J. PHYS. IV FRANCE **7** (1997)
Colloque C5, Supplément au Journal de Physique III de novembre 1997

Precipitation Process in a Deformed NiTi Near Equiatomic Alloy

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Abstract: The precipitation process in deformed NiTi alloys was studied in the work. The alloys had a nominal composition of 50.6 at.% and 51.0 at% of nickel. Specimens were deformed by 5 - 10% and then aged at the temperature range 400 - 600°C. Electron microscopy studies showed that dislocations presence influence the precipitation process. This is especially visible in the Ni50.6%-Ti alloy were the particles nucleate at dislocations only. Ageing at 600°C causes healing out the dislocation and the precipitates do not occur in the alloy. Also in the alloy with larger content of nickel interaction between dislocations and precipitates is observed.

1. INTRODUCTION

The precipitation process in nickel-rich NiTi shape memory alloys has been intensively studied for last years [1-6] as it significantly influences both the structural and functional properties of the alloy. It is known that the precipitation sequence is as follows: $\beta_o \rightarrow \beta_1 + Ni_4Ti_3 \rightarrow \beta_2 + Ni_3Ti_2 \rightarrow \beta_3 + Ni_3Ti$ where β_o, β_1, β_2 and β_3 indicate changes in the matrix composition. The Ni_4Ti_3 particles precipitating in early stages of ageing have a rhombohedral structure and are uniformly distributed in the matrix. However, if the alloy is deformed after supersaturation and before ageing the presence of dislocations and their healing out can change the precipitation behaviour. On the other hand the precipitates occurring in the alloy can influence the recrystallization process. D.Treppmann el.al [7] have carried out systematic studies of influence of such a „combined reaction" on the alloy properties. They found out that the transformation temperatures and sequences strongly depend on the alloy structural properties such as dislocations and precipitates presence in the matrix.
The aim of this work was to study the early stages of the precipitation process in presence of dislocations in near-equiatomic NiTi alloys.

2. EXPERIMENTAL PROCEDURE

Two NiTi alloys with nominal composition of 50.6 at.% and 51.0 at.% of nickel were used in the studies. The specimens in form of plates were solution treated at 850°C for 1 h followed by cold rolling with a deformation degree in the range 5 - 10%. This low deformation degree allowed for observation of single dislocations in the sample. Then the specimens were aged at 300 - 600°C for 1 h.
TEM observations were carried out using JEM 200B and JEM 3010 microscopes on thin foils prepared by jet-polishing in a 7% solution of $HClO_4$ in CH_3COOH.
The transformation temperatures were determined by Differential Scanning Calorimetry (DSC).

3. RESULTS AND DISCUSSION

The alloy containing 50.6at.% Ni deformed by 5% and then aged at 400°C for 1 h shows presence of dislocations uniformly distributed in the matrix. In some regions dislocations form arrays of parallel lines. All of them are decorated by very fine, semicoherent particles (Fig. 1).

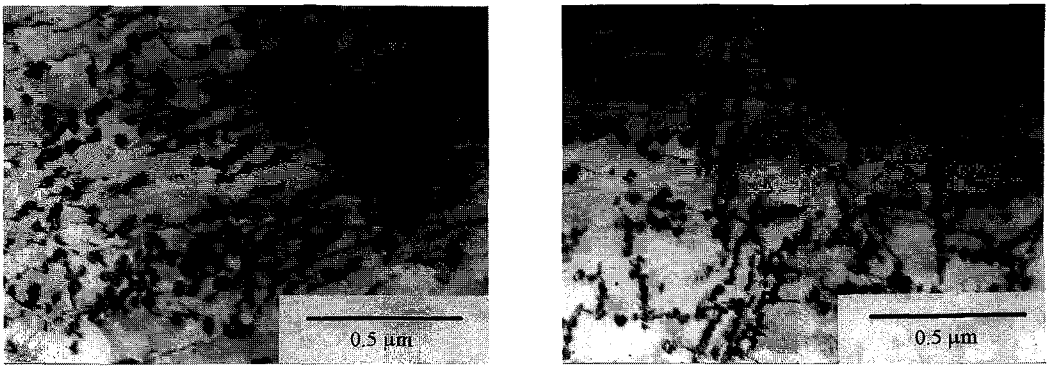


Figure 1: Structure of the Ni50.6at.%-Ti alloy deformed by 5% and aged at 400°C/1h

It was difficult to obtain a good diffraction pattern from these particle but at certain orientation weak additional spots were visible which allow to prove that these are particles of Ni_4Ti_3 phase (Fig. 2). Ageing of the alloy without previous deformation did not caused the precipitation process. Moreover, ageing the alloy at higher temperatures caused disappearing of both dislocations and precipitates.

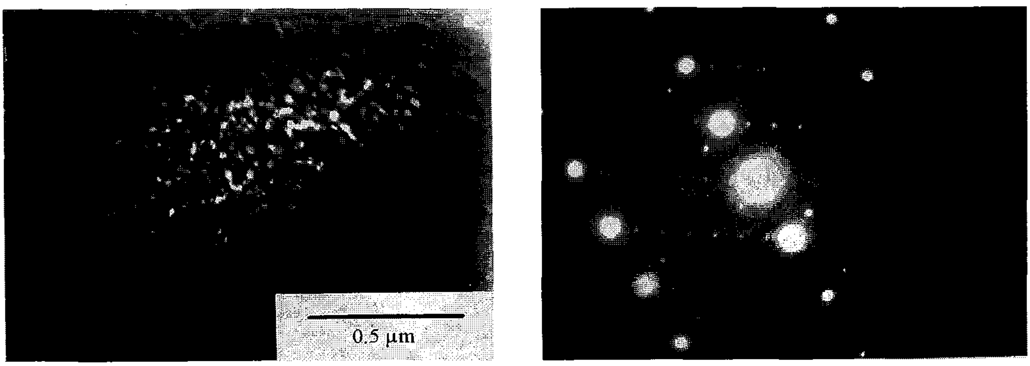
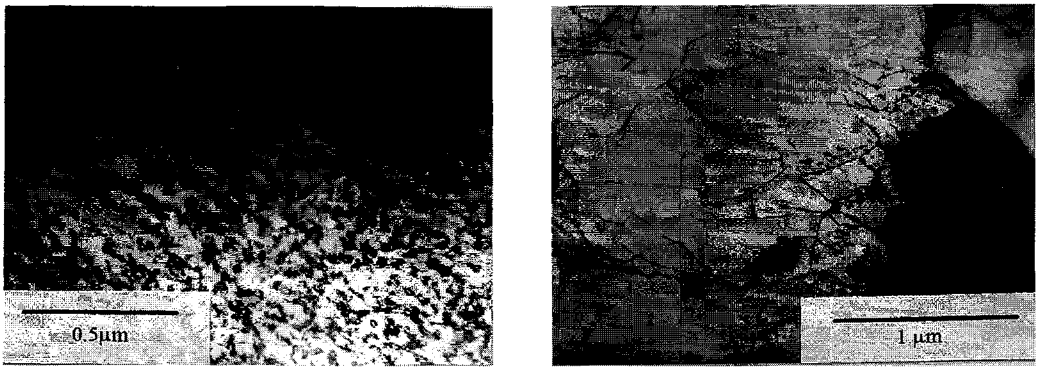


Figure 2: Dark-field image of Ni_4Ti_3 particles and the corresponding diffraction pattern in [233] orientation of the Ni50.6%-Ti alloy deformed by 5% and aged at 400°C/1h

The same alloy deformed by 10% and then annealed at 400°C for 1h also shows dislocations decorated by precipitates (Fig. 3) although in these specimens the dislocation density is much higher and the precipitates are visible only in areas of a relatively small dislocation density where it was still possible to detect single dislocations. Ageing of a 10% deformed specimen at 500°C/1 h leads to formation of low-angle boundaries but the precipitates dissolve at this temperature. This peculiar behaviour of the Ni_4Ti_3 precipitation process is probably due to the fact that the alloy composition was only slightly exceeding the lower limit of nickel content from which the precipitation process occurs. Thus the presence of dislocations which are places of lower energy for particles nucleation allows for precipitation, if the dislocations are absent in the sample the precipitation process does not occur.

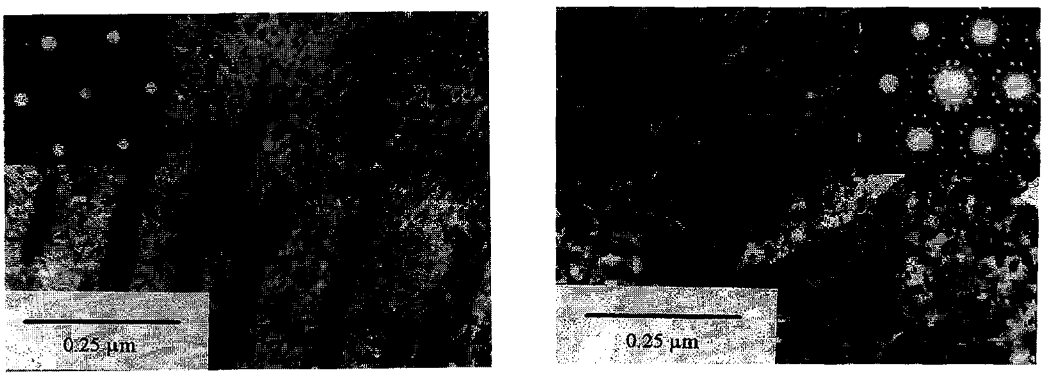


a) b)

Figure 3: Structure of the Ni50.6at.%-Ti alloy deformed by 10% and aged at 400°C (a) and 500°C (b)

Since this was the first time that the heterogeneous precipitation of Ni_4Ti_3 particles was observed, it was interesting to find out whether in an alloy with higher nickel content the same would happen. Thus, a second alloy with a nominal composition of 51.0at.% of nickel was thermomechanically treated and the electron microscopy studies were carried out on the samples.

A complex structure occurs in the alloy specimens deformed by 5% and then aged at 400°C/1h (Fig. 4). First of all the R-phase is present in the alloy at room temperature which is indicated by very strong 1/3 <110> spots on the diffraction patterns. Then the precipitation process of the Ni_4Ti_3 phase is very intense in these specimens. The particles are coherent with the matrix and give a very strong strain field contrast on the microscopic images. In the place where dislocations are visible the precipitates tend to nucleate at the dislocation lines.



a) b)

Figure 4: Structure of the Ni51.0at.%-Ti alloy deformed by 5% and then aged at 400°C/1h (diffraction patterns in the corners show extra spot from the R phase (a) and Ni_4Ti_3 precipitates (b))

However, at some places it was possible to observe that the precipitation process has a heterogeneous character (Fig. 5). The average length of the particles is about 30 nm and they were much larger than in the same alloy aged at 400°C without previous deformation.

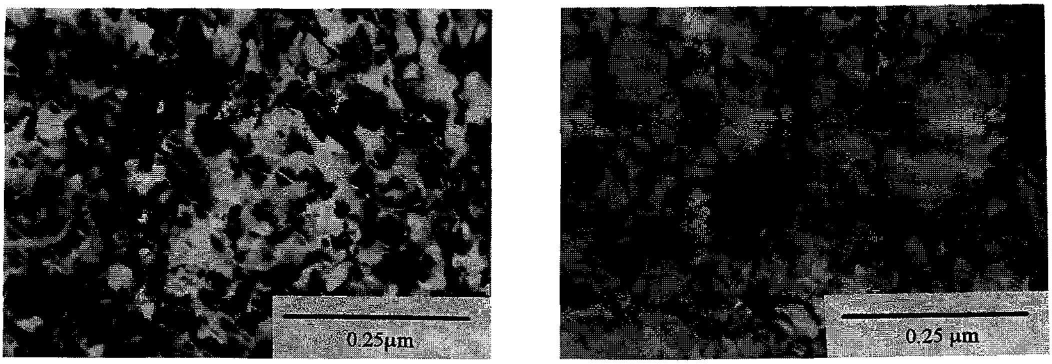


Figure 5: The Ni_4Ti_3 particles precipitation at dislocations in the Ni51.0at.%-Ti alloy aged at 400°C/1h

Ageing of the alloy at 500°C/1h causes significant increase of the Ni_4Ti_3 particles. They are in the range of about 30 nm to 100 nm long and make obstacles for the moving dislocations. Fig. 6a shows interaction of dislocations with lenticular precipitates, bending of dislocations on the particles is visible. Also, since the dislocations cannot move freely here the low-angle boundaries were rarely observed in these specimens. On the other hand, the precipitates in these specimens are uniformly distributed in the matrix and in many places no influence of the dislocation presence on the precipitation is observed (Fig. 6 b).

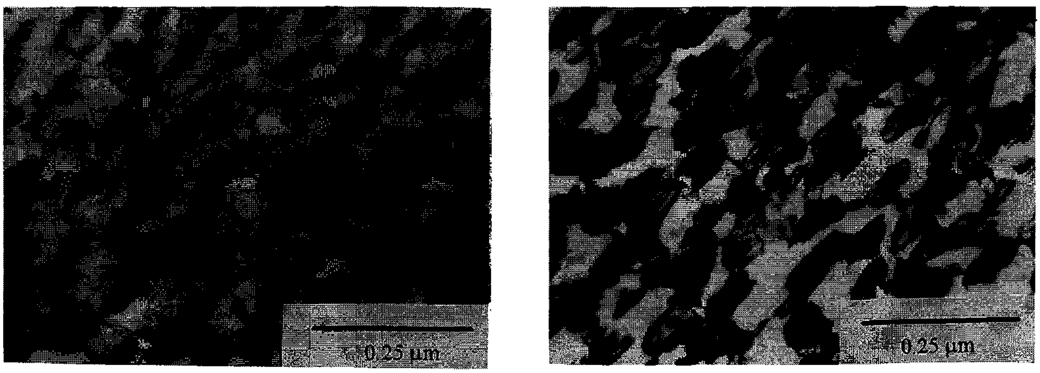


Figure 6: The structure of the Ni51.0%-Ti alloy deformed by 5% and aged at 500°C/1h

This observation is indirectly confirmed by the DSC measurements. The specimen of this alloy deformed by 5% and aged at 500°C/1h gives on the DSC cooling curve two distinct peaks, one with a maximum at 21°C caused by the B2 $\rightarrow$ R transformation, and the second one with a maximum at -26°C from the R $\rightarrow$ B19' transition. The martensitic transformation occurred in one stage, unlike other NiTi alloys deformed and annealed [8] where the specific configuration of dislocations caused two-stage martensitic transformation. In the alloy aged at 400°C/1h the M_s temperature is depressed to such low temperatures that it was impossible to detect it by scanning calorymetry. On the other hand, in the alloy containing 50.6%Ni deformed by 5% and aged at 400°C/1h and 500°C/1h on the DSC cooling curve additionally to the R-phase transformation peak, two peaks from the martensitic transformation are present. This means that the 5% deformation gives enough dislocations to form the specific configuration responsible for the two stages of the martensitic transformation. Thus the presence of relatively large particles in the specimen of the Ni51%-Ti alloy aged at 500°C/1h suspends the dislocation rearrangement into low-angle boundaries and in result a classical one stage martensitic transformation is observed in the alloy.

4. CONCLUSIONS

1. It is possible to cause a heterogeneous precipitation process in a NiTi near-equiatomic alloy by introducing dislocations before ageing which provide places for particles nucleation. Since the precipitation process changes the matrix composition to a lower content of nickel this can influence the characteristic temperatures of transformations in the alloy.

2. Deformation of the nickel-rich NiTi alloy prior to ageing increases the speed of the precipitation process. At the early stages of precipitation the particles seems to nucleate at the dislocations. But increase in the ageing temperature causes the precipitation process so dominating that in result the particles are uniformly distributed in the matrix.

3. Large particles of the Ni_4Ti_3 phase existing in the Ni51.0%-Ti alloy are obstacles for dislocations and as such can influence the recrystallization process. The effect of the particles presence on the recrystallization process needs further studies on the alloy with larger degree of deformation.

Acknowledgements

The author is grateful for the assistance given by D. Chrobak in obtaining the DSC data presented in this paper.
The author wish also to acknowledge the Polish Committee for Research (KBN) for financial support under the project No. 7TO8A04910.
The JEM3010 transmission electron microscope was presented to the Institute of Physics and Chemistry of Metals, University of Silesia by the Polish Foundation for Science.

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