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RESEARCH REGARDING THE POSSIBILITY OF OBTAINING NITINOL BY POWDER METALLURGY

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ABSTRACT

In the paper the obtaining of nitinol by pressing and sintering of a mixture of nickel and titanium powders is presented. The fabrication of NiTi alloys by powder metallurgy allows avoiding the usual problems related to classical casting obtaining methods (problems related to defects caused by segregation or excessive growth of the grains), it also assures an exact control of the chemical composition and offers the possibility of manufacturing a variety of components very close to their final shape.

Although the advantages of manufacturing products by powder metallurgy are certain, the first research presented in this paper in the case of nickel and titanium powders have showed some unwanted aspects related to powder metallurgy processing which are yet to be resolved, that is, the high oxide content, the high content of secondary phases, also the difficulty of obtaining dense materials. The main conclusion is that it is imperative to do the sintering in a protecting system (if possible in vacuum), because of the high content of oxygen observed in the measured sintered products.

KEYWORDS: powder metallurgy, Ti powder, Ni carbonil, NiTi, sintering, X-ray diffractometry, SEM

1. Introduction

Nitinol is a group of materials defining the alloys of the Ni-Ti family situated around the stoichiometric concentration (50% Ni). Nitinol, the material discovered in 1959, at the Naval Ordnance Laboratory (now Naval Surface Warfare Center) is the first commercial name which became the most known in time and accepted with the same name in the materials science, after the binary Ni-Ti system that it belongs to [1][2].

The first experiments related to shape memory phenomenon (pseudo-elasticity, simple shape memory effect, double ways shape memory effect, vibration damping effect, pre-martensitic effects etc.) have been made on monocrystals. Because monocrystals are easier to obtain on copper based alloys, these were the experimental materials which allowed, in the 70's, to establish the microstructural origin of the shape memory phenomenon, and also the connection between those and the martensitic transformation [3].

The special properties of the shape memory alloys make them extremely important in present, through their extraordinary usage potential in high tech domains as biomedical technologies, nanoelectronic systems, microelectronic systems or the complex bio and optoelectromechanical ones [4].

The technology of obtaining sintered products is fundamentally different from the classical metallurgical technologies, where the semi-products are manufactured through casting of melted metals and alloys, which, afterwards, are subjected to mechanical processing (forging, lamination, dye pressing etc.); thus getting to the end product involves a big number of difficult operations, expansive and long lasting.

In powder metallurgy the products are usually obtained without ever having the materials in liquid phase.

The complexity of powder metallurgy stands in the interaction between three necessary factors in order to make the end product. These factors are: powder, pressing and sintering. A high level of knowledge of the relationship between these ingredients is of utmost importance in order to make components with high resistance and in order to carry on requests regarding quality and costs. Recently, two new processing method using powder metallurgy named MARFOS (mechanically activated reactive forging synthesis) and MARES (mechanically activated reactive extrusion synthesis) have been studied in order to produce raw NiTi alloys, being considered promising technologies for producing raw intermetallic compounds [5].

2. Experimental results

The samples analyzed in this paper were made according to the diagram shown in Figure 1, starting from raw materials from metallic powders of nickel and titanium. From the homogenized mixture of the two types of metallic powders were realized by compression products that undertook afterwards a sintering process.

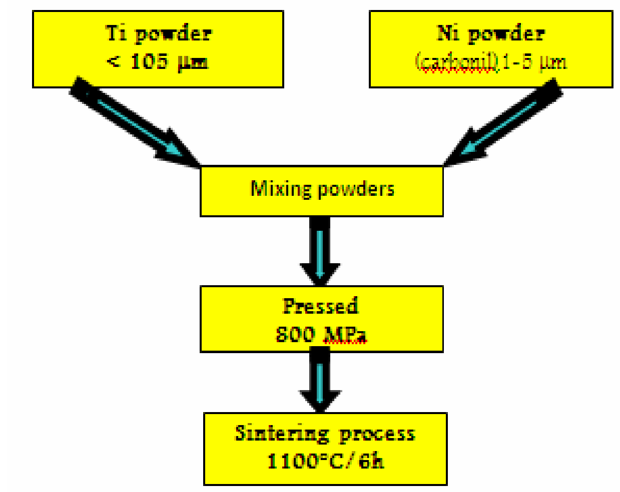


Fig. 1. *Processing scheme of the nitinol samples obtained from metallic powders*

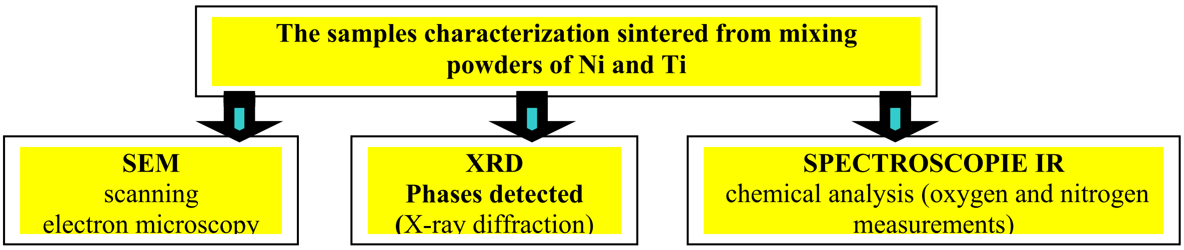


Fig. 2. *Characterization of the nitinol samples obtained by sinterring the mix of the metallic powders (according to the process presented in fig. 1)*

The nitinol samples made after mixing, homogenizing, compressing and sinterring the powders had a complex characterization in order to understand the nature of the resulted phases after diffusion (Figure 2).

2. Results and Discussion

The investigation through **X-ray diffraction (XRD)** presented in Figure 3, was made in order to identify the phases that came out after the diffusion processes in the sintered compressed products from the powder mix.

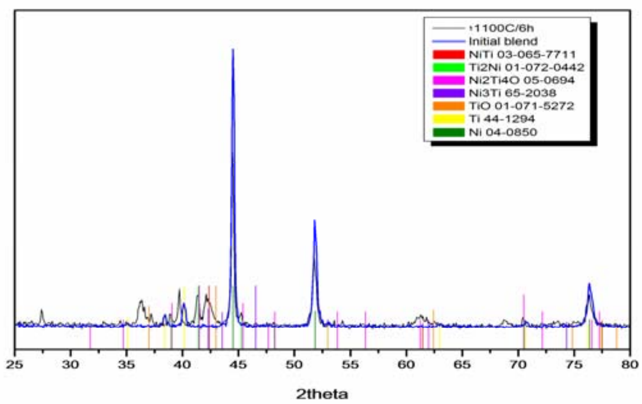


Fig. 3. *Phases detected (by XRD)*

One can notice that if, after the pressing step the phases were Ni and Ti, after the sinterring step intermetallic compounds and oxydic phases were formed: **NiTi, Ti_2Ni, Ni_3Ti, Ni_2 Ti_4 O, TiO, NiO.** Analyzing the binary equilibrium diagram Ti-Ni (Fig. 4), that gives back the areas of the phasic stability for the Ti-Ni alloys from liquid state to the environment temperature, one can notice that similar phases are being formed after invariant reactions (except for the oxydic ones).

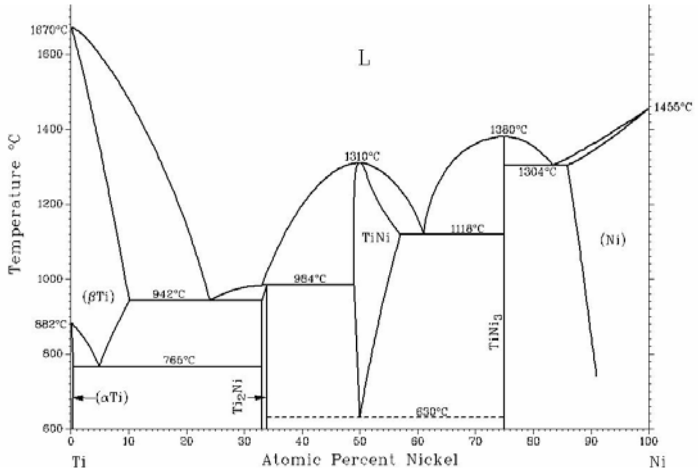


Fig. 4. *Scheme of the Ti-Ni binary phase diagram*

The invariant transformations that take place of Ti-Ni binary phase diagram are:

- three eutectic reactions:

$L_{24.5} \leftrightarrow \beta_{Ti_{11}} + Ti_2Ni$

$L_{60} \leftrightarrow TiNi + TiNi_3$

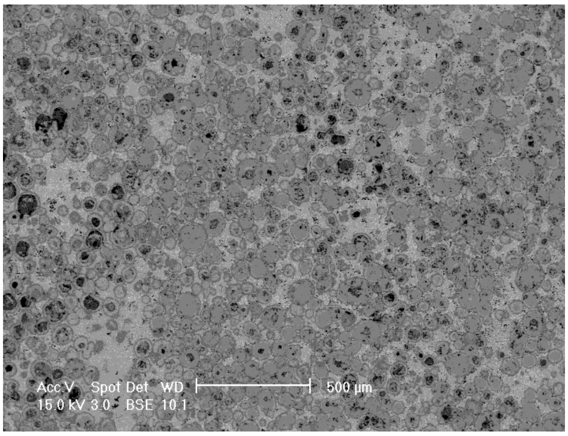
$L_{80.8} \leftrightarrow TiNi_3 + (Ni)_{85}$

- one peritectic reaction:

$L_{33} + TiNi \leftrightarrow Ti_2Ni$

- one eutectoid reaction:

$(NiTi)_{49.5} \leftrightarrow (Ti_2Ni)_{33.3} + (TiNi_3)_{75}$



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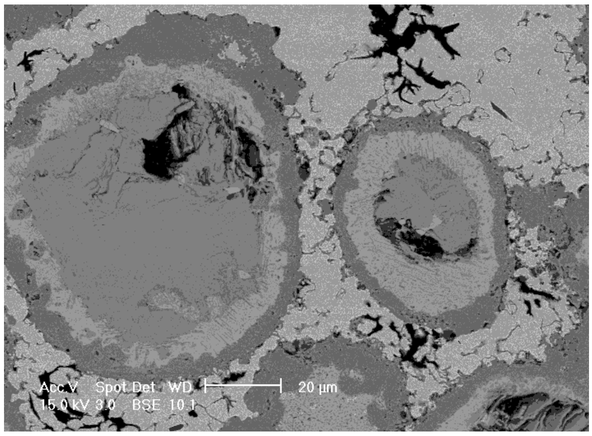

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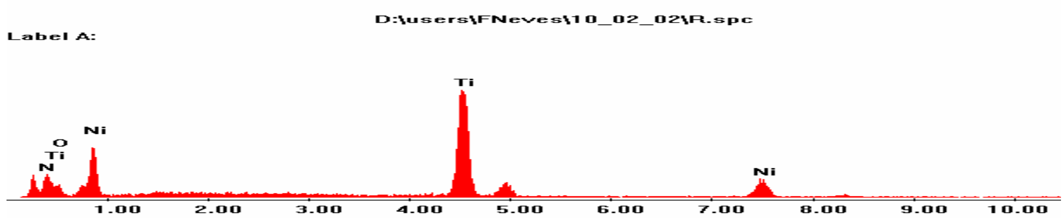


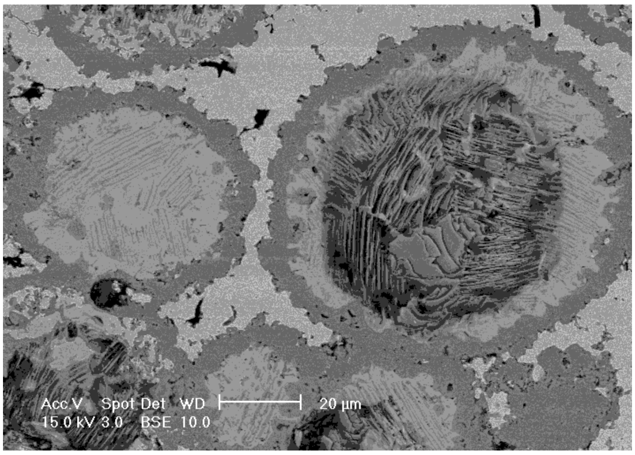
Total area of Fig. 5a

Fig. 5. *The SEM microstructure of the sintered products from Ni-Ti powder mix (a, b)*

The explanation of forming the oxydic phases was cleared out after making the spectral analysis, chemical analysis (oxygen and nitrogen measurements). Oxygen and nitrogen contents (wt%) (LECO - The ONH836 Oxygen/Nitrogen/Hydrogen Elemental Analyzer is designed for wide-range measurement of oxygen, nitrogen, and hydrogen content of inorganic materials, ferrous and non-ferrous alloys, and refractory materials using the inert gas fusion technique). As-pressed: oxygen 0.280.03; nitrogen 0.0410.007. As-sintered: ***oxygen over 15 (IR cell saturated);*** nitrogen 2.5490.358.

The results of the SEM analysis of the sintered compressed products in the given conditions are presented in Fig. 5.

Figure 6 presents the chemical composition of 4 zones with different microstructures resulted during sintering after diffusion.



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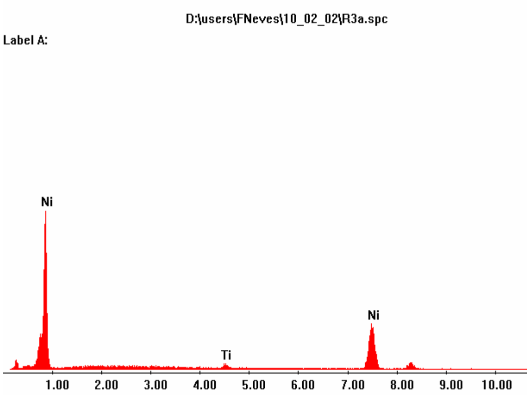
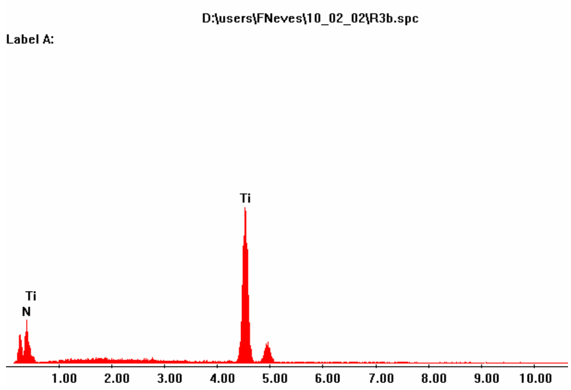
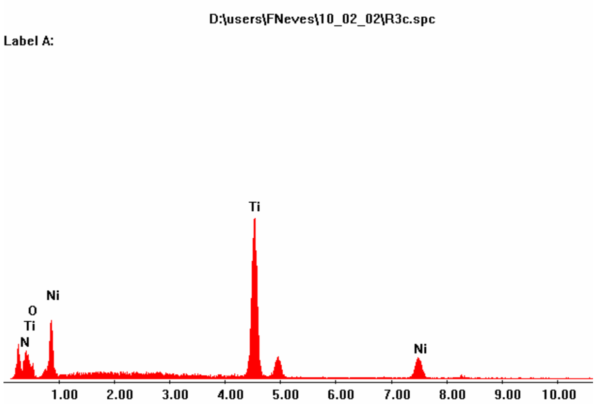


Area marked as 1 in Fig. 6a



Area marked as 2 in Fig. 6a



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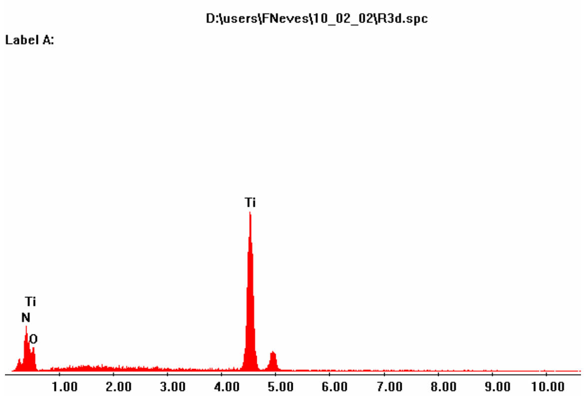

Area marked as 4 in Fig. 6a

Fig. 6. *SEM results sintered material*

3. Conclusions

The processing of Ni and Ti metallic powders of through technologies specific to MP lead to forming some materials known as nitinol.

The nitinol obtaining technology must be improved as the XRD, spectral and SEM analysis highlighted in the sampled obtained after sintering similar inter-metallic compounds with those from the binary system Ti-Ni (NiTi, Ti_2Ni, Ni_3Ti) and also oxydic phases (Ni_2 Ti_4 O, TiO, NiO).

The main conclusion of the present study is that it is required that the future sintering step to be made in a protection system (preferably vacuum) due to the high levels of oxygen detected in the sintered samples.

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