IN SITU EXPERIMENTS WITH SYNCHROTRON HIGH-ENERGY X-RAYS OF NI-TI ALLOYS PRODUCED BY POWDER METALLURGY

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ABSTRACT: The structural evolution that takes place during the homogenization heat treatments of powder metallurgical Ni-Ti alloys was studied by in situ synchrotron diffraction. It is proposed to get a deeper understanding of this phenomenonby using different types of thermal/mechanical cycles.This work also intends to prove the feasibility of in situ X-ray diffraction studies during thermomechanical cycles and to demonstrate the interest of the combined dilatometry (under compression) and diffraction data for the detailed analysis of the phase transformations in powder metallurgical Ni-Ti shape memory alloys.

Keywords: Powder metallurgy, Ni-Ti alloys, X-ray diffraction, structural phase transitions.

1. INTRODUCTION

Materials scientists devote their efforts in the development and optimization of the processing steps that are involved in the production of any kind of material and also in the understanding of the basic principles behind materials properties. Nevertheless, it should be kept in mind that all these factors are in some way interconnected. Static studies (studies that are performed after the material processing has been completed) are used many often but they do not give a sufficient answer to some important questions. For example, considering a metallic alloy that during his processing involves the application of a heat treatment or the use of a mechanical force or both, the question "How the material changed from state X to state Y?" may arise. So the use of dynamic studies is often more appropriate for answering to these type of questions. Nowadays, some in situ experiments are already available and the 3rd generation synchrotron source PETRA III at DESY, Hamburg, is one example of that.

Equiatomic NiTi-based intermetallic compounds are the most important shape memory alloys(SMAs) which exhibit unique properties such as superior shape memory effect (a largerecoverable strain up to 8%), favourable pseudoelasticity, excellent corrosion resistance, goodbiocompatibility, and appropriate mechanical properties [1, 2]. Owing to those unique characteristics these compounds are being used in a variety ofmedical and engineering purposes. Conventionally, the NiTi SMAs are madeby well-known methods related to melting and casting. These approachesare high energy consuming and imply difficulties in controlof the processed alloy composition [3, 4].

Intensive effort has been put to adopt alternative production techniques such as powder metallurgy (PM) for manufacturing Ni-Ti SMAs. Several conventional PM methods including self-propagating high-temperature synthesis (SHS), reactive sintering, hot isostatic pressure (HIP), hot extrusion and field-activated pressure assisted synthesis have been used for the fabrication of NiTi alloys [5 – 8]. In comparison with conventional PM routes, the introduction of a mechanical alloying step offers new possibility in obtaining micro and nanostructured powders with metastable structure that affect the consolidation process [9]. Recently, two promising approaches to produce nanostructured NiTi alloys via PM have been proposed [10, 11]. The work that was carried out has revealed the necessity of having a detailed knowledge of what happens in relation to the phase transformation during the homogenization heat treatments, in particular to the relation between the newly formed intermetallic phases and the solid solutions. To our knowledge, such information is lacking in open literature. In fact, investigating the constitution at high temperatures is difficult by microstructural characterization and phase analysis at room temperature. The reason is that different phase transformations will occur on cooling even when high cooling rates are applied. So, the proposed study aims to take advantage of the possibility to carry out in-situ studies of dynamic processes, where a combination of tem-

perature with mechanical forces may enhance the kinetics. The insitu analysis by XRD will enable to follow the details of these mechanisms.

2. EXPERIMENTAL

Mechanically alloyed powder mixtures were used for these sets of experiments. Those mixtures had a nominal composition of Ti-50Ni (at.%) and were prepared from elemental powders. The experimental conditions used for the mechanical activation are described in detailed in [12]. The mechanically alloyed powders were hot-pressed at 650 ºC using a pressure of 155 kN. Subsequently, the hot-pressed material was machined in order to have samples of approximately 9/9.5x4.5x4 mm for the replicas of the homogenization heat treatments.

In situ XRD experiments were carried out on the High Energy Materials Science Beamline P07 at PETRA III (DESY, Hamburg)that is operating with an X-ray monochromated incident beam (λ = 0.124 Å) with a cross-section of 0.1 mm x 0.7 mm. Thermomechanical cycles were achieved using an Bähr DIL-805 dilatometer(Fig. 1). The dilatometer is equipped with windows that allow the X-ray beam to pass in between the heating coil. The dilatometer is working in compression mode with maximum applicable force of 25 kN and a temperature range from RT to 1500ºC. At photon energies of 100 keV samples with 4 or 5mm thickness/diameter can be used, which is the standard dimension for the used dilatometer. To control the temperaturean R-type thermocouple spot was welded to samples surface in an area that stayed above the beam. Throughout each experiment complete Debye-Scherrer diffraction rings were acquired every 2 s by a 2D detector MAR-3450.

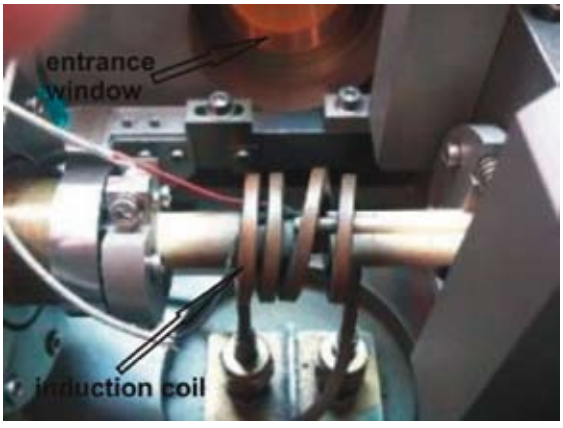

Fig. 1. Detailed view of the inductive heating section of the DIL-805 dilatometer with the X-ray beam entrance window visible; the sample (roughly, 5mm in diameter/thickness and 10 mm in length) with a spot welded thermocouple in the center is surrounded by the induction coil.

In order to study the effect of the internal stress on the kinetics of the homogenization treatment of the hot-pressed powder samples it was planned to carry out two different types of thermomechanical cycles. In one type of experiment no load was applied (sample PA) while on the other type of experiment a constant load of 0.5 kN was used (sample PB). In both cases, the heating was planned to go up to 950C with a holding time of 5 h. However, on the experiments where a load of 0.5 kN was applied it was observed a significant deformation of the samples (more details are given in the Results section). Due to this fact, those experiments were only carried out up to a temperature of 915ºC and without applying a holding stage. Both types of experiments were conducted under vacuum (10^{-3} Pa) and a constant heating rate of 20ºC/min was used.

3. RESULTS AND DISCUSSION

Here, we present the results of a first test illustrating the capabilities of the combined measuring techniques. Fig. 2 provides the change in dimension (in-plane direction) measured

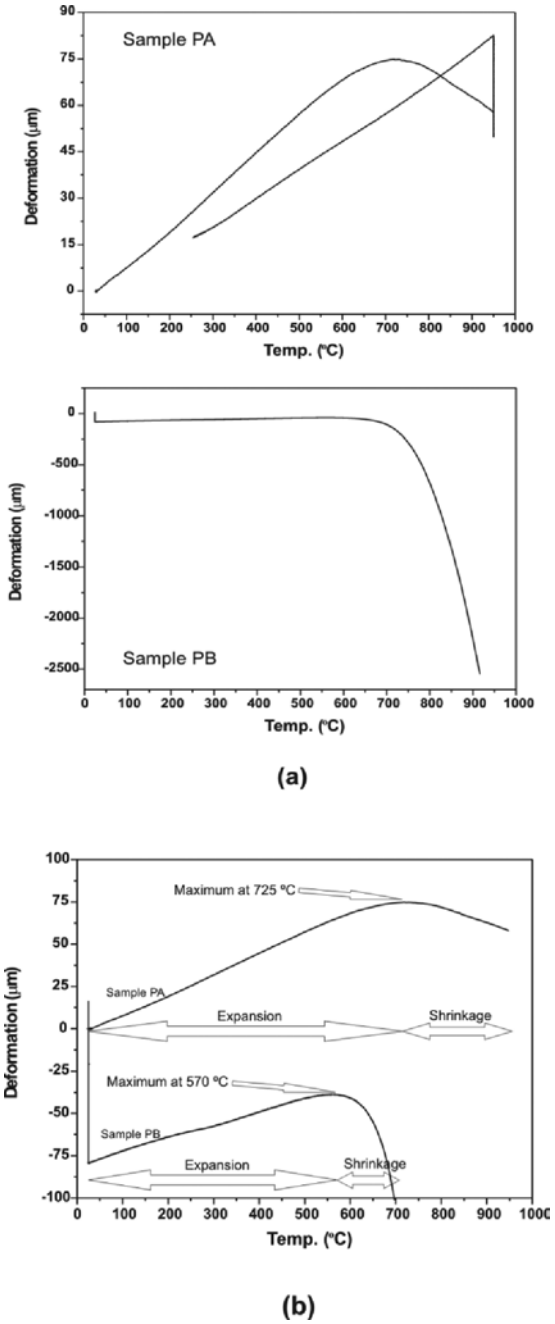

Fig. 2. Dilatometer curves obtained during the homogenization heat treatments of the Ni-Ti powder samples PA (without load) and PB (with a constant load of 0.5 kN): (a) full cycle and (b) zooming of the intersection area between expansion and shrinkage.

in the dilatometer for the Ni-Ti powder samples PA and PB as a function of time for the two thermomechanical cycles. As can be seen in Fig. 2(a), for the experiments where a constant load of 0.5 kN was applied (sample PB), it was measured a deformation of 2500 μm at 900ºC. In order to prevent any possible damage of the equipment it was decided that the following experiments would be performed only up to 915ºC, without a holding stage.

During the heating stage, the dilatometer curves can be divided into two different parts: the region of linear expansion and the region of shrinkage. The linear expansion is defined as the change in length dL divided by the initial length L_0. When the material specific temperature is reached where thermal expansion is balanced by shrinkage due to densification, no further increase in length is measured. At that point a maximum in the dilatometer curve arise. By further increasing of temperature shrinkage prevails over expansion, resulting in decreasing length of the sample. These regions are highlighted in Fig. 2(b) for the two different thermomechanical cycles. During cooling sample PA shows the usual thermal contraction (Fig. 2(a)). Ni–Ti powders were reported to show dimensional anisotropy during sintering, i.e. shrinkage in the axial direction (along the direction of compression) and the expansion in the radial direction (perpendicular to the direction of compression) [5, 13]. This anisotropy was reported to increase with increasing pressure and temperature.

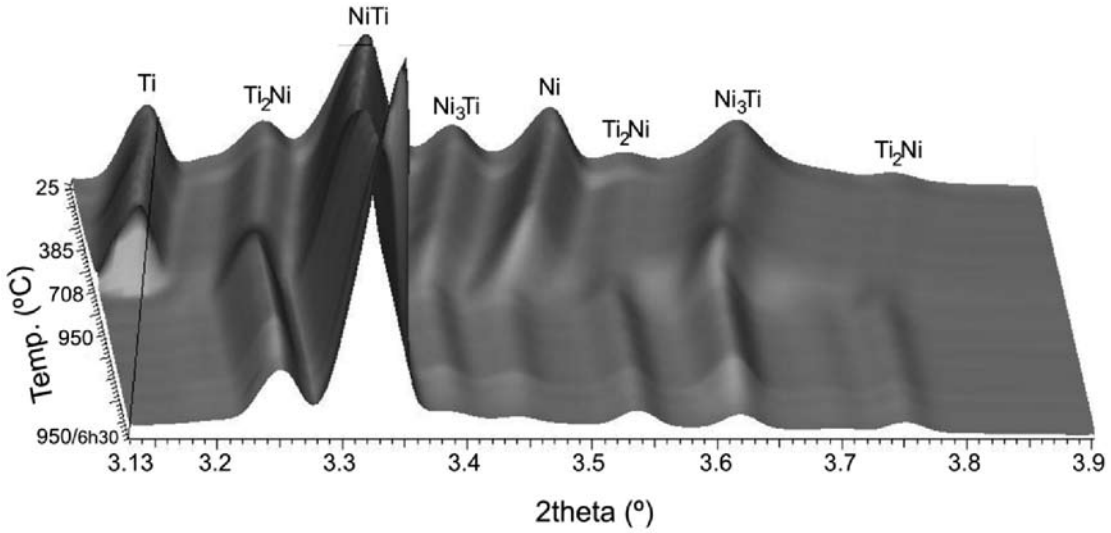

Fig. 3. XRD patterns obtained during the homogenization heat treatments of the Ni-Ti powder samples PA.

A lower expansion region of sample PB compared to sample PA can be seen in Fig. 2(b), indicating initiation of densification at lower temperature for sample PB. The temperature at which thermal expansion balanced the densification by sintering (appeared as maxima in dilatometer curves of Fig. 2(b)) was approximately 725°C for sample PA. For sample PB this temperature was approximately 570°C. Nevertheless, the relatively smoothness of both dilatometer curves may be an indication of a diffusion-assisted process.

Fig. 3and Fig. 4 shows the diffraction patterns obtainedduring the thermomechanical cycles of samples PA and PB, respectively. It can be seen that in the hot-pressed Ni-Ti powders (corresponding to a temperature of 25ºC in both figures) the reflection of the intermetallic phases NiTi, Ni_3Ti and Ti_2Ni were already indexed and coexisted with the reflections of Ti and Ni.Fig. 3 and Fig. 4 puts in evidence that heating the material resulted in a shift in all diffraction peaks positions to lower 2theta due to thermal expansion.With the increase in the temperature a continuously decrease in the reflections of Ni and Ti was observed. The reduction and disappearing of the Ti reflection wasreached in a more abrupt way fortemperatures around 710ºC and 740ºC for the samples PA and PB, respectively. Contrarily, the disappearing of the Ni reflection was done in a more gradual way. These two occurrences can be seen more clearly in Fig. 3. Associated to these two events is also the increase in the intensity of the diffraction peaks corresponding to the intermetallic phases. Taking Fig. 3 as an example, it can be easily observed the increment in the NiTi and Ti_2Ni phases simultaneously with the decrease of Ti and Ni.Moreover, the NiTi phase was found to increase significantly with the increment ofthe holding time at 950ºC, indicating a continuous incrementin the fraction of the NiTi phase during this stage.Summarizing, the phase transformation in both samples was done following the same path although between sample PA and sample PB it was observed a shift to lower temperatures in the maximum of the dilatometer curves. Nevertheless, these observations support the need of doing the homogenization heat treatments of Ni-Ti powder alloys at temperatures above 900ºC [10].

4. CONCLUSIONS

This study shows the feasibility of the simultaneous dilatometry and XRD in order to get a better understanding of the conditions for the homogenization of NiTi alloys produced by powder metallurgy. The obtained results support the need of doing the homogenization heat treatments of Ni-Ti powder alloys at temperatures above 900ºC. It is also shown that the complete conversion of the Ni and Ti solid solutions is achieved through a diffusion-assisted process.

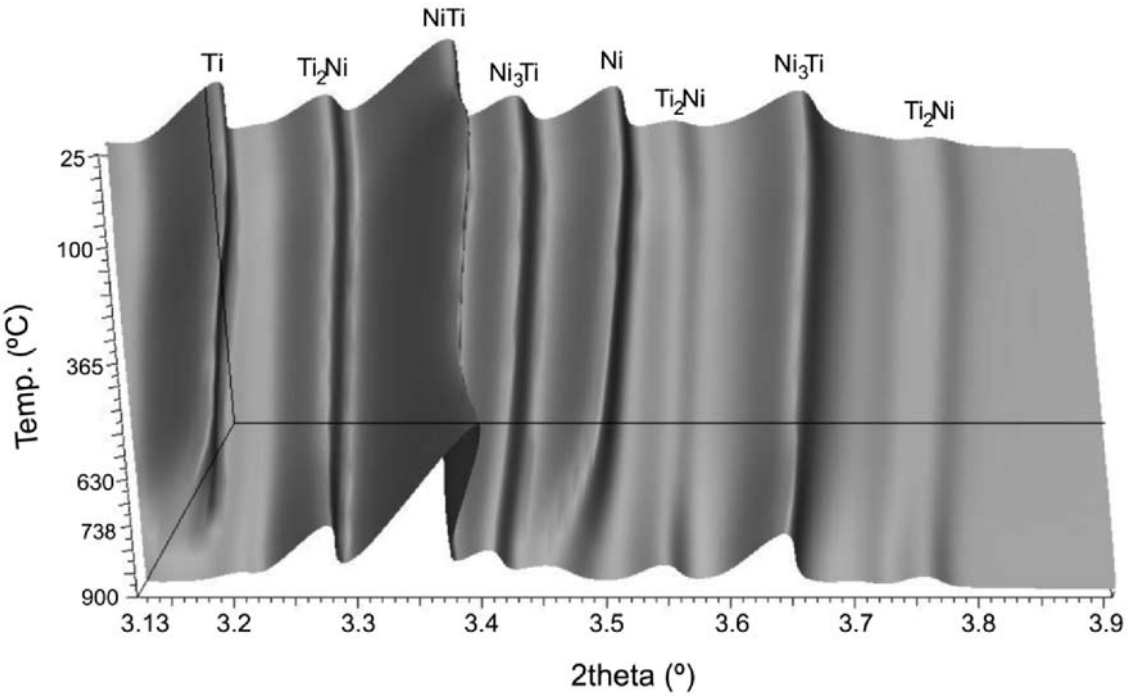

Fig. 4. XRD patterns obtained during the homogenization heat treatments of the Ni-Ti powder samples PB.

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REFERENCES

[1] K. Otsuka, X. Ren, *Intermetallics*, 7 (1999) 511-528.

[2] K. Otsuka, X. Ren, *Progr Mater Sci*, 50 (2005) 511-678.

[3] N. Nayana, Govind, C.N. Saikrishna, K. VenkataRamaiah, S.K. Bhaumik, K. Suseelan Nair, M.C. Mittal, *Mater SciEng*, 465 (2007) 44-48.

[4] J. Frenzel, E.P. George, A. Dlouhy, Ch. Somsen, M.F.-X. Wagner, G. Eggeler, *Acta Mater*, 58 (2010) 3444--3458.

[5] M. Igharo, J.V. Wood,*Powder Metal*, 28 (1985) 131-139.

[6] M. Bram, A. Ahmad-Khanlou, A. Heckmann, B. Fuchs, H.P.Buchkremerv, D.Stöver,*Mater SciEng*, 337 (2002) 254-263.

[7] N. Bertolino, M. Monagheddu, A. Tacca, P. Giuliani, C. Zanotti, U.A. Anselmi, *Intermetallics*, 11 (2003) 41-49.

[8] B. Bertheville,*J Alloys Comp*, 398 (2005) 94-99.

[9] C. Suryanarayana,*Rev Adv Mater Sci*, 18 (2008) 203--211.

[10] F. Neves, F.M. Braz Fernandes, I. Martins, J. B. Correia, M. Oliveira, E. Gaffet, T-Y. Wang, M.Lattemann, J.Suffner, H. Hahn, *Smart Mater Struct*, 18 (2009) 115003 (9pp).

[11] F. Neves, F.M. Braz Fernandes, I. Martins, J.B. Correia, M. Oliveira, E. Gaffet, T-Y. Wang, M. Lattemann, J.Suffner, H. Hahn,*ESOMAT 2009 - The 8th European Symposium on Martensitic Transformations*, P. Šittner, L. Heller, V. Paidar (Eds.), EDP Sciences (www.esomat.org),2009, 05023 (http://dx.doi.org/10.1051/esomat/200905023).

[12] F. Neves, F.M. Braz Fernandes, I. Martins, J.B. Correia, *Powder Metall*, in press 2012 (DOI:10.1179/17432901 12Y.0000000022).

[13] B.B. Panigrahi, M.M.Godkhindi,*Intermetallics*, 14 (2006) 130-135.