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Ni_3Ta high temperature shape memory alloys: effect of B addition on the martensitic transformation and microstructure

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Abstract

Shape memory alloys operating at high transformation temperatures are considered very attractive materials for enabling a new class of high temperature smart devices for different fields, such as automotive, aerospace and appliances.
In this work, the effect of B addition in the Ni_3Ta alloy was studied; B contents from 1 to 5 (at.%) were alloyed in the place of Ta. For the all studied compositions, the calorimetric investigations have shown martensitic transformation above 220 °C, which was stable during thermal cycling. The characteristic phases of Ni_3Ta alloyed with B were identified using both scanning electronic microscopy and powder X-ray diffraction analyses.

Keywords: HTSMA; Calorimetric Analysis; SEM; Powder XRD; Mechanical properties

1. Introduction

In the recent years, great efforts have been made on the development of Shape Memory Alloys (SMAs) to be applied at High Temperatures (HT), above at least 100 °C, for different potential industrial fields, such as the automotive, the aerospace and the mechanical and control fields [1-2]. A relevant number of works can be found in

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open literature, dealing with the microstructural and functional characterization of HT-SMA. For instance, ternary NiTiX alloys (with X = Zr, Hf, Pd, Pt) have shown promising functional properties with transformation temperatures in the range of 100-250 °C [3-5]. Other systems, different from those based on NiTi, were also studied as possible HTSMAs, such as CuZr [6] and RuNb [7] with intermediate and very high martensitic transformation (MT) temperatures, respectively. Also ferromagnetic NiMnGa as bulk and thin films [8] and Ni3Ta [9] showed HT shape memory effect and good thermal stability. Recently, a new approach to reach high transformation temperature using commercial austenitic Nitinol was proposed [10]. This new method consists in the the thermal cycling of stress induced martensite, a thermomechanical path firstly described in [11]. Firstov et al. [9] observed that the Ni_3Ta intermetallic compound exhibits reversible martensitic transformation MT at temperatures above 200 °C. The drawback underlined poor mechanical and workability properties. Rudajevova et al. [12] studied the mechanical behavior of this alloy in both the non-deformed and the pre-deformed states, confirming the potentialities of this system as HTSMA. In this context, the workability of Ni_3Ta system has to be improved for enabling manufacturing of semi-finished products. It is well known that B addition can reduce brittleness and enhance mechanical characteristics of several alloys, such as Ni based ones. For instance, an evident benefit of borum was found on the ductility and strength of Ni_3Al [13] and NiPdTi [14] alloys. It was seen that an adjunct of B as interstitial atom in the Ni_3Al lattice improves the ductility and reduces the occurring of intergranular fractures at room temperature [13]. The effect of B doping (0.2 at.%) in TiPdNi promotes the precipitation of micro size TiB_2 phase enhancing the mechanical properties at high temperature [14]. In the present work the effect of B addition in Ni_3Ta compound, in the place of Ta, was studied by calorimetric and microstructural analysis. The MT occurred above 220 °C and the thermal stability is achieved from the second thermal cycle. Moreover, results of a microstructural investigations carried out by of Scanning Electron Microscopy (SEM) and powder X-Rays Diffraction (XRD) were also reported.

2. Experimental

High purity Ni, Ta and B elements were melted with a vacuum arc melting system (Leybold mod. LK 6/45) equipped with a non-consumable tungsten electrode. The melting was performed in a water cooled copper crucible, under inert atmosphere (pure Ar) for avoiding the contamination of the liquid pool. The nominal compositions of the produced alloys are $Ni_{75}Ta_{(25-x)}B_x$ with x = 0, 1, 3 and 5 at.%. The obtained ingot buttons were re-melted six times in order to increase the chemical homogeneity. The material was fully annealed at 1400 °C for 4 h and cooled under pure Ar flow. A differential scanning calorimeter (DSC - Seiko model 520C) was used for studying the martensitic transformation. DSC scans were in the range of temperature [50 ÷ 400 ºC] using a heating/cooling rate of 10 °C/min. Microstructural investigation of ingot sections samples was performed by means of a SEM (Leo 1430), equipped with an Energy Dispersive Spectroscopic (EDS) microanalysis probe. Powder X-Ray Diffraction analysis was carried out at room temperature. Rietveld refinement using the software MAUD [15] was carried out on XRD profiles.

3. Analysis of Results and Discussion

A representative DSC scan of $Ni_{75}Ta_{24}B_1$ after 20 complete heating/cooling thermal cycles is depicted in Fig. 1; the direct and inverse MT occurred completely above 240 ºC. The stabilization of the MT was obtained at the third cycle, similarly to the evolution of the MT of the binary alloy [9]. The effect of the B on the characteristic temperatures at the third cycle is shown in Figure 2a. The temperatures of the direct MT did not look to be strongly affected by B content; the Martensitic Starting and Finish temperatures (Ms and Mf) were approximately 235 ºC and 270 ºC, respectively. On the contrary, the thermal behavior of the inverse MT, is affected by the B content. Indeed, Austenite Starting (As) and Finish (Af) temperatures increased from 285 ºC to 350 ºC and from 320 °C to 375 °C, respectively as B increase from 1 to 5 % at., a particular increment was detected for B content of 1 %.

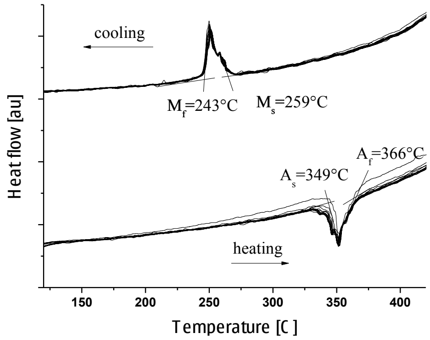

Fig. 1. DSC scan of the $Ni_{75}Ta_{24}B_1$during thermal cycling.

In Figure 2b a parabolic trend of the heats exchanged is shown in function of the B content; maximum value of heats exchanged at 3% at. of B content is found, at which the highest amount of the phase involved in the MT is present. The addition of B (up to 3%) increases the transformation temperatures of the reverse MT with respect to the binary system. It is detected a slight difference between the heats exchanged upon heating and cooling scans, so the net enthalpy during a complete thermal cycle indicates dissipation energy phenomena [16].

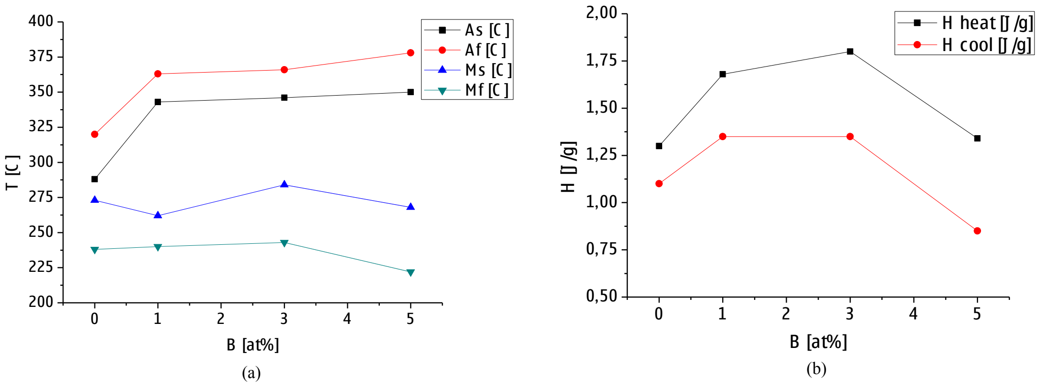

Fig. 2. Characteristic temperatures (a) and corresponding heats exchanged (b) during the MT.

BSE-SEM image, at room temperature (below Mf), of $Ni_{75}Ta_{24}B_1$ is shown in Figure 3a. The matrix is characterized by a Ni:Ta ratio equal to 3:1, as reported in literature by Firstov et al. for the binary compound [9]. The alloys have shown the presence of two secondary phases: Ni_8Ta and Ni_2Ta [9]. The B addition up to 1 at.% did not change significantly the microstructure with respect to the binary compound. In $Ni_{75}Ta_{24}B_1$ trace of Ni_8Ta phase was detected at the grain boundary mainly (see Figure 3a). However XRD analysis, at room temperature, have shown only the Ni_3Ta phase with two crystal structures (see Figure 3b) evaluated as P21/m and I4/mmm. It was found an increasing of the monoclinic phase at higher B contents. The observed trend is in agreement with the results (see Figure 2b) and to the experimental evidence of the martensitic transformation in Ni_3Ta that occured between the tetragonal phase, stable at high temperature, and the monoclinic phase, stable at low temperature [9].

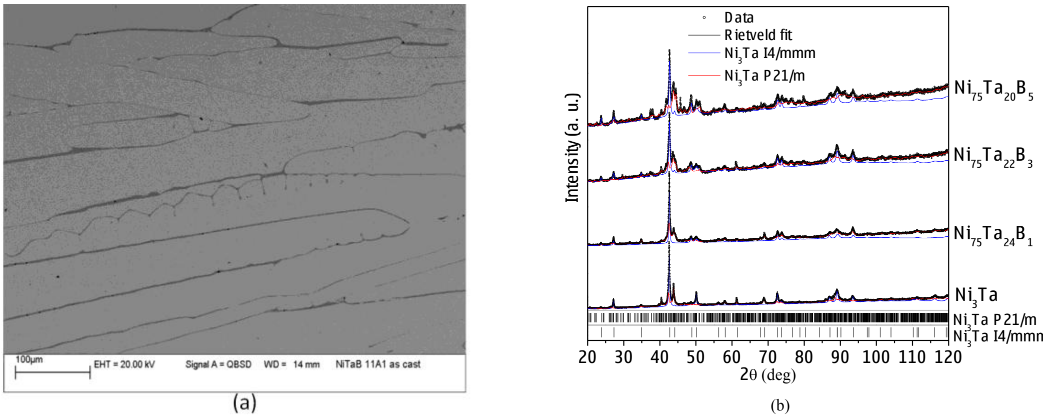

Fig. 3. SEM picture of $Ni_{75}Ta_{24}B_1$ (a) and XRD patterns collected at room temperature (b).

4. Conclusions

In this work, the effect of the B addition on the calorimetric properties and the microstructure of the Ni_3Ta system was studied. The following points can be highlighted:

- Ni_3TaB showed the MT at high temperature, above 220 °C. The MT was influenced by the amount of B in terms of characteristic temperatures and heats exchanged; on the contrary, the stability of the MT during thermal cycling was not degraded.
- The microstructural analysis Ni_3TaB alloys with B up to 5 % showed that quasi-pure phase was obtained in the; no evident modifications were seen by adding B with respect to the binary alloy.
- The amount of B was found to be correlated to the amount of the monoclinic phase, involved in the MT. The highest heats exchanged involved in the MT was detected at 3 at.% of B.

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