THE EFFECTS OF IMPURITIES CARBON AND OXYGEN ON THE TEMPERATURES AND ENTHALPIES OF MARTENSITIC TRANSFORMATION OF NiTi SMA

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Abstract. The martensitic transformation temperatures and enthalpies of NiTi SMA are strongly dependent upon the nickel content and impurities carbon and oxygen. Nickel is the high temperature phase stabilizing element and carbon and oxygen precipitate compounds that make the matrix richer in nickel content compared to initial nominal composition. As far as those impurities are inherent to processing techniques (VIM and EBM), its overall effects should be understood aiming scientific and technological aspects. This work shows that depending upon the degree of contamination the negative deviation of peak martensitic transformation temperature compared to reference data could be as large as 100°C while the values of enthalpies changes as a function of nickel content are overlapped by reference curve that by its turn presents a maximum around the equiatomic composition. Values of enthalpies changes plotted as a function of peak martensitic transformation temperatures present linear relationship with positive slope. It means that the lower the enthalpies the lower is the peak martensitic transformation temperatures and at end no phase change should occur.

Keywords*: NiTi, Martensitic Transformation, Impurities*

1. Introduction

Our research group has been working on NiTi SMA production since 1997 using two processes: electron beam melting (EBM) and vacuum induction melting (VIM) for obtaining ingot in pilot scale (Rigo et al. 2002 and 2005a, Otubo et al. 1998, 2003, 2004 and 2005). The contamination by carbon in VIM process is inherent to its process due to melting in a graphite crucible and it is extremely dependent upon the quality of the graphite used. Also, the production scale is a very important factor. The larger the scale the lower is the contamination by carbon due to decrease of contact area between the melt and graphite crucible (Rigo et al. 2002). For EBM process, no contamination by carbon occurs since it is melted in water cooled copper crucible. Therefore the carbon content in the final product comes from the initial raw material, mainly titanium. For both processes, the contamination by oxygen is much more dependent upon the raw materials as far as they operate in high vacuum (better than 10^{-2}Pa). The contamination by carbon and oxygen generates some consequences: firstly, higher the contamination more difficulty will be the mechanical processing due to material embrittlement and secondly, carbon and oxygen precipitate compounds that modify the original matrix composition that by its turn deviates the martensitic transformation temperatures and some others parameters such as enthalpy change. This work takes the several data already published by the group mainly in terms of carbon and oxygen contamination relating them to martensitic transformations temperatures and enthalpies changes and comparing to reference curve which is supposed to be free from carbon and oxygen interference (Rigo, Otubo and Mei, 2005).

2. Experimental Procedures

The NiTi SMA ingots were produced by two processes: VIM and EBM. Through VIM, the ingots were melted in graphite crucible and then cast also in a graphite mould varying the ingots size (1.5 and 4.3kg) and graphite quality (low and high porosity). The melting power ranged from 15 to 17kW and the melting chamber internal pressure from 1 to 10^{-2}Pa. The EBM ingots were prepared in a 80kW EB furnace with EB power of up to 13.5kW and melting chamber internal pressure up to 10^{-3}Pa. The ingots weighting from 0.175 to 2.2kg were melted in a water cooled copper crucible. A grade 1 titanium plate and electrolytic nickel were used as raw materials for both processes. The fabrication procedures can be found elsewhere (Rigo et al. 2002, Otubo et al. 1998, 2003, 2004 and 2005).

The martensitic transformation temperatures and respective enthalpies changes were taken from differential scanning calorimetry (DSC) data. It was used a STA 409 C DSC Netzsch equipment with cooling and heating rate of 5°C per minute. The temperature range was set between -140 and +150°C and the samples protected in inert helium gas. For details see reference (Rigo, Otubo and Mei, 2005).

3. Results and Discussions

Table 1 presents the chemical composition of 15 ingots produced by EBM and VIM processes. The nickel content varied from 48.62 to 50.58at%. The lower values of carbon content below 240ppm in weight were presented by the samples taken from EBM ingots. The carbon content from VIM ingots varied from 543 to 2,440ppm. The carbon contents in the commercial range, that is, 600ppm, were presented by VIM ingots melted in low porosity graphite crucible weighting 4,3kg while those with higher carbon contents were melted in high porosity graphite crucible with ingot weight of 1,5kg. The oxygen content has varied from a minimum of 358 to a maximum of 1536ppm irrespective of the processing technique depending only upon the initial raw materials nickel and titanium. Table 1 also shows the direct and reverse peak martensitic transformations temperatures M_P and A_P, its respective hysteresis A_P-M_P and enthalpies changes ΔH_M and ΔH_A (M for direct and A for reverse martensitic transformation respectively).

Table 1. Ingots chemical compositions and respective martensitic transformation parameters M_P, A_P, A_P-M_P and ΔH.

INGOT	Ni (at%)	C (ppm)*	O (ppm)	M_P (°C)	A_P (°C)	A_P-M_P (°C)	ΔH_M (J/g)	ΔH_A (J/g)
1	48.62	240	1,536	55.1	90.0	34.9	28.56	-27.05
2	49.50	70	1,050	58.3	91.0	32.7	30.23	-30.16
3	49.60	1,880	329	-26.5	-3.8	22.7	16.62	-18.28
4	49.63	240	1,482	13.9	46.7	32.8	21.45	-21.58
5	49.66	130	640	60.4	93.7	33.3	-	-
6	49.68	660	1,113	51.2	81.9	30.7	31.48	-31.73
7	49.74	140	640	55.0	86.3	31.3	23.9	-22.87
8	50.01	543	924	22.0	52.7	30.7	2666	-27.05
9	50.13	1,000	390	-46.0	-21.9	24.1	14.63	-14.87
10	50.17	1,100	621	-67.5	-39.1	28.4	9.08	-9.12
11	50.18	600	564	21.2	47.2	26.0	26.55	-26.74
12	50.21	2,440	358	-18.0	4.1	22.1	16.26	-16.50
13	50.42	520	570	-4.9	17.0	21.9	22.23	-23.37
14	50.49	580	837	-1.9	17.8	19.7	22.42	-23.92
15	50.58	150	1,055	-29.9	-10.8	19.7	16.93	-18.86

* ppm are in percent weight

The effect of carbon and oxygen content on the direct peak martensitic transformations temperatures M_P can be better visualized attempting to Figure 1 which is a plot of M_P as a function of nickel content. Before starting the analyze it is important to clarify some aspects of Figure 1. The outer curve is the reference curve obtained from specially prepared small arc melted samples of NiTi alloy with carbon content below its solubility limit and the effects of oxygen above its solubility limit were taken into account. Therefore the outer curve is supposed to be free from carbon and oxygen interference as pointed out in Rigo et al. (2005). The reference curve shows that for nickel content below equiatomic composition, there is little influence on M_P and above that same composition M_P decrease rapidly stabilizing the high temperature phase. Frenzel at al. (2004) shows similar curve for M_S (direct martensitic start temperature instead of M_P) which was initially compiled by Sawaguchi et al. (2003). Now let's compare data from VIM (square open black dot) and EBM (round open dot) with the reference curve. It can be observed that excepting two data, ingot 2 and 5, all the others are below or coincident to reference curve just mentioned.

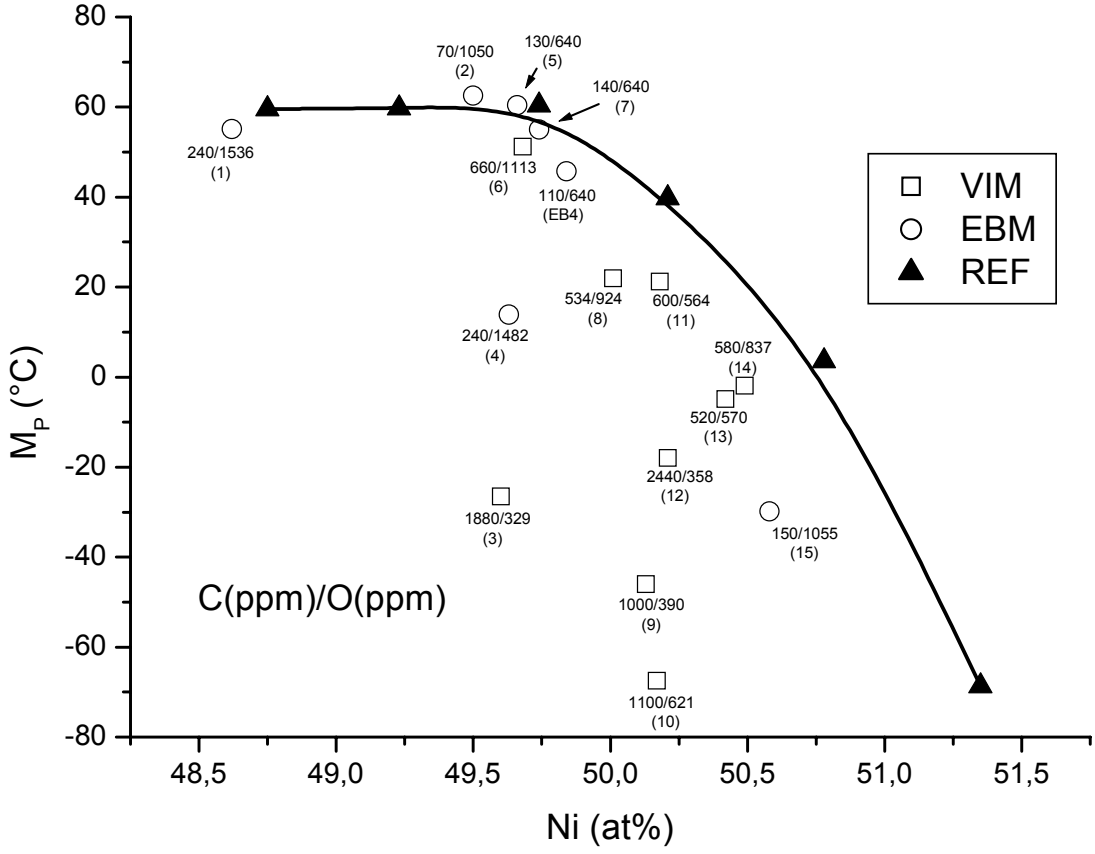

Figure 1. Peak martensitic transformation temperature M_P as a function of nickel, carbon and oxygen contents.

Let's start analyzing ingots 3, 9 and 12 which present carbon content above 1,000ppm or respectively 1,880, 1,000, and 2,440ppm but with oxygen content below 400ppm. Comparing to reference curve, ingot 3 with nickel content of 49.6at% should present M_P value around 60°C. Instead, its value is -26.5°C with negative deviation of ~86°C which is the behavior of an alloy with higher nickel content (~50.1at%). Ingots 9 and 12 also present similar behavior with M_P negative deviation of 58 and 88°C respectively.

Ingot 10 with 1,100ppm carbon and 621ppm oxygen presented the highest deviation value of 107°C in relation to reference curve. Although its nickel content is 50.17at%, the M_P value of -67.5°C presented by the ingot 10 is for an alloy of 51.3at%.

Another group of ingots is composed by ingots 8, 11, 13 and 14 which present carbon content in the range of 520 to 600ppm and oxygen in the range of 564 and 837ppm, that is, those values are average composition found in commercial products (ASTM F-2063-00, 2000). It should be observed that the deviation of M_P temperatures in relation to reference curve is much lower than the first group varying from a minimum of 18.5°C (ingot 11) to a maximum of 30.6°C (ingot 13).

The third group is represented by ingots 1, 2, 4 and 15 which are the samples from EBM ingots with very low carbon content (maximum of 240ppm) while the oxygen content is relatively high. Related to oxygen content, further two subgroups can be observed: ingots 2 and 15 with ~1,050ppm and ingots 1 and 4 with ~1,500ppm, that is, 50% higher in oxygen content. From the last two it is observed that for ingot 1 there is no influence on M_P while for ingot 4 the deviation on the same parameter was around 55°C. It means that the influence of oxygen contamination on martensitic transformation temperature is lower the lower is the nickel content below equiatomic composition as follow, 48.62at% for ingot 1 and 49.63at% for ingot 4. This tendency is also observed in ingots 2 (49.50at%Ni) and 15 (50.58at%Ni). Ingot 2 had its M_P value coincident with reference curve while ingot 15 presented a negative deviation of ~43°C.

The last group is also composed by the samples from EBM ingots. They are ingots 5 and 7 with carbon content below 150ppm and oxygen content of 640ppm. They are the samples with lowest level of contamination and as such their M_P are coincident with reference curve.

From the above we can see that the influence on M_P temperatures is larger the higher is the contamination by carbon and oxygen and that it is enhanced by the increase in nickel content. All the discussions done for M_P temperatures are valid also for A_P which are the peak reverse martensitic transformation temperatures. The only difference is that the temperatures are shifted to higher values as can be seeing in Table 1.

Summarizing it can be said that the increase in nickel, carbon and oxygen content, isolated or together contribute to lower the martensitic transformations temperatures mainly above nickel equiatomic composition. Nickel is the high temperature phase stabilizing element and carbon combines with titanium precipitating TiC particles and oxygen forms Ti_4Ni_2O complex oxide. These two compounds withdraw more titanium than nickel making the matrix richer in nickel explaining the negative deviation of M_P temperatures compared to reference curve.

Figure 2 shows the enthalpy change, ΔH_M as a function of nickel content. As for Figure 1, the outer curve of Figure 2 (triangle black dots) is the reference curve obtained from specially prepared arc melted samples (Rigo, Otubo and Mei, 2005) and others data are from VIM and EBM ingots (triangle open dots). The enthalpy change of reference samples presents a maximum of 35J/g around equiatomic composition and then decreasing for nickel content departing from that value. It means that the martensitic transformation is becoming more difficult as the nickel content depart from the equiatomic composition. Except for one point (ingot 4), all the data from VIM and EBM ingots presented lower values than the reference curve and the deviation from the same curve being larger the higher is their impurities content.

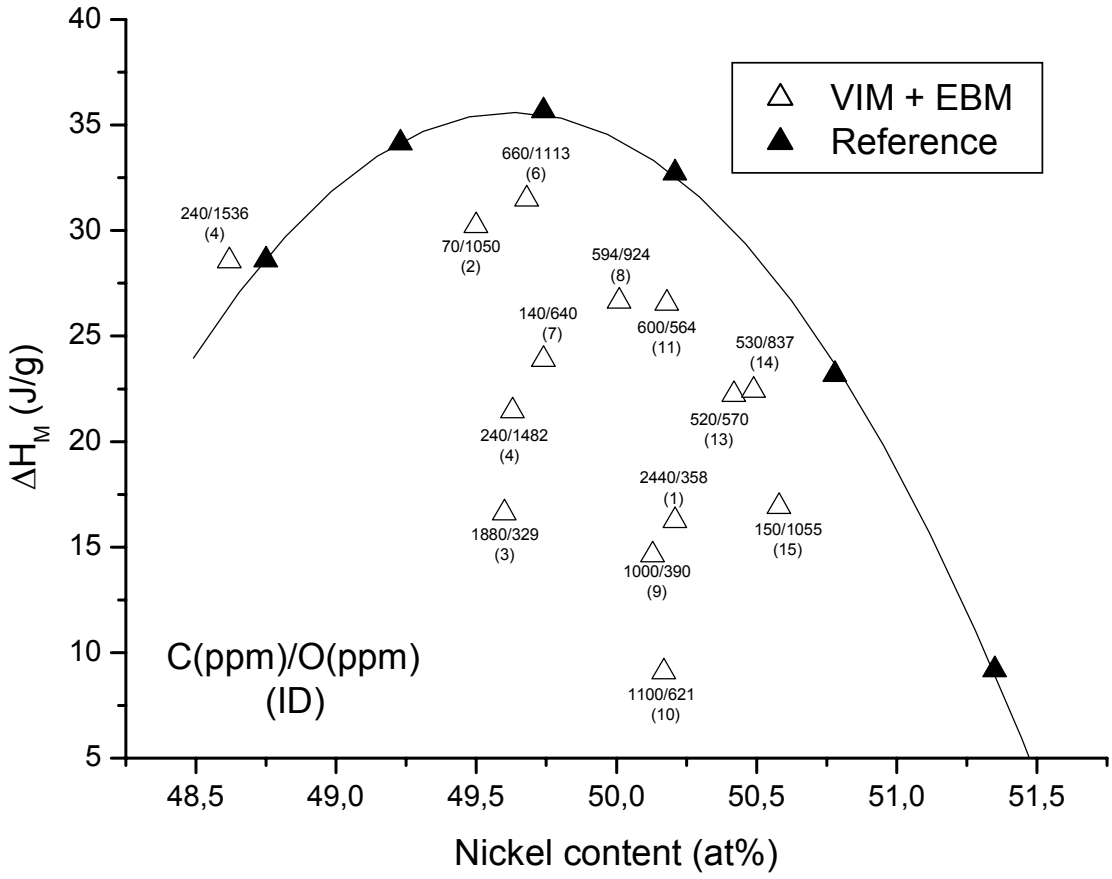

Figure 2. Enthalpy change as a function of nickel, carbon and oxygen content.

As shown in Figure 3, when the enthalpy change, ΔH_M is plotted as a function of peak direct martensitic transformation temperature, M_P irrespective of sample source or degree of contamination, its relationship is linear with positive slope. The enthalpies changes decrease as the M_P temperatures decrease indicating that the lower the martensitic transformation temperature more difficult is its transformation and at limit no transformation occurs at all.

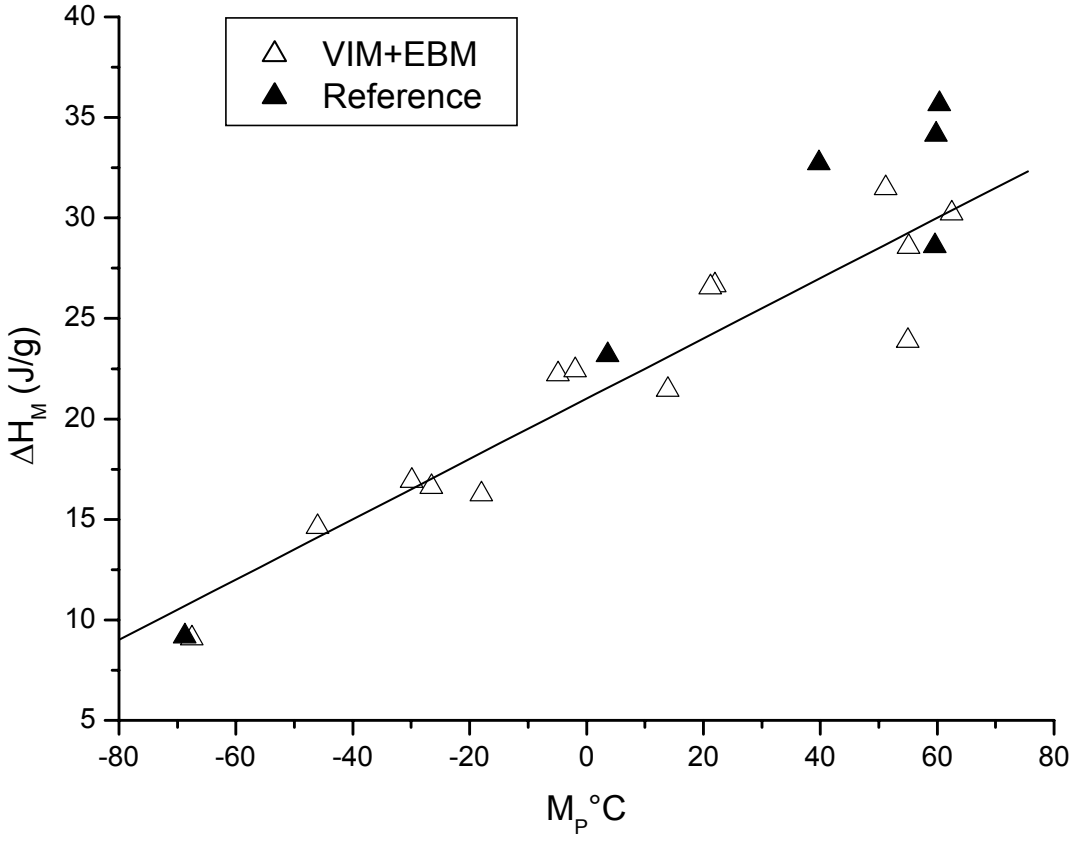

Figure 3. Enthalpy change as a function of peak direct martensitic transformation temperature M_P.

The last aspect that should be pointed out is the small hysteresis A_P-M_P presented by the NiTi samples as can be seeing in Table 1. Its values varied from a minimum of 19.7°C to a maximum of 34.9°C compared to 400°C for conventional steel. The narrow hysteresis is one of the characteristic of thermoelastic martensitic transformation of shape memory alloys **(**Verhoeven, 1975). Now restricting to the data presented in this work, Table 1, another interesting aspect that should be pointed out is that the values of hysteresis decrease as the M_P (or ΔH) decrease. At this point, care should be taken to analyze these hysteresis decreases. Usually small hysteresis is attributed to the easiness of martensitic transformation, that is, the easiness of forward and backward movement of martensite-martensite interface or martensite-austenite interface during heating and cooling cycles. That is not the case here because we are directing toward the lower M_P where martensitic transformation is getting more and more difficult. In that sense the decrease in hysteresis as the M_P temperature decreases is related to thermodynamic instability of martensitic phase which serves as potential for backward movement to high temperature phase. Studies are underway to better understand this topic.

4. Conclusions

This work has shown that:

The reference curve in Figure 1 shows that for nickel content below equiatomic composition, there is little influence on M_P and above that same composition, M_P decreases rapidly stabilizing the high temperature phase.

The increase in nickel, carbon and oxygen content, isolated or together contribute to lower the martensitic transformations temperatures mainly above nickel equiatomic composition.

The enthalpy change of reference samples presents a maximum of 35J/g around equiatomic composition and then decreasing for nickel content departing from that value.

Except for one point (ingot 4), all the data from VIM and EBM ingots presented lower values of enthalpy change than the reference curve and the deviation from the same curve being larger the higher is their impurities content.

The relationship between enthalpy change, ΔH_M and peak martensitic transformation temperature, M_P is linear with positive slope irrespective of sample source or degree of contamination.

The hysteresis A_P-M_P presented by the NiTi samples varied from a minimum of 19.7°C to a maximum of 34.9°C.

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