THE INFLUENCE OF THE THERMAL TREATMENT ON THE MICROSTRUCTURE AND FRACTURE FEATURES OF NiTi ALLOY

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Abstract

The aim of this work was to study the influence of thermal treatment of the NiTi alloy on the microstructure, fracture features, and phase composition. NiTi sheets with a thickness of 2 mm and a chemical composition of 56.3 wt% Ni and 43.7 wt% Ti were used for the experiment. The samples were subjected to solution treatment at 850 °C for 1 hour and subsequent aging at 450 °C for 1 hour, or only aging at the same temperature and time for the as-received state of the material. All steps were finished by water quenching. Experiments were carried out for four states of the samples, namely the as-received state, after solution treatment, solution treatment and aging, and only aging. The study of the microstructure was carried out using a transmission electron microscope. The samples were tensile tested at a strain rate of $6.67 \cdot 10^{-5}$ s^{-1} and the fracture surfaces were examined using a scanning electron microscope. Phase composition was estimated using XRD analysis.

Keywords: NiTi**,** thermal treatment, fracture, TEM, XRD

1. INTRODUCTION

The Niti alloy is a material that can exist in three states, each of which has different properties and behaviors. The main variable of this alloy is temperature, which affects the presence of these states: martensite, superelastic austenite, and stable austenite. Other properties of the alloy, such as modulus of elasticity, electrical resistance, and specific heat capacity, are also strongly dependent on temperature [1].

The heat treatment of NiTi alloys consists mainly of solution treatment and aging, where during solution treatment the structure is homogenized and the precipitates are dissolved, while during aging, lenticular Ni_4Ti_3 precipitates can be formed [2]. However, if the aging was carried out at high temperatures (slightly below the temperature of solution treatment), or for a long time, the Ni_4Ti_3 precipitates would begin to decompose into acicular Ni_3Ti_2 and granular Ni_3Ti, affecting the mechanical properties [3]. However, due to the formation of these precipitates, the nickel content in the matrix is disturbed, leading to an increase in transformation temperatures. In terms of aging, the volume fraction of precipitates was found to be determined by the aging temperature, while their size is related to the duration of the aging process [4].

The fracture mechanisms of NiTi alloys have been the subject of several research works [5-6], which have provided information on the feature of fracture surfaces under various conditions. Conclusions were drawn from the observations that the fracture surfaces of NiTi alloys have a quasi-cleavage character, when no macroscopic plastic deformation occurs at all. In the case of superelastic austenite, due to the transformation of stress-induced martensite, there is a further increase in deformation, which affects the fracture surface in a quasi-cleavage form rather than a purely cleavage one [7].

The aim of this work was to study the effect of heat treatment on the microstructure, fracture character and phase composition of NiTi alloy. Heat treatment promotes the formation of Ni_4Ti_3 precipitates, which affects the transformation temperatures of the alloy, thus also affecting the phase composition. It was assumed that the character of the fracture surfaces corresponds to the changes of the phase composition and microstructure due to the heat treatment. The structure and phases before tensile testing were observed by TEM, the phase composition was determined by XRD and the fracture surfaces of the tensile specimens were examined by SEM.

2. EXPERIMENT

The material investigated in this work was NiTi in the form of sheets with a thickness of 2 mm and a chemical composition of 56.3 wt% Ni and 43.7 wt% Ti purchased from EdgeTech Industries LLC, USA. Strips with dimensions of 250 mm x 10 mm were prepared from the sheets by means of water jet cutting, from which samples were subsequently taken for further experiments. Selected samples were tested in their as-received state, others were heat treated in a Linn HT1800 furnace in an argon atmosphere. Heat treatment consisted of solution treatment at 850 °C for 1 h followed by aging at 450 °C for 1 h or only aging under the same conditions. All heat treatments were finished by water quenching.

From the prepared strips in the as-received state, but also after each heat treatment, cylinders with the following dimensions were cut using electroerosion machining: 3 mm in diameter and 2 mm in height. Subsequently, these cylinders were cut into thin samples approximately with 0.4 mm thickness using a WS-25 High Precision Wire Saw with a Siemens LOGO TDE electronic control unit and an abrasive suspension (SiC particles and glycerol). The required thickness of 0.1 mm was achieved by manual grinding of the samples using SiC papers with P1200 grit. The thus prepared samples were then electrolytically thinned to a thickness suitable for TEM observation using a Struers TenuPol-5 device and an electrolyte composed of 10 % $HClO_4$ and 90% CH_3OH. The electropolishing parameters were chosen according to the literature [8] and subsequently adjusted as needed to achieve the best surface quality. Polishing was carried out under the following conditions: 10 V, - 30 °C, 30 mA. The polished samples were carefully immersed in distilled water to prevent further etching. The samples thus prepared were examined using an electron microscope STEM 1200X operating at 120 kV.

XRD analysis was used to detect the phases present in the structure. For this analysis, samples with dimensions of 10 mm x 10 mm were prepared and ground using SiC papers with P1200 grit to remove oxides from the surface. The samples were analyzed using a Bruker D8 Advanced diffractometer equipped with a CuKα cathode. The experiment was carried out under the following parameters: angle 30-110°, step size 0.025° and scan speed 3 s/step in 2Θ.

Fracture surfaces of the specimens in various thermal treatment conditions after tensile testing at the strain rate of $6.67 \cdot 10^{-5}$ s^{-1} were examined using a JEOL JSM-6490LV scanning electron microscope with an Oxford Inca X-act probe.

3. RESULTS AND DISCUSSION

3.1 TEM analysis

TEM images (bright field observation) of the microstructure of the NiTi sheet after various thermal treatments are shown in **Figure1**. The dislocation structure shown in **Figure 1a)** associated with the rolling process was observed for the samples in the as-received state. There was a very small amount of Ni_4Ti_3 precipitates with a dimension of approximately 1 μm. A detailed examination of the samples after solution treatment revealed Ni_4Ti_3 precipitates, but they were smaller in size than in the as-received samples. These precipitates were assumed to dissolve during solution annealing. However, they may have been too large to dissolve completely

under the given conditions. To completely dissolve the Ni_4Ti_3 precipitates, the temperature would have to be higher or the heat treatment time would have to be longer. Martensitic needles were observed in the structure, which are further internally twinned, as can be seen in **Figure 1b)**. In contrast, in **Figure 1c)** shows the microstructure of the solution treated and aged samples, which contain a large amount of Ni_4Ti_3 precipitates with a size in nanometric scale, but simultaneously the same precipitates with a size of around 0.5 μm were also present. It is possible that precipitates detected already in as-received state were partially dissolved during solution treatment, and during subsequent aging coarsened. It was also confirmed that aging of the samples under certain conditions leads to the formation of these precipitates [9]. The structure of the aged samples contained a large amount of nanosized Ni_4Ti_3 precipitates, as can be seen in **Figure 1d)**. Simultaneously, a very small amount of the same precipitates with a much larger size were observed. The larger precipitates, detected similarly in as-received samples, probably have grown further as a result of the effects of heat treatment. Therefore, aging promotes the formation of new precipitates that are homogeneously distributed throughout the sample structure, but at the same time supports the growth of already present precipitates.

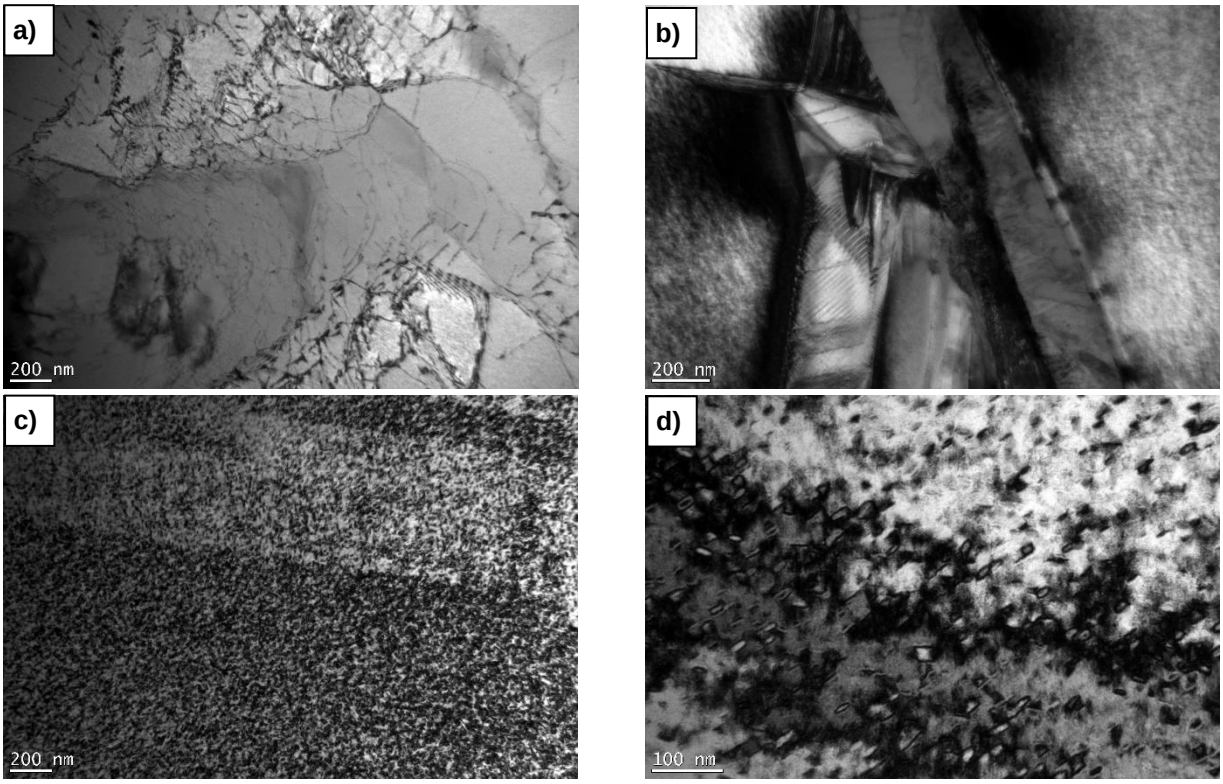

Figure 1 TEM images (bright field images) of microstructure of NiTi sheets after various thermal treatments, a) as-received, b) solution treated, c) solution treated and aged, d) aged

3.2 Fracture surfaces

The tensile testing was performed on the specimens in different heat treatment. The values of the tensile stress at break σ_f reached of 862, 1163 or 418 MPa for the as-received, aged or solution treated and aged stages, respectively. The fracture surface of the sample in the as-received state is shown in **Figure 2a)**. It is clear that this is a quasi-cleavage fracture, consisting of ductile dimples, brittle facets, and local cracks. **Figure 2b)** shows the fracture surface of the solution treated and aged sample. This sample was characterized by lower ductility and strength despite the elastic feature of the stress plateau region. The fracture surface corresponds to the phase composition of the sample that consisted of the R phase or martensite and $NiTi_2$ or Ni_4Ti_3 particles. The fracture surface is rather flat with cleavage character, and the crack can propagate very easily. The cleavage

facets reach a length of up to 200 μm with a width of 50 μm with a river character, which are largely oriented in the same direction. Sharp-edged structures most likely related to $NiTi_2$ particles or nickel-titanium oxides were also present. The fracture surface of the aged sample that is related to the best superelastic behavior of all tensile tested specimens, is shown in **Figure 2c)**. The surface looks rugged but cleavage with elongated quasi-cleavage facets. Sharp-edged structures were also observed that could be related to the broken particles. Among the quasi-cleavage facets, ductile micro-dimples around the observed precipitates can also be seen.

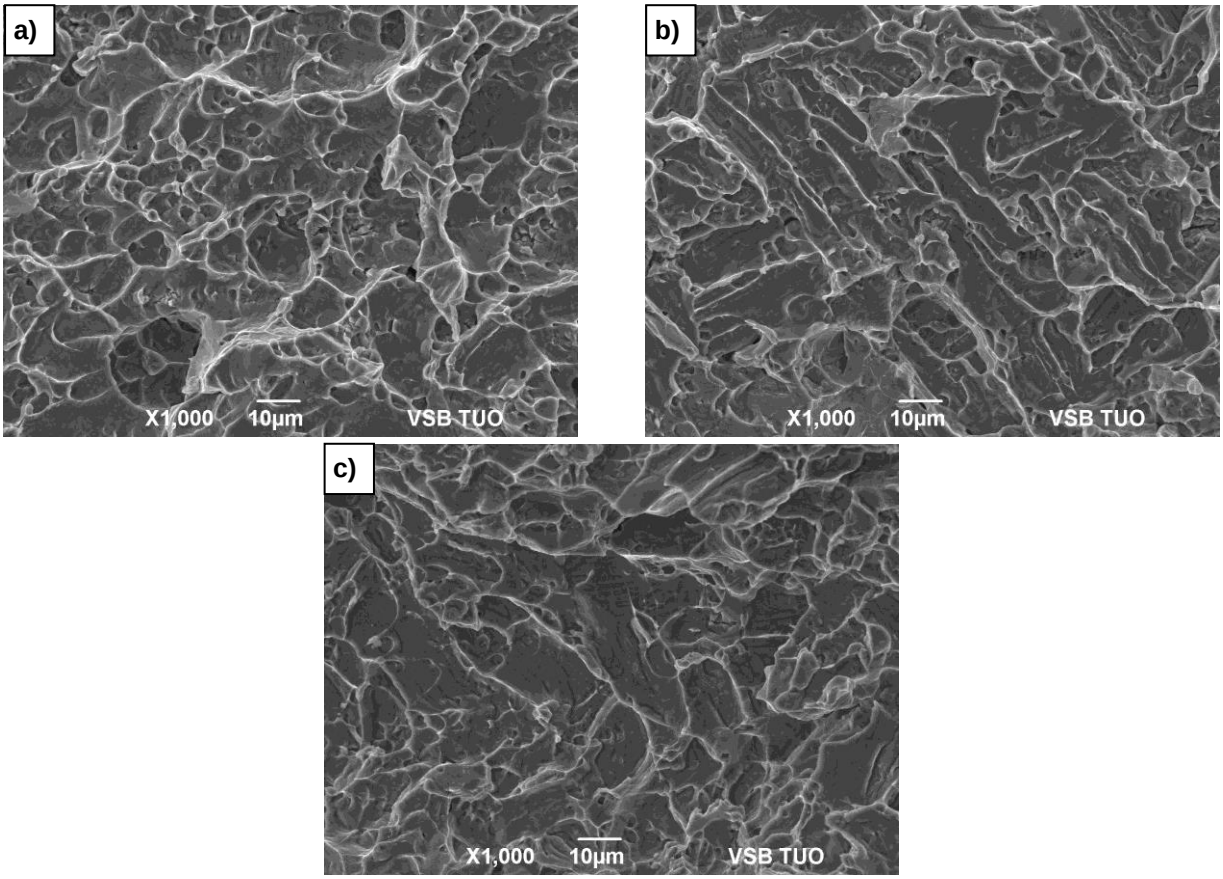

Figure 2 SEM images (secondary electrons) of the fracture surfaces of the NiTi sheet after various thermal treatment, a) as-received, b) solution treated and aged, c) aged

3.3 XRD analysis

The XRD spectrum of the sample in the as-received state, shown in **Figure 3a)**, revealed the presence of an austenitic matrix with a cubic lattice. Precipitates $NiTi_2$ and Ni_4Ti_3 were also observed, which is consistent with the TEM analysis, where these precipitates were detected.

Using XRD analysis of the samples after solution treatment, an austenitic matrix with a cubic lattice was determined, as in the samples in the as-received state. Similarly, $NiTi_2$ precipitates were also detected here. The spectrum in **Figure 3b)** shows peaks for Ni_4Ti_3 precipitates, of which only a small amount in the structure was revealed by transmission electron microscopy. A NiTi hexagonal phase detected by analysis can correspond to some variant of the martensite or R phase.

Similarly, as for the samples after solution treatment, in the structure of the solution treated and aged sample XRD analysis revealed the same phases. An austenitic matrix with a cubic lattice, $NiTi_2$ precipitates, and a

hexagonal NiTi phase was present as shown in **Figure 3c)**. Ni_4Ti_3 precipitates were also detected, which is consistent with TEM analysis.

The spectrum for the aged samples (**Figure 3d))** shows the same phases asfor the solution treated and aged samples. Specifically, it is an austenitic matrix with a cubic lattice, $NiTi_2$ and Ni_4Ti_3 precipitates, and a hexagonal phase. The hexagonal phase can represent the R phase or some variant of martensite [10]

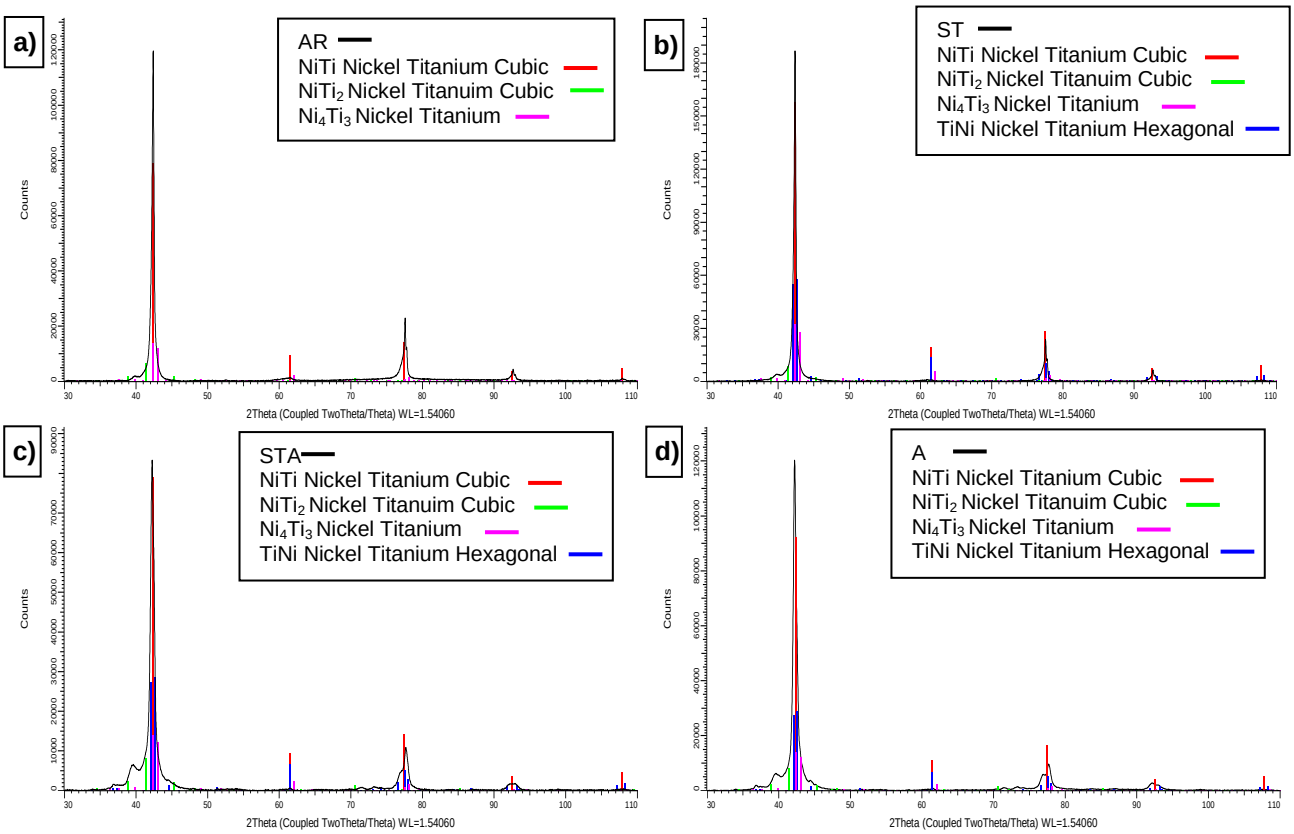

Figure 3 XRD spectra of NiTi sheets in different conditions, a) as-received, b) solution treated, c) solution treated and aged, d) aged

4. CONCLUSION

TEM analysis detected a dislocation structure in the as-received samples and a small amount of Ni_4Ti_3 precipitates. Ni_4Ti_3 precipitates were also detected in ST samples, but with a smaller size than in as-received samples due to the solution treatment process. A large amount of nanometric Ni_4Ti_3 precipitates were observed in the structure for the solution treated and aged and only aged samples.

The fractography study of all samples showed the quasi-cleavage character of surfaces with facets, micro-dimples, and local cracks. Cleavage facets of the largest size were observed for solution treated and aged samples, which also corresponds to brittle behavior during tensile tests. Sharp-edged structures were also revealed, which may be related to the cracking of secondary phase particles. Therefore, it is possible to conclude that the solution treatment and aging process led to increased brittleness and quasi-cleavage feature of the fracture with large facets, unlike the more ductile aged samples.

XRD analysis of as-received samples revealed only the presence of austenitic matrix, $NiTi_2$ and Ni_4Ti_3 precipitates, while in solution treated, solution treated and aged and only aged samples the hexagonal phases were also detected.

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