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Advances in Materials Processing Technologies

NITI SMA production using ceramic filter during pouring the melt[*]

O.D. Rigo[a], J. Otuboa,[b] C. Moura Neto[b] and P.R. Mei[a]

[a]Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas – UNICAMP, 13083-970, Campinas, SP, Brazil, email: pmei@fem.unicamp.br

[b]Instituto Tecnológico de Aeronáutica – 12228-900, S. J. Campos, SP, Brazil.

Abstract: The usual process to produce NiTi shape memory alloys is by vacuum induction melting (VIM) using graphite crucibles which contaminate the bath with carbon. Carbon reacts with titanium precipitating TiC influencing the matrix composition which affects the martensitic transformation temperatures. Furthermore, the presence of TiC makes the final product difficult for mechanically process using cold working steps. In this study we present preliminary results of our attempt to remove the TiC from the melt using ceramic filters during pouring and analyzed the efficiency of the filtering process and some results will be presented.

Keywords: NiTi; Shape memory; VIM; Ceramic filter.

1. INTRODUCTION

Although the NiTi shape memory alloys (hereafter called NiTi SMA) are known worldwide since the 1970's [1], the literature relating processing are few in comparison to that concerning characterization and martensitic transformation phenomena mainly due to production difficulties (there are very few producers in the world). In Brazil there are few research groups working on NiTi SMA and Koshimizu [2, 3] and Andrade [4, 5] did the pioneering works. Our group has been working on NiTi SMA processing since 1997 [6, 7, 8] using two processes: electron beam melting (EBM) and vacuum induction melting (VIM) in attempt to produce pilot scale ingots. The main problem in NiTi production is the contamination by carbon and oxygen making the final product brittle. Beside that, the contamination by carbon and oxygen causes deviation in the martensitic transformation temperatures to lower values. The main commercial process for producing NiTi SMA is by VIM using graphite crucibles and graphite ingot molds. The contamination by carbon comes from the graphite crucible, which reacts with both nickel and titanium. The use of other types of crucibles, such as MgO and Al_2O_3 contaminates the bath with oxygen [1]. The contamination by oxygen can also come from residual oxygen inside the melting chamber since the pressure is not so low (1 to 10 Pa). This work analyzes the efficiency of using ceramic filters to remove mainly TiC particles from the melt during the pouring process. The melting and casting were done in graphite crucibles and graphite molds producing 1.5 kg ingots.

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2. EXPERIMENTAL

The ingots were melted in a VIM furnace with the melting power ranging from 15 to 17 kW and the melting chamber internal pressure from 1 to 10 Pa.

Two distinct melting procedures were used: the first consisted of producing three ingots using extruded high porosity (low density) graphite crucibles and molds with no ceramic filter during pouring the melt. The charge consisted of grade 1 titanium plates intercalated with electrolytic nickel plates consolidated by TIG welding. This was then set over a NiTi block which was already inside graphite crucible. The NiTi block served as a melting starter. It should be noted that the carbon solubility in NiTi compound is lower than for elemental nickel and titanium. The ingots produced in this step were used as a reference. Using the same charge mounting procedure as described above, the second set of experiments consisted of using low porosity (high density) graphite crucibles and pouring the melt through a ceramic filter.

The ceramic filter was mounted inside a graphite holder, Figure 1, and the set mounted on the top of graphite mold, Figure 2. The mold shown in Figure 2 was also used in first stage with no ceramic filter. The final ingot dimension was 180 mm long by 19 mm in diameter weighing around 1.5 kg. The filters tested included SiC with 15 and 25 ppi (pores per inch) with maximum operating temperature of 1590°C and ZrO_2-PSZ (partially stabilized zirconia) with 25 ppi and maximum operating temperature of 1700°C.

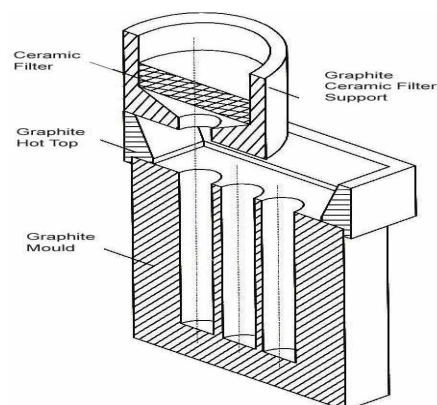

Figure 1. Ceramic filter inside the holder

Figure 2. Ceramic filter on the top of mold

3. RESULTS AND DISCUSSION

Table 1 presents the chemical composition of the ingots produced with and without ceramic filters: ingots 1, 2 and 3 were cast without ceramic filter showing very high and increasing values of carbon content from 2440 to 4010 ppm; ingots 4 to 11 were produced using ceramic filters during pouring and contain much lower carbon contents ranging from 990 to 2430 ppm.

The high carbon content in the ingots produced without filters is attributed to the use of extruded graphite crucible that presents high porosity promoting large actual contact area between liquid bath and graphite crucible surface and this contact area increases (for the same liquid volume) as the number of melts increases (using the same crucible), increasing the carbon content as presented by ingots 2 and 3. The low carbon content presented by the second set of ingots (4 to 11) compared to ingots produced in first stage is due to the use of high density graphite crucible.

Table 1.
Ingots chemical composition

Ingot	Filter	Ni (wt%)	Ti (wt%)	C*(ppm)	C (ppm)	O (ppm)	N (ppm)
1	-	55,31	remainder	2440	-	358	19
2	-	54,60	remainder	2750	-	-	-
3	-	54,89	remainder	4010	-	632	8
4	SiC	55,56	remainder	1400	1200	-	-
5	SiC	55,20	remainder	2430	-	-	-
6	ZrO_2-PSZ	55,26	remainder	1150	1100	621	3
7	ZrO_2-PSZ	55,21	remainder	1020	1000	390	9
8	ZrO_2-PSZ	55,35	remainder	1600	1680	636	13
9	ZrO_2-PSZ	55,45	remainder	990	1000	476	12
10	ZrO_2-PSZ	54,63	remainder	1800	1880	329	4
11	ZrO_2-PSZ	54,10	remainder	2300	2400	-	-

(*) Carbon content before filtering.

The higher carbon content presented by ingots 8, 10 and 11 is due to degradation of crucible inner surface, but still lower than the lowest values found in the first stage.

Also from Table 1, it can be seen that the carbon content is practically the same before and after filtering showing that the ceramic filter was inefficient in removing TiC precipitates although, as shown by SEM analyses, the adhesion of TiC on the porous surface is quite visible. The oxygen content varied from 329 to a maximum of 636 ppm and nitrogen content from 4 to 19 ppm showing no difference between two processes. It should be emphasized that the oxygen and nitrogen contents in the final product are much more dependent on the initial raw material than the melting process itself due to operation in vacuum.

Another aspect that should be analyzed is the dichotomy between the results presented in Table 1 that shows no difference in carbon content before and after filtering, and the SEM analyses showed clearly the adhesion of TiC particles on the surface of the ceramic filter. The explanation could be as follows: taking into account that the primary TiC particle dimensions are some orders of magnitude smaller than the pores dimensions, the basic retention mechanism of these particles during filtering is related to the occurrence of contact between those particles and the pores surface [9, 10, 11]. The probability of particle adhesion onto pores surface increases with increasing contact area and longer liquid paths through the ceramic filter channel. The thickening of TiC particles layer, or the agglomeration onto the pores surface occurs by the successive adhesion of those particles passing through the pores being higher in channels between adjacent pores. On the other hand, to keep enough fluidity during pouring it is necessary to superheat the bath between 150 and 200°C. Since the melting point of NiTi SMA (for the compositions tested) is around 1310°C, the bath temperature should be kept between 1450 and 1500°C. This temperature is sufficient to keep carbon in solution or to dissolve TiC particles. At the end, the bath passing through the ceramic filter should acquire a stationary equilibrium condition of adhesion and dissolution justifying the results shown in Table 1. Finally it should be emphasized that, although apparently the SiC

ceramic filter is more efficient to remove the TiC particles from the melt its use was interrupted because this type of ceramic is chemically bonded, being its maximum operating temperature of 1550°C, which is too close to the bath temperature (approximately 1500°C). In this range of temperature, the SiC filter is easily damaged, and its fragments are carried into the bath, and, consequently the final product contains higher carbon contents.

4. CONCLUSIONS

The change from a high porosity to a low porosity graphite crucible resulted in a drastic reduction of carbon content due to reduction in real contact area between crucible surface and the liquid bath. Independent of graphite type, its inner surface degradation as a function of usage is very high requiring reworking the crucible. Although SEM analyses have shown TiC particle adhesion onto the pores surface the chemical analyses show that the use of ceramic filter of both types is not efficient to remove those particles. The resulting carbon content before and after filtering is the same.

Since the TiC particle dimensions are some orders of magnitude smaller than the pores dimensions, the particle retention is related to the probability of contact between these particles and the pores surfaces being higher the longer is the liquid path through the ceramic filter.

The superheat of 150 to 200°C, necessary to keep the liquid fluidity through the ceramic filter, keeps carbon in solution or may dissolve the TiC particles generating a stationary condition of adhesion and re-dissolution.

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