Scale up of NiTi shape memory alloy production by EBM

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Abstract. The usual process to produce NiTi shape memory alloy is by vacuum induction melting (VIM) using a graphite crucible, which causes contamination of the melt with carbon. Contamination with oxygen originates from the residual oxygen inside the melting chamber. An alternative process to produce NiTi alloys is by electron beam melting (EBM) using a water-cooled copper crucible that eliminates carbon contamination, and the oxygen contamination would be minimal due to operation in a vacuum of better than 10^{-2}Pa. In a previous work, it was demonstrated that the technique is feasible for button shaped samples weighing around 30g. The present work presents the results on the scale up program that enables the production of larger samples/ingots. The results are very promising in terms of chemical composition homogeneity as well as in terms of carbon contamination, the latter being four to ten times lower than the commercially-produced VIM products, and in terms of final oxygen content which is shown to depend primarily on the starting raw materials.

1. INTRODUCTION

The usual process to produce NiTi SMA is by Vacuum Induction Melting (VIM) using high-density graphite crucibles to minimize the carbon contamination of the melt. The carbon is soluble in liquid nickel and it has great affinity to titanium. The contamination by oxygen comes from residual oxygen inside the melting chamber whose internal pressure is around 10Pa. An alternative process to produce NiTi alloy is by Electron Beam Melting (EBM). The EBM process is known since the 1950's and it has been extensively used mainly for refining refractory metals such as Mo, Ta, Nb and W and also reactive metals such as Ti, Zr, Hf and its alloys [1]. Its use for processing alloys such as Ti6Al4V [2, 3, 4] and superalloys [5] is more recent. In an EBM, the contamination by carbon is completely eliminated since melting is done in a water-cooled copper crucible and the contamination by oxygen is minimized 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. The disadvantage of the EBM process in alloy production comes from the fact that on melting and remelting it is difficult to control the nominal chemical composition due to the high vacuum operation, which causes some component evaporation. For the NiTi SMA, it should be noted that any small deviation in the chemical composition results in large changes in the martensitic transformation temperatures, especially on the nickel-rich side of the phase diagram [6, 7]. In recent work, Otubo et. al. [7] produced button-shaped samples of NiTi alloy weighing around 30g and showed that the use of EBM is a viable process. The weight loss after double melting was around 0.36% and was mainly Ni, which has a higher vapor pressure than Ti. Furthermore, the final carbon content was between 0.012 and 0.016wt% compared to 0.04 to 0.06wt% in the NiTi alloy commercially-produced by VIM. Matsumoto also presented some results on the preparation of NiTi and NiTi-based ternary alloys using EBM and demonstrated that the EBM is a viable process as long as the vapor pressure of the ternary addition is 1Pa or lower [8, 9]. The objective of this work was to scale up the NiTi alloy production by EBM by producing and characterizing larger EBM ingots.

2. EXPERIMENTAL PROCEDURE

The ingot production using 80kW EB furnace was divided into two stages:

First of all, a disc-shaped ingot (hereafter referred to as the disc ingot) was produced via a **static process** where the alloy components are charged and melted together. The charge materials consisted of 99.84wt% purity Grade 1 titanium and 99.95wt% purity electrolytic nickel, both as 1mm thick plate, cut in $100x100mm^2$ pieces, intercalated together and cast in a shell-shaped water-cooled copper crucible. The charge target composition was Ti55.1wt%Ni and the charge weight was approximately 345.6g. The EB power required to melt the entire charge was 10kW while that necessary to keep the bath liquid was 6.5kW; this was maintained for 15 minutes for homogenization. The melting chamber internal pressure varied from $8x10^{-3}$ to $8x10^{-2}$Pa during the melting/homogenization operation. The ingot was inverted and remelted three times resulting in a final ingot weight of 341.3g. Upon completion of every melting and remelting operation, the electron beam was extinguished by decreasing the power slowly and kept under vacuum for 60 minutes for complete cooling.

In a second stage, two larger and more complex ingots were produced using a **semi-dynamic process**, that is, by continuously feeding the alloying elements into the path of the electron beam. Specifically, bar-shaped charge pieces with the desired composition were fed horizontally and cast into a constant volume water-cooled copper mold with a tapered cylindrical geometry as follows: 39.5mm top diameter, 37mm bottom diameter and 52mm height. The feeding charge was prepared by intercalating $0.41x35x490mm^3$ grade 1 titanium plate (foil) with $0.89x35x490mm^3$ electrolytic nickel plate (foil) with a total weight of 980g. The plates were arc welded to each other ending up with linear nominal composition along the sandwiched bar of Ti54.9wt%Ni and final dimensions of $10x35x490mm^3$. The first ingot was produced by positioning the bar width (35mm) perpendicular to the beam direction. Unfortunately, this configuration was not adequate because any bar misalignment promoted dripping of the liquid drop outside the mold. Even so, using this configuration, a 330g ingot was produced. The second ingot was produced by positioning the bar thickness (10mm) perpendicular to the electron beam direction, thereby readily accommodating the small bar misalignment. With this configuration, it was possible to completely fill the crucible producing a 455g ingot. The pressure inside the melting chamber was kept between 2 to $4x10^{-3}$Pa with electron beam power of 6.5kW during continuous melting. Both ingots were kept under vacuum for 60 minutes after the EB power was turned off. The smaller ingot was used to analyze the chemical composition homogeneity along the ingot and the larger one was saved for mechanical processing tests.

The ingots were analyzed in terms of chemical composition by X-ray fluorescence (Ni), combustion method (C) and inert gas fusion method (O) and correlated with martensitic transformation temperatures measured by differential scanning calorimetry (DSC).

3. RESULTS AND DISCUSSION

The disc ingot produced using the static process and the two ingots produced with the semi-dynamic process were all visually shiny indicating that the 60 minute hold, under vacuum after the EB gun was turned off, was sufficient to completely cool and avoid oxidation.

After melting and remelting three times, the final weight of the disc ingot was 341.30g, which corresponds to a total mass loss of 1.2% (or 0.3% loss every per melting event). This is slightly greater than the 0.18% loss per melting reported for the button sample and is reasonable considering that the exposed area to the electron beam for the disc ingots is approximately 14 times larger than that for the button sample presented in earlier work [7]. The disc ingot was sectioned and a sample for chemical analyses was taken from middle radius at 1/2 height (1/2HMR). For the DSC measurements, samples were taken from the center at 1/2 height (1/2HC), from the middle radius

region (1/2HMR) and from near the edge (EDGE). Table 1 shows the chemical composition indicating that the relative nickel loss was larger dropping from the nominal composition of 55.1 to 54.7wt% due to its higher vapor pressure when compared with titanium. It is emphasized that the carbon contents (0.007wt%) of the EBM ingots are almost ten times lower than the 0.058wt% typical of VIM-processed ingots [unpublished work]. For comparison, the carbon content typical of commercial NiTi alloys produced by VIM varies from 0.04 to 0.06wt%. The final oxygen content for the disc ingot was 0.1050wt% and it depends primarily on the oxygen content in the initial raw material since the melting is done in vacuum. The composition homogeneity along the radial direction is included in Table 1 along with the peak temperatures or the martensitic transformation, M_P, and the reverse martensitic transformation, A_P, measured at three locations as mentioned before. Those results are plotted in Figure 1. The M_P temperature varied from 58.3 to 63.1°C and the A_P from 91.0 to 97.2°C; these are considered to be very small variations given the steep dependence of the M_p and A_p on chemical composition.

Table 1. Chemical composition and martensitic transformations temperatures for disc and 330g ingots.

Sample	Positions	wt%Ni(nominal)	wt%Ni	wt%C	wt%O	M_P(°C)	A_P(°C)
Disc Ingot	1/2HC	55.1				62.5	97.2
	1/2HMR	55.1	54.70	0.007	0.1050	58.3	91.0
	EDGE	55.1				63.1	95.8
Ingot (330g)	3/4H	54.9	54.79			45.7	78.3
	1/2HMR	54.9	54.90	0.011	0.064	41.0	71.6
	1/2H	54.9	54.90			38.5	71.3
	1/4H	54.9	55.00			23.6	48.0
*	VIM	55.5	55.61	0.058	0.0837	-1.4	17.8

* Unpublished result of VIM ingot
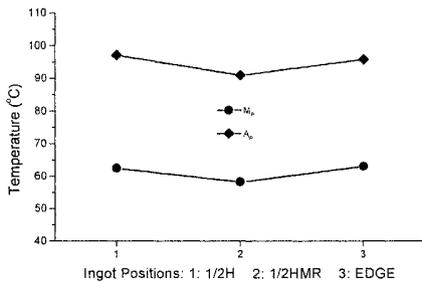
Figure 1. Direct and reverse martensitic transformation temperatures of disc ingot.
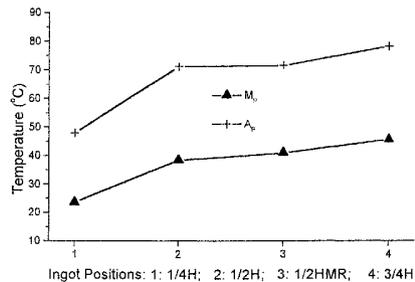
Figure 2. Direct and reverse martensitic transformation temperatures for 330g ingot.

Of the two ingots produced by continuous feeding and static casting, only the small 330g one was analyzed in terms of chemical composition and martensitic transformation temperatures. Samples for chemical analyses and DSC measurements were taken at: 1/4 height (1/4H); 1/2 height (1/2H) and 3/4 height (3/4H) from the bottom along the axis direction. To check the radial homogeneity, one more sample was taken at 1/2 height at middle radius (1/2HMR). The results are also shown in Table 1. The carbon content was almost twice, 0.011wt%, that in the disc ingot yet almost six times lower than the VIM ingot [unpublished result]. The oxygen content, 0.064wt%, was lower than that in the disc ingot and comparable to the VIM ingot. From Table 1, one can see that the nickel content decreased from 55.00wt% at the bottom (1/4H) to 54.90wt% at ½ height (1/2H) to 54.79wt% at ¾ height (3/4H). The aim nominal composition of 54.9wt%Ni was obtained only at ½ height. As shown in Table 1 and Figure 2, the direct peak martensitic transformation temperatures M_P, were 23.6; 38.6 and 45.7°C while

the reverse peak martensitic transformation temperatures A_P, were 48.0; 71.3 and 78.3°C respectively for 1/4H; 1/2H and 3/4H corroborating the composition data [6, 7]. The radial homogeneity can be seen by comparing data of samples 1/2H and 1/2HMR that exhibited close values. The decrease in nickel content from the bottom to top along the ingot axis is intimately related to the casting configuration used. In the continuous feeding and static casting process, the liquid pool level is raised as the casting proceeds. Therefore, when the pool level is near the crucible bottom, its exposure to the EB is lower minimizing the Ni evaporation. As the pool level increases, the intensity of the incident EB increases, thereby increasing component evaporation, mainly nickel. This kind of problem should not occur for continuous feeding and casting process. The scale-up program of NiTi production by EBM is now underway using the **dynamic process** of continuous feeding and continuous casting and the results will be published soon.

4. CONCLUSIONS

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

1. A **static process** of charge feeding, EBM and casting was used to produce a 341g disc ingot. The compositional homogeneity along the radius was confirmed by chemical analysis and martensitic transformation temperature data. The mass loss was determined to be about 0.3wt% per melting/remelting cycle.

2. A **semi-dynamic process** of continuous charge feeding, EBM and static casting was used to produce two large ingots. In this case, the nickel content decreased from the bottom to the top due to greater evaporation at the higher positions in the ingots. This problem should not occur in a truly **dynamic process** where the liquid pool height remains constant.

3. A significant advantage of EBM is that the carbon content in the final product is four to ten times lower than that in typical VIM ingots. Furthermore, the oxygen content depends upon the levels in the initial raw materials.

4. The charge preparation for EBM should compensate for the mass loss due to component evaporation.

5. The various results presented here confirm the earlier work showing that the production and scale up of NiTi by EBM is feasible.

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