Preparation of the NiTi Alloy by a Powder Metallurgy Technique

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Abstract
Approximately an equiatomic alloy of nickel and titanium, known as nitinol, possesses a lot of interesting properties such as superelasticity, pseudoplasticity, shape memory, good corrosion resistance and satisfactory biocompatibility. Therefore, it is used in a lot of branches, for example for fabrication of surgery implants. Due to disadvantages of commonly used manufacture methods, there is a search for their alternatives. Powder metallurgy can be one of them.

In this work, influence of particle size of initial powders on composition and properties of samples, which were prepared by a thermal explosion mode of self-propagating high-temperature synthesis (TE – SHS) powder metallurgy technique, was studied.

Keywords:
Nitinol, TE – SHS, memory shape alloys, powder metallurgy

1. INTRODUCTION
The NiTi shape memory alloy called nitinol is composed of nickel and titanium in approximately equiatomic ratio. Thanks to its ability to get austenitic and martensitic structure by stressing or changing temperature it possesses unique properties such as superelasticity, pseudoplasticity and shape memory [1]. Moreover, its corrosion resistance and biocompatibility make this material suitable for production of various types of devices including surgery implants [2].

Its transformation temperatures are very sensitive to chemical composition, which places demands on quality of manufacture process [3]. Commonly a vacuum induction melting (VIM), vacuum arc remelting (VAR) methods, or their combination (VIM/VAR) are used for fabrication of the NiTi alloy [3]. By the VIM method the batch of pure nickel and titanium is melted by induction field, which also provides sufficient homogenization of the melt. This process takes place in a graphite crucible situated in an evacuated chamber. Ingots fabricated by this method possess homogenous composition, but they are polluted by carbon, which originates from the crucible [2]. The VAR method is also realized in an evacuated chamber. The batch (pressed nickel and titanium) is melted by the electric arc between this consumed electrode and water cooled copper crucible. The melt is not polluted by copper, because it exists only for short time. On the other hand it causes that the product is inhomogeneous and the process has to be repeated several times. By using VIM ingots as the consumed electrode ingots, so called VIM/VAR ingots, are fabricated [3].

Powder metallurgy can be an alternative to these methods. The thermal explosion mode of self-propagating high-temperature synthesis (TE – SHS) is one of several approaches how to prepare NiTi alloy by a powder metallurgy technique [4]. By this method, a pressed mixture of nickel and titanium powders is heated to temperature lower than the melting point of the batch [4, 5]. Due to diffusion processes in the system, the melting point decreases. Moreover, formation of intermetallic phases, which is usually exothermic, increases temperature of the system. It causes occurrence of eutectic an peritectic systems and melting the batch, which improves homogenization of the system. Final structure of the product is influenced by factors such as heating rate and powder size of starting materials [5-11].
In this work we have focused on the influence of powder size of starting materials on properties of NiTi samples prepared by TE – SHS. Chemical and phase composition, microstructure, mechanical properties and transformation temperatures of the prepared samples were studied.

2. EXPERIMENTAL

Powders of pure nickel and titanium of different particle size were used as initial materials. First sample marked as CP in this paper, was prepared from coarse powders of irregular shape (main diameter 200 – 600 µm), which were obtained by mechanical machining of ingots. The second one (will be marked FP) was prepared by using fine powders of spherical shape (particle size ≤ 10 µm). These powders were mixed in the equimolar ratio and uniaxialy cold-pressed by a Heckert FPZ 100/1 machine by the pressure of 265 MPa into cylindrical green compacts with 12 mm in diameter and about 25 mm in length. Both of green compacts were sealed into evacuated quartz ampoules and were put into an electric resistance furnace, which was preheated to a temperature of 1100°C. After 20 minutes the ampoules were removed and cooled on air. After cooling the ampoules were broken and the samples were then cut into several pieces, from which metallographic cross-sections and samples for XRD, DSC analysis, compressive tests and measurements of the HV 5 hardness were prepared. Bulk chemical composition was measured by the TESCAN VEGA-3 LMU scanning electron microscope with the Oxford instruments INCA 350 EDX analyser (SEM-EDX). Microstructures were observed by the Olympus PME3 light metallographic microscope and SEM-EDX. The phase composition was studied using the XRD 3000 P - XRD system with a Co anode and SEM-EDX. DSC curves were measured by the Setaram-DSC 131 machine and the compressive tests were realised using the LabTest 5.250SP1-VM universal loading machine.

3. RESULTS AND DISCUSSIONS

3.1. Chemical composition

In the next table (Tab. 1) one can see that both of the prepared samples were depleted of nickel. It is probably caused by evaporating of nickel during process. The sample prepared from coarse particles was more depleted. It can be explained by slower reaction rate caused by longer period of existence of liquid phase, which arises during the process.

Table 1 Chemical composition of the prepared samples.

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<th>Ti [at. %]</th>
<th>Ni [at. %]</th>
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<tr>
<td>CP</td>
<td>51.86</td>
<td>48.14</td>
</tr>
<tr>
<td>FP</td>
<td>51.18</td>
<td>48.82</td>
</tr>
</tbody>
</table>

3.2. Microstructure

In Fig. 1, microstructures of the prepared samples are shown. Both of the samples had an as-cast structure, which indicates melting during the preparation process, and consisted of NiTi matrix and primary Ti$_2$Ni phase. In the case of CP sample, Ti$_2$Ni phase formed into polygonal and Chinese letter like shapes. The second mentioned shape predominated in this sample. The FP sample contained almost all Ti$_2$Ni phase in polygonal shape and total amount of this phase was smaller in the case of FP sample. On the other hand, porosity of this sample was significantly higher.
3.3. Phase composition

The X-ray diffraction patterns of the prepared samples are shown in the next pictures (Fig. 2 and 3). One can see significant differences in the phase composition of the prepared samples. While NiTi occurred as rhomboedric R-phase and orthorombic B19 martensite in the case of CP sample, in the FP sample it formed B2 austenite at room temperature. It is caused by different content of nickel in NiTi matrix (approximately 48.89 at.% for CP and 49.40 at.% for FP), which was determined by point EDX analysis. These differences lead to a shift of transformation temperatures. This claim is in good agreement with DSC measurement shown in the next part. Except NiTi phase, both of the prepared samples contained Ti$_2$Ni phase as well.
3.4. Transformations temperatures

In measured DSC curves (Fig. 4) one can see big differences in transformation behaviour. While transformations occurring during heating and cooling are obvious in the case of the CP sample, no distinct peaks were found in DSC curves of the FP sample. During cooling of this sample no changes were detected, which implies, that the NiTi phase occurred in the austenitic state in measured temperatures interval. It is in a good agreement with the XRD-analysis results. During heating, some weak endothermic peaks and a change in the slope of the curve were detected. These observations were not well justified and will be studied in the future. In the case of the CP sample, transformation of martensite or R-phase in austenite occurred (endothermic peak around 60°C) during heating. During cooling, the NiTi phase transformed from austenitic structure to R-phase and subsequently to B19 martensitic structure. Transformation temperatures are listed in Tab. 2.

**Fig. 4** DSC curves of the CP (a) and FP (b) samples.

**Table 2** Transformations temperatures.

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<tr>
<td>CP</td>
<td>42</td>
<td>70</td>
<td>43</td>
<td>30</td>
<td>30</td>
<td>-4</td>
</tr>
</tbody>
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3.5. Mechanical properties

One can see some differences in compression curves in Fig. 5. While compressibility of both samples is similar, yield point of the CP sample is markedly higher. It is probably caused by higher content of the Ti$_2$Ni phase (in Chinese letter like shape especially) and by lower porosity of this sample. No plateau, typical for superelastic alloys, was found in the compression curve of the FP. It is probably due to strong influence of presence of the Ti$_2$Ni phase and porosity especially.

Average HV5 hardness of the CP sample was moderately higher in comparison with the FP sample. Large variations in measured values, especially in the case of the FP sample, indicate inhomogeneities in their structures.

4. CONCLUSIONS

In this work two NiTi samples were prepared by a TE – SHS method. One sample was prepared from coarse powders the second from fine powders. The samples differed in their microstructure, phase constitution, mechanical properties and transformation temperatures. Purer NiTi phase was obtained by using fine powders as starting materials. On the other hand, this sample was more porous. Both of the prepared samples were depleted of nickel and contained Ti$_2$Ni phase. For preparation of pure NiTi phase, the process must be modified. Obviously the batch has to be enriched by nickel, or the process has to be realised in an inert atmosphere instead of the vacuum. Structure could be homogenized by annealing and mechanical treatment such as forging, or extrusion. These modifications will be studied in the future.

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