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MANUFACTURING AND ANALYSIS OF A HEAT-ACTIVATED STAPLE USING TI-NI-CU SHAPE MEMORY ALLOY

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Abstract. *Nickel-Titanium (Ni-Ti) shape memory alloys (SMA), commercially known as NiTiNOL, have unique features like shape memory effect (SME) and superelasticity (SE), due to solid-solid phase transitions between two phases, austenite and martensite. Additionally, these SMA presents properties that allow its use for orthopedic applications. Recently, a new 47Ti-32Ni-21Cu (% at.) SMA was developed using the Artificial Intelligence Material Selection (AIMS) methodology. The unique features of this TiNiCu SMA include reduced thermal hysteresis and transformation temperature range, as well as excellent cyclic stability. In this work, the aim was to manufacture and analyze this TiNiCu SMA for possible application in heat-activated orthopedic staples. The 47Ti-32Ni-21Cu (% at.) SMA was manufactured using the electric arc melting process and prototypes of orthopedic staples were produced through a rapid investment casting process. The post-processing step was followed by thermal and mechanical characterization tests. The staple prototypes had a low phase transformation temperature range and thermal hysteresis, also presenting mechanical strength to opening cycles and the ability to generate compressive force. Finally, it was concluded that it is possible to manufacture orthopedic staples with low thermal hysteresis from a 47Ti-32Ni-21Cu (% at.) SMA by rapid investment casting.*

Keywords: *Shape memory alloys, Ti-Ni-Cu alloys, orthopedic staples, investment casting.*

1. INTRODUCTION

Shape memory alloys (SMA) are materials that can be deformed and recover their shape by increasing the temperature. The possibility of recovery even under high mechanical loads and the capacity to absorb and dissipate mechanical energy, make the SMA widely used as sensors and actuators, for the impact absorption and damping of vibrations (Lagoudas, 2008).

The material thermal recovery occurs due to solid-solid phase transitions between two phases, through distortions in the crystalline lattice caused by shear. Therefore, SMA presents a martensitic phase at low temperatures that cause the emergence of the shape memory effect (SME), while the austenitic phase appears at high temperatures, allowing the superelasticity (SE) phenomenon. The SME is the ability of the material to be plastically deformed due the load application and to recover its original shape with the increase of temperature above the transformation temperature. The SE is the ability to be elastically deformed and recover its shape when the stimuli cease, without the need for temperature variation.

In general, the martensitic phase has a monoclinic crystalline structure (*B19′*), while the austenitic phase has a body-centered cubic structure (*B2*). Some Ni-Ti alloys also have an intermediate trigonal phase, called R-phase. The forward transformation ($B2 \rightarrow B19'$) occurs when the material cools down, with the start and end phase transformation temperatures called initial (M_s) and final (M_f) martensitic temperatures. If the transformation occurs in two steps ($B2 \rightarrow R \rightarrow B19'$), the characteristic temperatures of the R-phase are known as Rs and R_f. In the reverse process, in which the SMA is heated ($B19' \rightarrow B2$) or ($R+B19' \rightarrow B2$), it presents the initial (A_s) and final (A_f) austenitic temperatures (Lagoudas, 2008; Otsuka & Wayman, 1998).

According to Mahtabi et al. (2015), Ni-Ti SMA have unique characteristics such as excellent shape memory effect and superelasticity, associated with corrosion resistance and an unusual combination between mechanical strength and biocompatibility. Thus, these characteristics make Ni-Ti SMA widely used in the biomedical field (Duerig et al., 1999). In addition, the modulus of elasticity and the energy dissipation capacity of Ni-Ti SMA are close to those of hard tissues, such as bones and tendons (Morgan, 2004).

Orthopedic Ni-Ti compression staples are mainly used in the treatment of fractures, osteotomies, and arthrodesis of bones and tendons (Safranski et al., 2020). However, Ni-Ti SMA implants are usually stiffer than human bones, causing much of the mechanical load to be transferred to the bone through the implant. This can cause problems such as adaptive proximal bone remodeling, which results in slow healing, reduced bone density and stress concentration at the implant site (Aihara et al., 2019; Andani et al., 2016).

As a result, the SMA Ni-Ti concept for porous staples enables it to adjust different stiffness values to be closest to the specific bone location. Furthermore, the porous structures implants help the adhesion, allowing growth and integration of bone cells in the host tissue, and improving the exchange of body fluids (Yuan et al., 2018).

Ni-Ti SMA staples can be classified into three categories: room temperature superelastic (SE), body temperature activated (BT) and heat-activated (HA). SE staples have A_f temperature near or less than room temperature, while BT staples have an A_f temperature below human body temperature but above room temperature. The HA staples have A_s temperature near or slightly above body temperature, but the A_f is low enough to avoid the excessive heat application during the implantation process (Russell, 2009). When compared to other types, heat-activated staples have advantages as adequate stiffness, resistance to permanent deformation, in addition to improved handling, as established by Rethnam et al. (2009).

Recently, Trehern et al. (2022) developed a Ti-Ni-Cu alloy using Artificial Intelligence Material Selection (AIMS) technique. The authors proposed a new SMA composition corresponding to 47Ti-32Ni-21Cu (% at), having an austenite start temperature (A_s) near body temperature and an A_f temperature above body temperature, revealing that it is a heat activated alloy. This SMA demonstrated a reduced temperature hysteresis and excellent cyclic stability. Furthermore, studies have revealed that Ti-Ni-Cu alloys present a non-toxicity feature and good in vitro biocompatibility, besides possessing antibacterial properties (Li et al., 2016).

Therefore, this study aims to manufacture and characterize a heat-activated "U" shape staple prototype using this novel 47Ti-32Ni-21Cu (% at) SMA.

2. EXPERIMENTAL PROCEDURES

The steps of the manufacturing process used in this study is summarized in the schema of Figure 1. The experimental methodology was divided into two main parts: manufacturing and characterization of Ti-Ni-Cu SMA staples. The prototypes were produced by a rapid investment casting process, followed by thermal and mechanical characterization.

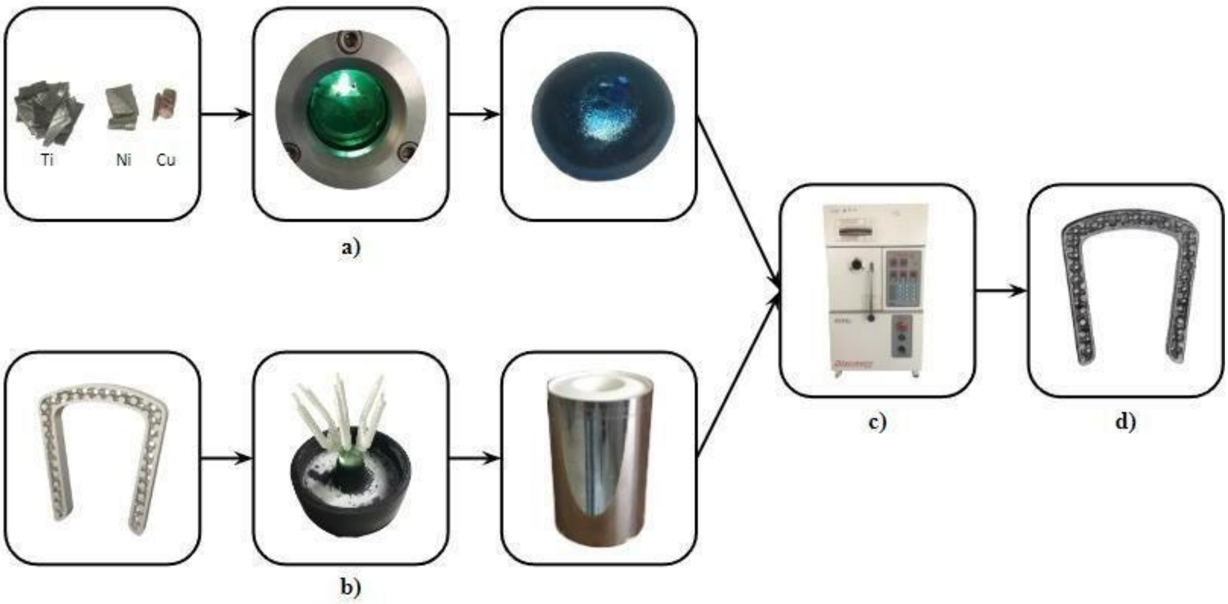

Figure 1. Ti-Ni-Cu staples steps manufacturing process. a) Ti-Ni-Cu alloy melting. b) Mold fabrication. c) Discovery all metals casting machine using the Plasma Skull Push Pull. d) TiNiCu SMA Staple.

2.1 Manufacturing of the Ti-Ni-Cu staples

The 47Ti-32Ni-21Cu (% at.) alloy, which corresponds to a 41,2Ti-34,4Ni-24,4Cu (% wt.) composition, was fabricated following the methodology validated by De Araújo et al. (2009). The pure metals Ti, Ni and Cu were cleaned in an ultrasonic bath, positioned on a copper crucible and covered by an argon atmosphere, to create an inert environment. A small bulk alloy with approximately 18 grams was produced by melting the pure metals through an electric arc rotation created by a non-consumable tungsten electrode. The bulk alloy was melted and re-melted four times with the goal to obtain a homogeneous alloy.

For the mold fabrication (Fig. 1b), a ceramic coating was used. Photosensitive resin staples and feed channels were manufactured using a three-dimensional (3D) resin printer. The porous orthopedic staples prototypes were modeled following the geometry and dimensions proposed by Silva (2023), as shown in Figure 2.

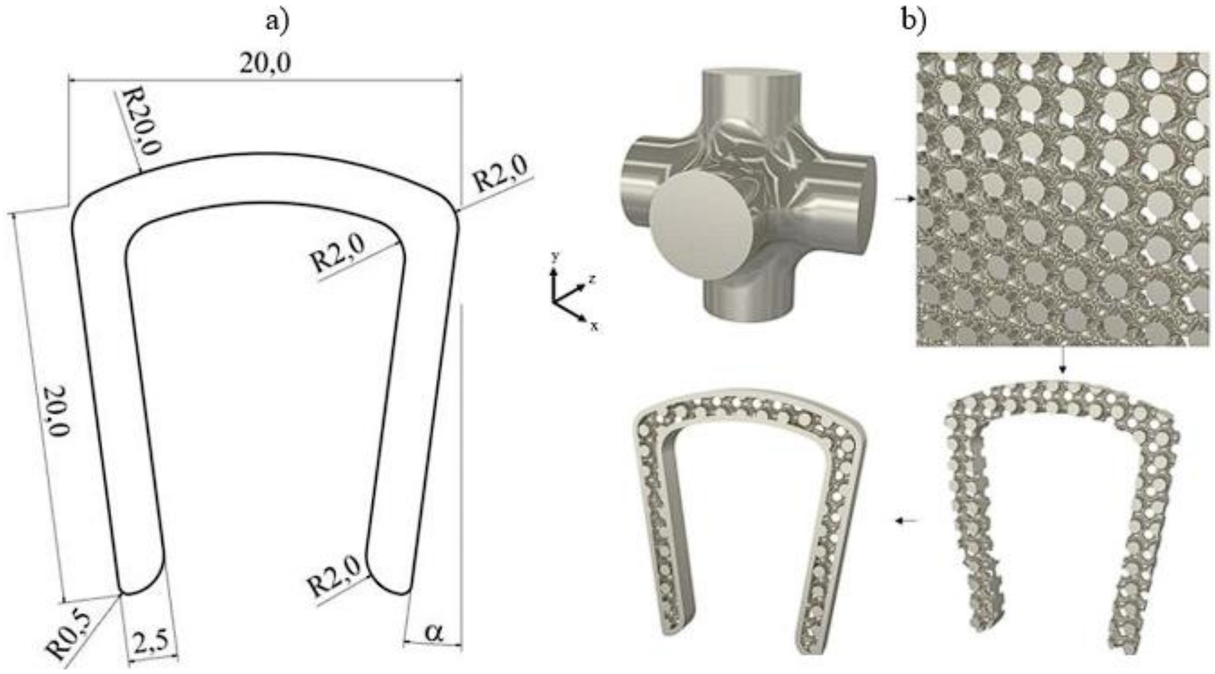

Figure 2. Porous Ti-Ni-Cu staple design. (a) Orthopedic staple front of view. (b) Modeling representation of the porous orthopedic staple using software CAD (Silva, 2023).

The 3D printed resin staple models were positioned on a plastic base in such a way that three staples could be produced by a single casting, as pointed out in Fig. 1(b). The mold was obtained by filling the ceramic coating (Micro Fit from Talmax Inc.) into the metallic ring with the resin staples. After the coating dried and cured, it was burnt in an electric furnace. For this, the temperature was increased at a rate of 30°C/min until 960 °C and it was held for 60 minutes, to evaporate the resin and supply the refractory material resistance and then cooled to 300 °C for casting.

With the Ti-Ni-Cu alloy and the mold, investment casting was performed by the Plasma Skull Push Pull (PSPP) method, using a Discovery All Metals casting machine from EDG Equipment's Inc. (Brazil). For this process, during melting the argon exerts a positive pressure pushing the liquid metal, while the vacuum exerts a negative pressure pulling the liquid metal. After that, the post-processing part began with the removal of staples from the mold, preceded by the removal of the feed channels. The coating excesses were eliminated by blasting with aluminum oxide. Then, the staples passed through a chemical cleaning using an acid solution composed of HNO3 – HF – H2O and washed in water. Finally, the staple was submitted to heat treatments of homogenization at 850 °C for 1 h and aging at 500 °C for 2 h, both under vacuum and naturally cooled at room temperature.

2.2 Characterization of the Ti-Ni-Cu SMA staples

The transformation temperatures of the Ti-Ni-Cu staple prototypes were determined by Differential Scanning Calorimetry (DSC) (model Q20 from TA Instruments). The temperature range was from −75 °C to 100 °C with a cooling/heating rate of 5 °C/min under a nitrogen atmosphere (ASTM F2004-17). The starting and final phase transformation temperatures were obtained by the tangent intersection method applied to the DSC peaks.

To investigate the mechanical behavior of the Ti-Ni-Cu SMA staples under different constant temperatures, quasi-static tensile tests combined with bending were performed on the staple's legs opening tests, in accordance with the technical specifications of the ASTM F564-17 standard. Therefore, the staples were submitted to loading-unloading cycles up to 5 mm of the crosshead at a displacement rate of 1 mm/min. Those isothermal tests were carried out at 30 °C, 37 °C and 60 °C temperatures. Beyond that, a force relaxation test was performed to measure the compressive force made by the staple under a constant displacement over time around body temperature (at 37 °C). All the tests were done using an electromechanical testing machine (model 5582 from INSTRON) equipped with a 5 kN load cell, thermal chamber and video extensometer with displacement control.

3. RESULTS AND DISCUSSION

3.1 Manufacture process

The Ti-Ni-Cu SMA staples produced by investment casting and submitted to surface treatments (aluminum oxide blasting and chemical cleaning) presented a satisfactory final aspect, as can be verified in Fig. 3. The porous staples showed no casting defects that compromised the product structure or caused some fragility. Therefore, the process was shown to be effective, and the staples could pass to thermal and mechanical characterization steps.

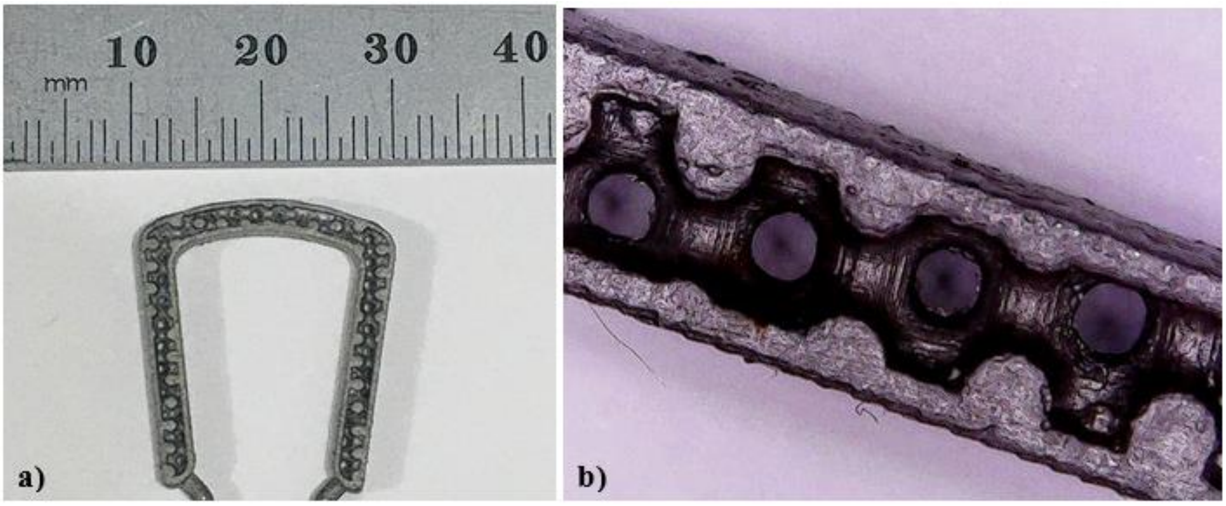

Figure 3. Ti-Ni-Cu orthopedic staple prototype. (a) Front view image (b) Close-up image of staple macro porosities.

3.2 Transformation temperatures

Figure 4 shows the DSC graphs of the Ti-Ni-Cu SMA staple in the as-cast and post heat treatment states. Therefore, under isothermal conditions of 30°C, the Ti-Ni-Cu SMA staple in the post heat treatment state will present shape memory effect behavior, with the start temperature of martensite phase transformation around 44.5 °C. Furthermore, it is possible to observe the shift to the right of the transformation temperatures after the heat treatments of homogenization followed by aging (post-heat treatment state), as well as an increase in the enthalpy of transformation, as shown in Table 1, presenting final temperatures of austenite phase transformation around 31.6 °C and 61.6 °C, respectively.

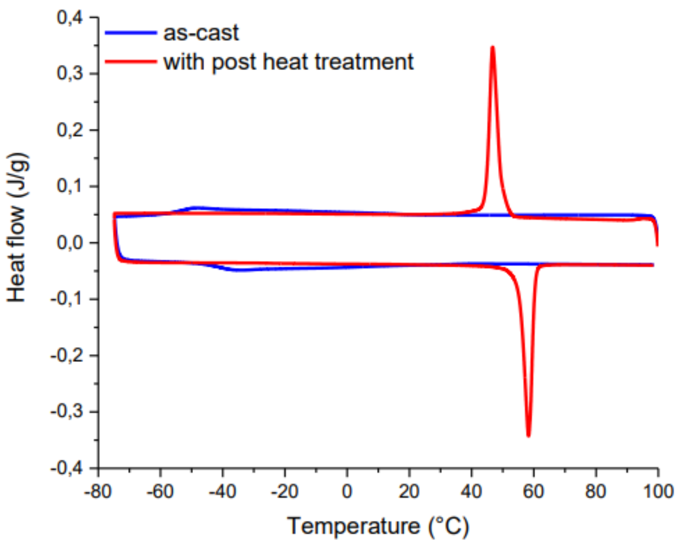

Figure 4. Thermal behavior characterized by DSC of the Ti-Ni-Cu SMA staple in the as-cast and post heat treatment states.

Table 1. Phase transformation temperatures, transformation temperature range, thermal hysteresis and enthalpy of transformation for the Ti-Ni-Cu SMA staple in the as-cast and post heat treatment states.

	As-cast	**Post heat treatment**
M_s (°C)	-9.9	49.9
M_f (°C)	-60.4	44.5
A_s (°C)	-48.4	55.3
A_f (°C)	31.4	60.4
Transformation temperature range (°C)	94.7	15.8
Thermal hysteresis (ºC)	41.2	10.5
Enthalpy of transformation – cooling (J/g)	7.7	13.0
Enthalpy of transformation – heating (J/g)	8.2	13.0

Furthermore, it was observed that after the heat treatments, there was a decrease in the thermal hysteresis and in the phase transformation temperature range. Thus, it can be concluded that the heat treatments applied were effective in stabilizing the transformation temperatures and eliminating the effects of the casting process (Montenegro et al., 2020).

3.3 Thermomechanical behavior

Figure 5 shows the quasi-static force vs. displacement behavior of the Ti-Ni-Cu SMA staple under isothermal temperatures conditions. This test was made to determine the compression force generated by the SMA staple under different temperatures. The orthopedic staple's ability to generate compressive force is important for immobilizing broken bones during the healing process.

Overall, an increase in the peak force and a decrease in the residual displacement are observed with increasing temperature. The increase in peak forces follows the Clausius–Clapeyron relationship. For the peak force at 30 °C and 60 °C, the values were approximately 40 N and 65 N, respectively. At 60 °C is usually considered the temperature that human body tissues can be damaged. Therefore, the heat activation temperature of the staples must be lower than this value (Russell, 2009).

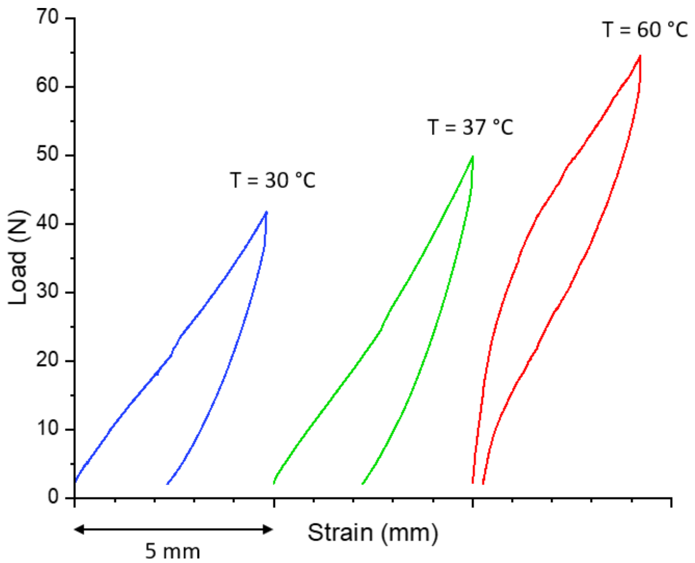

Figure 5. Force vs. displacement response of the Ti-Ni-Cu SMA staple for different constant temperatures.

3.4 Force relaxation

Stress relaxation describes the material's tendency to decrease its load generation when held under a constant strain or deflection (Anusavice et al., 2013). An orthopedic staple that exhibits rapid force relaxation may express a decreasing amount of compression force once inserted in the bone region. This effect likely will negatively impact bone healing. Thus, the force relaxation behavior was evaluated under a constant displacement at 37 °C for the Ti-Ni-Cu SMA staple in the post heat treatment state, as shown in Figure 6.

The SMA staple showed a peak force of approximately 50 N at the end of loading, equivalent to the maximum opening of the legs, stabilizing around 47 N after about 35 min, a reduction of approximately 6%. Thus, the staples can maintain a considerable compression force at human body temperature.

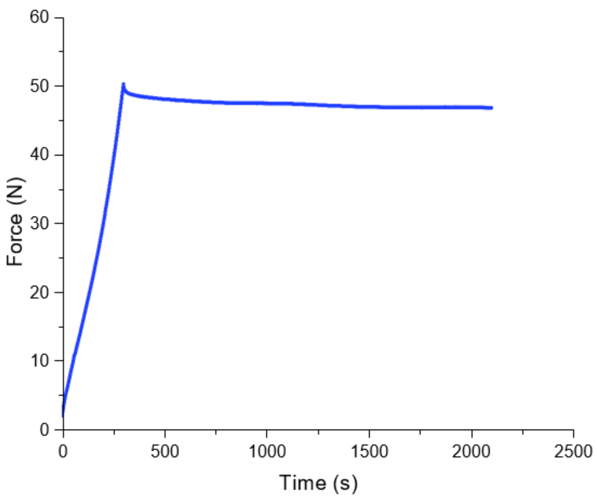

Figure 6. Force relaxation response over time for Ti-Ni-Cu SMA staple.

3.5 Orthopedic staple prototypes on a 3D printed foot

To illustrate the real-world application of heat activated Ti-Ni-Cu SMA staple prototypes, an artificial foot was 3D-printed in ABS using the Snapmaker A250 3D printer. The model used was the Full Size Anatomically Correct Human Foot Model, as described by Cults3D (2023). As shown in Figure 7, two staple prototypes were opened and installed in the Calcaneal/Cuboid Fision (I) and Talo/Navicular Fusion (II) regions, following Novastep's nomenclature (Novastep, 2023).

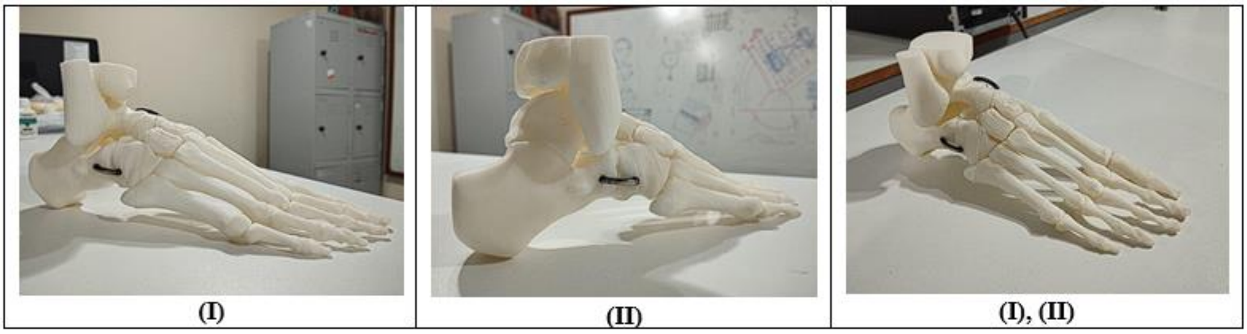

Figure 7. Ti-Ni-Cu staples installed on a 3D-printed Full Size Anatomically Correct Human Foot Model. (I) Calcaneal/Cuboid Fusion. (II) Talus/Navicular Fusion.

The installation of the staples on the model in Figure 7 was performed using a newly patented set of tools (Holanda et al., 2023), distinct from the one commonly employed at present (Novastep, 2023).

4. CONCLUSIONS

The rapid investment casting process proved to be effective for producing Ti-Ni-Cu orthopedic staple prototypes with good surface finish and mechanical strength. The Ti-Ni-Cu alloy presented phase transformation, mainly after the heat treatments employed. The heat treatments were responsible to stabilize the transformation temperatures and eliminate the casting process effect, resulting in a low phase transformation temperature range and thermal hysteresis.

The staples showed an A_s temperature above body temperature, but the A_f low enough to avoid overheating during the implantation process. Thus, the Ti-Ni-Cu staples can be used as heat-activated orthopedic implants. Through mechanical tests, Ti-Ni-Cu staples revealed the ability to produce and maintain compressive force at body temperature, indicating that it can be employed as orthopedic fastening, as demonstrated by the installation on a 3D-printed Full Size Anatomically Correct Human Foot Model.

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