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Original Article

Effect of dry cryogenic treatment on Vickers hardness and wear resistance of new martensitic shape memory nickel-titanium alloy

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ABSTRACT

Objectives: The aim of this study is to investigate the role of dry cryogenic treatment (CT) temperature and time on the Vickers hardness and wear resistance of new martensitic shape memory (SM) nickel-titanium (NiTi) alloy. The null hypothesis tested was that there is no difference in Vickers hardness and wear resistance between SM NiTi alloys following CT under two soaking temperatures and times. **Materials and Methods:** The composition and the phase transformation behavior of the alloy were examined by X-ray energy dispersive spectroscopy and differential scanning calorimetry, respectively. Fifteen cylindrical specimens and 50 sheet specimens were subjected to different CT conditions: Deep cryogenic treatment (DCT) 24 group: −185ºC, 24 h; DCT six group: −185ºC, 6 h; shallow cryogenic treatment (SCT) 24 group: −80ºC, 24 h; SCT six group: −80ºC, 6 h; and control group. Wear resistance was assessed from weight loss before and after reciprocatory wet sliding wear. **Results:** The as-received SM NiTi alloy contained 50.8 wt% nickel and possessed austenite finish temperature (A_f) of 45.76°C. Reduction in Vickers hardness of specimens in DCT 24 group was highly significant ($P < 0.01$; Tukey's honest significant difference [HSD]). The weight loss was significantly higher in DCT 24 group ($P < 0.05$; Tukey's HSD). **Conclusion:** Deep dry CT with 24 h soaking period significantly reduces the hardness and wear resistance of SM NiTi alloy.

Key words: Cryogenic treatment, nickel-titanium, shape memory, Vickers hardness, wear resistance

INTRODUCTION

The nickel-titanium (NiTi) alloy, which is used in the manufacturing of rotary endodontic instruments, is an exotic metal that can be subjected to thermomechanical treatment in order to alter shape memory (SM) and superelasticity.[1] Although NiTi alloys possess these unique properties, fracture of rotary instruments in the canal without warning is unavoidable when compared with stainless steel.[2] To overcome this difficulty, either new alloys could be used or the manufacturing process (machining or twisting) could be altered.[3,4]

There is a significant improvement in the design and control of raw NiTi alloy over the last decade in relation to manufacturing process and material properties.[3,5-8] Based on the characterization experiments performed earlier, the martensitic SM NiTi alloys possess significant proportion of stable martensite phase at working temperature that is

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the body temperature.[5] Consequently, martensitic instruments deform easily and regain their original shape when heated above the transformation temperature during sterilization.[9] They possess active austenite finish temperature (A_f) of -55°C, and the superelastic (SE) property exists 50°C above the A_f temperature that is 105°C.[10] Despite the extreme flexibility, canal centering ability, and superior canal tracking,[9,10] these alloys do not possess the conventional stress-induced martensitic transformation as observed in SE NiTi alloys.[11]

The major drawback of martensitic instruments is their permanent plastic deformation following instrumentation.[12] Peters *et al.* reported that 82% of the SM rotary instruments plastically deformed postinstrumentation, of which 37% of the instruments did not recover their shape after sterilization.[12] Also, smaller SM instruments have a larger tendency to plastically deform than larger instruments for a given torque. Therefore, the operator should be cautious while reusing small rotary instruments.[13]

Cryogenic treatment (CT) is an inexpensive, one-time treatment of subjecting metals to very low temperatures that affects the entire core components rather the surface alone.[14,15] Based on the soaking temperature, the CT can be shallow (−80°C; shallow cryogenic treatment [SCT])[16] or deep (−185 to − 196°C deep cryogenic treatment [DCT]).[17,18] Based on the contact of specimens with liquid nitrogen, the process may be dry (not immersed) or wet (immersed).[19] CT of rotary endodontic instruments made up of SE NiTi alloy has shown increased cutting efficiency[19] and microhardness.[20] Improvement in steel tool life of 200% following CT has been reported due to phase transformation of retained austenite to martensite as well as to the deposition of fine carbide particles.[18,21] Both stainless steel[20] and SM NiTi alloys[10] have A_f temperature above the body temperature. However, the effect of CT on the mechanical properties of SM NiTi alloys remains unclear. Therefore, the purpose of this preliminary study is to evaluate the effect of dry CT temperature and time on the hardness and wear resistance of SM NiTi alloys. The null hypotheses tested were as follows:

- There are no differences in Vickers hardness and wear resistance between SM NiTi alloys following DCT and SCT (CT temperature)
- There are no differences in Vickers hardness and wear resistance between SM NiTi alloys following exposure to 6 h and 24 h (CT time).

MATERIALS AND METHODS

Raw SM NiTi alloy in the form of sheet and rod from the same ingot was obtained for the investigation.[22] The elemental composition was determined for the SM alloy using scanning electron microscope (CX-200; Coxem Ltd., Daejeon, South Korea) coupled to energy dispersive X-ray spectrometer.

The transformation temperature range was determined using differential scanning calorimetry (DSC). A small piece of alloy (10–12 mg) was cut using water-cooled, slow-speed diamond saw to avoid changes in the transformation temperature range. The phase transformation was monitored using a differential scanning calorimeter (DSC 204; Netzsch–Geratebau GmbH, Germany) over a temperature range from −70°C to 100°C. Cooling DSC curve was obtained by first heating the specimen from room temperature to 100°C and then cooled to −70°C. Heating DSC curve was obtained by subsequently heating the specimen to 100°C. The austenite starting and finishing temperature and martensite starting and finishing temperature were identified from the DSC curve in order to confirm the transformation temperature range of SM alloy.

X-ray diffraction (XRD) was performed on a specimen after polishing to identify the phases. The analysis was performed at room temperature on an X-ray diffractometer (MiniFlex II-C, Rigaku, Tokyo, Japan). The angular 2θ diffraction range was 10–100° at 0.02° steps and 2 s of step time. The XRD system was operated with Cu-K^{α} anode (λ = 1.5406 Å) with 40 kV accelerating voltage and 40 mA beam current. A silicon standard (640b Silicon Powder XRD Spacing, Standard Reference Material; NIST, Gaithersburg, MD, USA) was used to calibrate the diffractometer. The International Centre for Diffraction Data (ICDD) database (PDF release 2004; ICDD, Newton Square, PA) was used to identify the austenite and martensite phase peak.

Cryogenic process

Fifteen cylindrical specimens (10 mm height and 9 mm diameter) and 50 sheet specimens (15 mm × 15 mm square) were sectioned from the as-received NiTi sheet and rod with the help of wire electrical discharge machine (AQ300L; Sodick, Shaumburg, IL). The dry CT facility used in the present study has been utilized in the previous study.[19] Both cylindrical and sheet specimens were randomly divided into five groups of three and 10

each, respectively. The groups were categorized based on the soaking temperature and time as follows: DCT 24 group: −185°C, 24 h; DCT six group: −185°C, 6 h; SCT 24 group: −80°C, 24 h; SCT six group: −80°C, 6 h; and Control (Ctrl) group: No treatment. The cooling rate of 1°C/min (3 h) and warming rate 0.6°C/min (6 h) were kept constant for all experimental groups.

Vickers hardness

All cylindrical specimens (3/group) were mounted and the cut surface was ground and polished with sandpaper (Carbimet Paper Discs, Buehler: 240 and 600 grit) in a polishing machine (Bainpol, Chennai Metco Pvt Ltd, Chennai, India). Final polishing was done with alumina paste (Alpha Micropolish, Buehler: 6 μm, 1 μm and 0.5 μm particle sizes). Hardness measurements were performed in each specimen with Vicker's hardness tester (VM-50, Fuel Instruments and Engineers Pvt. Ltd., Kohlapur, India) at room temperature with 5 kg load and 15 s dwell time. Five indentations were made in each specimen with a square-based pyramidal diamond indenter at the center and at equidistant adjacent locations in each specimen (n = 15). The two diagonals of the indentations were measured to the nearest 0.1 μm with a filar micrometer and averaged. Hardness was taken as the maximum force divided by the area of contact.

Wear resistance

Fifty NiTi sheet specimens (10/group) were subjected to reciprocal sliding wear. Wear test was conducted on a reciprocatory friction and wear monitor as per the American Society for Testing and Materials standards.[23] The reciprocating speed was adjusted to 10 Hz with a stroke length of 10 mm and duration of 4 h with the vertical load of 10 N. The En-31 steel was selected as opposing material during reciprocating sliding wear in order to have higher hardness than that of NiTi alloy.[24] Physiological saline solution was used as coolant during the experiment. The SM NiTi specimens were weighed in an electronic weigh balance (Analytical Plus; Ohaus Corporation, Pine Brook, NJ) before and after the sliding test and their wear resistance were quantified by calculating the loss of weight.[25]

The significance for hardness and weight loss data was analyzed using one-way ANOVA followed by *post-hoc* multiple comparisons using Tukey's honest significant difference (HSD) test. Statistical analysis was performed using SPSS software version 16.0 (SPSS Inc. Chicago, IL) at a 0.05 significance level.

RESULTS

The elemental composition of the as-received SM alloy was nickel rich (nickel – 50.8 wt%; titanium – 48.4 wt%) with trace elements. The typical DSC curve of the raw material exhibited single well-defined peak on heating and two peaks on cooling [Figure 1]. The A_f temperature was found to be 45.76°C that is well above the body temperature. XRD pattern confirmed the presence of martensite phase at room temperature [Figure 2].

The Vickers hardness number (VHN) of specimens in all groups was above 200 VHN [Table 1]. The specimens in DCT 24 exhibited the least hardness (212 VHN) whereas the specimens in Ctrl showed the maximum value (238 VHN). The statistical difference in VHN of different groups was highly significant (P < 0.01; one-way ANOVA). The mean VHN of Ctrl was significantly higher than that of DCT 24 and

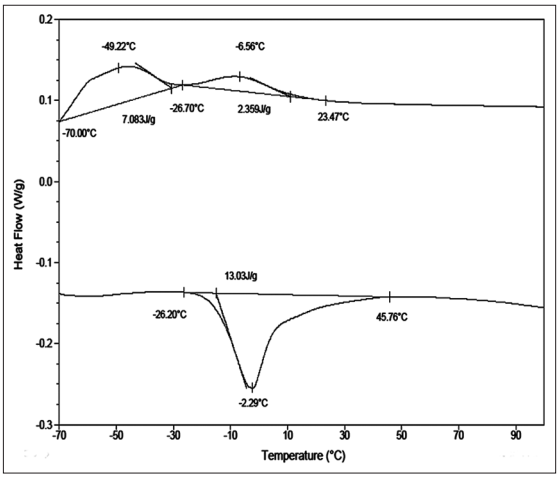

Figure 1: Differential scanning calorimetry curve of the specimen of the as-received nickel-titanium shape memory alloy

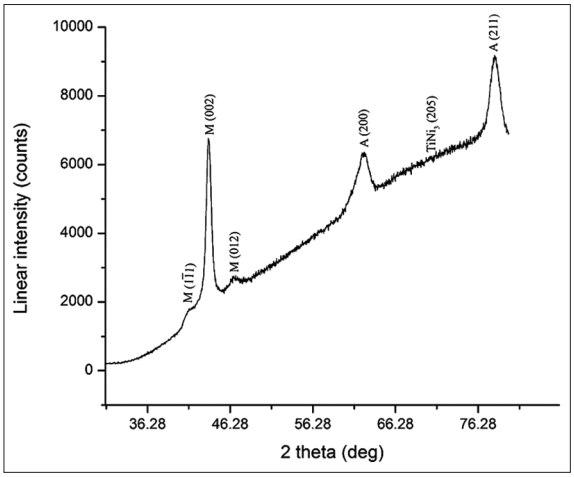

Figure 2: X-ray diffraction pattern of the as-received specimen at room temperature

Table 1: Inter-group comparison of the Vickers hardness values (*n*=15) from cylindrical specimens and weight loss values (*n*=10) from sheet specimens

	Vickers hardness† (VHN)	Weight loss† (×10⁻³ g)
DCT 24	212.27±4.85[a]	4.67±0.01[d]
DCT 6	225.60±8.60[b]	4.51±0.03[e]
SCT 24	234.27±15.05[c]	3.47±0.06[f]
SCT 6	237.33±8.47[c]	3.57±0.04[g]
Ctrl	238.33±11.26[c]	2.94±0.03[h]

†One-way ANOVA and Tukey's *post-hoc* test. Data are expressed as mean±SD. Values with different superscript letters indicate a self explanatory for significant difference between the groups (P<0.05). SD: Standard deviation, VHN: Vickers hardness number, DCT: Deep cryogenic treatment, SCT: Shallow cryogenic treatment, Ctrl: Control

DCT 6 (P < 0.05; Tukey's HSD). The mean difference in VHN of DCT specimens treated with 24 h and 6 h soaking period was highly significant (P < 0.01) in contrast to that of SCT specimen (P > 0.05).

The difference in mean weight loss following wet sliding wear in different groups [Table 1] was statistically significant (P < 0.01; one-way ANOVA). The mean weight loss in all the experimental groups was significantly (P < 0.01; Tukey's HSD) higher than that of Ctrl. The mean difference in weight loss of specimens treated with 24 h and 6 h soaking period was highly significant (P < 0.01; Tukey's HSD) in both DCT and SCT specimens.

DISCUSSION

CT of alloys during manufacturing has been successful in improving their hardness and wear resistance.[14,21,26] Although SM alloys are extremely flexible with longer fatigue life due to the presence of martensite phase at working temperature,[27] supplementary CT would further increase the volume of martensite[14] resulting in superadded benefits. The objective of this study is only to assess the effect of soaking temperature and time. Hence, the cooling rate and warming rate were maintained constant. The results of this study showed a significant difference in Vickers hardness and wear resistance of SM NiTi alloys between those treated with DCT and SCT. Therefore, the first null hypothesis was rejected. However, the soaking time had a significant influence on the properties of the SM NiTi alloy pertaining to DCT. Thus, the second null hypothesis was partially rejected.

The results of this study showed that the composition and transformation temperature range were closely approximating with that of the commercial SM files.[3] Nevertheless, the mechanical properties are more sensitive to the transformation temperature range rather than the composition.[1] The phase transformations were more prominent with a single stage (martensite → austenite) while heating and two stage (austenite → R-phase → martensite) while cooling.[3,28] Raw materials were selected prior to manufacturing for two reasons – To avoid the influence of manufacturing methods (machining/twisting) and thermomechanical processing on NiTi properties and the dimension of the specimens were customized according to the test requirements.

Hardness tests were performed on polished surfaces to ensure low surface roughness that might lead to errors in depth calculations. The average microhardness values of M-wire SM NiTi alloy, controlled memory SM NiTi alloy, conventional SE NiTi alloy, and fully annealed NiTi alloy were 390 VHN, 315 VHN, 353 VHN, and 200 VHN, respectively.[6,29,30] However, the as-received specimens in this study exhibited mean hardness of ~238 VHN as a result of cold working. When compared with the Ctrl group, there is a significant reduction in hardness value of the specimens in the DCT groups. In the SCT groups, significant reduction in hardness of specimens was appreciated neither between them nor with the Ctrl. The reduction in hardness of the specimens following DCT could be speculated to the complete transformation of retained austenite into martensite phase.[18] Microstructural characterization of the same alloy performed earlier using optical microscope, scanning electron microscope, and XRD has confirmed the reduction in volume of austenite and increase in martensite.[31] This highlights the importance of deep dry CT in a controlled manner, which avoids the thermal shock as observed in wet CT.[19] In contrast, deep wet CT increased the microhardness of SE NiTi instruments.[20]

The weight loss data of the specimens in the experimental groups showed a relatively higher value in DCT 24 suggesting its poor wear resistance. This could be correlated with the reduction in hardness and increase in martensite content of the specimens.[24] The wear resistance of the martensite phase is relatively lower than the austenite phase as they undergo plastic deformation due to their low strength.[32]

The soaking period plays an important role in significantly altering the hardness of SM NiTi specimens as far as DCT is concerned. Longer soaking time of 24 h yielded favorable results by providing adequate time for the transformation of retained austenite to martensite phase. The SM NiTi alloys show remarkable fatigue resistance and flexibility due to the presence of proportionately higher martensite phase.[4]

Accordingly, the hardness is reduced resulting in a decrease in likelihood of instrument fracture during use.[33] However, the wear resistance was significantly affected in both DCT and SCT group between 24 h and 6 h soaking period.

CONCLUSION

Dry CT appears to be a promising supplementary method in the manufacturing of SM NiTi endodontic instruments. Under the given experimental framework, deep dry CT with 24 h soaking period significantly reduces the hardness and wear resistance of SM NiTi alloy. Further investigation is required to evaluate the impact of CT on cutting efficiency and fatigue life of the instruments made out of this new SM alloy.

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Conflicts of interest

There are no conflicts of interest.

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