INFLUENCE OF THE REPROCESSING BY PLASMA MELTING AND INJECTION MOLDING ON THE THERMOMECHANICAL PROPERTIES OF A NI-TI SMA MANUFACTURED BY VIM

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Abstract. *Shape Memory Alloys (SMA) metallic materials that can change their mechanical and physical properties with temperature variation and mechanical loading, surprising engineers and researchers. In this way, one can develop thermomechanical actuators capable, for example, of generating force by blocking the shape recovery or change the natural frequency of a mechanical system in a way it does not go into resonance. The obtaining processes of these SMA are countless, each one with its specific limitation and particularity. This study aims to evaluate the influence of rapid solidification of a Ni-Ti SMA that was originally manufactured by Vacum Iinduction Melting (VIM) and reprocessed by Plasma Melting (PM) followed by injection molding into different metal molds (steel, brass, aluminum and copper). The influence of this reprocessing was analyzed through Differential Scanning Calorimetry (DSC), Electrical Resistance as a function of Temperature (ER-T) and Dinamical Mechanical Analysis (DMA) to determine the effects on transformation temperatures, damping and stiffness. The results demonstrate that using the copper mold one could provide greater uniformity of the material properties. Thus, there is the possibility of obtaining different kinds of SMA mini-actuators by PM injection in a copper mold and that includes different shapes and sizes that can be studied further.*

Keywords: *Shape Memory Alloys, plasma melting, vacuum induction melting, solidification, thermomechanical characterization.*

1. INTRODUCTION

Shape Memory Alloys (SMA) are functional materials which can recover from being deformed when heated. These materials are challenging because they can work either as sensors and actuators at the same time (Lagoudas, 2008). NiTi-based SMA has attracted much interest for its potential use as a functional material in many engineering applications such as an active, adaptive or smart structure as well as certain biomedical application. Applications of SMAs are related to several areas as aerospace, automotive, telecommunications, health, among others (Monteiro Jr., et al, 2013).

The thermomechanical behaviors associated with these alloys are Superelasticity (SE) and Shape Memory Effect (SME) (Otsuka and Wayman, 1998). SE or pseudo-elasticity is exemplified by large inelastic strains induced during loading that are recovered during unloading due to reversible stress-induced phase transformation between austenite and martensite. In the SME inelastic strains are induced during loading due to orientation of martensite variants from self-accommodated microstructure; residual strain upon unloading is still recoverable by phase transformation of this oriented martensite into austenite via heating. Subsequent stress-free cooling from austenite to martensite results in a self-accommodated microstructure – this process exhibits no macroscopically observable deformation. Actuation may be achieved via a special case of the SME in which the applied load is not removed from the alloy as it is thermally

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cycled through phase transformation between oriented martensite and austenite microstructures (Stebner and Brinson, 2013).

Although two families of these alloys, copper and NiTi based, are commercially available, NiTi alloys are the most explored because of their superior Shape Memory Effect (SME) and Superelasticity (SE). Due to their unique properties such as corrosion resistance and excellent biocompatibility there are many attempts to develop new applications. However, the complicated manufacturing and processing of these alloys place obstacles to diffuse applications (Elahinia et al. 2011). The main inconvenient of melting NiTi alloys besides the chemical composition control, it is extreme reactivity at melting temperatures. For example, the titanium reacts with oxygen, nitrogen and carbon to form oxides, nitrides and carbides respectively. In order to avoid atmospheric contamination and to ensure high ingot purity, the melting process of NiTi alloys is carried out in vacuum or inert atmosphere (Otubo et al. 2004).

Among the different processes of these alloys there are Air Induction Melting (AIM), Vacuum Induction Melting (VIM), Vacuum consumable and non-consumable Arc Melting (VAM), Electron Beam Melting (EBM), Powder Metallurgy (PM), Rapid Solidification (Mainly melt-spinning) and Mechanical Alloying (MA) (Zhang, et al., 2005; 2006).

The VIM process is used for melting titanium, nickel alloys, stainless steel, cobalt, and special alloys. In VIM, the result of electrodynamic forces provides excellent agitation of the melting mass ensuring greater chemical and microstructural homogeneity of the ingot. Carbon is highly soluble in nickel which has a high affinity with titanium. For this reason, the major inconvinient of VIM is the carbon contamination of the ingot (Rigo et al., 2005). Even so, this process is one of the most commercially used today.

Another technique that has been used in laboratory scale production of alloys and even mini-actuator is the Plasma Skull Push-Pull (PSPP). On that process the metal is molten in a thin layer on its own, in a protective atmosphere of argon, and then injected into a metal mold, leading to obtain the desired shape (De Araujo et al., 2009). PSPP process can be considered as a combination of PM and AIM. Even though the PSPP process is an efficient and commercially available for the production of alloys for dental care applications, De Araujo et al., (2009) applied this technique to develop various types of SMA. At first there were produced Cu-based alloys which are usually produced by other processes (AIM and PM) and then the PSPP process was used for the other families of SMA.

In this context, this worked aimed to evaluate the influence of rapid solidification of a NiTi-based alloy which was originally manufactured by VIM and reprocessed by PSPP process followed by injection molding into different metal molds (steel, brass, aluminum and copper). The influence of this reprocessing was analyzed by the following characterization techniques: Differential Scanning Calorimetry (DSC), Electrical Resistance (ER) and Dinamical Mechanical Analysis (DMA) to determine the effects on the transformation temperatures, damping and stiffness. The study of this reprocessing had the objective of improving the PSPP process for the production of SMA mini-actuators obtained directly in the desired form, eliminating other manufacturing steps, such as machining.

2. EXPERIMENTAL PROCEDURE

The material used to evaluate the reprocessing effect on SMA by PSPP process was a NiTi-based alloy. This alloy is commercially known as VIM70 was manufactured by VIM process and supplied by Villares Metals S.A. The Fig.(1a) shows the ingot (16 x 130mm) with chemical composition of 55.10Ni-44.9Ti (% weight).
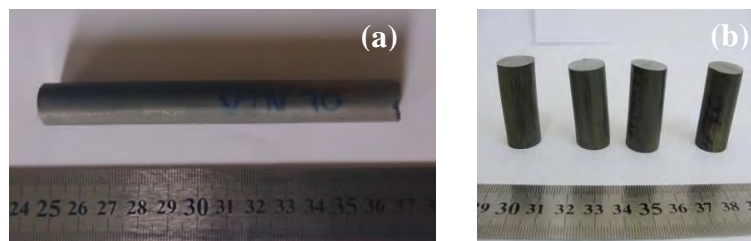

Figure 1. NiTi Ingot: (a) VIM70 provided by Villares Metals S.A. (b) Small NiTi billets.

The ingot was cut in four small billets (Fig.1b) with a metallographic precision cutter. Each billet was set with a weight of approximately 42.60 + 0.50 grams was introduced into the plasma furnace as the raw material, being injected into four metalic mold made of different materials. Fig. (2) shows a typical PSPP process sequence PSPP for a SMA manufacturing. Initially, Ni and Ti were pilled up on a melting pot (Fig. 2b) and placed under a protective argon atmosphere. The melting of the raw elements is rapidly carried out with a plasma rotating torch created by a tungsten electrode (Fig. 2e-1), creating a small "button" (Fig. 2e-3). In order to assure a reasonable homogeneity of the molten material, there were carried out five remeltings. The final product was obtained when the remelted "button" (Fig. 2e-4) was injected into a metallic mold (Fig. 2f), resulting on the designed product.
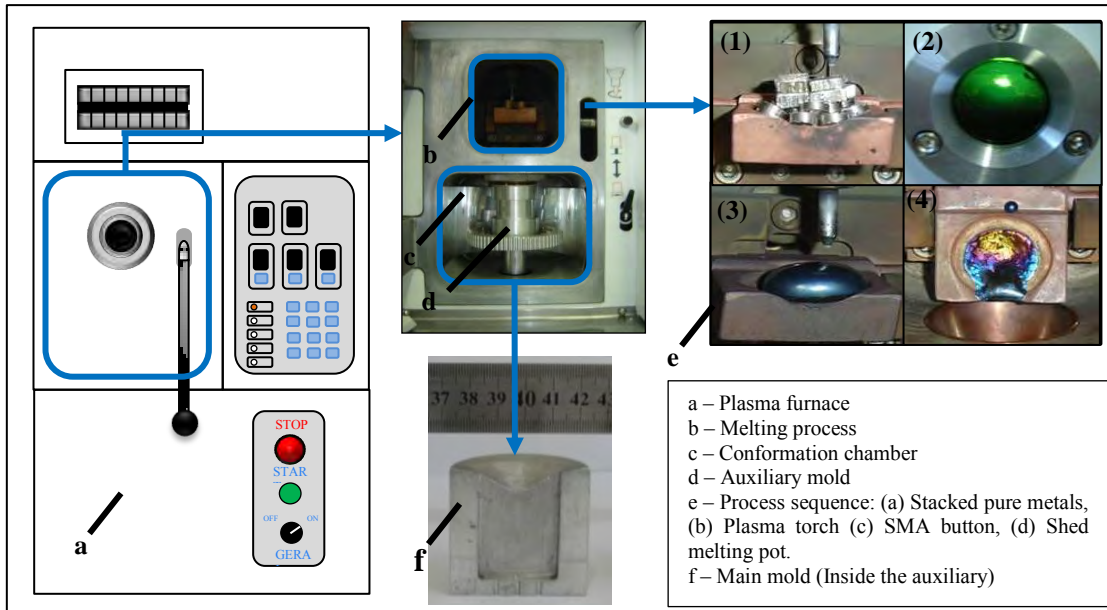
Figure 2. PSPP reprocessing sequence of NiTi-based SMA.

The design of the molds for the manufacturing process was defined to have a prismatic geometry with 30mm x 25mm x 5mm, as shown in Fig. (3a). This geometry allows one to cut thin specimens in order to perform the characterization by electrical resistance as a function of temperature and DMA. The molds were manufactured from steel, brass, aluminum and copper (Fig. 3b) in order to evaluate the influence of the alloy's solidification under different thermal conductivities (W/mK) (45, 75, 204 and 386, respectively for each mold).
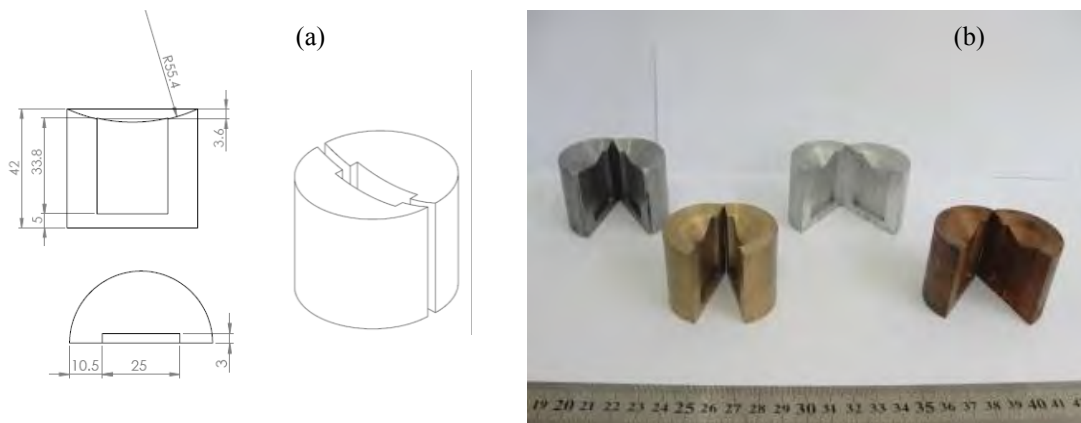

Figure 3. Metallic molds used for PSPP process:
(a) Technical drawing (b) Molds made of steel, bronze, aluminum and copper.

All specimens were melted with the same temperature, pressure and vacuum conditions and the same exposure time to the plasma torch. After melting, all specimens were cut in the longitudinal direction of the bar, shown in Fig. (4a). The slices were taken from the bottom of the bar because it represents the part that undergoes the greater influence on the solidification process. These slices measured about of 25mm x 6mm x 1mm.

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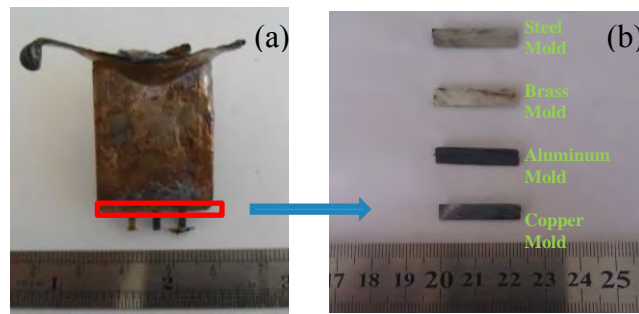

Figure 4. Melting product (a) prismatic NiTi bar (30mm x 25mm x 5mm). (b) NiTi Slices injected into different metal molds (shown).

As a way to evaluate the obtained results, one could observe the reprocessed specimens under two aspects: surface finishing and mold filling. The characterization of the specimens in this work aimed to compare the NiTi alloy obtained by VIM with the same alloy reprocessed by PSPP injected into different metal molds.

The thermal characterization was carried out using the Differential Scanning Calorimetry (DSC) technique using a calorimeter from TA Instruments, model Q20. The tests were carried out at a temperature range from 100 °C to -70 °C with a heating and cooling rate of 5 °C/min.

Another technique used to determine the transformation temperatures of SMA is the variation of Electrical Resistance as a function of Temperature (ER-T). This technique is based on measure the variation of electrical resistance of the material during heating and cooling. The specimens used in this step were the slices obtained from cutting the prismatic bar towards its cross section. The test of ER-T was carried out using a adjustable thermal bath with silicone oil, where each sample was subjected to thermal cycles of heating and cooling at a temperature range between 120 °C and - 10 °C, while measuring at the same time the variation on the electrical resistance through a data acquisition system. Each sample was subjected to a current of 0.4A during the test.

The DMA was performed by an equipment from TA Instruments (DMA Q800) that was used to measure the damping capacity of the specimens. The tested samples were the same used in the thermal characterization by ETR. The test was made by performing a complete cycle, cooling and heating samples. The standard parameters for the dynamic test of metallic materials were: frequency of 1 Hz, heating/cooling rate of 2 °C/min and oscillation amplitude of 5 μm (Villar et al., 2010).

3. RESULTS AND DISCUSSIONS

The analysis of reprocessing of the NiTi alloy initially was carried out by visual inspection of the surface finishing and mold filling of the bars, shown in Fig. (5). One can notice the specimen that obtained the better surface finishing and mold filling was the one injected into the copper mold. It is noteworthy that the specimen with the highest surface oxidation was injected into the steel mold.

Figure 5. Visual aspects (finishing) and mold filling after reprocessing by PSPP with subsequent injection into molds made of steel, bronze, aluminum and copper.

T test result. The DSC thermogram was not able to detect the R-phase as shown in the ER-T in Fig. (6). This shows the importance of the ER-T for thermal characterization of these alloys, which shows greater sensibility in comparison with DSC. The problem of ER-T is the limitation for cooling.
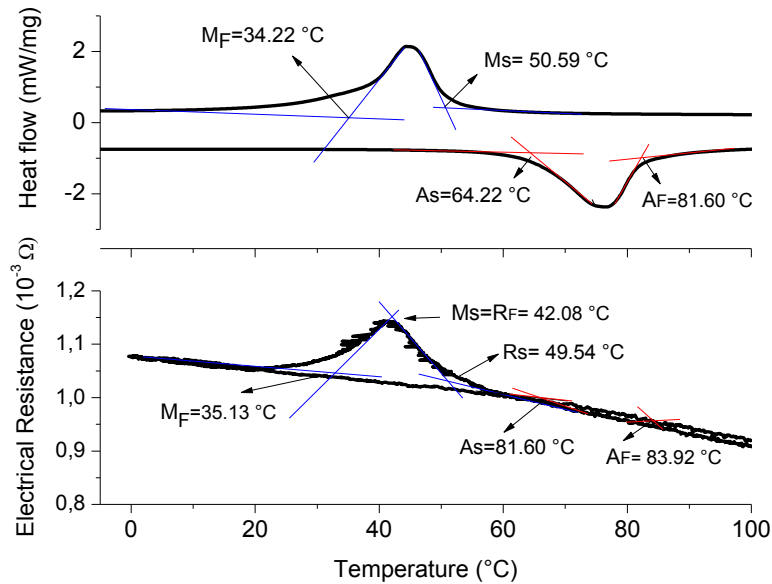

Figure 6. DSC thermogram (above) and ER-T results (below) for a NiTi reprocessed by PSPP.

The small differences on the transformation temperatures measured in the raw material are related to the chosen techniques. However, the obtained results were quite reasonable. Table 1 shows the transformation temperatures obtained from the two techniques.

Table 1. Transformation temperature of a NiTi alloy originally manufactured by VIM measured by DSC and ER-T.

Tecnic \Temperature (°C)	M_F	M_S	R_F	R_S	A_S	A_F
DSC	34.22	50.59	-	-	64.22	81.60
ER-T	35.13	42.08	42.08	49.54	66.48	83.92

In DSC thermograms performed on the reprocessed specimens are shown in Fig. (7). The results lead to believe that the solidification may cause disturbances in the peaks, interfering on the phase transformation, particularly during heating. These disturbances may also represent the presence of R-phase. The alloy's transformation temperatures decreased after reprocessing. This reduction is shown to be characteristic from PSPP process, taking into account the injection into different molds.

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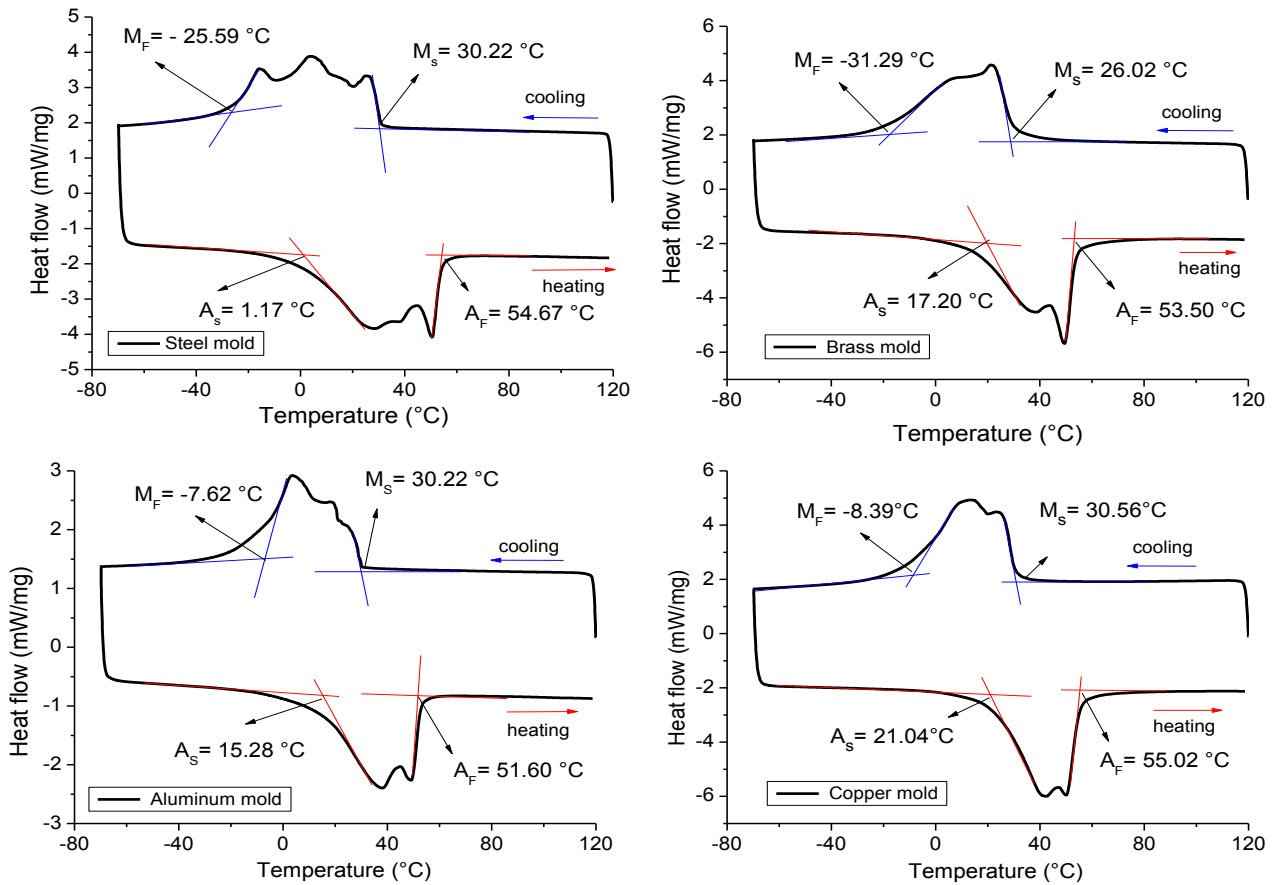

Figure 7. DCS thermograms of a NiTi alloy reprocessed by PSPP in four different metal molds.

Although the transformation temperatures, in Tab. (2), present some variations between the molds which have different thermal conductivities, the transformation temperature A_f remained almost unchanged.

Table 2. Transformation temperature of a NiTi alloy provided by VIM and measured by DSC.

Specimen\Temperature (°C)	M_F	M_S	A_S	A_F
Steel	-25.59	30.22	1.17	54.64
Brass	-31.29	26.02	17.20	53.50
Aluminum	-7.62	30.22	15.28	51.60
Copper	-8.39	21.04	21.04	55.02

The electrical resistance curves versus temperature clearly confirm the presence of R-phase in the alloy composition with this chemical composition, even though the sample has not reached its full transformation during cooling. There also were light peaks in the direct transformation during heating.
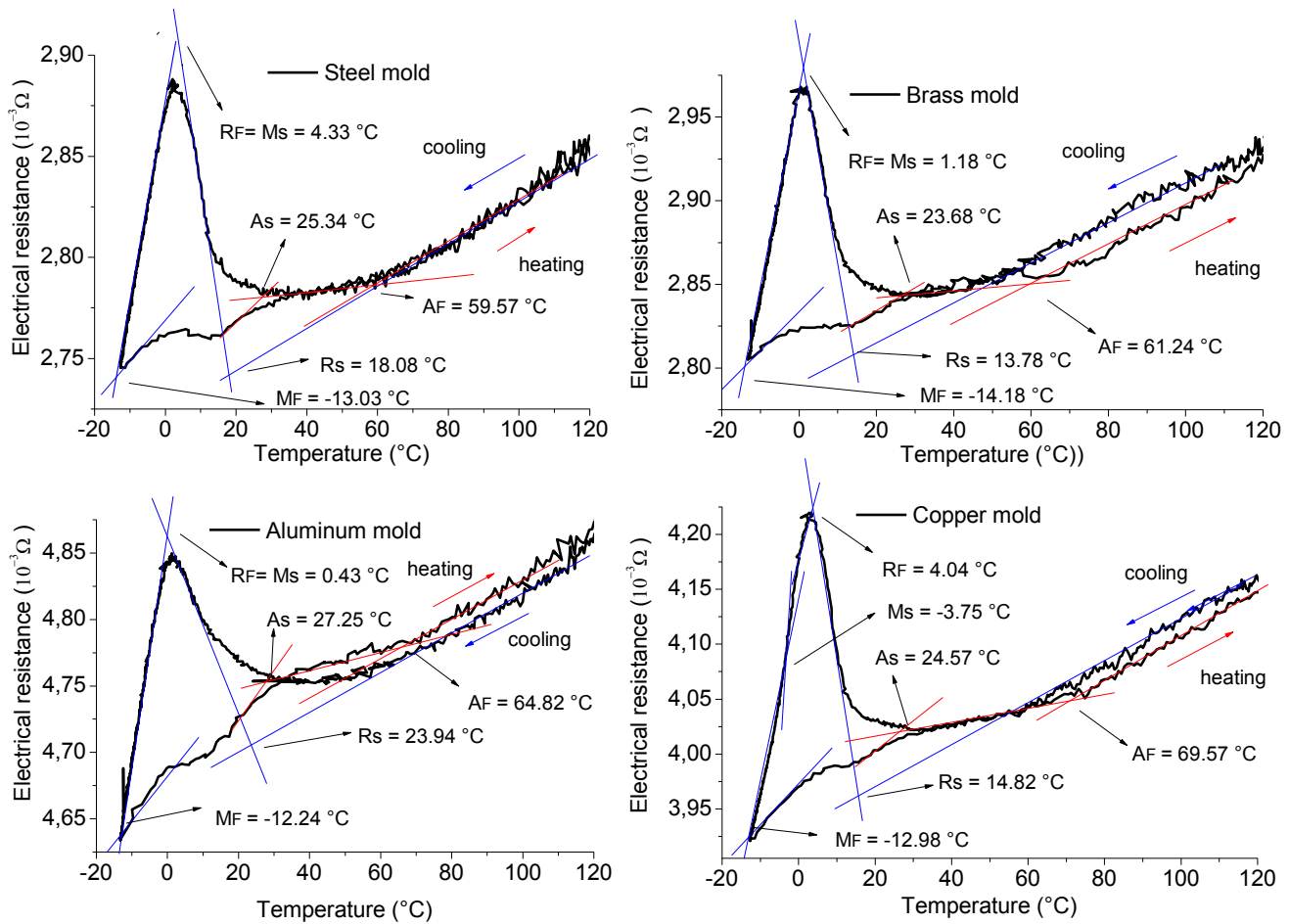
Figura 7. Curvas de ER-T NiTi for samples reprocessed by PSPP in four different metal molds.

Table 3 shows that the transformation temperatures generally do not change greatly from mold to mold. The equality presented with for the temperature M_F is hidden due to the cooling capacity of the system, which reaches a maximum temperature of -15 °C and, as it has been noticed in DSC thermograms, there were samples which presented M_F well below that value.

Table 3. Transformation temperature of a NiTi alloy provided by VIM and measured by ER-T.

Sample\Temperature (°C)	M_F	M_S	R_F	R_S	A_S	A_F
Steel	-13.03	4.33	4.33	18.08	25.34	59.57
Brass	-14.18	1.18	1.18	13.78	23.68	61.24
Aluminum	-12.24	0.43	0.43	23.94	27.25	64.82
Copper	-12.98	-3.75	4.04	14.82	24.57	69.57

Regarding the DMA curves, one can observe that the samples in this paper show the same behavior, with their damping values very close. The curves are shown in Fig. (8).

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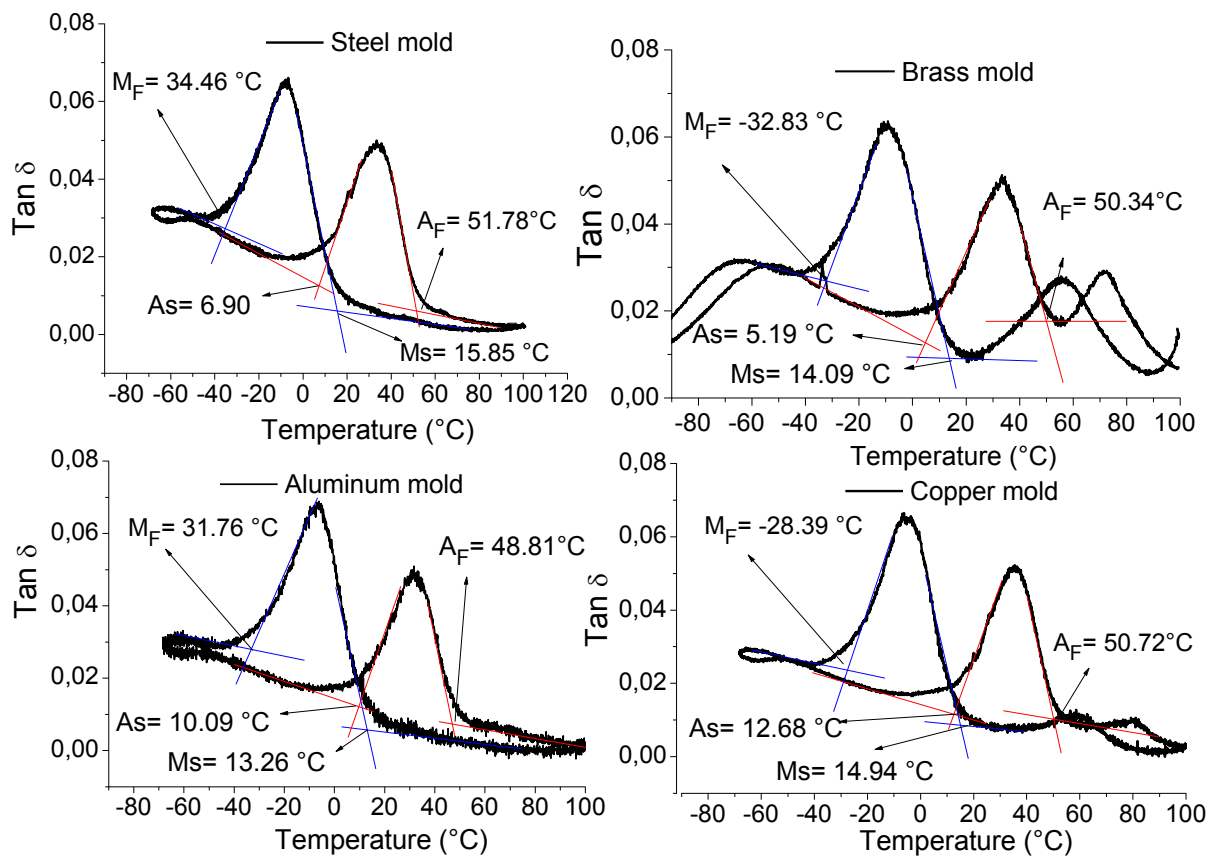
Figure 8. Curves de DMA NiTi for samples reprocessed by PSPP in four different metal molds.

The stiffness as a function of temperature of the samples is greater the greater the thermal conductivity coefficient is, except the sample manufactured in the steel mold, which had the greatest elastic modulus having the lowest thermal conductivity. This fact can be explained due to greater contamination of the sample cast in steel mold. Carbon is soluble in the liquid nickel and has a great affinity to titanium. Thus, it is impossible to prevent contamination by C, producing a solid solution in Ni-Ti phase, forming precipitates of TiC.

Table 4. Transformation temperature of a NiTi alloy provided by VIM and measured by ER-T.

Sample\Temperature (°C)	M_F	M_S	A_S	A_F
Steel	-34.46	15.85	6.90	51,78
Brass	-32.83	14.09	5.19	50.34
Aluminum	-31.76	13.26	10.09	48.81
Copper	-28.39	14.74	24.57	56.72

Table 4 shows that the transformation temperatures generally do not change greatly from mold to mold. The same results were obtained from DSC tests, differently from what was expected, which was to have higher transformation temperatures, once the the material is under load.

4. CONCLUSIONS

After this work, it is not totally clear that the use of different molds with different thermal conductivities may influence on the thermomechanical behavior of these alloys in the remelting process, with respect to the transformation temperatures of the SMA. Regarding to the material's stiffness there is an influence that should be further investigated.

Although the results do not clearly assure, the copper mold showed better results in general, due to the lower amount of oxides present on the surface. A study of sample's contamination with carbon and/or oxygen or by the volatility of any alloy's element must be conducted to better understanding. Perhaps the melting of copper-based alloys might

contribute to this study, as they are easier to observe the effects of different of heat transfer rates. Also would be interesting to conduct a study to better understand the micro structural variables as well as the inconvenients of the reprocessing.

The PSPP process was found to be suitable to manufacture SMA, but it has to be better understood as its use as a reprocessing mechanism and for manufacturing of mini actuators. From this study, it is expected that a new manufacturing method of mini actuators may be developed.

5. ACKNOWLEDGEMENTS

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