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Ni_4Ti_3 Precipitation during Ageing of MARES NiTi Shape Memory Alloys Studied by FEG-SEM

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The use of a high-brightness field-emission gun (FEG) in scanning electron microscopy (SEM) is a powerful technique to examine microstructures at very high spatial resolution down to nanometer level and has significantly enhanced our ability to solve challenging materials problems, allowing studies of nanoprecipitates.

Martensitic transformation determines almost all important properties of NiTi shape memory alloys (SMAs), including shape memory effect. Moreover, any compositional inhomogeneities in the matrix of NiTi SMAs affect the martensite start temperature, Ms, because it depends on the concentration of Ni in the matrix: for Ni content exceeding 51.5 at.% Ms is lower than -200 ºC [1]. There is a very good way to adjust the transformation temperature of NiTi alloys for Ni-rich alloys even after the alloys have been made. It is possible to use ageing treatment to rectify the transformation temperature due to incorrect initial composition of Ni-rich NiTi SMAs. The principle behind this method is the (metastable)-equilibrium between TiNi and Ni_4Ti_3 precipitates since the formation of those Ni-rich precipitates affects the composition of the retained matrix [1-2]. Although Ni_4Ti_3 is considered as a metastable phase compared with the equilibrium Ni_3Ti precipitate, it is quite stable at temperatures below 600 ºC and under normal ageing condition only Ni_4Ti_3 is observed. The ageing temperature and time dependence comes from the evolution of the density and size of Ni_4Ti_3.

Recently, it was proposed an innovative process to produce NiTi SMAs using mechanical activation of an elemental powder mixture followed by hot extrusion, called MARES (mechanically activated reactive extrusion synthesis) [3-4]. Homogenization treatment at 950 ºC/ 24 h, in argon, followed by water quenching lead to the formation of a microstructure consisting of a NiTi matrix, with a composition range of 55 - 56 at.% Ni, and a relatively uniform dispersion of Ti_2Ni [4]. To adjust the NiTi matrix composition, ageing treatments were carried out on the homogenized samples.

In order to contribute to a better understanding of precipitation processes in NiTi SMAs, the present work is an to attempt to measure the concentration variations at the precipitate-matrix interfaces by using a Philips XL30 FEG-SEM equipped with a backscattered electron (BSE) detector and an integrated EDAX energy dispersive X-ray microanalysis system. Samples with 2 mm thickness were cut from the 6 mm diameter Ni-50Ti (at.%) MARES rod and specifically heat-treated to form the Ni_4Ti_3 precipitates: after homogenization treatment the samples were aged in argon at 400 ºC and 500 ºC during 7 and 48 h. Subsequently the samples were water quenched or furnace cooled.

The microstructural observations of the aged samples using BSE (figure 1 and figure 2) were able to resolve two levels of contrast in the matrix: light gray areas, corresponding to the lenticular precipitates, and a medium gray area. These two levels of contrast are related to the variation in the backscatter coefficient that occurs due to changes in atomic number (Z-contrast). Although EDAX has lower resolution, the composition evaluated for the lenticular precipitates (58 at.% Ni) and for the medium gray area (53 to 56 at.% Ni) corroborates with the information obtained by the BSE signal. The lenticular precipitates may be assumed as Ti_3Ni_4 and the medium gray area as NiTi, according with the Ti-Ni phase diagram [1]. At 400 ºC/ 7 h (figure 1 (a)) the Ni_4Ti_3 precipitates were located in limited areas of the matrix. No significant changes were observed when the ageing time was increased to 48h (figure 1 (b)). Ageing at 500 ºC/ 7h resulted in a homogeneous distribution and high density of the Ni_4Ti_3 precipitates (figure 2 (a)). At this temperature the increase of the holding time from 7 h to 48 h caused the coarsening of the precipitates (figure 2 (a) vs figure 2 (b)). As expected, the presence of the Ni_4Ti_3 precipitates reduced the Ni concentration in the NiTi matrix from 56 at.% to 53 at.% (figure 1 (b) vs figure 2 (b)), foreseing an increase in Ms.

As conclusion, FEG-SEM may be considered as an expedite technique to study these microstructures allowing to verify the density and size of Ni_4Ti_3 precipitates and to prove that Ni content was dependent on their local volume fraction.

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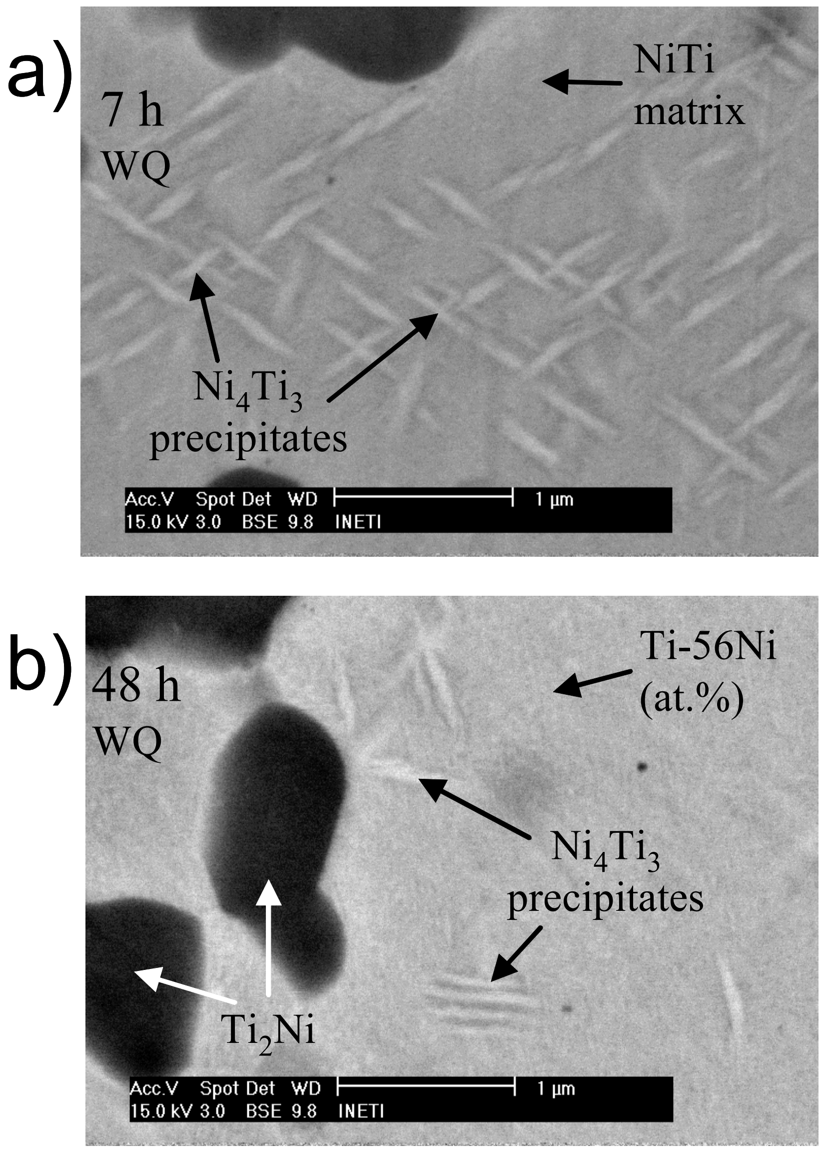

Figure 1. (a) SEM/BSE micrograph for the samples aged at 400 ºC during 7 h followed by water quenching (WQ) and (b) SEM/BSE micrograph and EDAX phase analysis for the samples aged at 400 ºC during 48 h followed by water quenching (WQ).

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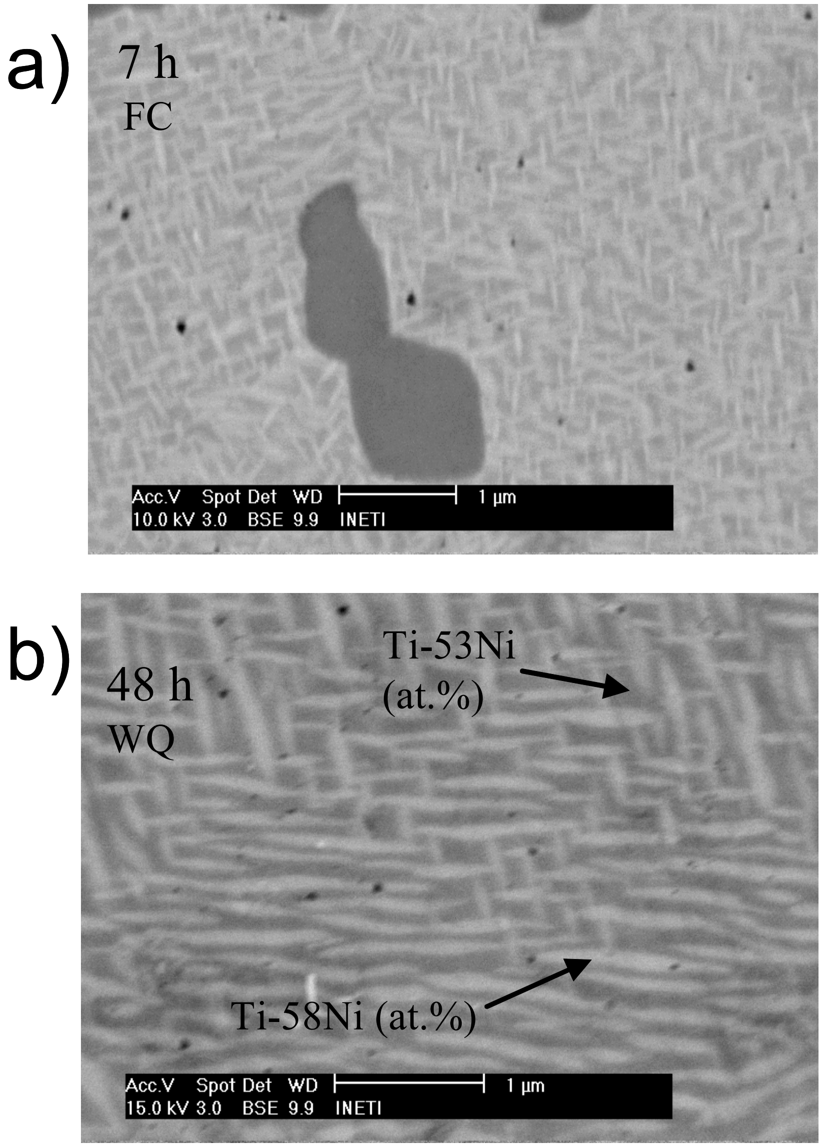

Figure 2. (a) SEM/BSE micrograph for the samples aged at 500 ºC during 7 h followed by furnace cooling (FC)and (b) SEM/BSE micrograph and EDAX phase analysis for the samples aged at 500 ºC during 48 h followed by water quenching (WQ).

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