-rich nitinol to investigate the hardness and density of the new composition. The samples have been produced by the compaction process of the powder using a hydraulic press with subsequent heat sintering to form solid circular disks. The addition of WC into NiTi for enhancing the mechanical property of hardness was evaluated. The addition of different materials in NiTi opens the possibility of assessing several different applications with desired functional properties. Small varying mass

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percentages of WC were added to NiTi to enhance the strength of the combined powder with a view to not significantly alter the shape memory properties of the produced NiTi composite part.

Materials and Methods

Powder Mixing and Compaction

Pre-alloyed nickel titanium powder was sourced from Fort Wayne Metals, Castlebar, Ireland with an elemental composition of 52.39 at.% Ni and 47.61 at.% Ti with a purity of 99.999%. The particle size distribution of NiTi powder is 12.3 µm (D_{10}), 27.4 µm (D_{50}) and 47.6 µm (D_{90}). A hydraulic press was used for the compaction process of the NiTi powder. The compaction parameters applied were the compaction pressure (ton), holding time (min), and varying powder mass to achieve highly compact powder to produce disc samples geometry of 20 mm diameter. Although the best results were achieved from the compaction of the pre-alloyed NiTi powder at 2.4 MPa, a holding time of 15 mins, and a NiTi powder mass of 2.4g; however, it was still not sufficiently compacted enough to continue onto the sintering process as shown in Figure 1.

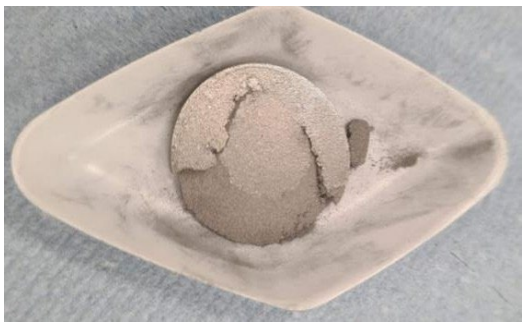

Figure 1: Pre-alloyed NiTi powder compacted at 22 tons, holding time of 15 mins and mass of 2.4 g.

Due to the failure of the achieving fully compact discs, separate nickel and titanium powders sourced from Fort Wayne Metals, Castlebar, Ireland was used with a purity of 99.996%. A Resodyn LabRam1 acoustic mixer was used to thoroughly mix the sample powder. A three-step mixing process was used with each step lasting 30 seconds with increased acceleration gravity (g) levels of 40g, 60g, and 70g in each step. These newly mixed samples of NiTi were then tested for compaction under different parametersand instant improvements to the samples post compaction were obtained. However, there were microcracks observed on the samples. A preliminary pilot test to investigate the optimum set of mixing ratios, it was found that the addition of water soluble 2% PVA (Polyvinyl Alcohol) to the powder mixture and compaction at a load of 25 tons, holding time of 15 mins, and the mass of the powder at 6.5g to achieve a significant and improved compaction results followed by efficient removal of the parts from the die as shown in Figure 2.

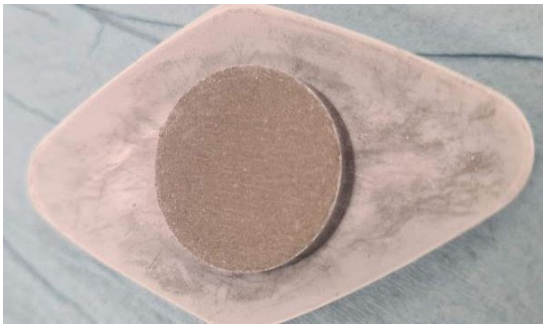

Figure 2: Self-mixed NiTi powder was compacted using the parameters of load 25 tons, hold time of 15 mins, mass of powder 6.5g and PVA added at 2% of the mass of the NiTi powder.

Once the parameters that are best suited for the compaction of NiTi was found, WC was mixed into the powdered samples at increasing mass percentages of 5%, 10%, 15% and 20% of the total mass of the powder mixed according to Table 1. These self-mixed NiTi powders and WC were then compacted under the previously found parameters for compaction of the self-mixed NiTi powder.

Table 1: Varying masses of WC added to self-mixed NiTi powders for compaction.

Mass division of WC and NiTi		
WC %	**NiTi (g)**	**WC (g)**
0	40	0
5	38	2
10	36	4
15	34	6
20	32	8

Sintering

Sintering was done to each of the compacted samples with the use of a heat furnace. Due to the high melting point of NiTi, heat sintering method was employed to keep the purity of the samples post processing. Pre-testing was conducted for the heat sintering of the compacted samples by holding the samples inside the heat surface for 3 hours with a temperature 1200 ºC (as this was between the ideal sintering temperature between nickel (1091 ºC) and titanium (1251 ºC)). However, this resulted in the samples tested completely melted and incapable of any use. The samples were then sintered in steps until the heat furnace reached a temperature of 1000 ºC holding it for 3 hours before the heat furnace was cooled down in the same steps by which it was heated. Figure 3 shows the sintering process used for the samples. The samples post sintering under these steps were seen to produce ideal samples.

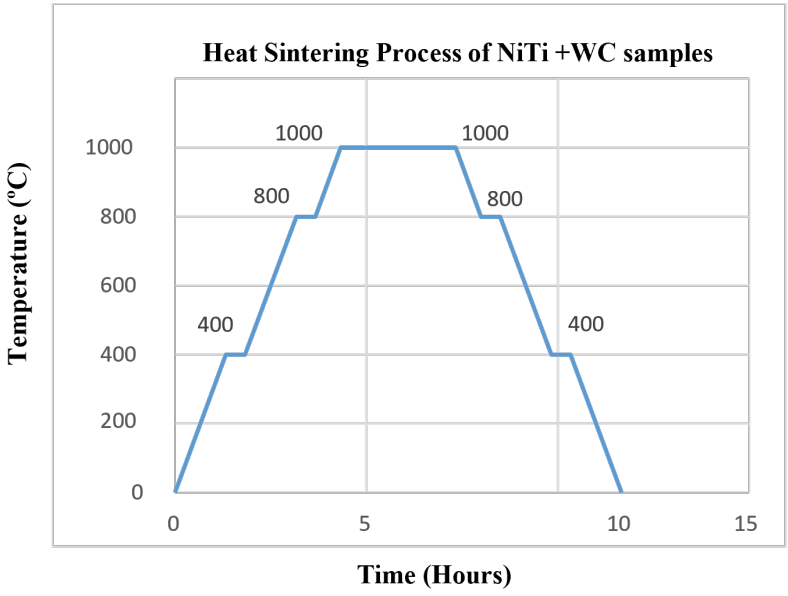

Figure 3: Sintering steps conducted until the heat furnace reached 1000 ºC with holding time for 3 hours before it was cooled down in steps.

Metallographic preparation of the samples

All the sintered samples were mounted in resin for ease of use during the grinding and polishing process of the surface. The samples were grinded using abrasive paper that went up in grit size value from P80 to P4000. Once all samples were grinded diamond polishing was done to the

surface of the samples to achieve a smooth mirror-like finish on all samples to make them available for testing as shown in Figure 4. The samples were polished using diamond suspensions in decreasing number of particle sizes from 9µm, 6µm, 3µm and 1µm.

Figure 4: Polished sample surface of NiTi + 10% WC.

Characterization Techniques

Morphological characterization was conducted using a scanning electron microscope (SEM), Zeiss EVO LS-15, on all powders which comprised of pre-alloyed NiTi, self-mixed NiTi, and NiTi with varying amounts of WC. This inspection was conducted to analyze the even mixing of all powders before compaction. Energy dispersive X-ray spectroscopy (EDS), INCA, Oxford Instruments EDX system was used in combination with SEM to carry out an elemental analysis on all the samples being used. This technique helped to understand the composition of all powdered and sintered samples by showing the average mass percentage value of each element present within each sample.

As there were many defects found within the topography of the sintered and polished samples it was almost impossible to see the composition of the material using optical microscopy, thus backscattered images were used to get the structural composition of the polished samples. This was done with the addition of the backscatter sensor to the SEM directly above the sample which detects backscattered electrons from the sample onto the sensor and produces high-quality images of the microstructure of the sample a small distance inside the sample being viewed. EDS was then used to map out the different elements present within the sample shown by each color contrast specific to a different element.

Vickers Hardness test was carried out on each of the samples to obtain a value for hardnesson each of these samples. A small indentation is made on each of the samples with a load of 0.98 N with a holding time of 20 secs. The average Vickers hardness was reported after 5 measurements were done on each sample. Density measurements were carried out on all the sintered samples using the Archimedes principle. The measurements were carried out using ethanol as fluid. Three measurements were conducted, and the average density has been reported.

Results and Discussion

Morphological characteristics of the powder samples

The SEM metallography images show clear structural difference between the NiTi particles and WC particles as shown in Figure 5 and Figure 6, respectively. The NiTi powder showed particles were circular and round consistently throughout the sample with little to no impurities or defects to the particles. On the other hand, WC was observed to have a much smaller particle size (ranging from 1-5 µm) and was very random in shape which is a commonly supplied form for this material [12].

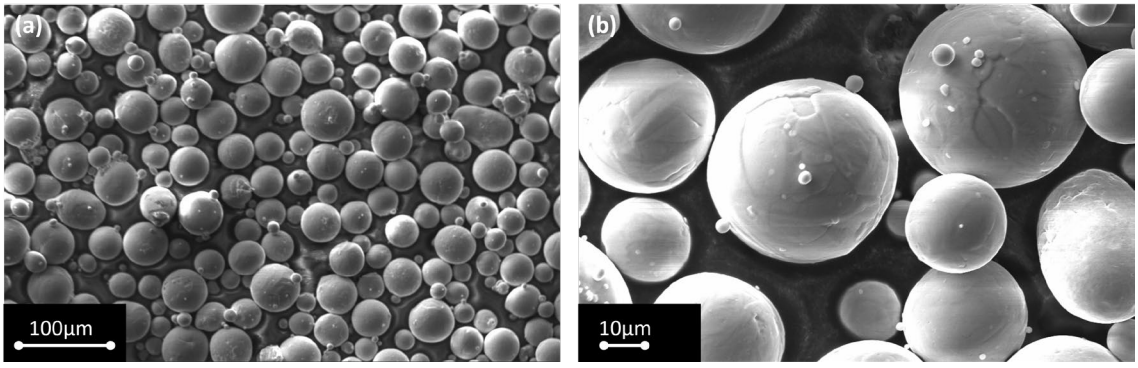

Figure 5: SEM image of self-mixed NiTi powder.

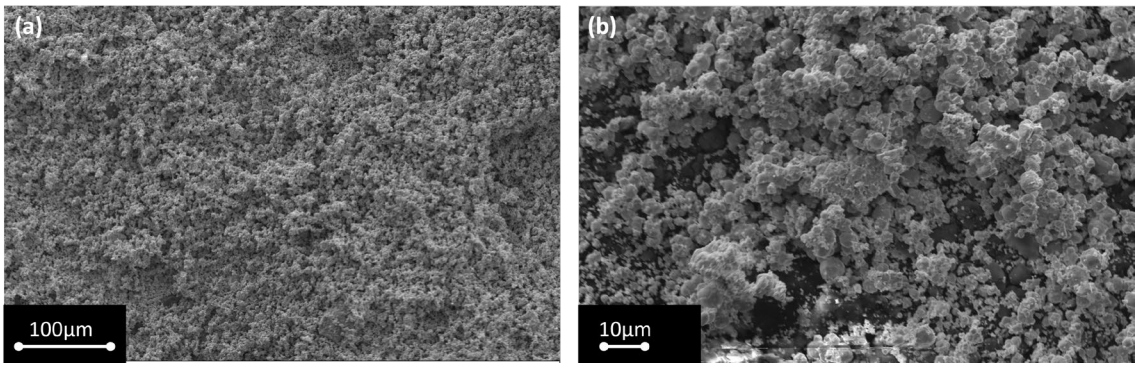

Figure 6: SEM image of WC powder.

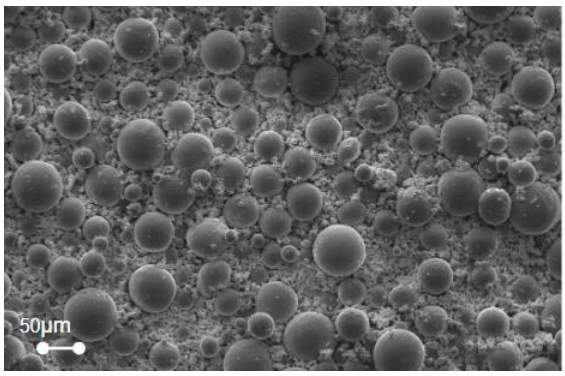

Figure 7: A constant and uniform mixing of both powders were observed of mixed NiTi + 10% WC powder.

As observed in Figure 7, all powders were found to be uniformly mixed with expected amounts of both NiTi and WC in all areas of the sample. EDS was conducted on all samples, and it was found that there was a steady increase in the WC in the average atomic mass percentage of the WC as more WC was added.

Backscattered scanning electron microscope images helped analyze the inner microstructure of each sample. The three distinct color contrasts were observed in the backscattered images of each of the samples as depicted by Figure 8.

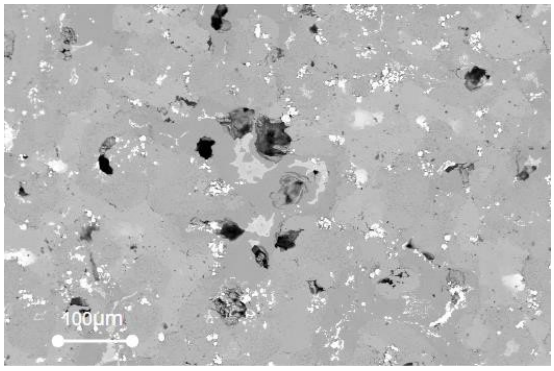

Figure 8: Backscattered scanning electron microscope image of NiTi + 10%WC.

Effect of addition of WC on the density of the samples

Due to the higher melting point of WC than that of NiTi, the WC particles would not form an alloy with NiTi after the sintering process. However, WC particles still retain all their properties post sintering which will increase mechanical properties such as hardness and density while being encapsulated in the ductile and biocompatible environment of the NiTi.

It was observed that there was a linear increase in the density of the samples with an increase in the WC percentage as shown in Figure 9. This is primarily because WC is a very dense material and as WC was not melted during the sintering process it still retains all its properties. Along with the reduction in the number of pores present throughout the sample, it also increased the density of the samples.

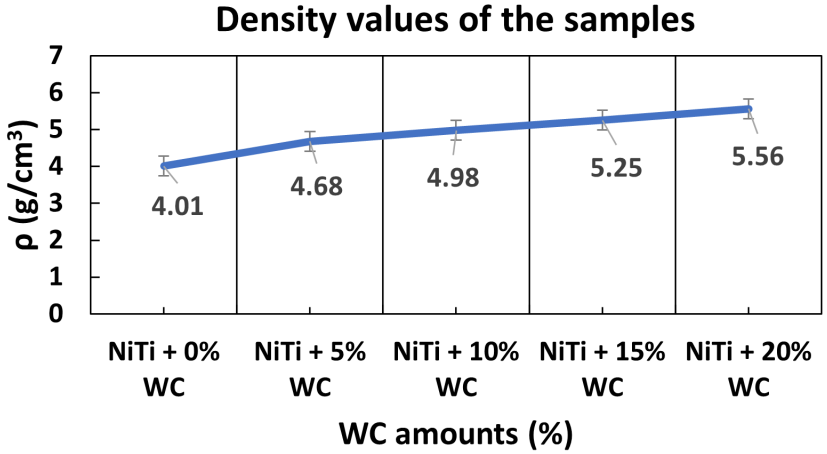

Figure 9: Density of the sintered samples after the compaction process with varying WC amounts.

Effect of addition of WC on the hardness values of the samples

A steady linear increase in the Vickers Hardness values was observed as the mass percentage of the WC powder present within the samples was increased as shown in Figure 10. From analysis of all samples, it was seen that the sintered samples containing only NiTi had a lot of pores which resulted in the reduction of the hardness value of the sample. These pores were formed because of either the parameters used for the sintering process or due to the evaporation of the PVA from inside the sample leaving void spaces. The number of pores visible in the samples gradually decreased as the amount of WC increased. This is because the areas in which the pores were formed

were filled with the WC powder which resulted in significantly fewer void spaces throughout the sample thereby increasing both the hardness and strength of the material.

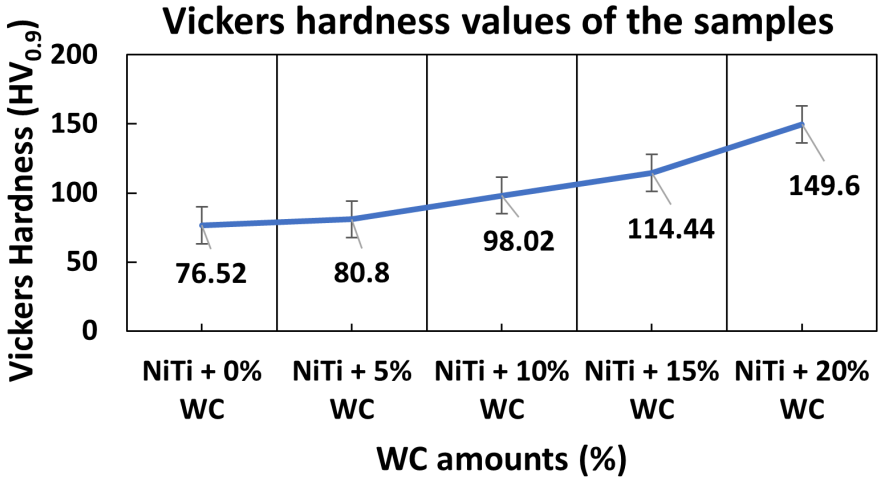

Figure 10: Vickers Hardness values was observed for all samples with varying WC %.

Conclusion

In this work, the advantages of adding tungsten carbide (WC) in different amounts to nickel-rich nitinol were investigated. Due to its extraordinarily high melting point, it was found that the WC powder did not entirely melt in any of the samples. The evaporation of PVA left gaps in the sample, but this powder-filled them and provided structural support for the NiTi resulting in fully dense solid samples. The sample's hardness increased with increasing amounts of WC. These are all extremely crucial elements to consider when creating any stent and will lower risk factors like restenosis and stent distortion. Further work will be carried out to evaluate the influence of addition of WC to NiTi on radiopacity and biocompatibility of the produced samples. As NiTi is still used as the primary element for the fabrication of the stent, it still inhibits all important properties such as shape memory, corrosion resistance, and biocompatibility along with the mechanical advantages of WC, making the addition of WC to NiTi stents a potential advantage for the fabrication of stents.

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