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A Novel Fabrication Method for Nitinol Shape Memory Alloys

S.A. Rizvi[a] and T.I. Khan[b]

Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Canada

[a]shabbar_rizvi@yahoo.com, [b]tkhan@ucalgary.ca

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Abstract. Nitinol (NiTi) shape memory alloys are widely used in a variety of biomedical applications, such as dental implants, cervical and lumbar vertebral replacements, joint replacements and stents. In this study, commercially pure Ti and Ni foils ~100 um thick were diffusion bonded in vacuum. The experimental conditions were optimized to achieve a near equiatomic composition to produce NiTi SMA thin foil of approx. 5-8 micron thick. The cross-sectional surfaces of joint were subjected to metallographic investigation using optical microscope after grinding, polishing and etching. Scanning electron microscope equipped with EDX system was utilized to characterize the bonded layer and compositional analysis. Differential scanning calorimetry (DSC) technique was employed to determine the shape memory effect. The samples were subjected to X-ray diffraction analysis in order to establish phase structures formed during the diffusion bonding stage. An ultra fast femto-second laser facility was utilized to ensure the production of complex shapes or patterns within micron scale.

Introduction

The near-equiatomic nickel–titanium alloy (NiTi or Nitinol) is one of several shape memory materials that can remember a pre-set shape when heated even after plastic deformation. These alloys exhibit unusual mechanical properties i.e. superelasticity and shape-memory effects which are related to a thermo-elastic phase transformation near ambient temperature, martensite twinning and inhibition of slip by fine Ni-Ti precipitates, that enable multifunctional applications involving high recovery strain [1]. These alloys have good corrosion resistance and biocompatibility, which enable them to be widely used in numerous applications [2-6]

One major application for NiTi shape memory alloys is in biomedical devices. Their good biocompatibility compared with conventional stainless steel and titanium (Ti) alloys makes them suitable for prosthetic implants.

A variety of production techniques have been used to fabricate nitinol and include powder metallurgy using elemental Ni and Ti powders, self-propagating high-temperature synthesis (SHS), spark plasma sintering (SPS) , hot isostatic pressing (HIP) with argon expansion, capsule-free HIP (CF-HIP) and conventional sintering (CS) [7,8]. In these processes partial powder densification and exothermic synthesis of the intermetallic NiTi occurs and undesirable non-equiatomic Ni–Ti phases often remain due to incomplete NiTi formation. These phases are often difficult to remove, even after prolonged high-temperature homogenization treatments [9].

The martensitic transformation in bulk NiTi SMA shows excellent properties of actuation, however, micro-actuators using the transformation have a limitation in their actuation speed. This is because the micro-actuators operated by temperature variation require heating and cooling time necessary for inducing the forward and reverse transformations. However in thin film SMA, thermal mass is much smaller than the bulk NiTi alloys. The large surface to volume ratio of the NiTi thin films result in faster cooling. Hence, the frequency response of thin film SMA is higher than that of bulk SMA. Nevertheless, the large actuation stresses and strains of NiTi SMA can still be retained in the thin film form. Therefore Ni-Ti shape memory alloy (SMA) thin films are attractive candidates for powerful micro-actuators. Thin film SMA has been recognized as the promising and high performance material in the field of micro-electromechanical system (MEMS) [2,10]

Since the 1990's, various physical vapour deposition techniques have been used to fabricate thin NiTi films, which includes magnetron sputtering [11], ion beam sputtering [12], Electron cyclotrone

sputtering (ECR) [13], Laser ablation [14], Pulsed laser deposition [15], Flash evaporation[16], electron beam deposition [17] and vacuum plasma spraying [18]. NiTi SMA thin films deposited either by sputtering techniques (involves challenges in controlling chemical composition and costly heat treatment procedures to attain the shape memory effect) or manufactured by conventional metal deformation processes are costly, no guarantee of repeatability and ineffective to produce complex, miniature micron scale devices. Due to the lack of understanding of the properties of thin film SMAs and controlling their deposition parameters, they have not received as much attention from the MEMS community as other micro-actuator technologies [2]. Therefore, in the present study a novel technique is introduced for the production of NiTi shape memory alloys. This technique has the potential to increase reproducibility and reduce costs, which were associated with long processing time. Commercially pure Ti and Ni foils were diffusion bonded in vacuum and bonding parameters were optimized to achieve a near equiatomic NiTi composition. The NiTi alloy was then examined for the shape memory effect and characterized using metallurgical analysis.

Experimental Procedure

Commercially pure Ti and Ni foils with surface roughness approximately 0.2-0.4μm Ra were used for diffusion bonding. The foils were cut to small square samples with dimensions of approximately 15 mm x 15 mm. The thickness of titanium and nickel foils was about `100μm and 25μm respectively. The surfaces were prepared and ultrasonically cleaned for 10 minutes. The diffusion bonding system was employed to bond Ti and Ni foils together. The foils were placed in between the Si_3N_4 ceramic plates to avoid the sticking of the NiTi foils to the steel plates, used to apply load to the samples. A uniaxial load of 5MPa was applied to the samples. Diffusion bonding was carried out at temperatures from 650-880°C for the duration of 0.9ks to 4.5ks under vacuum at $5x10^{-4}$mbar. The heating rate was controlled at 2.5°C/sec. K-type thermocouple was used to monitor the temperature. The samples were allowed to cool to room temperature in the vacuum. The experimental conditions were optimized to achieve a near equiatomic composition to produce NiTi shape memory alloy (SMA). The cross-sectional surfaces of the bonded sample were cut, cold mounted and subjected to grinding and then polished using 1μm diamond paste. The samples were chemically etched in Krolls reagent and in a solution containing H_2O, HF and HNO_3 at a ratio of 5:1:4. The samples were then washed ultrasonically in acetone for 10 min and then in deionized water for 10 min. The transverse section through the thin foil was examined using standard metallographic characterization techniques. Scanning electron microscope model JEOL JXA 8200 equipped with EDS/WDS system was utilized to characterize the microstructure and composition across the bonded layer. Differential scanning calorimetry (DSC) technique was employed for the characterization of the shape memory effect. Martensitic transformation temperatures were measured by Perkin Elmer Instruments, Pyris DSC-1 in the nitrogen atmosphere while heating and cooling at the rate of 10°C/min. over a temperature range of 25°C to 130°C. For X-ray diffraction analysis, a Rigaku Multiflex XRD was used with the wavelength of 1.54Å Cu-Kα X-ray source at 40KV. The ultra fast femto-second laser facility was utilized to cut out the thin foil and ensure the production of complex shapes or patterns within micron scale.

Results and Discussion

The microstructure of the diffusion bonded Ni and Ti foils is shown in Fig. 1. The joint microstructure showed a smooth bond interface, which consists of several reaction layers. Examination of the bond interface using SEM analysis revealed five distinct zones, as shown in Fig. 2. The composition of these zones was determined quantitatively by wavelength dispersive spectroscopy and the results are summarized in table 1. The results showed that the stoichiometry of the reaction zones correspond to the formation of Ni, Ni_3Ti, NiTi, Ti_2Ni and Ti respectively. The compositional profile across the joint region is shown in Fig. 3. This analysis showed that a 1:1 ratio of NiTi phase was obtained within a zone of approximately 9μm width.

Table 1: Quantitative compositional analysis of the distinguished phases, see fig. 2

Zones	Ni (%)	Ti (%)	Ni:Ti (~ ratios)
A	96-99	0.0-0.5	1:0
B	75	24	3:1
C	50-53	46-50	1:1
D	35	64	1:2
E	4-7	93-97	0:1

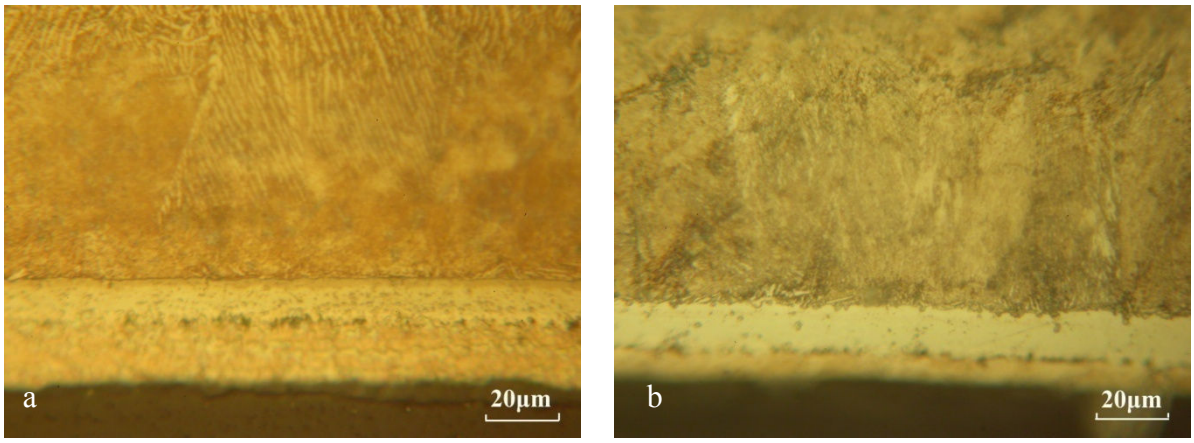

Fig. 1: Optical micrograph showing the cross-section of the bonded joint (a,b) bonded at different conditions

From the XRD analysis (see Fig. 4), it was revealed that the bonded structure was mainly NiTi along with the major phase of pure Ni. The peaks from the minor phases i.e. Ni_3Ti, Ti_2Ni and Ti were also observed. The peaks corresponding to the minor phase, Ti_2Ni were difficult to identify as some of the peaks lie in the range 2θ=40-47°. However, this phase was identified from a careful study of the other available peaks. The detection of this minor phase in the XRD spectrum supported the quantitative WDS analysis given in table 1.

The differential scanning calorimetry (DSC) trace for the diffusion bonded Ni-Ti sample is shown in Fig. 5. During the heating stage, one broad endothermic peak at 79°C and two sharp endothermic peaks at approximately 86°C and 98°C were observed. There were also a few more other minor peaks which probably correspond to some endothermic phase transformations/precipitations.

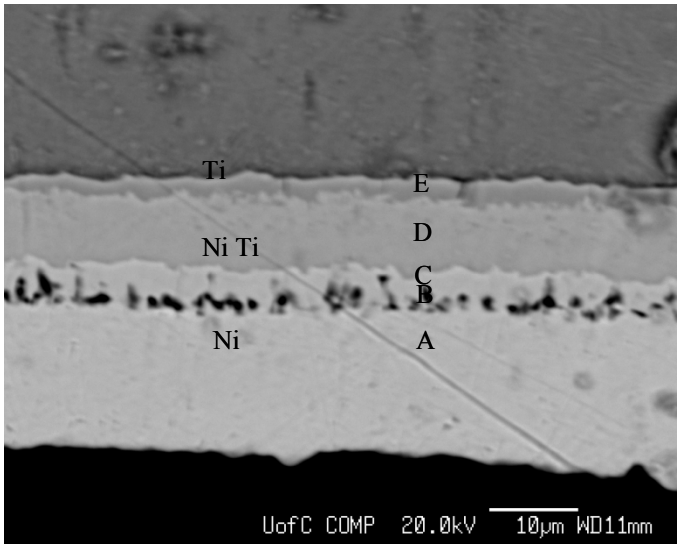

Fig. 2 SEM micrograph illustrating the formation of distinct phases of Ti-Ni SMA with near equivalent composition

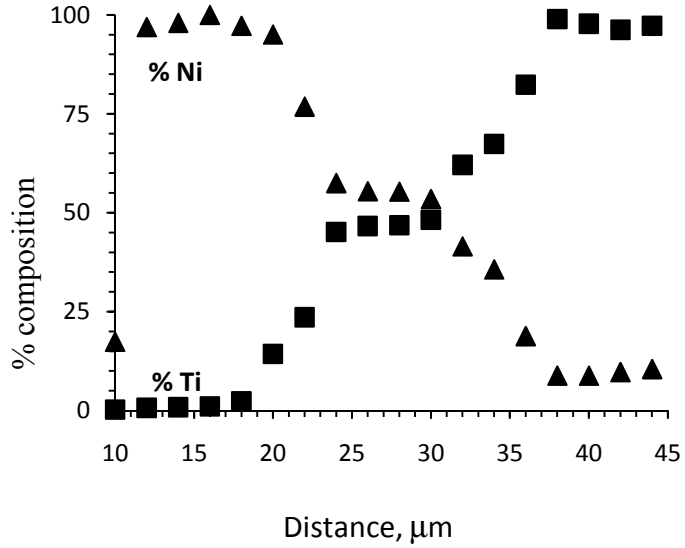

Fig. 3 Compositional line spectrum showing the Ni rich nearly equi-atomic composition in the diffused region of ~ 8-9 µm.

During cooling these peaks shifted to lower temperatures. One broad exothermic peak at 47°C and two sharp peaks at about 57°C and 82°C were observed. Other smaller peaks corresponding to exothermic precipitations were also visible in the range of 110-125°C temperature.

Both Ni and Ti rich precipitates/phases may affect the martensitic transformation temperatures in the Ni-Ti SMA. Therefore, a number of peaks obtained in the DSC trace for the martensitic transformations were increased and these Ni/Ti rich precipitates/phases could be responsible for the multiple transformation steps. The Ms temperature would also be affected by a change in Ni content, i.e. Ms temperature decreases with an increase in Ni content. J. Khalil-Allafi [19] had also shown that peaks for DSC trace regarding martensitic transformations could be complex with the formation of Ni rich precipitates.

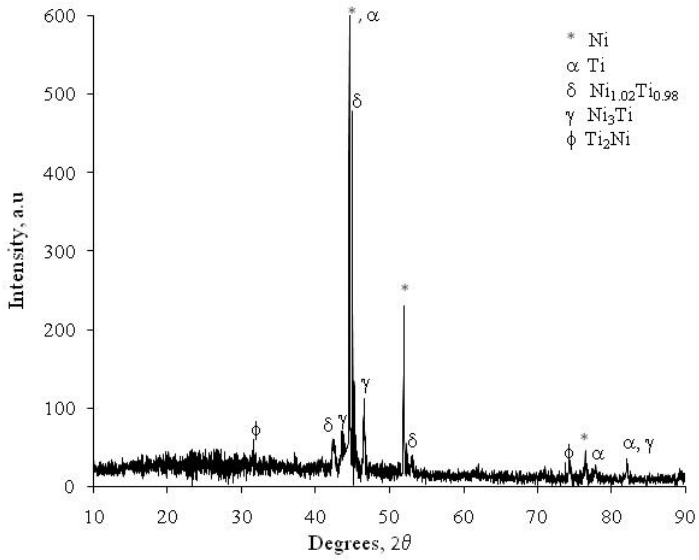

Fig. 4 XRD Spectrum illustrating the formation of NiTi phase along other phases formed during Ni and Ti diffusion bonding

Upon heating, the austenite phase (cubic) transformation from martensite/R phase started at 62°C, with a peak at 79°C and finished at 88°C. Upon Cooling, the R/martensite-phase transformation from austenite started at 61°C, with a peak at 47°C and finished at 39°C. This indicated that the R/martenisitic phase was dominant at room temperature and austenite at higher temperature (>90°C), see fig. 5. The hysteresis for the R-martensitic/austenite (B2) transformations was about 50°C.

The transformation temperatures in the sputter deposited films were reported to be below zero by E. Wibowo [5] in Ni rich Ni-48.6at%Ti. It was reported that the excess of nickel in NiTi films can lower the transformation temperatures to below the room temperature. J.D. Busch [11] also stated that transformation temperatures decrease by approximately 25°C per 0.2 at% Ni as the nickel content increases. However, S. Sanjabi [10] obtained martensitic transformation (R phase) from austenite in Ni rich $Ni_{51}Ti_{49}$ alloy at room temperature, with the transformation from R phase to martensite was reduced to below -50°C. N. Frantz [20] also demonstrated that transformation temperatures above room temperature could be obtained in Ni rich NiTi films. Similarly, the transformation temperatures for R phase martensite and austenite in this study were not far from room temperature and well within the temperature range of human body. Therefore, NiTi films produced by diffusion bonding have the potential to fabricate SMA for medical devices. The lower temperature for martensitic transformation from R phase could not be revealed due to the limitation of the DSC equipment. The DSC working temperature range was from 25°C to 650°C. Therefore, further DSC measurements at sub-zero temperature will be necessary and this work is in progress.

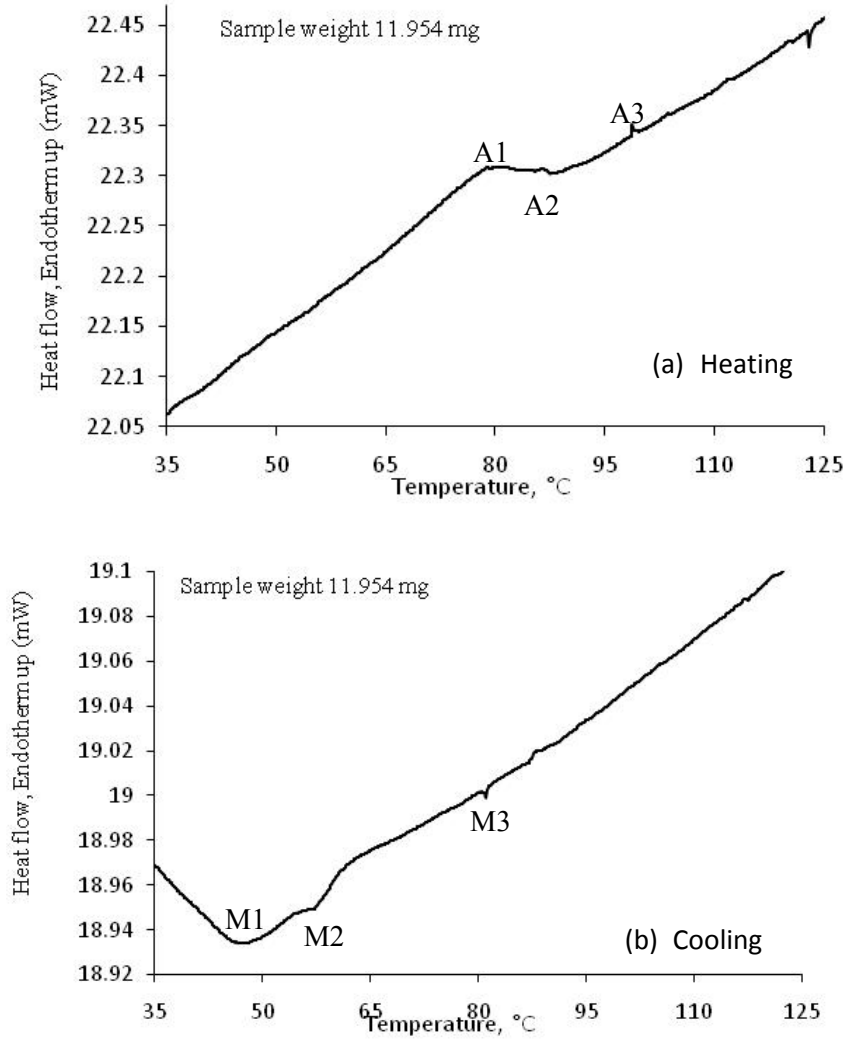

Fig. 5 DSC thermogram of a NiTi thin foil during: a) heating; b) cooling.

Conclusions

Diffusion Bonding was used as a method of fabricating a NiTi shape memory alloy. This alloy was successfully developed by the diffusion bonding technique. Optical and scanning electron microscopy equipped with wavelength dispersive spectroscopy confirmed the formation of TiNi phase along with Ni_3Ti and Ti_2Ni in the reaction layer. XRD analysis also confirmed the formation of Ni rich NiTi equiatomic phase. Differential scanning calorimetry (DSC) showed clearly that a martensitic transformation is seen when the alloy was heated and cooled. The transformation temperature was within the room temperature range, depicting the suitability of this alloy for use in smart medical devices.

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