

NiTi SHAPE MEMORY ALLOYS PRODUCED BY ELECTRON BEAM MELTING: PRELIMINARY RESULTS

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ABSTRACT

NiTi alloys known since the early 70's present one of the best performance in terms of shape memory effect with shape recovery up to 7%. The transformation temperature of these alloys could be varied from -50°C to +110°C depending upon the chemical composition and thermomechanical treatment. Now, the fabrication process for these alloys is not a easy task due to the contamination by carbon and oxygen in a usual vacuum induction melting (VIM). This work will present the preliminary results of the production of these alloys by electron beam melting (EBM). If by one hand, this process has the advantage to avoid the contamination by oxygen and carbon, by other hand it presents difficulty to control the chemical composition due to operation in high vacuum. The work will presents three nominal composition: Ni₄₄Ti, Ni₄₅Ti e Ni₄₆Ti. The preliminary results of EBM melting look promising with nickel content loss smaller than 1 wt% and final carbon content ranging from 0.012 to 0.016 wt%.

Keywords: Shape Memory Effect, NiTi alloys, Electron Beam Melting.

PRODUCTION OF LEAGUES OF NiTi WITH EFFECT OF MEMORY IN WAY FOR COALITION IN BUNCH OF ELÉTRONS: PRELIMINARY " RESULTS (1)

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SUMMARY

The leagues of NiTi, known since the decade of 70, developed initially by the NASA for hydraulic joining in military airplanes, introduce one of the best actings in terms of effect of form memory (EMF) with form recovery of up to 7%. The transformation temperature can be varied from -50oC to +110oC, depending on the chemical composition of the league. However, the production of those leagues is not an easy task due to contamination for oxygen and carbon in the usual processes he/she saw coalition for induction oven to vacuum (I CAME). This work will present the results preliminaries of obtaining of that league through coalition for elétrons bunch (EBM). If on one side this process has the advantage of avoiding the contamination for oxygen and carbon, on the other hand it presents difficulty in the control of the chemical composition due to operation in high vacuum. The work will present three nominal compositions: Ni₄₄Ti, Ni₄₅Ti and Ni₄₆Ti. One of the objectives is also the production of a system for liberation of solar panel of satellite using as atuador the league of NiTi.

Key words: Effect of Memory in Way, Leagues of NiTi, Coalition for Bunch of Elétrons.

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1. INTRODUCTION

The term EMF is used to describe the capacity of material rights, after they be deformed plasticamente, they return to the original form with the heating. Normal leagues when deformed besides its elastic limit they present permanent plastic deformation. Physically, EMF is associated to the transformation martensítica reversible cristalograficamente.

According to Miyazaki and Otsuka [1] and in the references there mentioned, the first leagues with EMF were developed in the decade of 50 in Au-cd (1951) and In-Tl (1953). Later on the leagues of NiTi were developed [2] and you tie the copper base. More recently, it was also verified that tie the base of iron as Faith-Pt, Faith-Pd, Faith-Ni-Co-you, Faith-Mn-itself [1,3] and you call inoxidable as developed them for this group starting from 94 [4-9] they presented the phenomenon of EMF. In most of the non ferrous leagues, EMF is associated to the transformation martensítica termoelástica, whose main characteristic is to present small transformation histerese, OH - MI, where MI, is at the beginning the temperature of the transformation martensítica in the resfriamento and OH it is at the beginning the temperature of the reversion of the martensita in austenita in the heating. That martensita can also be induced by external force (traction, compression, dobramento, etc.) giving as consequence the deformation in the way. The recovery of that deformation with the heating is what is denominated EMF.

The leagues of NiTi, known since the decade of 70, developed initially by the NASA [2] for joinings of hydraulic tubes of the airplanes F-14, they possess one of the best actings among the leagues with EMF presenting recovery in way of the order of 7% (the inoxidable leagues developed by this group present form recovery of up to 4%). They have applications in the areas: naval, aeronautics, nuclear, automobile, of domestic usefulness, of robotics and also in the doctor (orthopedics, ortodontia, etc.). They are leagues with great resistance to the fadiga and the corrosion and highly biocompatíveis. Of there its use in medical applications. The temperature in which happens the form recovery can vary since -50oC up to +110oC, depending on the chemical composition of the league. However it is a league quite difficult of being elaborated due to easiness of contamination by carbon and oxygen. It also presents difficulties in the mechanical conformação needing special procedures.

The most usual method of obtaining of the league is through coalition in induction oven to vacuum, using cadinho and lingoteira of special graphite. The contamination for carbon comes from the graphite that so much reacts with the nickel as with the titanium. The carbon is highly soluble in the liquid nickel and it possesses a very big likeness for titanium. To minimize the contamination, the special graphite of high density is used and it lowers porosidade. The use of another cadinho types as MgO and the alumina can provoke the contamination for oxygen [2]. The contamination for oxygen can also bring to an agreement due to the residual oxygen inside the oven, whose internal pressure of the coalition camera is of the order of 10 Shovel.

An alternative process for the obtaining of leagues of NiTi would be the coalition in an oven of electronic bunch. In this process, the contamination for carbon would be completely eliminated because he/she is founded in cadinho or crystallizing of refrigerated copper the water and the contamination for oxygen would be minimum because it is operated with better vacuum than 10-2 Shovel. It should be observed that in the coalition and refusão for electronic bunch one of the parameters most difficult of her to control it is the chemical composition for the fact of working in high vacuum with the matters cousins' concomitant evaporation. The uniformity of the chemical composition is fundamental for this league because small variations can result in great differences in the temperatures of phase transition. In this work it will be presented the first results of obtaining of the league NiTi through coalition for elétrons bunch in laboratory scale where was produced small samples in button form being varied the chemical composition of the initial load. Later on he/she intends to obtain small ingots seeking to study process parameters as: coalition rate, control of the superficial quality of the ingot and, mainly, control of the chemical composition along the ingot. Once made possible the obtaining of the league, the second stage will be to develop the process of mechanical conformação and treatment termomecânico being obtained products in agreement with its application: bars, wires, ribbons, foils, etc. TO this respect, one of the objectives is the production of the league for posterior use of the making of a device for liberation of solar panel of satellite [10] in a work group with INPE, ITA, UNICAMP and IPEN.

2. It LEAVES EXPERIMENTAL

2.1 elaboration of the leagues

For beginning of the experiences, three samples were elaborated in button form: the first with nickel excess (Ni44%Ti), the second estequiométrica (Ni45%Ti) and the last with excess of titanium (Ni46%Ti). The percentages are in weight. They were used as departure material the nickel eletrolítico with 99,84% of purity in form of small squared bars of 20x20mm² and the titanium 99,56% of purity in vareta form with 8 diameter mm. The two materials were laminate the cold for thickness of approximately 1 mm and cut in small pieces, decapados in a solution of HNO₃ + HF, washed and evaporated for then to do the composition of the initial load. The initial load of the samples varied between 20 and 30 g. The samples were melted in an oven of electronic bunch of 80 potency kW (LEW, model EMO80) with the use of a cadinho of refrigerated copper the water. The used potency varied of 2 to 4 kW and the internal pressure of the camera of 4 to 7x10⁻² Shovel. In the sense of allowing the homogeneização, all the samples suffered a second coalition. In each stage, the samples were heavy for verification of the losses. The break of the vacuum was made after ten minutes of resfriamento.

2.2 characterization of the leagues

For the preliminary characterization of the samples they were done: analysis chemical semiquantitativa through EDS (microscope Jeol, model JKA-840A); chemical analysis for humid road for the nickel (gravimétrica) and the titanium (volumétrica); analysis for combustion for the carbon; analysis for coalition for the nitrogen and analysis for emission espectrometria for plasm (EPS) for the iron. The determination of the present phases was made by difração of rays X (Rigaku D-Max 2000 with rotative door sample) and the determination of the transition temperatures for thermal analysis (DSC with the thermal analisador STA409C of Netzch) being varied the temperature between -70oC and +270oC and with heating rate (resfriamento) of 5oC/min.

3. RESULTS AND DISCUSSIONS

3.1 elaboration

The illustration 1 presents the samples obtained in button form after the second coalition with brilliant aspect and without oxidation. The table 1 presents the mass losses in percentile terms of the samples after the first and the second coalition in relation to initial mass. It is verified that the total losses (nickel + titanium) they were small being the maxim of 0,45% for the league Ni45Ti. The table 2 presents the absolute chemical composition of the elements after the second coalition. Observe that the text of obtained carbon was relatively low (0,012, 0,015 and 0,016% respectively for the leagues Ni445Ti, Ni45Ti and Ni46Ti) compared to the leagues melted with grafite cadinho in induction oven to vacuum that you/they present text of carbon in the strip from 0,03 to 0,08% [2]. The text of residual iron was practically constant when it is compared the three samples. The text of nitrogen varied of 40 to 95 ppm in weight that can be considered low. Of the table 2 it can also be observed that there was a fall in the nickel text while the one of titanium presented a small increase for the leagues Ni44Ti and Ni46Ti while the league Ni45Ti practically didn't have its altered composition. This can be visualized better in the table 3 where he/she is considered only the relative texts of the nickel and of the titanium as it had been done when of the composition of the initial load. In this table it is visible the relative loss of the nickel that is minimum in the league Ni45Ti. That is, this sample was very close of the composition estequiométrica with text of titanium of 45,2%.

It represents 1. Samples of the league NiTi in form of buttons

Considering the compositions after the second coalition, the samples Ni44Ti, Ni45Ti and Ni46Ti became Ni44,4%Ti, Ni45,2%Ti and Ni46,8%Ti respectively. Termodinamicamente the larger loss of the nickel is waited because the pressure of vapor of balance of this element is larger than the one of the titanium.

It controls 1. Percentile variation of mass after to 1a and 2a coalition

SAMPLE	loss after 1a coalition (% in weight)	relative loss after 2a coalition (% in weight)	total loss (% in weight)
Ni44Ti	0,09	0,28	0,37
Ni45Ti	0,22	0,23	0,45
Ni46Ti	0,05	0,21	0,26

It controls 2. Composition chemical end of the samples after the second coalition

Elements	Ni44Ti (% in weight)	Ni45Ti (% in weight)	Ni46Ti (% in weight)
C	0,012	0,015	0,016
N	0,0040	0,0045	0,0095
Faith	0,20	0,19	0,21
Ni	55,3	54,5	52,8
You	44,1	45,0	46,5

It controls 3. Comparison among initial composition and after the second coalition

SAMPLE	initial composition (% in weight)			composition after to 2a coalition (% in weight)		
	Ni	You	Ni	You	Ni	
Ni44Ti	56,1	43,9	55,6	44,4	-0,5	
Ni45Ti	54,9	45,1	54,8	45,2	-0,1	
Ni46Ti	54,0	46,0	53,2	46,8	-0,8	

3.2 present phases

For optic microscopia the presence could be observed of having precipitated in net form in all the samples being ruder in that with larger text of titanium. Analysis for difração of rays X revealed presence of the following phases in all the samples: NiTi, phase estequiométrica, Ti2Ni, rich phase in titanium and Ni3Ti, rich phase in nickel. In spite of one not to have been done analyzes quantitative of the present phases, it could be observed the following facts in terms of relative intensity I/Io: the league Ni44Ti (Ni44,4Ti) it presented picks relatively high of the phase Ni3Ti, precipitate that happens when the text of Ni is above the estequiométrico and, in the sample Ni46Ti (Ni46,8Ti) that presents titanium in excess, as it was of waiting, the relative intensity of the picks related to the phase Ti2Ni was quite pronounced. In the sample almost estequiométrica, Ni45Ti (Ni45,2Ti), the two phase appeared practically in the same proportions. Theoretically, the rich league in nickel should not present the precipitation of the phase Ti2Ni and the rich league in titanium, it should not present the phase Ni3Ti and the league estequiométrica it should almost present only the phase NiTi [11]. The aparecimento of those phases can be attributed to flotations in the composition of the analyzed samples because the same ones meet in the state coalition brute. New you analyze for difração of rays X they should be accomplished after a treatment of homogeneização of the samples. Analysis for EDS on top of the precipitated of the sample Ni46Ti, after a light chemical attack, it showed that the nickel texts and of titanium they were respectively of ~35% and ~65% revealing to be really of Ti2Ni whose theoretical values are 39% of nickel and 61% of titanium.

3.3 transformation temperatures

As it was mentioned in the introductory phase, the variation in the chemical composition contemplates in a quite drastic way in the temperatures of transformation of the phases as it can be seen in the table 4. The transformation temperatures were obtained starting from the curves of calorimetria sweeping diferencial (DSC). The temperatures MI and OH they are as having defined previously and MF is the temperature of end of the transformation martensítica and AF the temperature of end of the reversion of the martensita in austenita. To facilitate the interpretation they are defined more two parameters: MP that is the temperature in which the rate of transformation of the austenita in martensita is maximum and AP that is the temperature in which the rate of reversion of the martensita in austenita is maximum. In the case of the league Ni44Ti it was not possible to measure the temperatures MI and MF because there was disturbance in the curve of DSC during the resfriamento

with liquid nitrogen but certainly they are below 0oC because the temperature OH it was of just 1,6oC. The league Ni45Ti has the transformation martensítica it completes around 15oC (MF) and the league Ni46Ti around 40oC. The increase of approximately 0,8% in the text of titanium when he/she happens of the sample Ni44Ti for the sample Ni45Ti and of 1,6% when he/she happens of this for the sample Ni46Ti they provoked an increase respectively in the temperature AP of 35 and 48oC. Still in the same sequence, the temperatures at the beginning of the reversion of the martensita in austenita OH they were 1,6 respectively, 44,0 and 78,1oC showing the influence of the chemical composition in the transformation temperatures. Another fact that should be observed is the small transformation histereses OH - MI, that was of the order of 10oC in the two leagues with text of higher titanium. Low values of transformation histerese are characteristic of leagues that present transformation martensítica termoelástica. For reference, they were also placed in the table 4, data of temperatures of transformation of a league of Ni44,9%Ti [12] whose are valued they place among those presented by the league Ni45Ti and Ni46Ti. Theoretically, these values should locate among those presented by the league Ni44Ti and Ni45Ti. However it should be observed that the transformation temperatures besides they vary with the composition, they also vary in agreement with the history termomecânica of the sample, what would justify those discrepancies [13].

These preliminary results showed the importance of the control of the chemical composition that you/they control the temperatures of transformation of the phases for its time. Domain of another factors as treatment termomecânico also owes been taken into account because they can alter those temperatures and also the properties of effect of form memory and pseudo-elasticity.

They are goals for the future the continuity of the coalition experiences in the sense of having the domain of the control of the final chemical composition being varied parameters as initial load, potency of the bunch, pressure in the camera, etc. it is also Intended to increase the production scale being obtained material in form of ingots seeking mainly practical applications. One of those applications is the development of a device for liberation of solar panel of satellite based on an atuador with effect of memory so that it is of the interest of INPE and it is a project group among INPE, ITA, UNICAMP and IPEN.

It controls 3. Temperatures of transformation of phase measures through DSC

SAMPLE	MI (oC)	MF (oC)	OH (oC)	AF (oC)	MP (oC)	AP (the)
Ni44Ti (Ni44,4Ti)	-	-	1,6	39,5	-	15,2
Ni45Ti (Ni45,2Ti)	34,0	15,1	44,0	66,5	22,8	50,7
Ni46Ti (Ni46,8Ti)	69,7	40,6	78,1	116,0	54,1	98,4
Ni44,9Ti [12]	58,5	30,1	66,9	97,2	44,3	86,8

4. CONCLUSIONS

Starting from the results preliminaries of this work, some conclusions can be reached:

- THE total loss of the matter excels for double coalition it was relatively small and the texts of carbon went from two to six times below that that is obtained he/she usually saw coalition in induction oven to vacuum;

- THE double coalition provoked a relative loss of nickel mainly in the league Ni44Ti and in the turned league Ni46Ti them richer in titanium when compared the initial composition. The league Ni45Ti was close of the estequiométrico with small nickel loss;

Independent · of the composition, all the samples presented precipitation of the phases NiTi₂, Ni₃Ti and of the phase estequiométrica NiTi with the following provisos: the rich league in nickel, Ni44Ti, it presented pronounced picks of the precipitate Ni₃Ti and the rich league in titanium, Ni46Ti, the one of the precipitate NiTi₂ as it was of waiting. Aparecimento of phases in areas not foreseen in the phase diagram they can be attributed to small flotations in the chemical composition of the samples that you/they meet in the state coalition brute;

- The results of measures of transformation temperatures showed the importance of the control of the chemical composition because small variations of these can provoke great differences in the first ones;

- Concluding, it can be said that the obtaining of leagues of NiTi through coalition for electronic bunch is viable needing for so much of a larger domain on the parameters of the process as potency of the bunch, internal pressure of the camera, load of the departure materials, etc., to compensate eventual losses.

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