PREPARATION OF THE NITI SHAPE MEMORY ALLOY BY THE TE-SHS METHOD – INFLUENCE OF THE SINTERING TIME

Jaroslav ČAPEK, Vojtěch KUČERA, Michaela FOUSOVÁ, Dalibor VOJTĚCH

Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, capekj@vscht.cz

Abstract

A NiTi shape memory alloy, known as nitinol, has been intensively studied for last five decades. This big interest is caused by its unique properties, such as pseudoplasticity, superelasticity, shape memory, as well as good corrosion resistance and sufficient biocompatibility. Unfortunately, its common manufacture methods (vacuum induction melting, vacuum arc remelting) possess some disadvantages, such as a contamination or an insufficient homogeneity of the fabricated ingots. Therefore, new fabrication methods have been recently intensively studied. The self-propagating high-temperature synthesis seems to be a promising approach to the NiTi fabrication. It has been performed in both (thermal explosion and plane wave propagation) regimes. The thermal explosion one seems to be more suitable for the fabrication of compact materials.

In this work, the NiTi samples were prepared by the thermal explosion mode of self-propagating high-temperature synthesis (TE-SHS). The influence of a sintering time on the samples properties, such as microstructure, transformation and compression behaviour, as well as hardness HV 5 was studied.

Keywords: NiTi, powder metallurgy, thermal explosion mode of self-propagating high-temperature synthesis

1. INTRODUCTION

Recently, an approximately equiatomic alloy, known as nitinol, has been intensively studied. It is due to its unique properties, such as pseudoplasticity, superelasticity, shape memory as well as good corrosion resistance and sufficient biocompatibility. These properties predetermine this material to applications in a lot of branches, such as military, aircraft, aerospace and medical industry [1].

The NiTi alloy is commonly produced by a vacuum induction melting (VIM), a vacuum arc remelting (VAR), or by their combination (VIM/VAR). Apart from the fact that these methods are very expensive, they have other disadvantages. During the VIM process, the melt could be contaminated by carbon originating from a graphite crucible. The VAR process does not lead to any contamination, because the melt exists only for a short time. On the other hand it causes inhomogeneity of ingots. Therefore, the process has to be repeated several times, which increases costs of the ingots [2]. Due to these disadvantages, new producing methods of the NiTi alloy have been explored [2].

A self-propagating high-temperature synthesis (SHS) seems to be a very promising approach of the NiTi alloy preparation. This method is based on fast heating of green compacts prepared from elemental powders or from mechanically pre-alloyed powders to temperatures under melting point of pure elements. After heating, diffusion processes take place, which causes a decrease of melting point. Moreover, the system can locally reach eutectic or peritectic composition [3, 4]. It causes that a liquid phase is formed and improves further diffusion and homogenization. Moreover, reactions occurring in the system are exothermic, which leads to another temperature increase and subsequent diffusion acceleration [3-5].

The preparation of the NiTi alloys has been described by both, plane wave propagation (PWP) and thermal explosion (TE) of SHS modes in available literature [4]. The PWP mode consists of an ignition at one end of
the sample and subsequent propagation of the heat wave caused by exothermic reactions through the whole sample. While the PWP-SHS is usually used for preparation of porous NiTi alloys, the TE-SHS is preferred for preparation of compact NiTi. The thermal explosion mode of SHS is based on fast heating of the green compact in its whole volume [4].

Except the NiTi the SHS products usually contain other phases, e.g. unreacted nickel and titanium, or phases Ni$_x$Ti$_y$. Fortunately, this problem can be solved by subsequent heat treatment [6]. Pores, which are presented in the SHS products, can be removed by subsequent hot working.

Despite a lot of studies about preparation of the NiTi alloys by SHS methods have been published [7-10], only a few of them have been concerned on the thermal explosion mode of self-propagating high-temperature synthesis.

In this work, NiTi samples were prepared by the TE-SHS method. The influence of the sintering time on chemical and phase composition, microstructure, mechanical properties, hardness and transformation behaviour was studied.

2. EXPERIMENTAL SETUP

Nickel powder (≤5 µm, 99.98 wt. %) and titanium powder (≤50 µm, 99.9 wt. %) were used as starting materials. The powders were blended in an equiatomic ratio and subsequently uniaxially cold pressed using the LabTest 5.250SP1-VM universal loading machine into cylindrical green compacts with diameter of 10 mm and length of 30 mm. The green compacts were sealed into evacuated quartz ampoules to protect them from oxidation during sintering. The ampoules were put into an electric resistance furnace, which was preheated to the temperature of 1100 °C. As a consequence, heating rate about 500 °C·min$^{-1}$ was reached.

After different time periods of 2, 3, 5, 10 and 20 minutes, the ampoules were removed from the furnace and quenched into water at ambient temperature. The cooled samples were cut into several pieces and subsequently examined. Chemical composition of the prepared samples was measured by the TESCAN VEGA-3 LMU scanning electron microscope equipped with the Oxford instruments INCA 350 EDX analyser (SEM-EDX). Metallographic cross-sections were prepared and microstructure was studied by the OLYMPUS PME3 light metallographic microscope (LM) and by the SEM-EDX in BSE regime. Phase composition was examined using the XRD 3000 P - XRD system with a Co anode. Transformation behaviour was studied in the temperatures interval 0 – 100 °C by the SETARAM-DSC 131 machine, compression tests realized using the LabTest 5.250SP1-VM universal loading machine. Moreover, Vickers hardness HV 5 was also measured.

3. RESULTS

3.1. Chemical and phase composition

The EDX measurements showed that all prepared samples were depleted of nickel. The depletion was about 1.5 at. % for all of the samples. It could be explained by evaporation of nickel during combustion. The depletion did not depend on the sintering period, because the liquid phase, the presence of which significantly extends evaporation, exists only for few seconds. B2 NiTi and Ti$_2$Ni phases were found by the XRD analysis and confirmed by the SEM-EDX. The nickel content in the NiTi matrix slightly increased with increasing sintering time (Table. 1).
Tab. 1 Nickel content in the NiTi matrix

<table>
<thead>
<tr>
<th></th>
<th>2 min</th>
<th>3 min</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (at. %)</td>
<td>49.48</td>
<td>49.49</td>
<td>49.52</td>
<td>49.57</td>
<td>49.65</td>
</tr>
<tr>
<td>Ti (at. %)</td>
<td>50.52</td>
<td>50.51</td>
<td>50.48</td>
<td>50.43</td>
<td>50.35</td>
</tr>
</tbody>
</table>

It suggests that more Ti$_2$Ni phase formation takes place at longer sintering period. This phenomenon can be explained by low content of nickel in the samples. During longer sintering time period, composition of the matrix gets closer to the thermodynamically stable composition (50 at. %), on the other hand, amount of the Ti$_2$Ni phase has to necessarily increase.

3.2. Microstructure

The microstructure observation was in good agreement with results of the XRD analysis. The samples consisted of the NiTi matrix and polygonal shaped Ti$_2$Ni particles (Fig. 1). In Fig. 1, it is also obvious that prolongation of the sintering time led to coarsening of the Ti$_2$Ni phase up to sintering times of 10 min. After 20 min, finer and more homogeneously distributed Ti$_2$Ni phase was observed. Moreover, features of Ti$_2$Ni spheroidization can be observed in Fig. 1d. It can be attributed to the diffusion processes leading to homogenization of material composition.

Fig. 1 SEM micrographs of the sample sintered for a) 2 min, b) 5 min, c) 10 min and d) 20 min

3.3. Mechanical properties

No significant influence of the sintering time on compression behaviour was observed (Fig. 2a). However, there are some differences between the compression curves of the samples explanation of this phenomenon
is complicated by the pore presence. None of the compression curves showed the plateau, which is characteristic for superelastic materials. On the other hand, all of them showed changes in their slopes and consisted of several nearly linear parts. It indicates that some stress induced transformation could take place.

![Graph showing mechanical behaviour of the prepared samples](image)

**Fig. 2** Mechanical behaviour of the prepared samples, a) compression behaviour, b) hardness HV 5

More relevant information about mechanical properties was obtained by the hardness measurement (Fig. 2b). The hardness increased with the sintering time up to 10 min. After 20 min of sintering, the hardness significantly decreased. The increase of the hardness can be explained by the coarsening of the harder Ti$_2$Ni phase, as well as the low hardness of the sample sintered 20 min could be attributed to the microstructure changes, concretely to the sferodization and refininement of the Ti$_2$Ni phase.

### 3.4. Transformation behaviour

While during cooling no transformation changes were detected at any sample, the austenitic transformation was detected during heating of samples sintered for 2, 3 and 5 min (Fig. 3). Differences in peak positions and intensities are probably caused by a different content of nickel in the matrix and probably also by volume of lattice defects, which were not detectable by the usined methods. In the case of the samples sintered for 10 and 20 min, the transformations are probably shifted to lower temperatures, due to the higher content of nickel in the matrix and lower volume of the lattice defects. Also the martensitic transformations of all samples probably take place at lower temperatures than 0 °C during cooling.
NiTi samples were prepared by the TE-SHS method from elemental powders. All samples were depleted of nickel independently on the sintering time. All samples consisted of the B2 NiTi matrix and Ti2Ni particles. Time of sintering influenced microstructure, hardness and transformation behaviour. No relationship between the sintering period and compression behaviour was found.

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REFERENCES

