NiTi SHAPE MEMORY ALLOY INGOT PRODUCTION BY EBM

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ABSTRACT

In an earlier works, producing small ingots, it was shown that the use of EBM is a viable process to produce NiTi shape memory alloy. In those works two processes were tested: a static process where the alloy components were charged and melted together in a shell-shaped copper-cooled crucible resulting in a disc shaped ingot and a semi-dynamic process by continuously feeding the alloying elements into the path of the electron beam and casting into a constant volume cylindrical water-cooled copper mold. For the disc ingot the weight loss per melting was around 0.3wt% per melting with reasonable homogeneity along the radial direction. The cylindrical ingot presented small variation in chemical composition along the ingot axis due to differential exposure of the melt to the electron beam. To improve the homogeneity along the axis direction and also to scale up the NiTi production, quite more complex dynamic process of continuous feeding and casting larger ingot is now underway and preliminary results will be presented.

Key words: NiTi, Shape Memory, Electron Beam Melting, Martensitic Transformation

INTRODUCTION

The usual process to produce NiTi shape memory alloy (hereafter called NiTi SMA) is by Vacuum Induction Melting (VIM) using high-density graphite crucibles to minimize the carbon contamination of the melt. As can be seen in others works of this group in this congress [1, 2], the influence of graphite quality of the crucible used is quite large in terms of bath contamination by carbon. Carbon combine with titanium precipitating TiC particles resulting in an alloy matrix much richer in nickel content than the nominal composition consequently lowering the martensitic transformation temperatures [2, 3, 4].

An alternative to VIM process is the electron beam melting (EBM) to produce NiTi SMA. This process is known since the 1950's for refining refractory metals such as Mo, Ta, Nb and W and also reactive metals such as Ti, Zr, Hf and its alloys [5]. More recently this process has been used to produce alloys such as Ti6Al4V[6,7,8] and very clean superalloys [9]. By other hand, its use to produce NiTi SMA is not common. Beside this group that has been working on the development of EBM process to produce NiTi SMA since 1997's [4,10] only Matsumoto in 1991 produced some small samples [11,12]. In EBM process the carbon contamination is completely eliminated due to melting in a water-cooled copper crucible and oxygen contamination is minimum due to operation in high vacuum (better than 10^{-2}Pa). Therefore, the carbon and oxygen contents in the final product depend only on the initial raw material. One of the disadvantages of working in high vacuum during melting and remelting is the difficulty of controlling the nominal chemical composition due to some component evaporation changing the martensitic transformation temperatures, especially on the nickel-rich side of the phase diagram [3,4] . There are basically three possibilities of melting and casting using 80kW EB furnace installed at Unicamp: The first one is a static process where the elements (nickel plus titanium) are charged at ounce with desired nominal composition onto water cooled copper crucible that serves also as casting mold. By this process it is possible to produce samples from few grams up to maximum of 350g limited by EB power required to melt the charge and also by the loss of composition homogeneity. The second one is a semi-dynamic process where the raw materials are continuously fed and cast into constant volume cylindrical water-cooled copper mold. Here the limitation is the mold height that cannot be too large, being its maximum around 50mm. Large axial height of the mold promote differential EB incidence being lower when the melt pool level is at bottom then increasing as the pool level raise as the melting proceeds. Consequently there is axial composition change resulting in martensitic transformation temperature variation. The maximum weight that can be cast by this process is around 500g. This two processes were already tested and results published elsewhere and the carbon content in final products was very low and ranged from 0,007 to 0,016% compared to 0,04 to 0,06% of VIM processed ingots[2,4,10]. The third process

whose results will be presented in this work is a dynamic process with continuous feeding and continuous ingot casting overcoming the above limitations and scaling up the size and weight of the ingots. The shape memory alloy development project is supported by Fundação de Amparo a Pesquisa do Estado de São Paulo and beside the development of alloy production itself, another objective is to promote its use in areas such as robotic, medicine and space applications.

EXPERIMENTAL PROCEDURE

The EB furnace, model EMO 80 with 80kW EB power that pertains to Unicamp (DEMA/FEM) and used in this work to produce NiTi SMA ingot is shown in figure 1. In a dynamic process the raw material (nickel + titanium) is laterally fed continuously into path of vertical electron beam that melts the charge. Simultaneously the melted product drops onto water-cooled copper extractor that is mounted inside the water-cooled copper mold. The nickel used in this work was also produced by dynamic process casting 50mm in diameter ingot. This ingot was machined to 45mm in diameter to remove the surface defects, heated to 950^{o}C and hot rolled to 18mm in diameter. From 18mm in diameter the bar was cold rolled down to 4x4mm^{2} square rod. The nickel melting stage served as experience for further NiTi SMA alloy processing by EBM. They were used 18 pieces of 0,41mm thick by 35mm wide by 975mm long grade 1 titanium sheet imported from Kobe Steel plus 9 pieces 975mm nickel bars. The nickel bars and titanium sheets were intercalated each other and then encased inside a two U shaped titanium box. The set was consolidated by TIG welding. The figure 2 shows the mounting sequence of feeding charge with nominal composition along the length of 54,7wt%Ni. The EB power used was 6,5kW with melting chamber internal pressure of 2 to 4x10^{-3}Pa. It was used a 40mm in diameter copper mold. During melting and casting it was observed that the dimensions of feeding bar of 35x35mm^{2} was not adequate for 40mm in diameter copper mold. Any small misalignment of the feeding bar promoted dripping of the liquid drop outside the mold. To avoid this kind of problem, the feeding bar configuration was changed to 25x40mm^{2} rectangular bar positioning the thinner side normal to beam incidence direction. The second charge was melted and casted over the first ingot that was remelted twice to improve the surface quality.

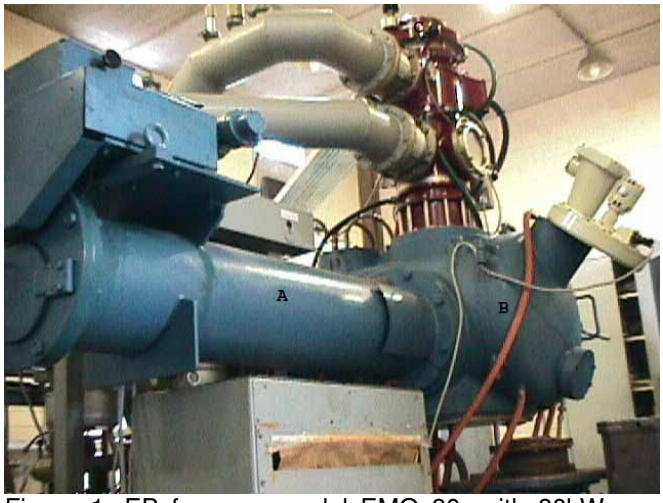


Figure 1. EB furnace, model EMO 80, with 80kW EB power. (A) lateral feeding system; (B) melting chamber and (C) electron gun

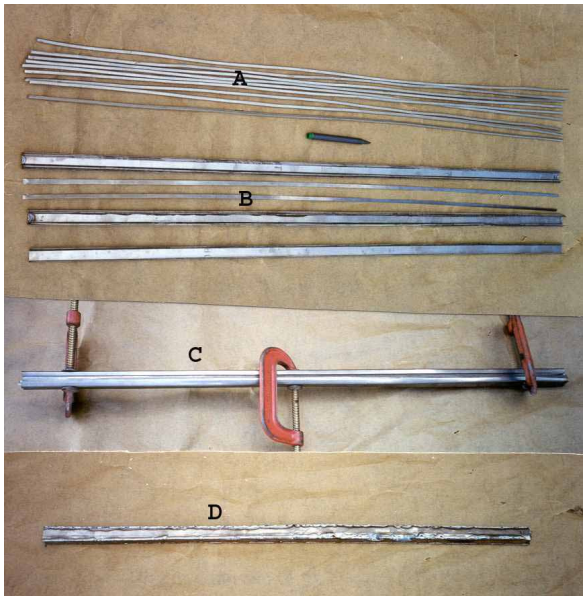


Figure 2. Mounting sequence of feeding charge. (A) nickel bars; (B) titanium sheets; (C) assembling Ni+Ti for welding and (D) TIG welded charge.

RESULTS AND DISCUSSIONS

The figure 3 (upper) presents the 40mm in diameter by 300mm long ingot weighing around 2.5kg after first casting. It can be seen some surface oxidation and the presence of cold junctions and also some cracks. To eliminate those surface defects the ingot was remelted twice as shown in lower part of figure 2. The remelted ingot also presents some surface defects aminly near right end that correspond to ingot bottom where the solidification starts. The surface defects disappear when the melting and casting process acquire a dynamic stationary equilibrium. After one melting and two remelting the final ingot weight was 2,2kg with 40mm in diameter and 270mm long. To check the chemical composition homogeneity, samples were taken from ingot bottom and ingot top after discharging about 5mm from both ends. Then from each end, three samples were taken going through radial direction as follow: one from the center (TC or BC), one from the middle radius (TMR or BMR) and one from near the border (TB or BB). T is for Top position and B for Bottom position of the ingot.

Figure 3. EBM ingot: upper, after first melting; lower, after two remelting.

The ingot homogeneity was checked analyzing the direct and reverse martensitic transformation temperatures from DSC measurements as shown in table 1. The oxygen and carbon content is also shown in Table 1. The following analyses will be done in terms of M_P and A_P, which are the pick temperatures of direct and reverse martensitic transformation. Starting from ingot top position, we can see that both pick temperatures presented very small variation of 2°C for M_P and 1,6°C for A_P denoting good radial homogeneity. Now for ingot bottom position after discharging 5mm the difference on M_P data is 6°C and on A_P is 3,4°C indicating that the process dynamic stationary equilibrium could not be achieved up this height. Now if we compare the average values of pick temperatures between bottom part and top of the ingot, the difference is around 1°C that is very good result. That is, the ingot presents good composition homogeneity along radial axial directions. This aspect can be seen clearly in figure 4 that presents M_P and A_P values at the both positions. Although in terms of operational aspect is much more difficulty to control the dynamic process of continuous feeding and continuous ingot extraction, once the stationary equilibrium is reached, the result of final ingot in terms of chemical composition uniformity is superior when compared do semi-dynamic process of continuous feeding and static casting[Hawaii e Icomat02]. Beside that the scaling up is only possible in dynamic process. With EMO 80 used in this work it is possible to produce ingot of 800mm long with 100mm diameter.

Table 1. Direct and reverse martensitic transformation temperatures of EBM ingot and VIM processed ingot.

Sample	%Ni (nom.)	%C	%O	M_F	M_P	M_I	A_I	A_P	A_F
TC	54,7	0,013	0,064	51,0	**58,8**	65,1	78,9	**93,3**	97,6
TMR				49,7	**58,2**	65,6	77,0	**92,6**	97,9
TB				49,0	**56,8**	65,0	79,5	**94,2**	99,1
BC				45,8	**54,4**	63,7	77,3	**90,3**	97,5
BMR				54,3	**60,4**	65,7	81,9	**93,7**	97,5
BB				48,0	**56,1**	65,4	79,5	**93,1**	99,9
VIM-1	55,5	0,058	0,0837	-13,8	-1,4	5,0	6,0	17,8	25,6

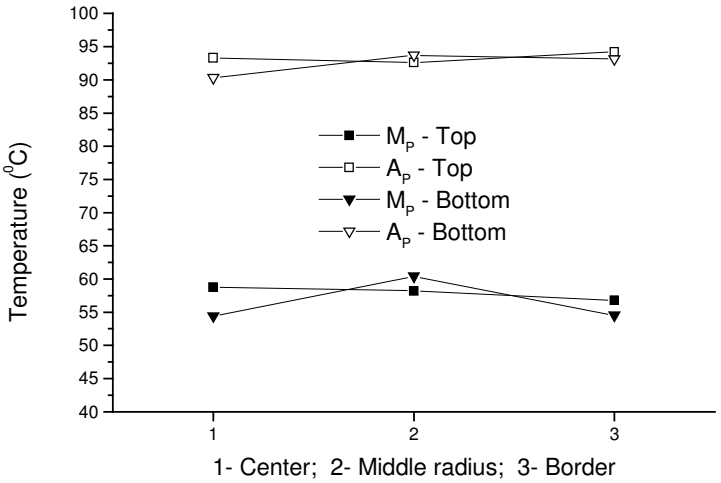
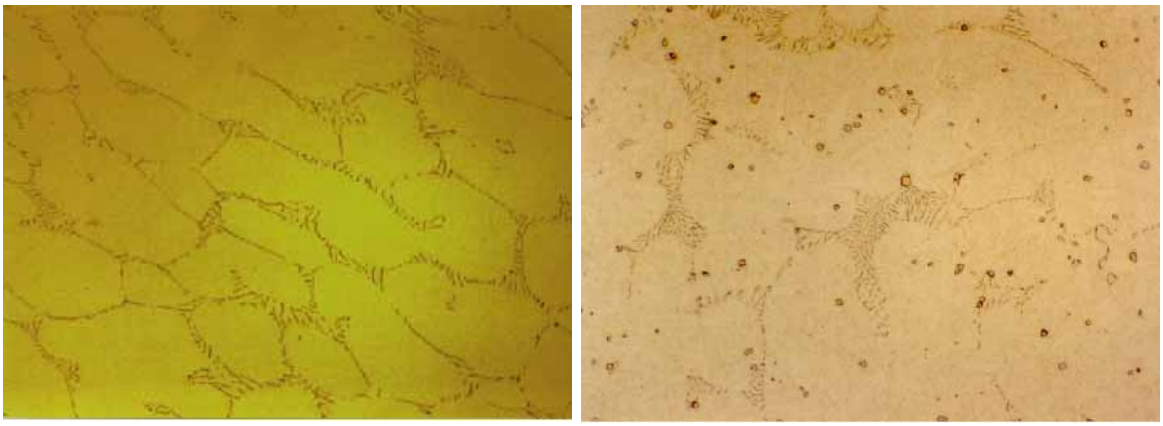


Figure 4. Direct and reverse pick martensitic transformation temperatures, M_P and A_P as a function of radial direction at ingot top position and bottom position.

Another aspect that should be emphasized is the low values of carbon content that was 0,013wt% presented by EBM processed ingot compared to about 0,06wt% of VIM product, that is, almost five times lower. This aspect could be seen from micrographies. Figure 5a shows the micrography of EBM ingot and no TiC particles is seen as far as the carbon content is lower than solubility limit of 0,025wt%. Figure 5b is from VIM ingot and the orange colored TiC particles are clearly seen.

This work confirm the earlier results( ) showing that the use of EBM process to produce NiTi SMA is perfectly viable and that the use of dynamic process for scaling up is also possible. The researches are in progress to analyze operational aspects of EBM to scale up the process. The possibilities to produce much clean material than ever made certainly will be important in areas such as medical application opening new possibilities. Also the possibilities of producing clean material with low carbon content open the necessity to reanalyze data such as martensitic transformation temperatures and other shape memory properties.



(a) (b)

Figure 5. (a) TiC precipitates free EBM ingot, 0,013wt%C (400X) and (b) Orange colored TiC precipitates from VIM ingot 0,058wt%C (200X)

CONCLUSIONS

It has been shown that electron beam melting can be scaled up to produce relatively large ingots of NiTi shape memory alloys. The specific conclusions from this work are summarized below.

By dynamic process of continuous charge feeding and continuous casting it was produced a 270mm long by 40mm in diameter ingot weighing around 2,2kg after one melting and two remelting.

The radial homogeneity was very good confirmed by small variation of around 2^{o}C and 6^{o}C in pick martensitic transformation temperatures for the top position and bottom position respectively.

The homogeneity along the length was also very good with the average of pick temperature difference of only 1^{o}C.

The carbon content of EBM ingot was 0,013wt% that is almost five times lower than the values presented by VIM processed ingot.

The oxygen content depends upon the raw material as far as the melting chamber internal pressure is very low (10^{-3} to 10^{-2}Pa).

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