EFFECT OF HEAT TREATMENT ON TRANSFORMATION TEMPERATURE AND MICROHARDENESS PROFILE OF A TiNiCuNb ALLOY

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ABSTRACT

NiTiCu are shape memory alloys (SMAs) that can be characterized by their low transformation hysteresis, low sensitivity to heat treatments and chemical composition variations that present brittle behavior for Cu additions greater than 10at%. Previous studies show that the addition of Nb in TiNiCu alloys results in the formation of a ductile Nb-rich phase, which favors the alloy's ductility. Because heat treatments are efficient in adjusting the properties of SMAs, this work aimed to evaluate the susceptibility of a TiNiCuNb alloy to heat treatments. For this, an ingot of atomic composition $Ti_{49}Ni_{36}Cu_{10}Nb_5$ was produced in an electric arc furnace and heat treated at 800°C and 600°C for 2h followed by water quenching at room temperature. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed to evaluate the present phases and their respective distributions and morphologies. The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC). Microhardness measurements along the transverse and longitudinal axes were performed to evaluate the mechanical properties. All techniques were applied to samples in the as-cast and heat-treated conditions. The as-cast microstructure was constituted by a TiNi matrix, β-Nb/TiNi eutectic constituent, Ti and Ti_2Ni particles. After heat-treatment at 800°C, additional β-Nb particles appeared in the form of fine and dispersed precipitate within the TiNi matrix, these precipitates were not observed in the sample heat treated at 600°C. The thermal evaluation using DSC, showed that the heat treatment caused the increase of the transformation temperatures. In the mechanical evaluation, a decrease in the average microhardness and an increase in the homogeneity of mechanical behavior along the section with the heat treatment of the alloy was observed especially after the 800°C heat-treatment.

Keywords: *Shape memory alloys, transformation hysteresis, heat treatment, transformation temperatures, microhardness.*

INTRODUCTION

Shape memory alloys (SMAs) are functional alloys that exhibit shape memory effect and superelasticity, both related to the occurrence of a reversible martensitic transformation. NiTi-based alloys are SMAs used in the actuator, buffer and dental industries, due to their ability to

recover large deformation amplitudes[10]. To increase the field of applications of binary NiTi alloys, their properties can be adjusted by adding elements to the binary alloy and even adding elements to the ternary alloys.
Studies of ternary alloys have shown that it is possible to increase the fatigue life of NiTi alloys by adding Cu, creating low hysteresis alloys. However, these alloys present high transformation temperatures and superelasticity at temperatures higher than room temperature, in addition to having very low formability when Cu >10 %at.[2,9,13-14,18]. The addition of some elements to the NiTiCu base alloy can be used to improve formability and lower the transformation temperatures. Previous works observed that the addition of Nb is related to a ductile phase appearance, increasing the ductility of the alloy and reducing the transformation temperatures[4-8,16-17,19-20].
On the other hand, heat treatments are a powerful tool to adjust the alloy's properties. This technique proved to be effective for binary alloys, being able to change the transformation temperatures and improve the fatigue life of the alloys[12]. However, ternary alloys with copper addition (NiTiCu) show a low sensitivity to heat treatments and composition changes[1,15]. In quaternary NiTiCuNb, heat treatments have been reported by (4) to have effects on the transformation temperatures, the tensile strengths, the maximum elongation and the critical stress for martensite induction[4]. However, this topic has not yet been widely explored
In this context, this work aims to evaluate the effect of heat treatments on the microstructure, microhardness, and martensitic transformation of an alloy in the NiTiCuNb system ($Ti_{49}Ni_{36}Cu_{10}Nb_5$).

MATERIALS AND METHODS

The alloy was produced by melting the elemental constituents (>99.5% purity) in a water-cooled copper mold into a 30g ingot by arc-melting under argon-controlled atmosphere. To assure chemical homogeneity, the ingot was remelted 6 times.
Heat-treatments were caried out at 600°C and 800°C, both for 2 hours, in a tubular furnace under an argon-controlled atmosphere. The samples were cooled in water at room temperature. These samples will be referred to, respectively, as HT600 and HT800, according to the heat treatment temperature. The as-cast sample will be named AC. Thermodynamic equilibrium simulations were performed in ThermoCalc using TCNI8 v8.1 to evaluate the equilibrium phases.
Scanning electron microscopy analyzes using backscattered electrons (FEI – Inspect S50) were performed on metallographically prepared samples. No etching was performed., Microhardness measurements were made along the longitudinal and transverse axes in these same samples. Measurements were made with 1 kgf for 10 seconds (Future Tech FM 700). One-way ANOVA statistical analysis with $p < 0.05$ was performed.
Samples were subjected to XRD analysis (Panalytical Empyrean) with 2θ varying from 30° to100° in a 0.02°/s scan speed using Cu-kα radiation. The ICSD database were used for peak indexation.
DSC analyses were performed in a Shimadzu DSC-60 to evaluate the reversible martensitic transformation. The test thermal cycle started at -100°C and samples were heated to 100°C, then cooled down to -100°C at the heating/cooling rates of ±10°C/min. As, Af, Ms and Mf transformation temperatures were obtained by the tangent method.

RESULTS AND DISCUSSION

Thermodynamic simulation

Using the equilibrium calculator (ThermoCalc), the volume fraction of equilibrium phases as a function of temperature in the $Ti_{49}Ni_{36}Cu_{10}Nb_5$ alloy was obtained. These results are graphically presented in Figure 1.

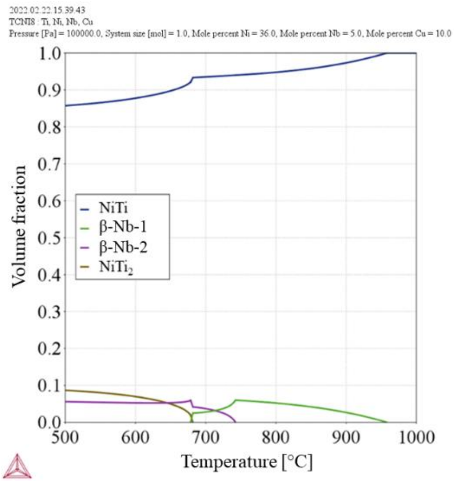

Figure 1 - Volume fraction of equilibrium phases as a function of temperature in the $Ti_{49}Ni_{36}Cu_{10}Nb_5$ alloy

From the thermodynamic simulation, the presence of four phases was identified: NiTi (B2), $NiTi_2$, β-Nb-1 and β-Nb-2. At 600°C NiTi (87.8%), $NiTi_2$ (6.9%) and β-Nb-1 (5.3%) are expected while at 800°C, only NiTi (94.8%) and β-Nb-2 (5.2%) are predicted under equilibrium conditions. The β-Nb-1 and β-Nb-2 phases are Nb-rich phases, but with different concentrations of Nb. Using a single point calculation tool, β-Nb phase has a higher concentration of Nb (90.7%) than the β-Nb' phase (52.7%).

Microstructure evaluation

The XRD spectra obtained for the three samples are presented in Figure 2. The austenitic phase (B2 - NiTi) is identified in all samples. The martensitic phase (B19 – NiTi) is identified in the heat-treated samples. It was also possible to identify the presence of $NiTi_2$, β-Nb and metallic Ti phases. It was not possible to identify which of the two Ti phases, α-Ti or β-Ti, is present due to the overlap of their peaks.

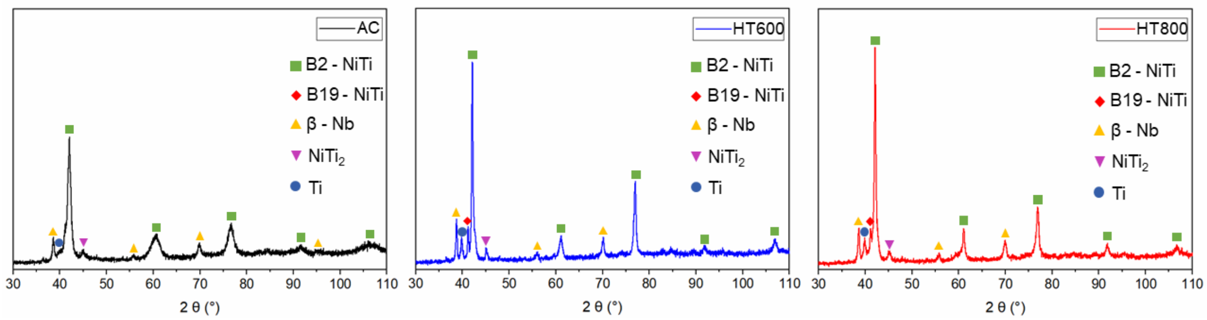

Figure 1 - XRD spectra for the three samples (AC, HT600 e HT800)

Backscattered electron images obtained by SEM are presented in Figure 3. The gray phase was identified as the NiTi phase. The white phase is a Nb-rich phase, identified as β-Nb on the XRD pattern. The dark gray phase is the $NiTi_2$ intermetallic phase. The black phase was identified as metallic Ti. The β-Nb phase appears mainly associated with the NiTi phase in the form of a lamellar eutectic constituent. The $NiTi_2$ phase appears dispersed in the matrix and in regions close to the eutectic with various morphologies. These phases and morphologies are observed for all samples. However, fine, and dispersed precipitates were observed in the matrix phase on the HT800 sample, as highlighted in Figure 3(f). The contrast in the images by backscattered electrons and previous results(10) indicate that the precipitates observed in this alloy may also be β-Nb.

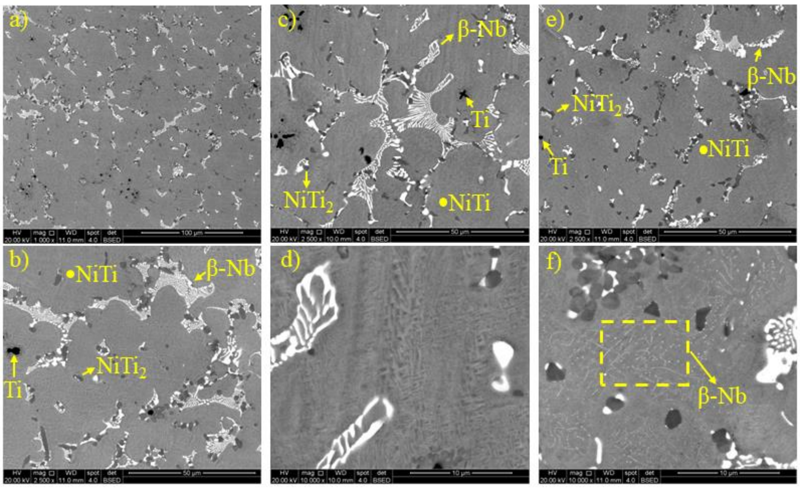

Figure 2 - Backscattered electrons images obtained in the SEM analyses of (a - 1000x and b - 2500x) AC; (c - 2500x and d - 10000x) HT600; (e - 2500x e f - 10000x) HT800

Differential scanning calorimetry

The curves obtained during thermal cycling of the AC, HT600 and HT800 samples are shown in Figure 4. it can be observed that heat treatments caused increases in transformation temperatures, as depicted in Table 1. Moreover, the heterogeneous characteristics of the transformation peaks in AC may be due do chemical heterogeneities resultant from the casting process. In HT600 the martensitic transformation occurred in a narrower range of temperatures. In HT800, a two-peak transformation took place during heating

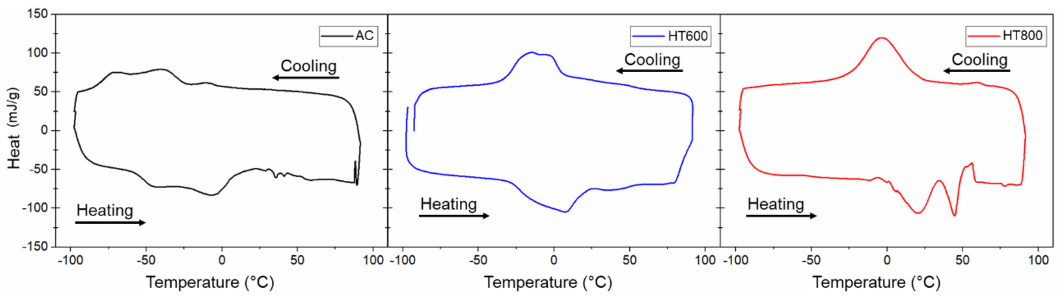

Figure 4 - DSC curves for the three samples AC, HT800 e HT600

Table 1 - Temperature of start and finish of the direct and reverse martensitic transformations

Sample	Ms (°C)	Mf (°C)	As (°C)	Af (°C)
AC	-26.2	-78.6	-54.9	4.9
HT600	-1.9	-40.6	-18.4	28.1
HT800	18.7	-21.7	-1.4	48.5

The increase in the transformation temperature indicates that the martensitic transformation occurs more easily after heat-treatments are performed. This can be due to the occurrence of recovering processes, which alters the dislocation substructures, and/or precipitation of β-Nb precipitates, which also affects the NiTi chemical composition. Additionally, the changes on the transformation peak shapes indicate the occurrence of more uniform martensitic transformations. The two-peak transformation in HT800 can be related to changes in the chemical composition differences of the matrix phase in regions closer to and further away from the β-Nb precipitate. On the other hand, these changes on the transformation temperatures implies different regions of stability for the austenitic and martensitic phases. So that heat treatments can be used to adjust the transformation temperatures of these alloys, and, for the same application temperature, they can present different functional properties.

Microhardness

Average microhardness of 217.5 ± 17.8 HV, 209.1 ± 12.2 HV and 200.1 ± 8.7 HV were obtained for HT600, HT800 and AC, respectively. No significant statistical difference was observed between HT600 and AC at a confidence level of 0.05 (ANOVA).
Histograms were prepared using the measurements made for each sample to assess their mechanical homogeneity, as shown in Figure 5. It is possible to observe that the AC sample presented a disperse distribution around the 210 – 220 HV interval. In HT600, a slightly smaller dispersion is achieved. In HT800 sample, the measurements are more concentrated around the 190 – 210 HV interval.

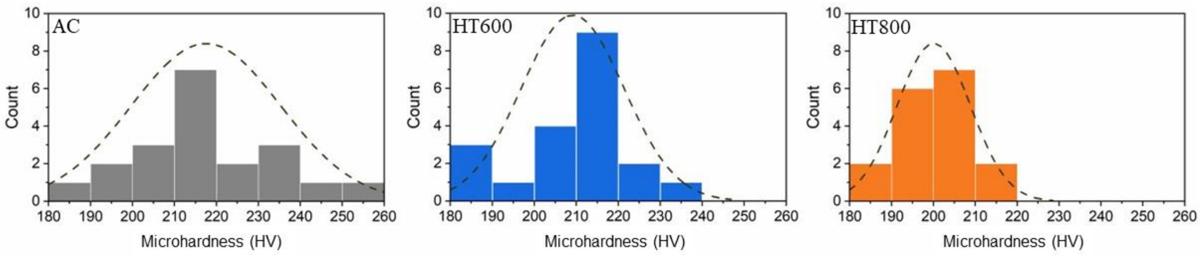

Figure 5 - Histogram of microhardness results for the three samples AC, HT800 e HT600

Hence, a more uniform dispersion and a slight decrease in the average was obtained in HT800 in comparison to AC and HT600. In HT600, no statistical difference was observed when compared to AC, however, an increase in the homogeneity of the mechanical behavior can be observed. Associated with the DSC results, these results indicate that recrystallization did not occur at 600°C, although recovery mechanisms may have taken place resulting in higher mechanical and transformation homogeneity, and also favoring the occurrence of the reversible martensitic transformation at higher temperatures. In HT800, the decrease in the average hardness and the more uniform mechanical properties may be associated with the precipitation of β-Nb and a possible occurrence of recrystallization.

CONCLUSIONS

In this paper, the $Ti_{49}Ni_{36}Cu_{10}Nb_5$ alloy were produced and the effects of heat treatments in the microstructure, martensitic transformation, and microhardness was evaluated. All samples (AC, HT600 and HT800) were constituted by matrix NiTi phase, a eutectic NiTi/β-Nb constituent, $NiTi_2$ precipitates and Ti metallic. For the HT800 sample the formation of a fine and dispersed β-Nb precipitates, within the matrix phase was observed. The submission of the alloy to heat treatments increased its transformation temperatures. As the applicability of these alloys is directly related to their functional properties, it is notable that the heat treatment of these alloys can become a powerful tool to adjust the transformation temperatures for different fields of application of these alloys. Regarding the effect of heat treatments on the mechanical behavior, it was possible to notice that performing the heat treatment at 800 °C was effective to reduce the microhardness of the alloy and make it more homogeneous.

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