Theme: Shape Memory Alloys

MELTING AND HEAT TREATMENT OF AN Ag HIGH-CONTENT NiTiAg SHAPE MEMORY ALLOY – A MICROSTRUCTURAL AND THERMAL VIEW*

Gilberto Álvares da Silva[1]
Jorge Otubo[2]

Abstract

New elements have been inserted in NiTi lately, resulting in ternary alloys with specific characteristics beyond Shape Memory Effect and Superelasticity. Among all others alloying elements, the Ag additions itself gives potential antibacterial activity to that smart material. So on, the elaboration procedures of ternary NiTiAg alloys was studied in order to obtain a melting procedure to ensure further studies on this alloy. Microstructural and thermal analyses were used to evaluate the VAR-remelting production of NiTiAg with 4.0% wt silver content. The microstructure is composed by a NiTi matrix, pure Ag precipitates, and, scarcely, TiC inclusions. Heat treatments at high temperature could not dilute those Ag particles, but could lead to the precipitation of new ones. The silver element reduces the temperature of the martensitic transformation, yielding a material with superelastic behavior, beyond induces the R-phase on cooling stage of this alloy.
Keywords: NiTiAg; VAR remelting; Heat treatment; Shape memory alloy.

[1] *Metallurgical Engineer, ITASMART, Instituto Tecnológico de Aeronáutica, São José dos Campos, São Paulo, Brasil.*
[2] *PhD in Mechanical Engineering, ITASMART, Instituto Tecnológico de Aeronáutica, São José dos Campos, São Paulo, Brasil.*

1 INTRODUCTION

The NiTi Shape Memory Alloys, first produced in 1960's [1], are known by two unique behaviors, thermally or mechanically activated: the shape memory effect (SME) and the superelastic effect (SE), respectively. The former ensures the recovery of the original shape by heating, even after large deformations, while the latter ensures the maintenance of a constant applied force in correspondence of significant displacements and its recovery; both owing to a peculiar crystallographic phase transformation.

With the shape recovery reaching 8%, transformation temperatures ranging from -50°C to 110°C, in addition to mechanical properties comparable to those of engineering materials, the NiTi shape memory alloys still presents biocompatibility [2] and some other features, being, therefore, the most used, studied and economic important shape memory alloy ever made.

Chemically, the NiTi is an intermetallic compound, near-equiatomic in composition, with low solubility, if any, of both forming-elements. Carbon and oxygen are accounted as impurities, so generally unwanted, as well as for the hydrogen. Alloying elements have been added intentionally to control others functional properties besides SME and SE, towards attain new applications. Those NiTi-based ternary systems result in solid solutions, intermetallic compounds and elementary precipitates [3].

The primary objectives of these alloying additions have been to increase austenite strength, increase creep resistance, increase/decrease hysteresis and transformations temperatures, increase corrosion resistance and radiopacity. The advantages gained by deliberately adding ternary elements to accomplish that goals are generally offset by losses in other properties or by intolerable increase in cost [4]. Still, applications exist that can only be serviced by ternary alloys.

Despite the broad-spectrum antibacterial effect of silver element is well known [5,6], until the last ten years it was not thought as a possible introduction to NiTi to give an antibacterial functional to that smart material. Back in 1991, silver has already been introduced in NiTi in studies about the feasibility to produce such alloy via Electron Beam Melting technique [7]. With the aid to provide antibacterial effects, silver was firstly introduced in NiTi system in 2006, when additions were only about 0.2 weight percent [8]. New investigations were made five years later [9], with Ag content of 2.8 weight percent. Those earlier studies find that NiTiAg has higher strength than NiTi, similar corrosion resistance and cyto-biocompatibility with NiTi alloys; moreover, exhibits reduced bacteria adhesion [8,9]. Oh et al. [8] and Zheng et al. [9] used VAR-remelting technique to produce its own ingots, and reported difficulties in melting procedure due to the higher vapor pressure of silver element. Zamponi et al. [10], after Quandt and Zamponi [11], used a multilayer-like co-sputtering technique to achieve high Ag concentration, up to 16.8% in weight, in NiTi thin films, whereupon silver was added as pure Ag nanoparticles, and revealed that Ag additions until high contents did not alter the shape memory transformation behavior.

The biological performance of silver in human body is dose dependent; the elementary Ag is ionized slowly, and the presence of Cl^- in body fluid reacts with Ag^+ to form the low soluble AgCl salt [9], therefore, yielding low inhibitory rates over the bacterium. So, an overestimated Ag-content shape memory alloy could be needed to solve those biomedical issues.

Aiming to assess metallurgical data on NiTiAg VAR melting processing, this work shows the first data set collected from the melting process of an Ag high-content NiTiAg shape memory alloy, from a microstructural and thermal point of view.

2 MATERIAL AND METHODS

By using a lab scale vacuum arc remelting furnace, was produced three ingots of 15 mm in diameter weighing 100 grams of $Ni_{53}Ti_{43}Ag_{4\%wt}$ SMA. The starting metallic charge was composed by 2.5 mm in diameter and 99.3 mm length NiTi equiatomic wires and 0.5 mm thick, 2.5 mm wide and 99.1 mm length silver 99.99% plates. The VAR furnace was operated with an electric current of 275 A, a voltage of 20 V, under an argon (Ar) atmosphere, optionally (Figure 1). The metallic fed was loaded systematically in the water-cooled copper crucible, which is the also the ingot mold. After the metallic load was charged in the furnace, its chamber was purged, blowing off the chamber until its internal pressure was near 10^1 Pa, then, filling it with Ar gas, and pumping it again. This purge cleaning process was done three times before the chamber was filled with Ar until $7,5x10^4$ Pa to melt. The charge melting was made in 5 steps: the melting process itself to consolidate an ingot, and four re-melts, each one tilting the ingot 90° around the longitudinal axle of ingot mold.

Two ingots was solution-treated on a special array in which the ingot was placed inside a quartz tube of 1 inch diameter, under a positive Ar pressure with laminar

Figure 1: Lab scale VAR furnace. (a) Chamber view and (b) metallic charge mounted in the crucible/ingot mold.

flow, and its tube was put on a split tubular furnace. Solution treatment was made at 900°C for 1 and 5 hours, followed by a quench in water.

Specimens from the as-cast and solution-treated ones were collected to microstructural and thermal analysis. For microstructural analysis, the samples were sectioned in a low speed saw, grind with SiC papers from 600 grit down to 1200 grit and polished with 1 µm diamond suspension and 50 nm colloidal silica; they were also ultrasonically cleaned after each step with distilled water. For etching was used Kroll's reagent and $CH_3COOH-HNO_3-HF$. Microstructural analysis, as well as, qualitative chemical analysis were performed in a Tescan Vega3 XMU Scanning Electron Microscope, equipped with an x-act SDD 10 mm² EDS detector controlled by Aztec software – Oxford Instruments.

Heat reaction data and transformation temperatures were accessed in a differential Scanning Calorimeter – Netzsch Pegasus DSC 404 c – under a heating rate of 5

K.min^{-1}. The samples with, approximately, 40 mg, were extracted from the original ingots in a low speed saw, and acid cleaned before analyzed.

All procedures were accomplished in *ITASMART* facilities at Instituto Tecnológico de Aeronáutica.

3 RESULTS AND DISCUSSION

3.1 Melting of NiTiAg

Compared to the others melting processes used to NiTi elaboration, VIM and EBM, the VAR is the less dynamical. In this, there is no mixing in the bath as occur in VIM or hot-metal-dripping such in EBM; the homogenization is due only to the convection

Figure 2: Superficial Ag segregation at the bottom of a $Ni_{53}Ti_{43}Ag_{4\%wt}$ ingot.

stream in hot liquid metal. Besides, in the lab scale VAR furnaces, the electrode are generally made by tungsten and not by the metallic charge itself. Both characteristics reduce the homogenization of the bath, requiring some careful in order to avoid segregation problems during the ingot solidification; for instance, it is important that the metallic charge was homogeneously assembled along the crucible. That is why the metallic charge was prepared carefully in specific dimensions; the NiTi wires and Ag plates length was equal the length of ingot mold (Figure 1).

In addition to the aim of obtain an ingot with chemical composition as better as can be made elsewhere, the idea of that complex charge assemble is overcome the problem of low rate recovers and low solubility reported in earlier studies about NiTiAg SMA [8,9]. The melting procedure composed by 5 steps, ensures that, after the consolidation of the ingot (step 1), this is re-melted four times, having, the melt, to accommodate in the ingot mold at the end of each step, promoting a long exposure of the metals to themselves in liquid state.

The solubility limit of the Ag in NiTi is described to be 0.26% in weight [8], what, considering the size of Ag atoms, is expected that limited substitutional solid solution occurs. Therefore, all the excess of solute tends to precipitate in the matrix as pure Ag particles, or be segregated in interdendritic regions and/or in the ingot surface. Experimentally, all the silver surface segregation is located at the bottom of the ingot, i.e., in the contact area between the ingot and the crucible (Figure 2). The silver high density, help the descendent movement of its element when all the components are in liquid state, what enables all silver amount, that did not reacts with NiTi, to be confined in the bottom of the ingot. Therefore, once the arc are removed from the

![69º congresso anual da abm - Pan American Materials Conference - 2014 - 1st Brazilian-German Symposium on Materials Science and Engineering]

ISSN 1516-392X

ingot and the water-cooled copper crucible rapidly cools down the liquid metal, the solute-saturated NiTi matrix is quickly solidified, retaining that pure silver in excess liquid for more than 300°C, with no possibility of reaction or diffusion in NiTi, yielding surface segregation.

To evaluate the silver low recovery rate, the vapor pressure, an indication of a liquid evaporation rate, was measured for the silver element at the melting temperature of NiTi (Equation 1):

$$P_{V,Ag,1310°C} = 10^{-2} psia.\frac{51,71 mmHg}{1 psia}.\frac{10^5}{760 mmHg} \rightarrow P_{V,Ag,1310°C} = 68 Pa$$

Considering the chamber internal pressure of the Ar atmosphere used in the melting process, no loss of Ag would be expected to boil when the NiTi alloy is melted.

As the temperature is the only variable in the calculus of vapor pressures, from the chamber internal pressure, the temperature in which Ag should start boiling was calculated (Equation 2):

$$P_{forno,T} = P_{v,Ag,T}.\frac{51,71 mmHg}{1 psia}.\frac{10^5}{760 mmHg} \rightarrow P_{v,Ag,T} = 11 psia \rightarrow T \cong 2.207°C$$

Regarding that is being used a plasma arc as heating source, temperatures like 2.207°C is easily achievable. Therefore, the silver loss by evaporation reported earlier could be an operational problem, demanding better control of the variables like arc current and voltage, as well as, experience from the furnace controller.

Varying the chamber internal pressure does not seen to be an effective way to control the silver loss. Despite higher internal pressures leads to higher boiling temperatures and reduced arc power, once energy from this is lost in interactions with gas particles, the increase in boiling temperature is so small to be controlled via an arc electric; e.g., for the highest internal pressures used, 1,15x10^5 Pa, the silver boiling point has been increased just to 2.290 °C, calculated from Equation 2.

3.2 Microstructural Analysis

Transversal sections of the as-cast ingot, etched for macrograph, reveal the absence of chilled and equiaxial grains. Just columnar grains can be seen, which grows upward, accordingly to the heat extraction sense (Fig.3). Each columnar grain is formed dendritically, rejecting solute to the solid/liquid (S/L) region. Analyzing the Figure 4, it is noted that the solute accumulated in the S/L interface are not re-distributed in solid or liquid phases as solidification theory states; it would happen if the solute atoms do not have high atomic radius as silver has, and the solidification process does not happen as fast as it is. Still, accordingly to the solidification theory, what happens is a non-equilibrium solidification, with a high S/L interface velocity, resulting in solute rejection by the solid and its accumulation at the S/L interface, hindering the solute re-distribution, next, the interdendritic segregation.

Melting a shape memory alloy is expected that the major constituent of the alloy be that one which promotes the shape memory effect; NiTiAg microstructure is composed by an NiTi matrix with pure silver particles randomly distributed (Figure 5). The NiTi matrix maybe presents some substitutional solid solution with Ag.

The silver particles has a random distribution, ranges from tens of nanometer to tens of micrometer in diameter, and its size does not depend on the silver content of the alloy (Figure 6) [12]. Metallic nanoparticles exhibit increase chemical activity due to

their large surface to volume ratios and crystallographic surface structure, because of it nanoparticles are persuaded in these alloys. Titanium carbide second phase particles, here impurities, are made with carbon from titanium of the metallic charge and, at this stage, it not seems to be hazardous to the shape memory effect. Any second phase particles containing silver was found.
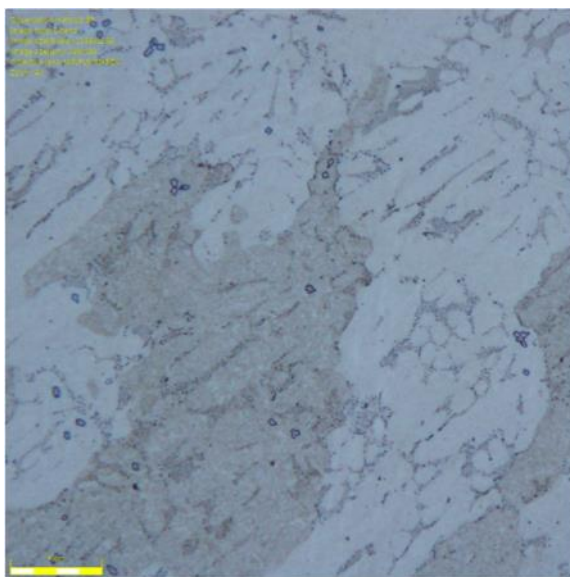

Figure 3: Cross section macrograph of $Ni_{53}Ti_{43}Ag_{4\%wt}$ as-cast ingot.

Figure 4: Interdendritic solute segregation on Ni53Ti43Ag4%wt alloy.
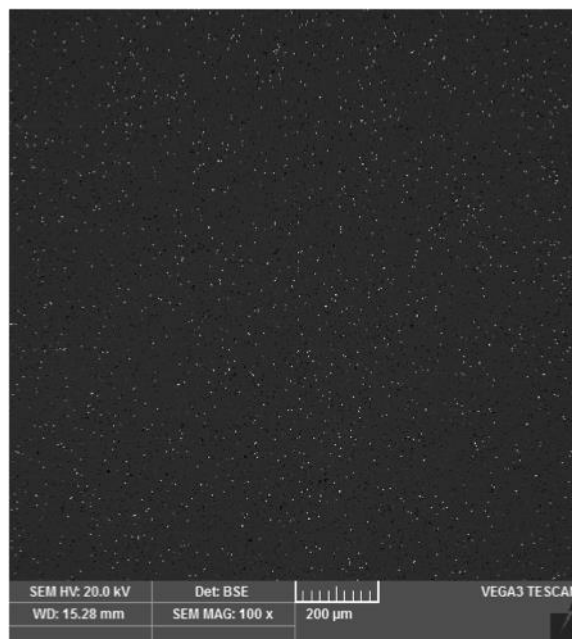
Figure 5: Microstructure of Ni53Ti43Ag4%wt; NiTi matrix with some silver in solid solution and pure Ag particles randomly distributed.

3.3 Heat Treatment

The heat treatment was performed at 900 °C in order to work for both NiTi matrix and silver, once silver diffusion could be hampered by its large atomic radius. The ingot heat-treated for one hour shows an increase in number of Ag particles throughout all the section, but it occurs mainly at grain boundaries and interdendritic regions, resulting in a cellular-like structure (Fig.7). Therefore, the heat-treatment at 900 °C for one hour seems not dilute the silver precipitates, but create new ones, by removing silver from the substitutional solid solution with the NiTi.

After heat treatment for five hours, the sizes of precipitates are smaller than seen before (Fig. 8). So, two possible situations are occurring during the heat treatment: the previous precipitates started to be diluted by heat treatment at 900 °C in five hours, or the precipitation process keeps happening, generating smaller precipitates
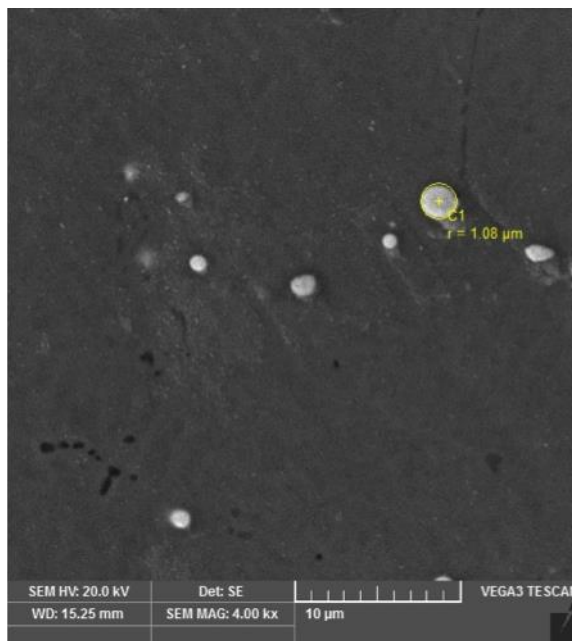
Figure 6: Silver particles on a NiTi matrix. Particles size ranges from tens of nanometers to tens of micrometers, and does not depend of the silver content in the alloy.
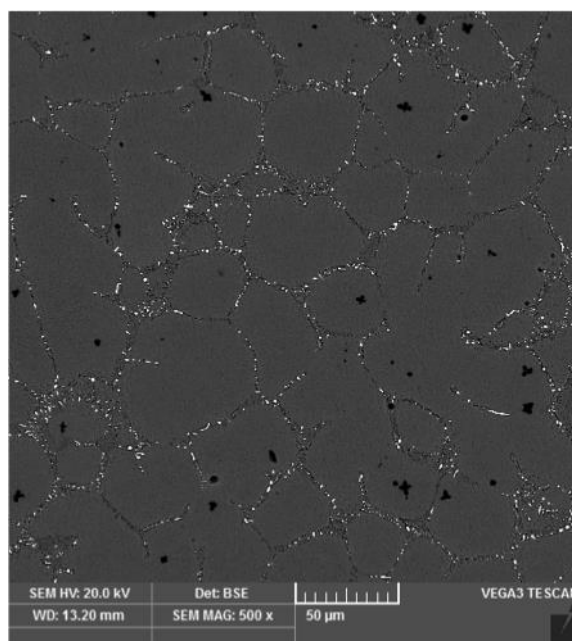

Figure 7: Microstructure of Ni53Ti43Ag4%wt after heat treatment at 900˚C for 1 hour. Increase in Ag pure precipitates by removing it from solid solution.

due to the lower content of silver in substitutional solid solution. The heat treatment did not induce the precipitation of any new phase in the alloy.
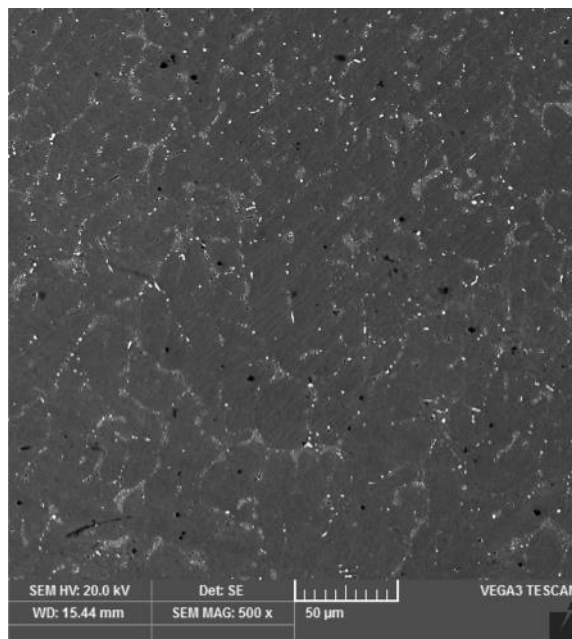

Figure 8: Microstructure of Ni53Ti43Ag4%wt after heat treatment at 900°C for 5 hours. Smaller Ag particles precipitated. Any cellular-like structure.

3.4 Thermal Analysis

Thermal analysis is the most controversial topic in the development of NiTiAg. Oh [8] stated small silver additions, until 0.26 weight percent, to increase austenitic transformation temperature. On the other hand, Zheng [9] shows a multiple-stage transformation behavior for NiTiAg, in which the direct martensite transformation temperature is reduced by an Ag addition of 2.8 weight percent.

Figure 9 shows the DSC curves for as-cast NiTi near-equiatomic, the base material, and NiTiAg$_{4\%wt}$. Ag acts reducing the martensitic transformation temperature, being an austenite-stabilizer element, i.e., the silver element has the same effect of nickel in NiTi shape memory alloys; other elements such Fe, Al, etc, works similar [5]. This behavior was demonstrated to exist in alloys with Ag additions ranging from 0.25% to 4% in weight [12].

The DSC curves were useful also to validate the VAR melting process to produce Ag high-content NiTiAg alloys, since Ag influences the transformation temperature directly as a function of its content [12]. So, a homogenous ingot should present constant transformation temperatures through it cross section, once the major problems in segregation are in this direction, due to the density difference among the alloying elements. In top and center position of the cross section, the phase transformation temperature are the same, while in bottom position, this temperature are quite smaller (Figure 10), though its difference are minimal, less than 5°C. It is understood as an influence of higher silver content in this region of ingot, a consequence of the alloy melting procedure and solidification process explained earlier.
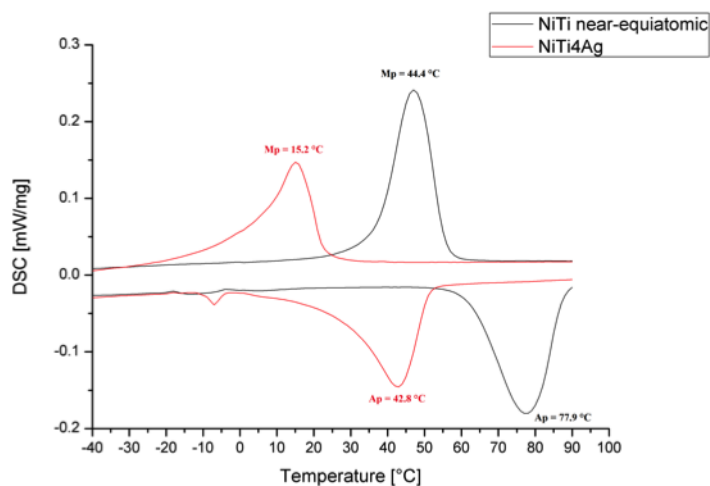
Figure 9: DSC chart for near-equiatomic NiTi and $Ni_{53}Ti_{43}Ag_{4\%wt}$, showing the influence of silver addition over the Martensitic Transformation Temperatures.
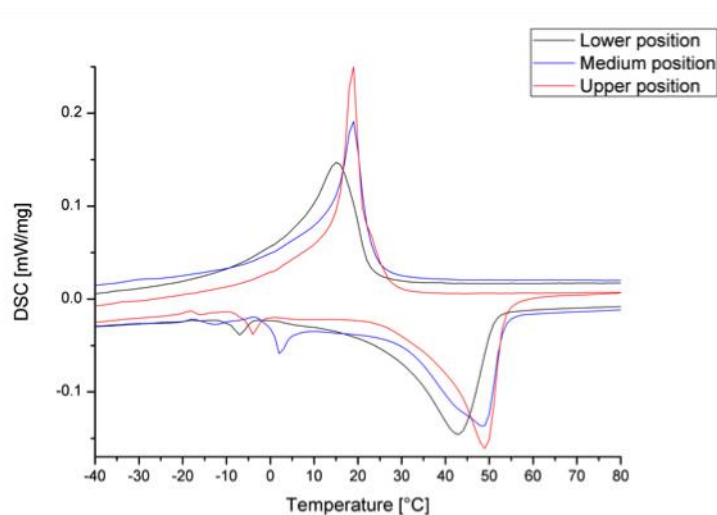

Figure 10: DSC data along the cross section of the $Ni_{53}Ti_{43}Ag_{4\%wt}$. Great homogeneity could be assessed by melting the alloy in VAR.

R-phase were found in DSC charts for $Ni_{53}Ti_{43}Ag_{4\%wt}$ after thermal cycling, confirming the tendency of a multiple-stage transformation from austenite to martensite, as reported by Zheng in rolled and heat treated samples [9]. This phase are characterized by the ascendant new peak, which arises from the initial single peak of the transformation on cooling (Figure 11). In this multiple-stage phase transformation, the austenite phase transform into R-phase with a lower enthalpy associated, reflected by the small peak in the DSC charts. Cooling down, the R-phase transforms into the martensitic phase, with a higher enthalpy associated, resulting, therefore, in two peaks on the cooling segment.

The DSC chart of heat-treated samples made clear its influence over the phase transformation. The phase transformation temperature is decreased down to -5°C, in both samples and the R-phase is induced (Figure 12). There is a great agreement between the temperature of the R-phase in samples thermally cycled and heat-treated.

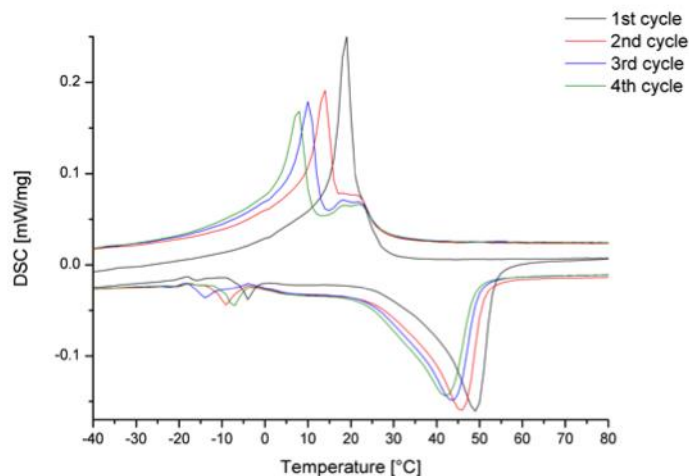**Figure 11**: Thermal cycling of Ni$_{53}$Ti$_{43}$Ag$_{4\%wt}$. Multiple-stage phase transformation characterized by the R-phase.

As the heat treatment reduces the transformation temperature and, at the same time, leads to the precipitation of new Ag particles, is viable think that the alloy under study is super-saturated. Samples heat-treated for one and five hours has similar martensitic transformation temperatures, what implies that after one hour of heating, the matrix are already established. Further heating, just enables the diffusion of silver atoms. It confirms the very low solubility of Ag in the NiTi lattice, as well, as the power of silver in reducing the transformation temperature.
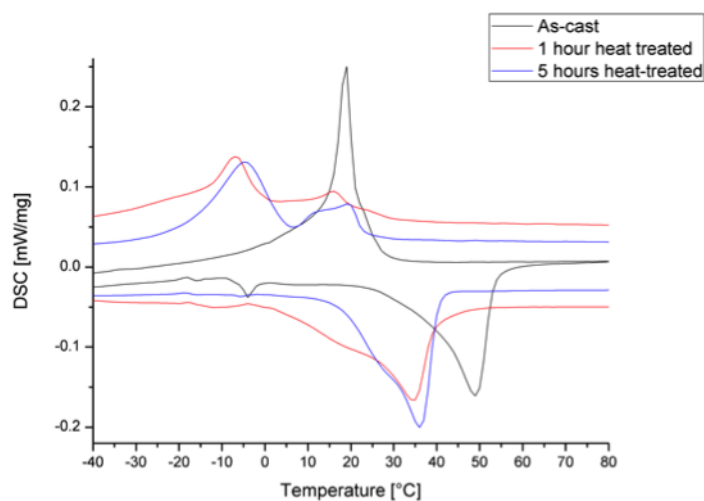

Figure 12: DSC curves for as-cast and heat-treated specimens.

4 CONCLUSION

The concluding remarks melting of Ni$_{53}$Ti$_{43}$Ag$_{4\%wt}$ ingots in VAR furnace are the following:
1. The VAR furnace can be used to melt this alloys, even with high silver content, but a great knowledge about the arc current and voltage, in addition to experience in controlling the arc is needed;
2. The heat treatment of this alloys have to be deep explored in order to specify what happens during it, and what the best procedure.

3. The thermal analysis was important to determine the transformation temperatures and how the Ag behaves in the alloy. Despite new studies should be done in order to prove the influence of silver in the performance of the alloy.

Acknowledgments

REFERENCES

1   Buehler WJ, Gilfrich JV, Wiley RC. Effect of low-temperature phase changes in mechanical properties in alloys near composition of TiNi. J. Appl. Phys. 1963; 34:1475-1477.
2   Haider W, Munroe N, Pulletkurthi C, Puneet KSG, Sushma A. A comparative biocompatibility analysis of ternary Nitinol Alloys. JMEPEG. 2009; 18:760-764.
3   Hodgson DE, Wu MH, Biermann RJ. Metals Handbook. 2nd ed. Materials Park: ASM International; 1990.
4   Duerig T, Pelton A, Trepanier C. Nitinol: alloying and composition. Materials Park: ASM International; 2011.
5   Liau SY, Read DC, Pugh WJ, Furr JR, Russel AD. Interaction of silver nitrate with readily identifiable groups: relationship to the antibacterial action of silver ions. Lett. Appl. Microbiol. 1997; 25: 279-283.
6   Gupta A, Silver S. Silver as biocide: Will resistance be a problem?. Nat. Biotechnol. 1998;16: 888.
7   Matsumoto, H. Addition of an element to NiTi alloy by an electron-beam melting method. J. Mater. Sci. Lett. 1991; 10: 417-419.
8   Oh KT, Joo UH, Park GH, Hwang CJ, Kim KM. Effect of silver addition on the properties of nickel-titanium alloys for dental applications. J. Biomed. Mater. Res-A. 2006; 76:306-314.
9   Zheng YA, Zhang BB, Wang BL, Wang YB, Li L, Yang QB, Cui LS. Introduction of antibacterial function into biomedical TiNi shape memory alloy by the addition of element Ag. Acta Biomater. 2011; 7:2758-2767.
10   Zamponi C, Wuttig M, Quandt E. Ni-Ti-Ag thin films. Script Mater. 2007; 56:1075-7.
11   Quandt E, Zamponi C. Superelastic NiTi thin films for medical applications. Adv Sci Technol. 2008; 59:190-7.
12   Alvares da Silva GHT, Matieli, JE, Otubo J. Effect of silver content on the martensitic transformation temperatures in NiTiAg Shape Memory Alloys for biomedical applications. Proceedings of the International Conference of Shape Memory and Superelastic Technologies, Pacific Groove, CA, USA. May, 2014.

_____
* Technical contribution to the 69th ABM International Annual Congress and to the ENEMET, July 21st -25th, 2014, São Paulo, SP, Brazil.

1613