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# Prospects of using powder metallurgical method to produce Nitinol shape memory dental implant

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## Abstract

This study tried to fabricate a new type of shape memory dental implant for implantation in bone socket as a tooth root replacement and using its shape memory effect to give the implant the ability of self-fixation. Specimens were fabricated via powder metallurgical method and elemental powder sintering technic. The produced specimens consist of mere Shape memory NiTi intermetallic with fewer amounts of other undesirable components such as $Ni_3Ti$ and $Ti_2Ni$. Shape, size and percentage of the pores were adjusted by addition of urea as space holder to make them suitable for bone ingrowth application. Porosity percentage and Pore mean size were %30 and 100 µm respectively in the specimens produced without space holder whereas these values reaches to %70 and 400 µm for the samples produced by space holder technic. Also addition of space holder converted the pores type from closed pores to interconnected one. Aging heat treatment is applied to adjust the austenite and martensite transformation temperatures to arouse at body tissue. As, $A_p$ and $A_f$ temperature were obtained equal with 25.11, 37.5 and 49.77oC respectively. Practical and mechanical tests results show the strain recovery of %2 after deformation and subsequent rising of temperature (superelasticity) as well as the excellent shape memory effect of the specimen.

**Keywords: Shape memory dental implant, porous Nitinol, powder metallurgy**

## Introduction

Porous NiTi alloy has attracted much interest as capable biomaterials for using in biomedical applications due to the combination of unique properties such as superelasticity and shape memory effect. Acceptable biocompatibility, good corrosion resistance and promising osteointegration potential reported specially for porous NiTi alloy [1, 2]. Porous NiTi with unique combination of mechanical and chemical properties, shows promising potential for bone implantation and in which a highly convoluted tissue can growth and secure within the porosity [1]. Because of these properties, the alloy has attracted a lot of attention as a biomaterial for medical application in orthodontic wire, orthopedic devices, guide wires, stents, filters and etc. [1-3].

One of the big challenges in the modern dentistry is the conservation of teeth in severe periodontal diseases which could not be saved by conventional treatment method [3]. The conventional titanium dental implants are difficult to be implemented surgically, especially in cases that bone tissue deficit is occurred. A dental implant is the portion that is implanted into the dental socket and then prostheses runs on it [4]. In the case of conventional titanium screw implants, however, need of long time for implant fixation prolongs the treatment period and consequently causes excluding of jawbone from functional loading [5]. This is due to this fact that conventional screw implants are implanted in two stages and four to six month are required at least, for jaw bone to integrate with the implants. This results in atrophy and weakening of jawbone. Moreover, weak initial fixation which is provided by only 5 mm immersion of the screw into alveolar, as well as the small displacement of implant in bone socket prevent the bone formation and reduce its strength [5]. Development of non-removable implant prosthetics is hence, an urgent need of dentistry in these days. In addition to reduction the treatment period, immediate implantation also prevents atrophy of the jawbone after removal of a tooth [5].

Recently new generation of dental implants with unique properties of NiTi shape memory alloy is introduced in few studies. [4] These dental implants provide high biological inactivity, shape memory effect and hyperelasticity similar to hysteresis of biological tissues as well as single stage immediate implantation [5]. Kotenko and et al [5] have recently introduced a new superelastic NiTi dental implant which is inactive in the biological environments. These implants provided a basis for artificial supports of non-removable prostheses by a short completion time (within 1 month) with 100% success. In another study Afonia and coworkers [3] studied the results of clinical treatment of severe periodontal diseases by application of the new nanostructured shape memory dental implants. One type of these implants is trans radix implant which is used to enforce teeth and attach it to the jaw bone. By application of these implants the conservation of those teeth which were recommended for deleting by conventional treatment methods became possible. There are a few reports concerning the NiTi shape memory dental implants in the literature and the above mentioned researches have done simultaneous with percent work. More studies, therefore, is necessary to optimize the fabrication methods and develop these types of implants. Moreover, the above mentioned dental implants are fabricated by the milling method which is very expensive way in the case of nitinol alloy. Application of powder metallurgy method could hence, be a good approach to produce near net shape parts. In addition to facilitate the production process, powder metallurgy method could produce porous structure which is suitable for biomedical application. Similarity of Young's Modulus of porous NiTi to bone tissue, arousing the bone formation, appropriate distribution of stress and prevention of stress shielding are the brilliant aspects of porous NiTi in comparison by dense NiTi [6]. Furthermore ingrowth of body tissue to open pores structure could bring better fixation of the implants in body tissue and its excellent biological stability in the jawbone. [1, 7-9].

The aim of the present study, therefore, is to fabricate a new shape memory NiTi dental implant via powder metallurgy method which could reduce the production steps. Then aging heat treatment is applied to adjust its shape memory effect to arouse at body temperature to give the implant the ability of quick self-fixation after implantation in bone socket. Also by using the space holder agent, size and percentage of the porosity is controlled to be useful for biomedical application.

## Materials and methods

### Designing and fabrication of the powder metallurgy die

First of all shape and size of the specimen is designed by solid work software. As it can be seen in Fig. 1 the desired shape for implant is designed as dual-radical. First die is fabricated in two pieces. But due to the asymmetric and complicated shape, and its small dimension's, the two pieces die couldn't be able to produce green samples. Because powder accumulation prevents the lower parts to be compacted. The other three pieces die thus, is fabricated to resolve the problem (Fig. 2). In this die, pressure is applied vertically and all parts of the specimen are compacted uniformly. The dies were fabricated by the spark and wire cut system.

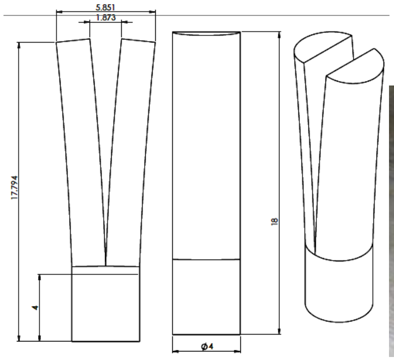


Fig.1- Schematic design of the implant

Fig.2- Three pieces powder metallurgy die made from2714 steel

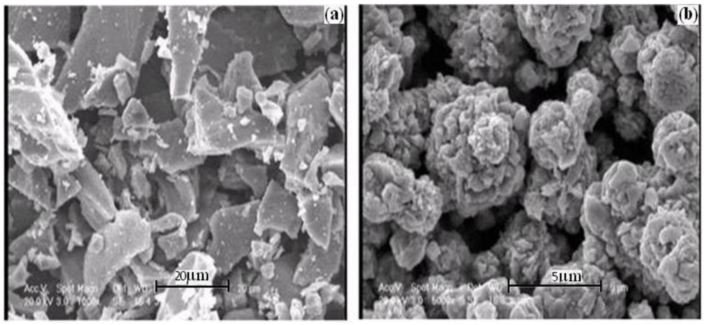


Fig.3- SEM morphology of raw: (a) TiH2 and (b) Ni powders.

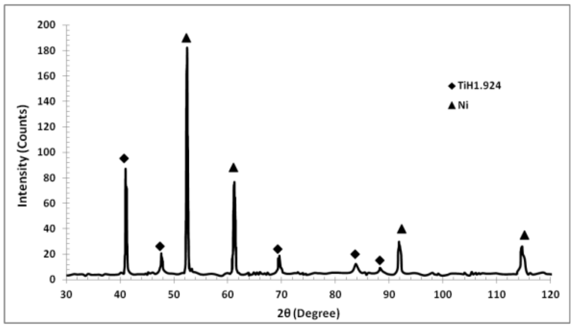


Fig.4. XRD pattern of the Ni-Ti powder mixture

## Initial powder characterization

Mixtures of nickel powder (99.9% purity, Merck, GmbH) with an average particle size of ~10 µm and titanium hydride (99.99% purity, Alfa Easar) having average particle size of ~50 µm were used to fabricate porous NiTi specimens. Fig. 3 shows the morphology of the initial powders. Ni particles were almost spherical while Ti powder had an irregular shape. X-ray diffraction pattern of the powders mixture also, is presented in fig. 4.

## Green samples compaction

The powders were mixed together with the atomic ratio of 50-50 by the vibration machine and then pressed up to 500 MPa by uniaxial hydraulic press to green compacts. The Urea powders with particle size of about 400-500 µm were mixed with some Ni-Ti powders as a space holder to produce samples with high porosity (desired percentage of the porosity was 70%) and large pore size (100-500 µm). In these samples at first the required Ni and Ti powders are weighted and then the urea powders with the volume ratio of the 70% were added and finally mixing process is carried out up to 30 min.

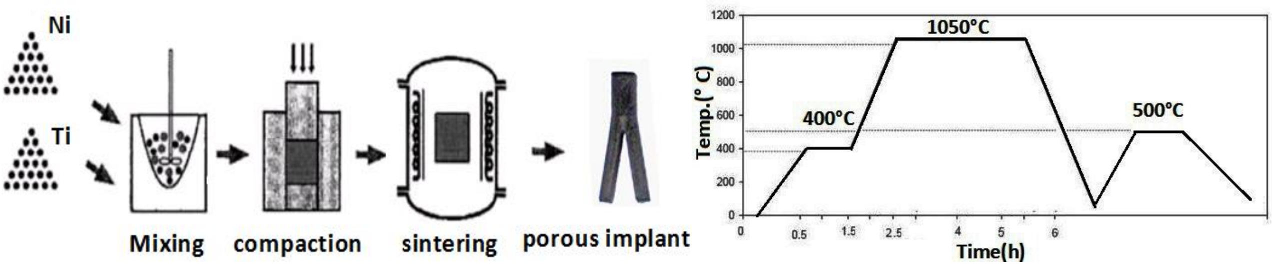


Fig.5. a) schematic illustration of the production process, b) sintering and heat treatment plan

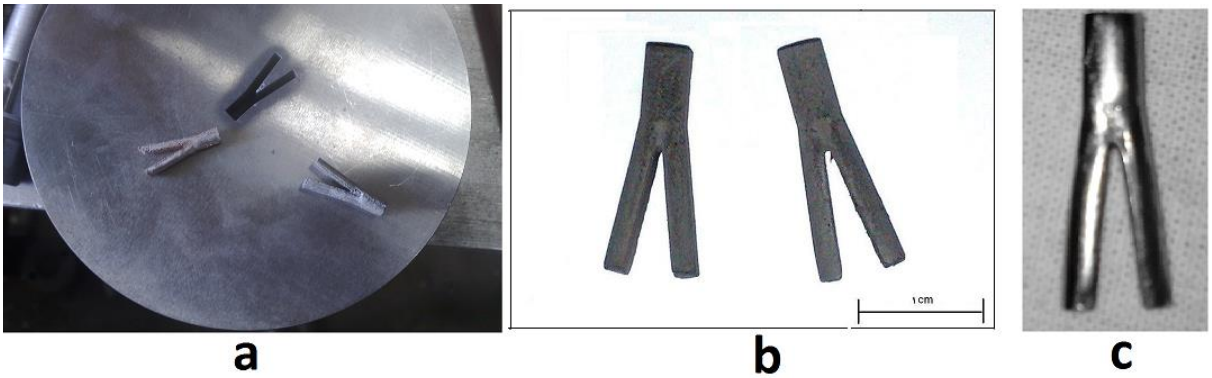


Fig. 6 a) green sample, b) sintered sample, c) heat treated and polished sample

**Sintering process**

Elemental powder sintering technique is used to fabricate porous NiTi specimens. Alloying process in fact, is occurred by diffusion of two elements in each other in this case. Fig. 5-shows a schematic of production process for the specimens. Because of the alloy sensitivity to even small amount of any impurity, sintering process was carried out at 1050°C for 3h in a high vacuum furnace. Regarding the presence of hydrogen in the powder composition, samples were kept at 400°C for 1 h to allow hydride powder to be decomposed (fig. 5-b). Also heat treatment of the sintered samples was performed to improve shape memory effect. Heat treatment is carried out at 500°C for 1 h under an argon atmosphere followed by furnace cooling. Fig. 6 a, b, c shows the green sample, sintered sample and heat treated polished sample respectively.

**Characterization**

A Philips X-ray diffractometer using Cu Kα radiation (k = 1.54056 A °) is applied to characterize the phase composition. The morphology of the powders and microstructure of the sintered samples were examined using a LEO scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) unit as well as an optical microscope. To achieve a more polished surface polishing operations beginning with alumina powder and finally with diamond paste lasted until completely smooth surface is created. Samples were etched in the etchant solution of H2O -%75HNO3 -%10HF%10. Differential scanning calorimetry (DSC, DSC 1 Mettler-Toledom, Switzerland) is used to determine the transformation temperature of porous samples. The test is carried out using a heating rate of 10 °C /min between the temperatures of -50 and 100 °C under an argon atmosphere.

## Results and discussion

### Structures and phase composition

Fig. 7 shows x-ray diffraction pattern of the specimen sintered at 1050°C for 2 h. As can be seen the specimen structure completely consists of B2-NiTi phase and no elemental nickel and titanium compounds were detected in the spectrum. This is important, because formation of undesirable

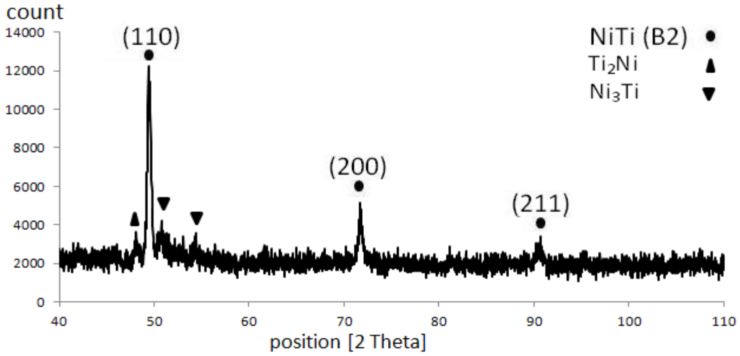


Fig.7. XRD patterns of Ni50 Ti50 mixed powder sintered at 1050°C for 3h

non-equiatomic compounds such as $Ni_3Ti$ and $Ti_2Ni$ have always been a challenge in production of shape memory NiTi parts [10-12]. This is due to this fact that the formation of above mentioned undesirable compounds is thermodynamically preferable [10-13]. Existences of these compounds deteriorate shape memory effect of the sintered samples. Non-existence of elemental Ni and Ti confirmed that they have diffused at sintering temperature and provided a homogenous NiTi. Regarding the high sintering temperature, formation of NiTi intermetallic is accelerated due to the liquid phase sintering. According to the Ni-Ti binary phase diagram, a eutectic phase with composition of 22.4 weight percent of Ni at 942°C will be formed. Since the sintering process is performed at 1050°C, partial liquid phase sintering is occurred. High purity of the powders and hydrogen content of the Ti particles also, improved formation of homogenous NiTi. Regarding this fact that Ti powders is produced under hydrogen atmosphere, there is some hydrogens in powders composition, especially in the surface layers. Hydrogen aggression from the powders particles before the sintering process facilitates formation of homogenous NiTi. Hydride powder is decomposed at 400°C during the sintering process according to the below reaction:

$$TiH_2 \xrightarrow{400\ ^{o}C} Ti + H_{2\,(g)} \qquad (1)$$

By decomposition of $TiH_2$ and Hydrogen aggression, a new surface appears on the particles. This new and active surface will accelerate atomic diffusion and sintering process. Consequently reactions completion time and sintering duration decreases substantially. In fact high purity of the powders and non-existence of the undesirable phases such as oxide phases favors formation of the NiTi intermetallic.

## Samples porosity

Fig. 8 shows the shape, size and percentage of the porosity for both of the samples produced without the space holder and with 70% vol. urea as a space holder. Porosity Percentage of the specimen produced without the space holder is relatively low by about the 30%. Pore mean size is also below the 100μm for this specimen. Shape of the pores moreover, is circular and there are little angular pores. This type of pores is desirable for the parts produced by powder metallurgy

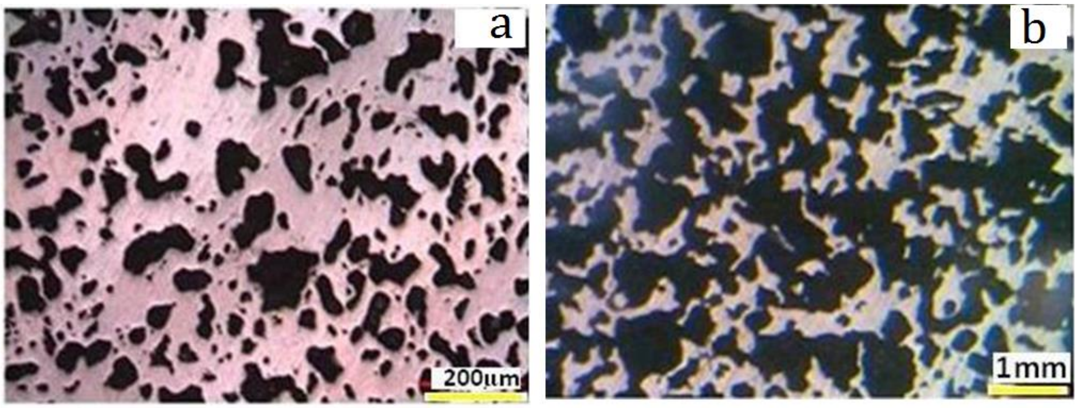


Fig.8. shape, size and distribution of pores a) without space holder and b) with 70% vol. urea space holder

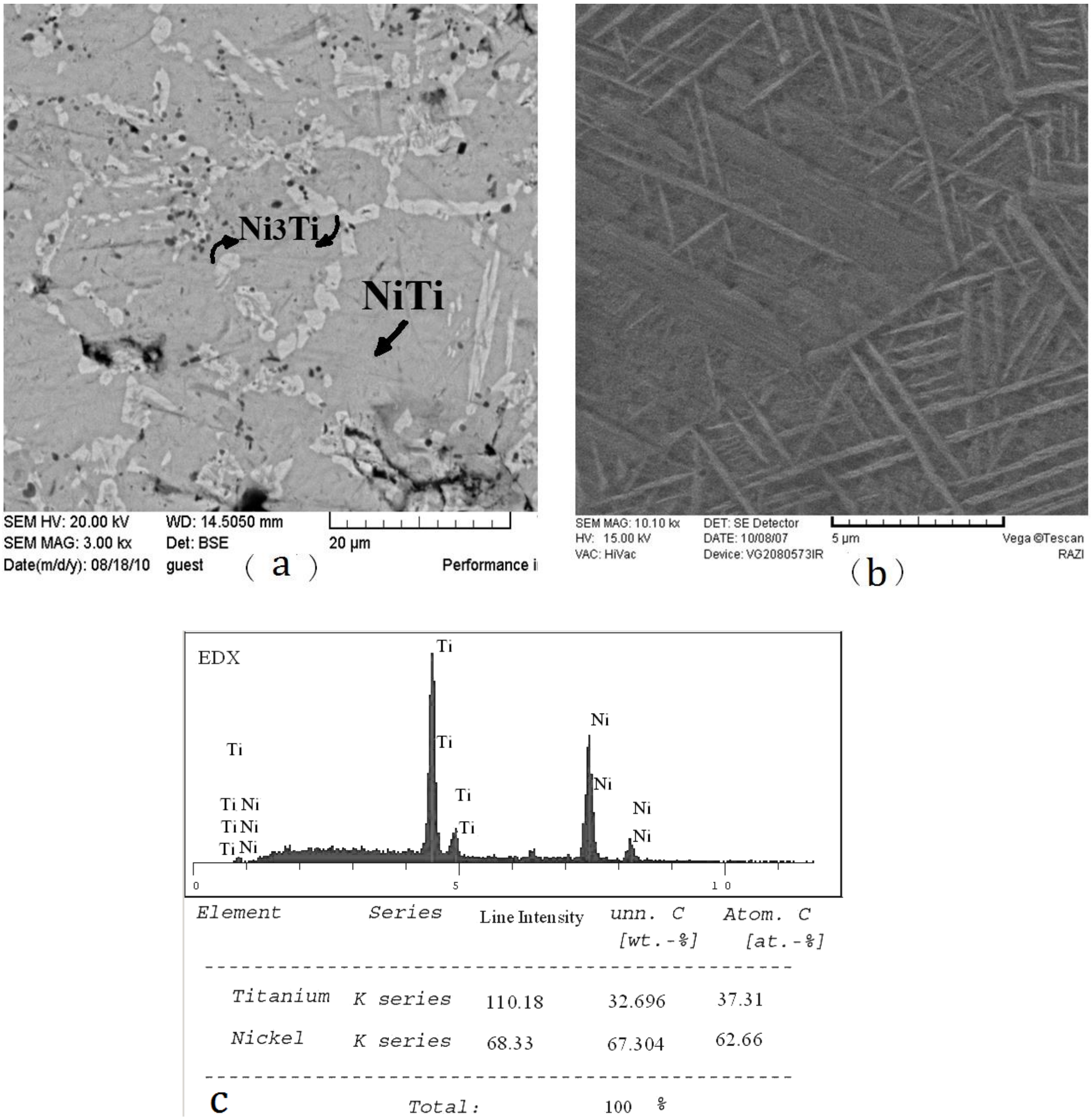
method, because elimination of sharp corners decreases the stress concentration which brings better mechanical properties likes' tensile strength. As it is clear the pores are closed that is due to their low percentage. Based on the researchers reports, open and interconnected pores with porosity percentage of higher than 60% is necessary for bone ingrowth and osteointegration [14-16]. As it can be seen in fig.7-b, addition of urea as space holder has reached the percentage of the porosity to about 70% and altered pores type from closed to open and interconnected one by mean pore size of about 400μm. Regarding this fact that suitable size for bone ingrowth is reported to be 100-500μm [9, 17], the samples produced by space holder agent are suitable for bone ingrowth application. Increasing the porosity percentage furthermore, could decrease yang's module and approach it to the yang's modules of bone tissue. Based on the previous researches results, the amount of yang's module for porous samples in the tensile state is obtained to be 19.8 Gpa which is very similar to yang's module of bone tissue (20 Gpa) [10].

## Microscopic investigations

Based on the XRD results, NiTi intermetallic which is necessary for appearance of the shape memory effect is formed in the specimens. A microscopic investigation is performed to observe phases formed during the sintering process. SEM micrograph of the sintered samples shows that the NiTi intermetallic is dominant phase which is appeared in the martensitic state so that the martensitic plates are easily distinguishable (fig. 9 a and b). This confirms XRD results truly. According to the DSC examination results (fig. 10) martensitic phase stability temperature is near to the room temperature so appearance of the martensitic phase is not unexpected. Moreover effect of the applied stress and strains during the sample preparation should not be neglected in this case. However metallographic investigation shows that the NiTi intermetallic is formed homogenously. Also there are some light phases around the NiTi phase in this figure which is precipitate in the grain boundaries. EDS analysis is performed to recognize this phases. Based on the EDS results (fig. 9 -c), these phases are the Ni rich compounds. Regarding this fact that there was a little amount of $Ni_3Ti$ in the XRD spectrum, these phases are attributed to the Ni rich component of $Ni_3Ti$. Deviation of the alloy composition towards Ni could be described by the hydrogen content of the titanium powders. Extra Ni is precipitated as a Ni rich phases during the cooling in the furnace and aging process.

## Transformation temperatures

Austenite and martensite transformation temperatures are very important parameters for a shape memory part which is due to work in the body tissues. Because the shape memory effect in this



| Element | Series | Line Intensity | unn. C [wt.-%] | Atom. C [at.-%] |
|---|---|---|---|---|
| Titanium | K series | 110.18 | 32.696 | 37.31 |
| Nickel | K series | 68.33 | 67.304 | 62.66 |

Total: 100 %

Fig.9. SEM micrographs of the specimen after aging: a) Martensitic structure and precipitates in the grain boundaries, b) martensite needles in the higher magnification, c) EDS Analysis on the bright grain boundary precipitates

alloy originates from the reversible austenite to martensite transformation and vice versa. In fact some strains which induced to specimen in the martensitic state are recovered and restore initial shape of the specimen during heating and second formation of Austenite phase. Austenite and martensite transformation temperatures therefore, play the main role in determination of shape memory parts efficiency. Based on DSC examination results illustrated in fig.10, transformation temperatures obtained for the implant is desirable for implantation in body tissues. Austenite start ($A_s$), peak ($A_p$) and finish ($A_f$) temperatures are obtained to be 25.11 $^{o}$C, 37.5 $^{o}$C and 49.77 $^{o}$C respectively. martensite start ($M_s$), peak ($M_p$) and finish ($M_f$) temperatures also, are obtained to be 9.68°C, 3°C and -22.69°C respectively. This shows that by cooling the specimen to temperature below -22.69$^{o}$C (Af) fully martensitic structure will be formed in the sample. In the martensitic state the sample is very flexible and easily bent, so it could be deformed to desired shape. Considering that the body temperature is equal to 37 $^{o}$C this results are very suitable, because the implant restores its initial shape after preliminary deformation at temperature below -22.69$^{o}$C (Af) and subsequent heating in body tissue.

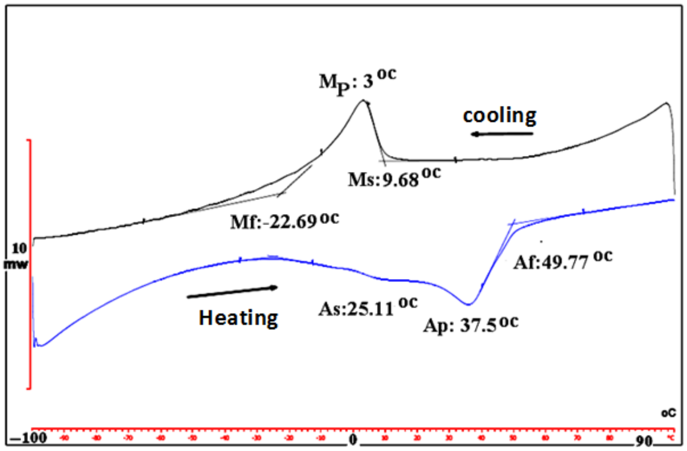


Fig.10. DSC curve of the sintered and aged specimen during heating and cooling

## Shape memory examination

From the DSC examination results, it is easy to detect that the shape memory effect and in fact austenite to martensite transformation will be occurred in the specimen. Practical shape memory examination hence, is performed for the specimen. The specimen is cooled by immersion into the liquid nitrogen to temperature below -22.69 oC and its radicals are brought together. The implant therefore, attains a shape convenient for insertion into the bone socket (Fig. 11-b). So it could be implanted into the previously treated and prepared bone socket. By placement of the implant in body temperature and occurrence of the martensitic transformation, the specimen recovers the

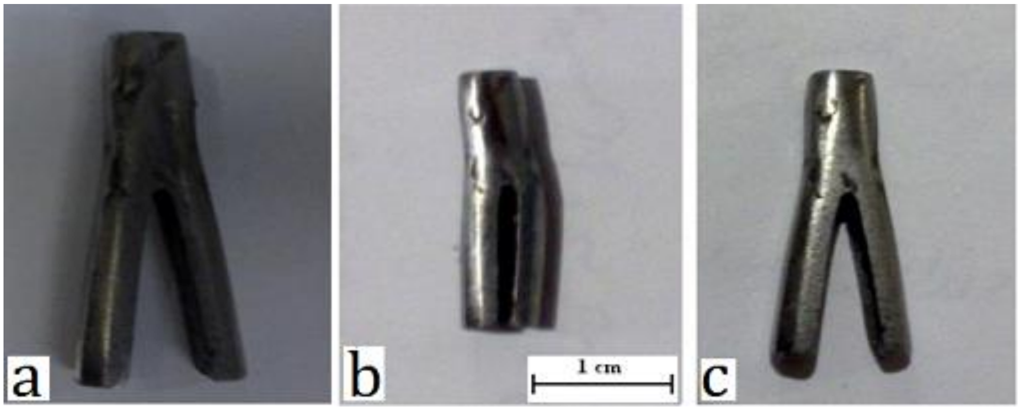


Fig. 11. specimen: a) in the austenite state and before deformation b) in the martensite state and after deformation c) after restoring initial shape and second formation of austenite structure

strains and restores its initial shape. By provided deformation the implant radicals are pushed into bone tissue and provides strong fixation of the implant into the bone. In the in vitro examination the specimen placed on a heater after immersion in the liquid nitrogen and bending the radicals together. As we expected the specimen became very flexible and easily bend after immersion into liquid nitrogen and occurrence of the martensitic transformation. Fig. 11 (a) and (b) show the specimen before bending in the austenite state and after bending in the martensite state respectively. As can be seen in fig. 10 (c) By rising the sample temperature its initial shape is restored. Based on the DSC examination results shape memory transformation is occurred in temperature ranges of 25-49 °C particularly at 37°C (Ap). Regarding kind of the applied stress, bending test is performed on the specimen to investigate its shape memory effect. Force-deflection curve of the specimen under bending stress is shown in fig. 12. In the austenite state a deformation of 2 mm is applied on the specimen that nearly all of this strain is recovered. This show the excellent superelasticity of the specimen which could develop damping property of the implant during functional loading in the jawbone. As it is obvious 110 N is needed to induce a

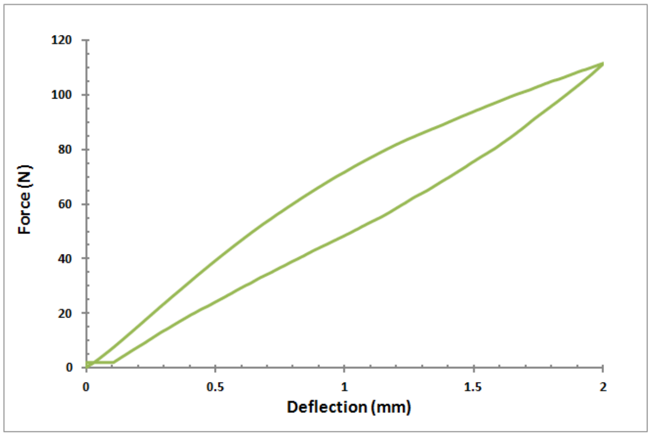


Fig.12. Force - deflection curve of the specimen under bending stress

deformation of 2 mm. investigation of the shape memory parts behavior show that the amount of recovered strain is similar in both of the superelastic and thermoelastic samples. So it could be stated that by recovering of the strains and formation of the austenite phase the same amount of load (110N) is applied to the surrounding tissue. This amount of load can help the implant to stabilize in the bone socket for the first time and after this self-fixation good superelasticity of the specimen will be useful for damping the stresses during functional loading.

## Conclusion:

In this research, Shape memory tooth implant for implantation in bone socket is fabricated from the NiTi alloy by powder metallurgical method. Application of powder metallurgical method provides single stage near net shape fabricating of the specimen. Shape memory specimen is produced successfully by elemental sintering of the mixed powders. Based on the XRD examination results the specimen structure almost consists of NiTi intermetallic and the amount of other undesirable compounds is very slight. According to the DSC examination, transformation temperatures of the specimen are very convenient to arousing in body temperature. Practical testing of the shape memory effect also, confirmed results of the XRD and DSC examination and the specimen showed good shape memory effect. Using the space holder agent has formed open and interconnected pores with mean pore size of about 400μm and porosity percentage of about 70% which is suitable for bone ingrowth and body fluid transition. According to the results of bending test a deformation of 2 mm could be recovered in this specimen. This amount of strain could be applied a load of 110N to the surrounding tissue which provides Strong stabilization of the implant in bone socket. Also superelasticity of the implant is very unique characteristics which could give excellent damping effect to the implant in the jawbone during functional loading.

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