Effect of Nb Content in the Microstructural and Thermal Characteristics of NiTiNb Shape Memory Alloys

Maria Eurenice Rocha Cronemberger[a], Vitória Honorato Franco Menezes[a], Rodrigo da Silva[a],

Ícaro G.R. Santos[a], Vitor L. Sordi[a], Sebastião Elias Kuri[a], Carlos Alberto Della Rovere[a]*

[a]Universidade Federal de São Carlos (UFSCar), Programa de Pós-Graduação em Ciência e Engenharia de Materiais (PPGCEM), Rod. Washington Luís, 310 km 235, CEP 13565-905, São Carlos, SP, Brasil

The influence of Nb content variation on the microstructural and thermal characteristics of NiTiNb alloys was evaluated since these aspects are relevant to the control and adequacy of its shape memory properties for application purposes. The aim of this study was to observe how the Nb content acts in the formation of Nb-rich precipitates and the eutectic structures, which can make this alloys more complex. Microstructural characterization of the alloys was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and microanalysis by energy-dispersive X-ray spectroscopy (EDS), besides the thermal characterization by differential scanning calorimetry (DSC), and the comparison between the Nb alloys and the NiTi binary alloy. The results demonstrated a proportional dependence between the amount of β-Nb phase in the microstructures and the amount of Nb dissolved in the NiTi matrix with the Nb content. Although it was found that the increase in the Nb content causes the decrease of the martensitic (Mi) and reverse (Ai) transformation temperatures, the magnitude of thermal hysteresis was not significantly changed.

Keywords: *Shape memory alloy, NiTiNb alloys, niobium, microstructural characterization, SEM/EDS*

1. Introduction

In practical terms, phase transformation temperature and thermal hysteresis are important parameters to determine the engineering application and performance of shape memory alloys (SMA)[1]. Considering this, it is desirable and perfectly possible to control both the transformation temperature and the thermal hysteresis by thermos-adjusting the chemical composition of the alloy and/or using thermo-mechanical treatment[2].

In the case of the binary alloy system NiTi, of well-known commercial importance, the addition of a third element (Zr, Hf, Pd, V, Al and Nb) has proven to be efficient in controlling and adjusting the transformation temperature, as well as improving its shape memory characteristics and resulting in the widening of the range of the alloy's applications[3–7]. It can also help to control the thermal hysteresis amplitude, increase the austenitic resistance, reduce or increase the martensitic resistance, improve corrosion resistance and suppress the R-phase transformation[8]. Among the possible elements, the choice of niobium (Nb) as a third element is quite attractive, considering that the NiTiNb alloys exhibits large transformation hysteresis and an improvement in the shape memory effects, which is very useful for applications in pipe couplings, for example[1, 5, 6, 9].

Although the use of NiTiNb alloys containing 9 at% Nb is more representative compared to the others, its preparation is more complex[5] due to the formation of Nb-rich precipitates.

In that sense, some researches are considering the reduction of the Nb content in these alloys to evaluate the impact of the eutectic structure in the alloy's properties[4, 5, 10, 11]. According to them[1, 5, 10, 11], it seems consensual that the addition of low Nb contents is not enough to reduce the transformation temperatures and to extend the thermal hysteresis of the alloys. However, regarding the variation of microstructures, according to Nb content of the alloys, there still have adverse aspects to be evaluated, since it seems not to be fully established. Such as the formation of the eutectic phase, that is simply treated as phase β-Nb in most previous work[5, 10, 12–14], while it presents as a microconstituent composed of a lamellar structure of NiTi and β-Nb phases.

In addition, regarding the role of this structure, the Nb content in solid solution in the matrix and the influence of the ratio between Ni and Ti contents in the thermal characteristics should also require clarification. In this sense, as it understands that the subject is not exhausted and that systematic research has not yet been conducted sufficiently, the purpose of this work is to expand the study about the role performed by the Nb in the microstructural and thermal characteristics of NiTiNb alloys, searching to optimization of the Nb content in these alloys. Thus, this study focuses on the microstructural and thermal characterization of NiTiNb alloys with different quantities of Nb to evaluate how the deviation in the composition of the alloys affects these characteristics, due to its relevance for understanding and improving the shape memory alloys' characteristics.

*email: carlosdrovere@gmail.com

2. Materials and methods

The study was carried out in NiTiNb alloys that presented three different compositions. In that case, Nb content varied whilst keeping the proportion between Ni and Ti constant at 1.07. The nominal composition of the alloys is indicated below in Table 1.

Ingots of approximately 30 g were prepared from high purity elements, i.e. Nb pieces Alfa Aesar 99.8%, Ni pieces Alfa Aesar 99.9% and Ti unalloyed bar, in accordance with ASTM Standard F67, 99.3%, using the electric arc-melting furnace process with tungsten electrode and water-cooled copper crucible under inert atmosphere (Ar). The calculations for weighing the elements were done to obtain a constant Ni/Ti atomic ratio of 1.07 for all the alloys, varying the Nb content (3, 6 and 9 at%). An NiTi alloy with the same proportion between the elements was produced and used for comparison.

The alloys were homogenized at 850 °C for 2 hours and hot rolled at 850 °C until they reached a width of approximately 5 mm. Solution annealing was performed at 850 °C for 1 hour, followed by water quenching [5, 11, 15].

The samples were cut into cylinders with a diameter of 5 mm by electric discharge machining (EDM), embedded in cold curing polyester resin, wet sanding with granulometry grades varying from 150 to 600 mesh and polished with 1.0 μm alumina suspension, followed by chemical etching with Kroll's reagent (10 mL HF + 30 mL HNO_3 + 50 mL H_2O) [16].

The microstructural characterization of the alloys was performed using X-ray diffraction (XRD), scanning electrode microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Three regions were selected for each composition of the alloy, and each region's matrix, eutectic phase and Nb-rich precipitates (β-Nb particles) was analysed by EDS.

The transformation temperatures of the alloys were verified through DSC tests (differential scanning calorimetry), using samples of approximately 40 mg. These samples undergo a thermal cycle between 150 °C and -80 °C, with a heating and cooling rate of 10 °C/min, as specified by the ASTM F2004 [17].

The martensitic transformation start and final temperatures were measured for each alloy, when possible, and identified as Ms and Mf, respectively. The reverse transformation start and final temperatures (As and Af), as well as the transformation temperature peaks (Mp and Ap, representing the martensitic transformation temperature and the reverse transformation) were measured as well when possible.

3. Results and Discussion

The SEM micrographs of the studied alloys, containing 3, 6 and 9 at% Nb are presented in Figure 1 (b - d), respectively. The micrograph for the NiTi alloy is presented in Figure 1 (a), for comparison.

Note that, unlike the NiTi alloy, the NiTiNb alloys show a distinguishable dendritic microstructure. This represents a typical hypoeutectic microstructure, which is mainly composed of a NiTi (α) matrix, identified in the micrographs as a dark grey region, surrounded by an interdendritic eutectic structure (α + β-Nb), identified as a light grey region in the grain boundaries, whose formation result of an eutectic reaction, according to the pseudo-binary diagrams presented by Piao et al.[18] and Shi et al.[3] illustrated in Figure 2.

Figure 1 (b - d) also shows an increase of the eutetic structure's volumetric fraction with the increase of the Nb content in the alloys, showing that Nb cannot be completely dissolved in the NiTi matrix as predicted by the pseudo-binary diagram, which results in an eutectic phase, as observed by Ying et al.[11].

The EDS results shown on Table 2, present the average of the analysis results in the selected points (1: matrix; 2: eutectic phase; 3: β-Nb particles), as presented in Figure 3 (a), (b) and (c). The matrix NiTi (1) presents a certain Nb amount dissolved, which increases as a function of Nb addition in the alloys. The eutectic structure (2) also becomes more enriched in Nb, that is, the amount of Nb contained in this structure also increases with the increase of the content of this element in the alloy, as it was noticed by Jiang et al. and Xiao Fu et al. [1, 19].

Table 1. Nominal composition of the alloys (% atomic).

Material	Ni/Ti	Ni	Ti	Nb
NiTi	1	50	50	-
NiTi3Nb	1.07	50	47	3
NiTi6Nb	1.07	49	45	6
NiTi9Nb	1.07	47	44	9

Table 2. EDS results (% atomic).

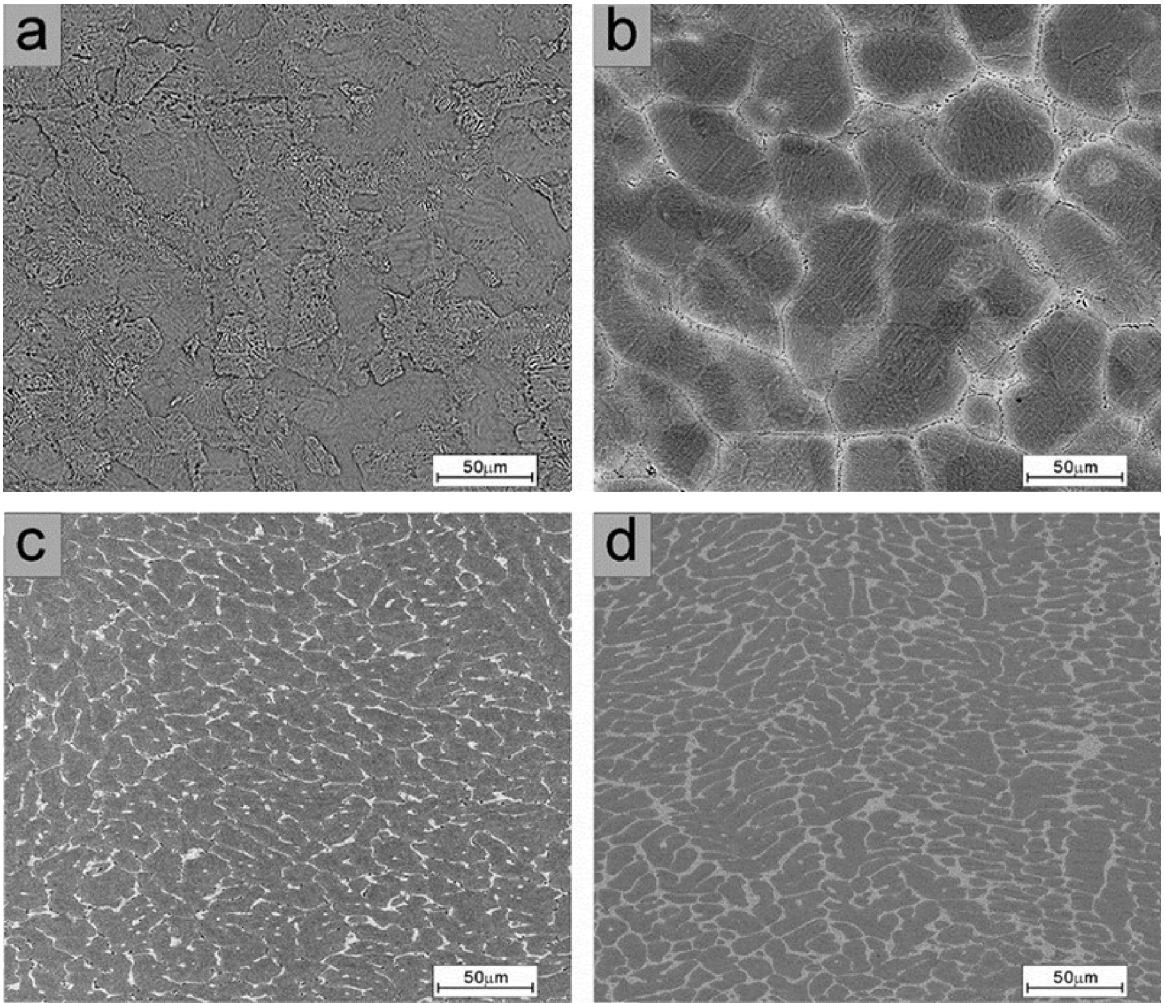| Material	Spot 1			Spot 2			Spot 3		
	Ni	Ti	Nb	Ni	Ti	Nb	Ni	Ti	Nb
NiTi3Nb	51.23	46.80	1.97	49.86	44.32	5.82	-	-	-
NiTi6Nb	50.32	46.06	3.62	42.99	41.02	15.99	33.61	36.34	30.05
NiTi9Nb	49.86	45.27	4.87	40.37	38.13	21.50	31.03	34.54	34.43

Figure 1. SEM micrographs of the solution annealing treated alloys (a) NiTi, (b) NiTi3Nb, (c) NiTi6Nb and (d) NiTi9Nb.
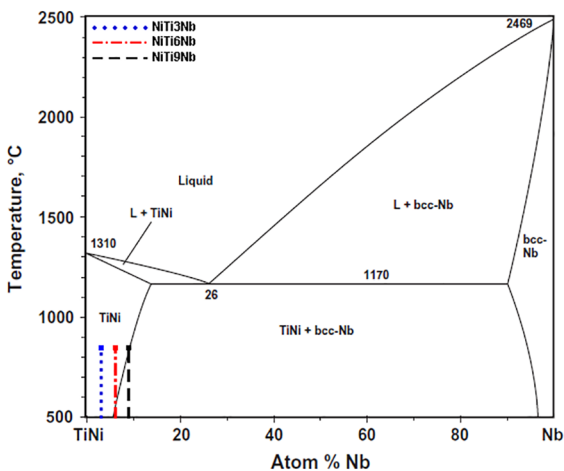

Figure 2. Phase diagram of the pseudo-binary "NiTi–Nb" system with studied compositions highlighted[3].

Analogously, Zhang et al., He et al. and Zhao et al. have reported fairly consistent EDS results in alloys with nominal composition 47 Ni – 44 Ti – 9 Nb (at%), demonstrating that there is a mutual solubility of both the Nb in the NiTi matrix and of both Ni and Ti in the β-Nb phase [5, 10, 20]. EDS analyses in point 3 show that the lighter regions of the eutectic phase can be identified as β-Nb particles (Nb enriched particles).

Besides the main phases already mentioned, some dark particles (represented in black) were found and identified as compounds containing Ti, Ni and Nb, similar to the ones pointed out as oxide particles $(TiNb)_4Ni_2O$ by Xiao Fu et al.[19], Zhao et al.[10] and Wei and Xinqing[12].

The XRD spectra obtained for the different compositions are shown in Figure 4. Besides presenting a primary phase, NiTi austenitic (B2) and martensitic (B19'), the binary alloy NiTi also shows two secondary phases, including Ni_4Ti_3 rich in Ni and Ti_2Ni rich in Ti, as observed by Chu et al.[21].

The peaks of these phases are suppressed with the Nb addition. As a result, only the phase Ti_2Ni can be observed with low intensity in the samples containing 3 at.% Nb[13]. The samples of the alloys containing 6 at.% Nb and 9 at.% Nb do not present peaks corresponding to secondary phases. In these cases, besides the NiTi (B2 and B19') matrix, the β-Nb phase can be observed[1, 13, 18, 22].

On the contrary, the results for the alloy with 3 at.% Nb do not show a crystalline peak for the β-Nb phase, suggesting that the β-Nb particles in the eutectic phase (α + β-Nb), finely distributed in small quantities, cannot be detected. The reason for that is possibly due to its small volume when compared to the matrix volume, or due to it being covered by the noise resulting from the analysis. By means of XRD analysis, He et al.[5] have observed only low intensity peaks for alloys with similar composition and they did not observe β-Nb particles through SEM analysis. Finally, the presence of carbides, oxides or free Ti and Ni was not detected, just as the analysis presented by Li et al.[13]. This suggests that the dark particles (shown in black), identified as possible oxide particles (like previously mentioned) are probably present in a very small volumetric fraction.

Figure 5 shows the resulting curves from the DSC analysis, making possible to observe the behaviour of the samples during thermally induced transformation. The exothermic peak on cooling represents the transformation from austenite phase to martensite phase, and the endothermic peak on heating is related to the reverse transformation from martensite to austenite phase. The transformation temperatures (Ms, Mf, As and Af) were determined from the intersections of two tangential lines to the cooling and heating peaks through the inflection points[17] and are shown on Table 3.
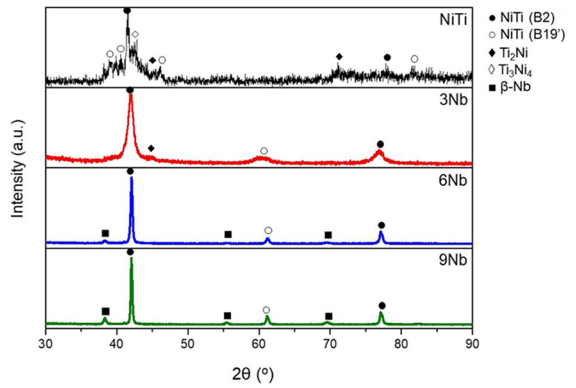

Figure 4. XRD spectra of the alloys NiTi and NiTiNb with different amounts of Nb.
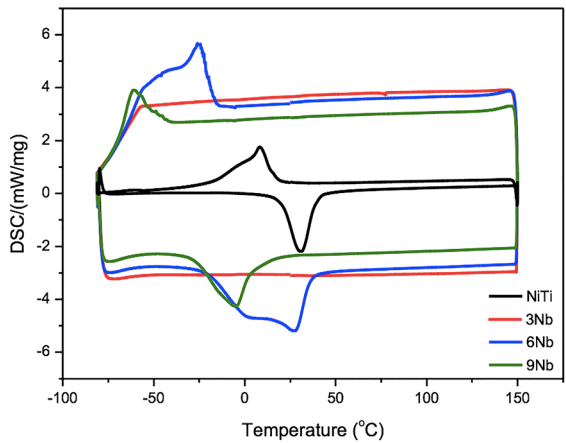

Figure 5. Resulting curves from the DSC analysis for the NiTi and NiTiNb alloys with different Nb contents.
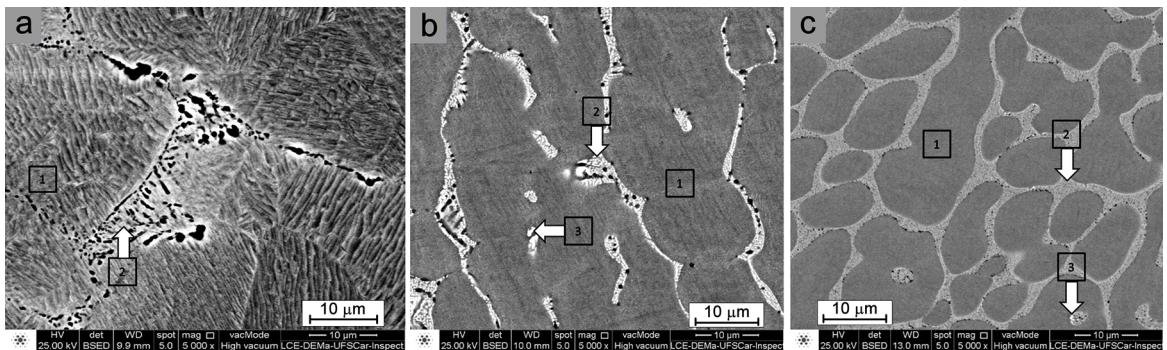

Figure 3. SEM micrographs of the alloys (a) NiTi3Nb, (b) NiTi6Nb and (c) NiTi9Nb, indicating the points chosen for the EDS analyses: (1) matrix, (2) eutectic phase, (3) β-Nb particles.

Table 3. Transformation temperatures (°C) obtained by the DSC curves.

Material	Ms	Mf	Mp	As	Af	Ap	(As-Ms)	(Ap-Mp)
NiTi	5	-16	8	20	39	31	15	23
NiTi3Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NiTi6Nb	-16	-33	-25	17	37	28	33	53
NiTi9Nb	-53	-70	-61	-28	2	-5	25	56

n.d.: not determined

This could not be done for the alloy with 3 at.% Nb since the curve for its thermal behaviour shows no exothermic or endothermic peaks, meaning that there are no variations in the heat flow that would allow the identification of the characteristic transformation temperature.

The NiTi and NiTi9Nb alloys exhibit one-step phase transformation (B2 → B19'), in which the exothermic peak on cooling represents the transformation from the austenite, B2, to the martensite, B19', and the endothermic peak on heating is related to the inverse transformation from martensite, B19', to austenite, B2, as observed by He et al. [5], Ying et al.[11], Fu et al. [19]. According to Tong et al.[14], the absence of an intermediate phase transformation (R-phase) in ternary alloys can be related to de significant quantity of Nb in solid solution in the matrix, increasing the energetic barrier for the intermediate phase transformation.

However, in the curve for the alloy with 6 at.% Nb, two peaks can be seen both for the cooling and the heating processes, which suggests that this alloy exhibits a two-step transformation (B2 → R → B19'). The first peak, in cooling, represents a transformation from B2 to R and the second peak, in the lower temperature, indicates a transformation from R to B19'[23].

According to literature[24–26], there are many reasons possibly leading to R-phase transformations in NiTi alloys, both related to the composition, as well as to mechanical and/or thermal treatments of these alloys. Zheng et al.[26], for example, mention the lack of homogeneity in the matrix as being responsible for the R-phase transformation. It is also possible to suggest that the Nb content dissolved in the matrix, which is lower than the amount found in the sample with 9 at.% Nb, is not significant enough to raise the energy barrier for the R-phase transformation. In this case, however, more investigations are necessary to clarify this hypothesis.

The martensitic transformation for the alloy with 6 at.% Nb initiates (Ms) in -16 °C, while in the alloy with 9 at.% Nb the starting temperature for the martensitic transformation is -53 °C, being both values considerably lower than the ones obtained for the NiTi alloy (5 °C). Similar results were obtained by Fu et al[19] and Jiang et al.[1], who reported that the higher the Nb content, the lower the martensitic transformation temperatures. According to Shi et al.[3], the lowering of the starting temperature for the martensitic transformation is partially due to the fact that Nb atoms usually substitute the Ti atoms, changing the Ni/Ti ratio in the matrix and resulting in the lowering of the Ms, which confirms the EDS results presented in Table 3.

Thermally induced transformation hysteresis (As - Ms) result in approximated values for the samples with 6 and 9 at.% Nb, at 33 °C and 25 °C, respectively.

These values are higher than the thermal hysteresis for the binary alloy at 15 °C, but it is possible to conclude that there is no substantial increase in the hysteresis when Nb is added to the alloy. Jiang et al.[1] showed that, in order to increase the hysteresis of the NiTi alloy's transformation, it is necessary not only to reduce the starting temperature for the martensitic transformation, but to increase the temperature for the reverse transformation (As) simultaneously. This does not happen with the studied alloys, which presented a decrease in temperature for the reverse transformation as well, with a temperature of 17 °C for the alloy with 6 at.% Nb, a value close to the ones observed for the binary alloy's As (20 °C). For the alloy with 9 at.% Nb the temperature observed was -28 °C.

According to Lin et al. [2], although the temperature for the martensitic transformation is strongly dependent of the chemical composition, the thermal hysteresis control can also be the result of the combination of a change in this composition and the application of thermomechanical treatments, such as thermal cycling, aging in alloys with high Ni content, and hardening followed or not by annealing. Zhao et al.[27] proposed that the plastic deformation of the Nb particles plays an important role in the increase of the NiTiNb alloy's transformation hysteresis, even for small deformations. The authors suggest that the presence of these particles decomposes the deformation of the martensitic structure in a reversible component (the NiTi matrix) and in an irreversible component (phase containing Nb), which makes the martensite reverse transformation difficult by maintaining the deformation of β-Nb particles. Additionally, Wei and Xinqing (2009) and Wang et al. (2012) noted that the Nb in solid solution can change the martensitic and reverse transformation kinetics under a proper pre-deformation, providing an elastic strain energy storage and martensite stabilization. Moreover, about the reverse transformation temperature, Jiang et al. (2016) explained its variation in terms of the variation of Gibbs free energy, which is composed of combination of the chemical free energy and elastic strain energy for transformation from martensite to austenite. According to the authors, when a great deal of elastic strain energy is stored in the martensite during martensitic transformation, the elastic strain energy contributes to increasing the driving force for the reverse transformation from martensite to austenite in the case of heating, which leads to the decrease in the austenitic transformation start temperature As. Thus, the solution annealing treatment after hot rolling of the studied alloys may have led to the plastic deformation energy relaxation of β-Nb particles stored at the interface of the martensite, avoiding the increase of the reverse transformation start temperature.

The comparative of the transformation temperatures' variation is shown in Figure 6, in which is possible to observe how the thermal behaviour of the alloys follows a similar pattern as a function of the Nb addition.
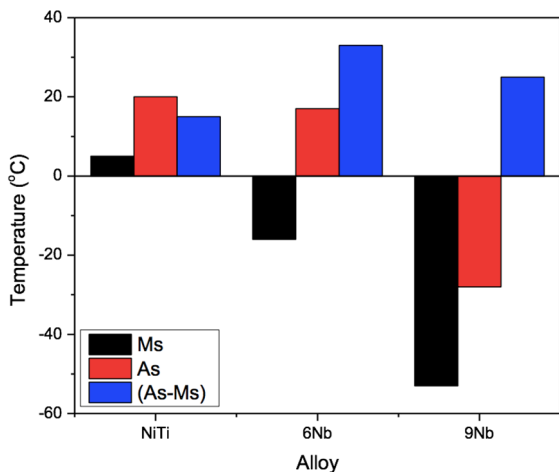
Figure 6. Martensitic transformation start temperature (Ms), Reverse transformation start temperature (As) and thermically induced transformation hysteresis (As-Ms) variations of NiTi, NiTi6Nb and NiTi9Nb alloys samples.

It can also be noted that as Nb content increases in the alloy, the martensitic transformation start temperature (Ms) and the reverse transformation start temperature (As) decrease, while the thermically induced transformation hysteresis (As – Ms) increases, although not significantly, as discussed above.

4. Conclusion

The influence of Nb addition in the microstructural and thermal characteristics of the three NiTiNb alloys - Ni50Ti47Nb3, Ni49Ti45Nb6 and Ni47Ti44Nb9 (at.%) - in comparison with a NiTi equiatomic alloy was investigated. The main conclusions are as follows.

The NiTiNb alloys show characteristic hypoetectic microstructure composed by a NiTi matrix involved by a eutectic structure, in which volumetric fraction increases with the increase of Nb content in the alloys.

Both the primary NiTi phase and the eutectic phase are Nb-enriched with the increase of Nb content in the alloys.

The Nb addition in the binary NiTi alloy and the increase of Nb content in the ternary alloys result in a decrease of the martensitic transformation start temperature, Ms, as well as the reverse transformation start temperature, As. However, the magnitude of the thermal transformation hysteresis of the ternary alloys has not been significantly changed with the Nb content.

5. Acknowledgements

6. References

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