AN INTERPLAY BETWEEN HEAT TREATMENT CONDITIONS AND B2↔B19' TRANSFORMATION IN Ni-Ti SHAPE MEMORY ALLOYS

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Abstract

This study investigates the influence of a heat treatment atmosphere on multistage martensitic transformations in a Ti-50.9at%Ni shape memory alloy. Evacuated quartz tubes were filled with hydrogen while the hydrogen partial pressure was carefully controlled in each experiment. The encapsulated specimens were subjected to heat treatments consisting of annealing and aging. After the heat treatment, the path of martensitic transformation was investigated using differential scanning calorimetry (DSC). On cooling, martensite initial temperatures decrease with the increasing partial pressure of hydrogen applied during the heat treatment. Moreover, the formation of martensite phase may not take place for partial pressures that exceed a certain limit. On the other hand, two- and multiple-step B2/R/B19' martensitic transformations are observed in specimens heat treated at lower hydrogen pressures. Results obtained using transmission electron microscopy (TEM) clearly show that the size of Ni4Ti3 precipitates becomes smaller in alloys that were heat treated at higher hydrogen pressures. The results are discussed in terms of a chain of events. It is suggested that diffusion of hydrogen into the specimen during the annealing step first influences the nucleation of the Ni4Ti3 phase. The sizes and distribution of the Ni4Ti3 precipitates than control the characteristics of B2/B19' transformation.

Keywords: Heat treatment atmosphere, nickel-rich NiTi shape memory alloys, differential scanning calorimetry, transmission electron microscopy.

1. INTRODUCTION

Processing of Ni-rich NiTi shape memory alloys generally involves thermomechanical treatments, which lead to the precipitation of a metastable Ni4Ti3 phase [1]. The presence of coherent Ni4Ti3 precipitates supports the formation of R-phase and thus results in splitting of B2/B19' transformation path into two steps: B2/R and R/B19' transformations [2-5]. Ni4Ti3 phase has a rhombohedral structure (space group R-3), lenticular disk-like shape and belongs to one of eight crystallographic variants that grow on {111}-planes of the B2 NiTi matrix [2].

Phase transition temperatures are important from a technological standpoint. In shape memory technology, the differential scanning calorimetry (DSC) represents a fundamental method which enables monitoring the bulk specimen behaviour in terms of initial and final transformation temperatures. The forward transformation B2/B19' is characterized by one exothermic DSC peak on cooling and the reverse transformation B19'/B2 by one endothermic DSC peak on the heating curve. The two step martensitic transformation make DSC chart more complex [1].

In recent years, multiple-step martensitic transformations B2/R/B19' (MMT) have received considerable attention. In spite of this effort, the mechanism of MMT transformations in the aged Ni-rich NiTi has not yet been fully clarified. It is generally accepted that MMTs are either associated with a microstructural
heterogeneity on a small scale (inhomogeneous Ni distribution in the NiTi matrix and/or coherent stress fields associated with the Ni₄Ti₃ precipitation) or a large scale (difference in the distribution and sizes of the Ni₄Ti₃ precipitates across the grain microstructure) [6-10].

Fujishima et al [3] has confirmed the influence of heat treatment atmosphere on the MMT. They pointed out that mainly the solution annealing step is the most significant for affecting the MMT path. The MMT can be suppressed by controlling the heat solution treatment atmosphere [3]. Fujishima et al explained the observed behaviour on the basis of compositional fluctuations that are induced during the solution annealing in air and are further intensified during the aging treatment [3].

The purpose of the present study is to provide new experimental data on the effect of heat treatment atmosphere on the MMT path and thus improve our understanding of the observed transformation behaviour.

2. EXPERIMENTAL PROCEDURE

The commercial nearly equiatomic Ti-Ni alloy SE508 (Ni: 50.8 at%, Ti: balance) was used in the present investigation. The alloy was purchased from EUROFlex® in the form of a cylindrical rod with a diameter of 12.7 mm. The cylindrical rod was cut into specimens of 20 mm in length. All the samples were mechanically polished and chemically etched for few seconds in the acid solution consisting of 43 vol% hydrofluoric acid and 57 vol% nitric acid. One of cleaned sample was wrapped with Ti-foil (99.6%) of 0.125 mm in thickness and then sealed in quartz tubes filled with argon (6.0) with a partial pressure of about 0.95 bar. The other samples were separately sealed in quartz tubes filled with hydrogen (2.5) with increasing partial pressures of 0.67, 0.80 and 0.95 bar. The sealed samples were solution treated at 1123 K for 1.8 ks, water quenched and subsequently aged at 723 K for 3.6 ks and water quenched again. After the heat treatments, disk-shaped samples of about 1.5 mm in thickness and 3 mm in diameter were spark-cut from the heat treated cylinders. These disks for DSC measurements were taken from both surface and bulk of the cylinders as shown schematically in Fig. 1. The DSC disks were further mechanically polished using 500-grit SiC paper and ultrasonically cleaned in water and ethanol. Samples for transmission electron microscopy (TEM) investigations were mechanically polished on 500, 600, 800, 1000, 1200 and 2400-grit down to about 0.15 mm and finally electropolished using electrolyte AS-I from Struers®.

![Fig. 1](image-url) A schematic drawing that illustrates positions of DSC and TEM samples (crosshatched areas) in the heat treated cylinders.
A differential scanning calorimeter of type 204F PHOENIX from NETZSCH was employed to investigate the path of martensitic transformations. The mass of DSC samples was between 30 and 50 mg and heating and cooling rates of 10 K/min were used.

A Philips CM12 TEM operating at 120 kV was used to conduct microstructural analysis in heat treated and DSC analyzed samples.

3. RESULTS AND DISCUSSION

3.1 Effect of hydrogen heat treatment atmosphere on MMT

In this section, we present data related to the influence of the hydrogen partial pressures on the Ti-50.8at%Ni alloy transformation behaviour as investigated by the DSC technique. The effect of the surface and the bulk of the heat treated cylinders on the transformation path was taken into account. Figure 2 shows the DSC curves obtained for specimens that were heat treated under indicated filling pressures of hydrogen. Figures 2a and 2b present the DSC charts of the disks taken from the surface and the bulk, respectively. There are three characteristic features that change with the heat treatment conditions: (1) the first (right) peak on cooling curves shifts towards higher temperatures with the increasing partial pressure of hydrogen.

This effect is more pronounced for the samples cut out of the bulk, see Fig. 2b. (2) The second (left) peak on cooling curves shifts towards lower temperatures with the increasing partial pressure of hydrogen, see Fig 2b. (3) MMT is effectively suppressed in specimens heat treated at high hydrogen pressures. In this case, the DSC disks taken out from the surface did not show the second transformation peak for partial hydrogen pressures of 0.8 bar and higher while a partial pressure of 0.95 bar is needed to suppress the second transformation peak on cooling in the bulk samples. We note that the heat treated samples in the low-pressure hydrogen atmosphere transform in three steps corresponding with the three peaks in contrast with

![Fig. 2 DSC curves of the Ti-50.8at%Ni alloy heat treated under different filling pressures argon (0.95 bar) or hydrogen (0.67, 0.80 and 0.95 bar). DSC disks were taken from (a) the surface and (b) the bulk of the heat treated cylinders.](image-url)
the heat treated sample in argon atmosphere that transforms in two steps corresponding with the two peaks on the cooling curves. Fujishima et al and Nishida et al [3, 11-13] have reported the three step transformation when the annealing step is performed in purified argon. The present DSC results are consistent with their findings.

3.2 Analysis of microstructure using TEM

Fig. 3 presents microstructures observed in TEM foils at 293 K. The foils were thinned from corresponding DSC disks taken out of the heat treated cylinders. The samples were heat treated in two different atmospheres: (1) figures in the left row (Figs. 3a and 3c) document the microstructure in the bulk of the specimen that was heat treated in a mixture of hydrogen and argon (1:1) with a total pressure of 0.95 bar, (2) figures in the right row (Figs. 3b and 3d), taken at the same magnification as the corresponding figures in the left row, demonstrate the alloy microstructure after the heat treatment under pure hydrogen with a partial pressure of 0.95 bar. In both cases, the microstructure was characterized by a homogeneous precipitation of the Ni₄Ti₃ phase. In each particular heat treated material state there was no apparent difference between the particle characteristics obtained for particles situated either at the grain boundary or in the grain interior regions. However, a considerable difference in terms of the particle size exists when the two investigated material states are mutually compared. This is clearly demonstrated in Figs. 3c and 3d. Average diameter of the Ni₄Ti₃ particles in the sample that was heat treated in the mixture of hydrogen and argon (1:1) was (76±18)nm (Fig. 3c) while the size of the particles in the sample heat treated in the hydrogen atmosphere was (37±6)nm (Fig. 3d). Thus the average diameter of Ni₄Ti₃ particles in the sample that was heat treated in hydrogen only (hydrogen pressure of 0.95 bar) is approximately half of the diameter of particles in the sample heat treated in the hydrogen and argon mixture (1:1, partial hydrogen pressure of 0.48 bar).

We first discuss the effect of the hydrogen partial pressure on the characteristics of the Ni₄Ti₃ particle population. It is obvious that the increase in the filling pressure of hydrogen leads to the decrease in the size of Ni₄Ti₃ precipitates, see Figs. 3c and 3d. Hydrogen atoms in NiTi lattice occupy tetragonal and octahedral sites and change lattice parameters [11]. Consequently, we suspect that these local distortions result in local stress fields that are responsible for an effective decrease of the nucleation barrier for the precipitation of the Ni₄Ti₃ phase. The effect of dissolved hydrogen eliminates the potential difference in the nucleation barrier between grain boundary and grain interior regions. As a result, a homogeneous distribution of Ni₄Ti₃ precipitates between grain boundary and grain interior regions is observed. Since the higher partial pressure of hydrogen during the heat treatment may result in higher density of the nucleation sites, the precipitates are smaller after the heat treatment under the higher partial pressure of hydrogen. Further work is needed to clarify this effect.

We now address the subsequent effect of the Ni₄Ti₃ particle populations on the MMT path. As mentioned in the section 1 of the present study, the presence of coherent Ni₄Ti₃ precipitate supports the formation of R-phase and thus results in splitting of B2/B19′ martensitic transformation in two steps B2/R and R/B19′ [2]. Since the R-phase nucleates at each particle matrix interface [2], the higher number density of precipitates (smaller particles resulting from heat treatments under higher hydrogen partial pressure) facilitates the R-phase transformation and leads to the shift of the corresponding DSC transformation peak on cooling towards higher temperatures. On the other hand, the presence of coherent Ni₄Ti₃ precipitate produces a strong resistance to large deformations associated with R/B19′ transformation [8]. Here the smaller particles (higher number density) have the opposite effect. Sufficiently dense Ni₄Ti₃ microstructures hinder the R/B19′ transformation, and for a certain critical size of particles the R/B19′ may be fully suppressed.
Fig. 3 Brief field TEM images a) and c) of the bulk of the specimen that was heat treated in a mixture of hydrogen and argon (1:1) and TEM images b) and d) of the bulk of the specimen heat treated in hydrogen atmosphere. Corresponding DSC curves (e) and (f) for the bulk samples heat treated in the mixture of hydrogen and argon (1:1) and in hydrogen atmosphere.
4. CONCLUSIONS

In the present study we have demonstrated the effect of hydrogen partial pressure applied during the heat treatment on the multiple-step martensitic transformations in Ti-50.8at%Ni alloy. Based on the obtained experimental DSC and TEM results, we can draw following conclusions:

1) The application of higher partial pressures of hydrogen during the heat treatment results in the reduction of the Ni₄Ti₃ particles size.

2) The denser Ni₄Ti₃ particle populations support the B2/R transformation and lead to the shift of the first transformation step on cooling towards higher temperatures.

3) The denser Ni₄Ti₃ particle populations hinder the R/B19' transformation and lead to the shift of the second transformation step on cooling towards lower temperatures. A critical particle size may exist below which the R/B19' transformation step is fully suppressed.

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REFERENCE
