Characterization of smart MARFOS NiTi shape memory alloys

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ABSTRACT: In the present study, structural characterization of NiTi smart shape memory alloys (SMAs), produced by an alternative powder metallurgy approach named mechanically activated reactive forging (MARFOS), was carried out by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was observed that MARFOS materials had a multiphase nanocrystalline structure. In addition, the transformation behaviour associated with the shape memory effect of the MARFOS aged materials was studied with differential scanning calorimetry (DSC). Multiple-step martensitic transformations could be observed in aged materials.

1 INTRODUCTION

Some materials have the ability to change shape or size simply by adding a little bit of heat, or to change from a liquid to a solid almost instantly when near a magnet. These materials are called smart materials (Grabe et al. 2009).

Varieties of smart materials already exist and are being researched extensively. These include piezoelectric materials, magneto-rheostatic materials, electro-rheostatic materials, pH-sensitive materials, smart gels and shape memory alloys (SMA's). The most known smart materials are SMA's (Grabe et al. 2009).

SMA's are metals that can be deformed and then returned to their original shape by heating. Arne Olander first observed these unusual properties in 1938, but not until the 1960's were any serious research advances made in the field of shape memory alloys. The most effective and widely used alloys include NiTi (Nickel - Titanium), CuZnAl, and CuAlNi (McNeese et al. 2000).

The scientific and technological interest devoted to NiTi alloys is very high due to their unique properties such as mechanical shape memory (superelasticity, associated with high pure elastic deformability), thermal shape memory (related with shape recovery upon heating of the material), pseudo-plasticity (associated to the high bendability of the material without fatigue and fracture) and biocompatibility (related to the high corrosion resistance and excellent cytocompatibility).

Several powder metallurgy techniques for producing NiTi alloys from elemental powders of Ni and Ti have been reported (Bram et al. 2002).

Among these methods, mechanical alloying has attracted significant attention since it opened new avenues for the synthesis of metastable nanostructured and ultrafine grained materials (Gu et al. 2005).

Recently, two innovative powder metallurgical processes named Mechanically Activated Reactive Extrusion Synthesis (MARES) and Mechanically Activated Reactive Forging Synthesis (MARFOS) were successfully set up for Ni–Ti alloys (Neves et al. 2007, 2008).

These two new approaches comprise a mechanical activation step (i.e. a short duration ball milling step) of elemental Ni and Ti powder mixtures, a densification step and a homogenization heat treatment step. With MARES and MARFOS the synthesis of Ni–Ti intermetallics was achieved at lower temperatures through a controlled synthesis reaction, instead of the usual strong exothermic reaction between elemental Ti and Ni powders. However, the characterization of the materials has been made using essentially X-ray diffraction and scanning electron microscopy analysis.

In this work, MARFOS NiTi alloys are also study by transmission electron microscopy and the transformation behavior associated with the shape memory effect is studied by differential scanning calorimetry.

2 EXPERIMENTAL

Commercially available micron size powders of pure Ni (ACROS ORGANICS, 99.9%, < 44 μm) and Ti (ALFA AESAR, 99.9%, < 105 μm) were mixed to give the desired equiatomic composition (Ni50Ti) and co-milled in a vario-planetary mill pulverisette 4 during 4 h. The rotation speeds of the disk (Ω) and vials (ω) were set, respectively, at 350 (clockwise) and 200 rpm (counter-clockwise). A ball to powder weight ratio of 7:1 was used.

Densification was conducted in a specially designed forging facility, built around a conventional tensile/compression test machine fitted with compression plates, and involved powders encapsulation in metallic cans. The cans were coated with lubricant, placed inside the dies and then heated by induction to a set temperature (700 ºC). The temperature was controlled with a thermocouple placed through the bottom of the die in direct contact with the can.

Additional solubilization (950 ºC for 24 h) and ageing (500 ºC for 48 h) heat treatments were conducted in the forged materials in order to promote homogenization and to adjust the composition of the NiTi matrix.

During the different steps of processing the materials were characterized by X-ray diffraction (XRD) (Rigaku diffractometer), with Cu-K_α radiation, and field emission scanning electron microscopy (SEM) (Philips XL30), with backscattered electron detector (BSE) and energy dispersive X-ray spectroscopy (EDS) analysis. Also, the microstructures of the solubilized and aged materials were studied with transmission electron microscopy (TEM) (JEOL 3000F, 300 kV microscope). Differential scanning calorimetry (DSC) graphs were recorded using a Perkin Elmer Diamond DSC calorimeter.

3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns obtained for the MARFOS materials after each step of the processing and a general view of the corresponding microstructures. Basically, they reflect the strong effect of each processing step on the constitution of the phases. As already mentioned, MARFOS combine a short duration ball milling and a relatively low temperature densification process. In the mechanically activated powders no intermetallic phase was detected and the high plastic deformation due to the MA resulted in a large contact area between the reactants and in the formation of layered structures with subsequent decreasing in the diffusion path lengths.

With the following densification step by forging, high density materials (99.4 % of theoretical density (Neves et al. 2008) were obtained but the layered structure was maintained. In fact, instead of forming directly the equilibrium phase, i.e. NiTi, the synthesis reaction involved the intermediate formation of other intermetallic phases (namely, Ti_2Ni and Ni_3Ti). Moreover, the metallic phases, Ni and Ti, were still present.

Homogenization was reached by diffusion during the following solubilization and ageing treatments (Fig. 1). Solubilization heat treatments resulted in a Ni-rich NiTi matrix (56 at. % (Neves et al. 2008)) and Ti_2Ni/Ni_2Ti_4O as secondary phases. The Ni content of the NiTi matrix was modified during ageing treatments due to Ni_4Ti_3 precipitation, with a lenticular shape, that caused the depletion of Ni content in the matrix and moved the alloy composition towards NiTi stoichiometry.

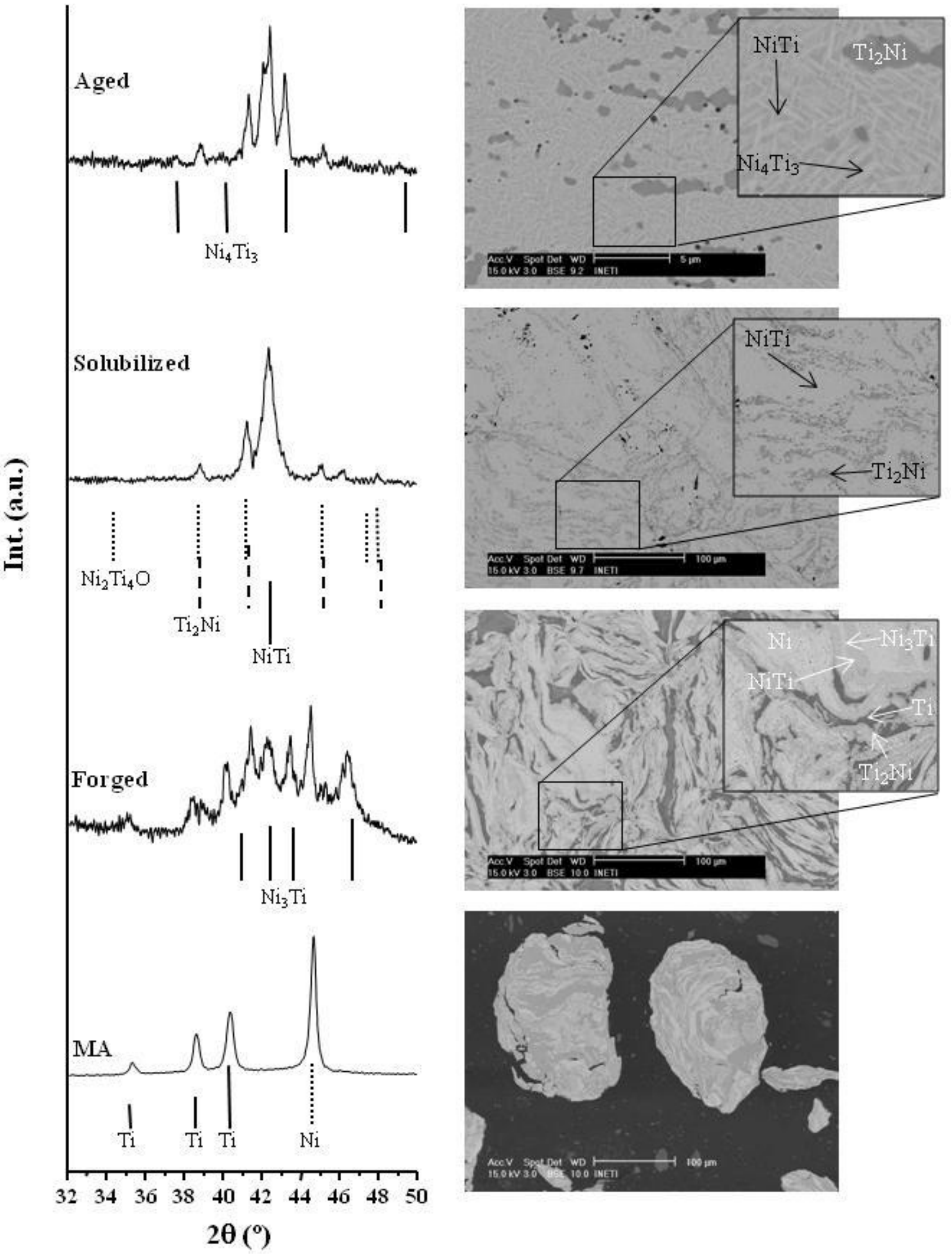


Figure 1. XRD patterns and typical SEM/BSE images of MARFOS materials.

Some of the aspects described above are understood by the thermodynamic characteristics of the Ni–Ti system, by composition fluctuations in the MA powder particles and also by the increase in the oxygen content during the processing due to the fact that some processing steps were executed under air atmosphere (from 0.50±0.02 wt % (mechanically activates powders) to 0.85±0.04 wt % (aged material)). These factors were presumably responsible for the formation of the different secondary phases and subsequently to the development of a NiTi matrix with Ni content higher than equimolar.

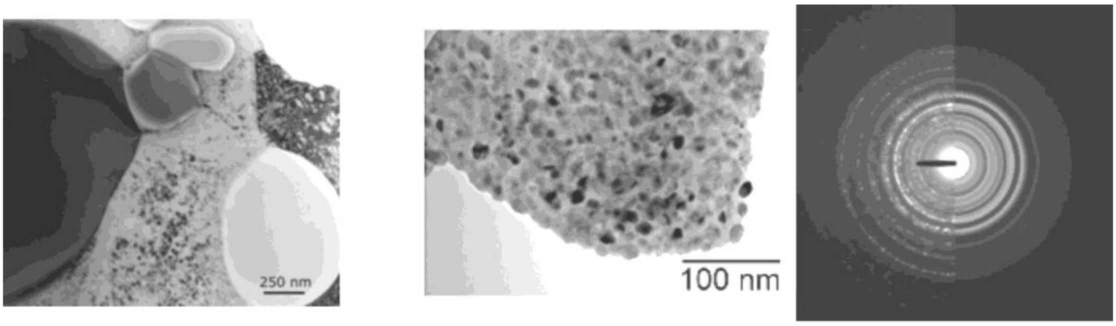
On the other hand, the presence of metallic phases in the forged material made the deformation easier, which explains at some point the high level of densification that was reached. Also, in nanocrystalline structures the grain boundaries occupy a large volume fraction of the structure, resulting in anomalously high diffusivity and capability for plastic deformation, enhancing densification (Suryanarayana et al. 2001).

The TEM bright field image in Fig. 2 (a) shows the Ti_2Ni grains embedded into a nanocrystalline NiTi matrix. The grain size of both phases was estimated to be in the range of 50 to several 100 nm. However, while the Ti_2Ni grains are single-crystalline with random orientation the NiTi grains exhibit a nanocrystalline substructure within the grains. The nanocrystals are equiaxed and are about 30 nm in size. As Fig. 2 (b) and Fig. 2 (c) reveals, the nanocrystalline substructure of the NiTi grains was maintained with the ageing treatment. However, TEM investigations are still going on in order to evaluate the Ni_4Ti_3 precipitates in the aged materials.

The transformation behaviour of the MARFOS aged materials, measured using DSC (Fig. 3), is of interest because it exhibited a multi-step transformation: a three-stage transformation on heating and an apparent single-stage transformation on cooling. It should be mentioned that the presence of the R-phase transformation was expected since this transformation occurs only in the presence of Ni_4Ti_3 precipitates (Otsuka et al. 2005).

Although the M to R transformation is identifiable, the R to M transformation on cooling is too diffuse to be detected with absolute certainty (Fig. 3). The peak temperatures for the most apparent transformations were $T_{A2\rightarrow R2}$ = 28.8 ºC (on cooling), $T_{M\rightarrow R}$ = 21.5 ºC, $T_{R2\rightarrow A2}$ = 34.5 ºC and $T_{R1\rightarrow A1}$ = 58.5 ºC (on heating).

The transformation behaviour of the MARFOS materials is probably related to microstructural features which were established during ageing. According to the literature (Otsuka et al. 2005) multiple-step transformations occur in Ni-rich NiTi alloys when the microstructure show not only large scale heterogeneities, associated with heterogeneous grain boundary precipitation, but also small scale microstructural heterogeneities, associated with precipitates and their surrounding matrix. Further work is required to clarify this point in MARFOS materials.



(a) (b) (c)

Figure 2. TEM investigation showing the nanocrystalline structure: (a) bright field image of the solution treated material; (b) bright field image and (c) SAED pattern of the NiTi matrix of the aged material.

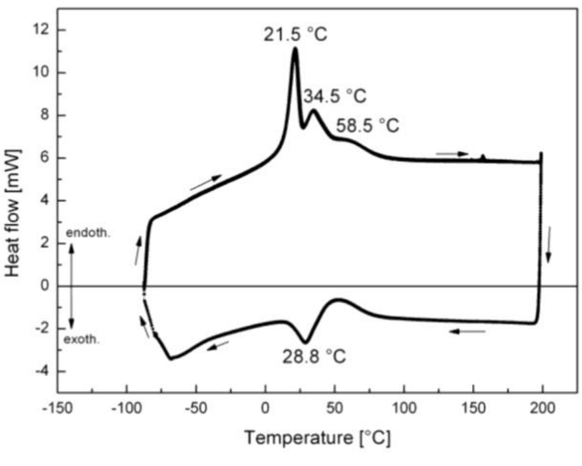


Figure 3. DSC graph of the aged sample.

4 CONCLUSIONS

Mechanically activated reactive forging (MARFOS) can be considered as a promising technique for the production of bulk NiTi alloys. Almost fully dense MARFOS materials, with a multi-phase nanocrystalline structure, have been produced. TEM analysis indicated that the Ti_2Ni grains are single-crystalline and NiTi grains exhibit a nanocrystalline substructure within the grains and this substructure of the NiTi grains was maintained with the ageing treatment. The multiple-step martensitic transformation occurs in aged NiTi alloys with a homogeneous distribution of Ni_4Ti_3 precipitates in the NiTi matrix.

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