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Influence of pre-heating temperature and ultrasonic vibration treatment on the structure and martensitic transformations in NiTi foams produced by SHS

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The structure and martensitic transformations in NiTi foams produced by self-propagating high-temperature synthesis under the action of ultrasonic vibrations (USV) at different pre-heating temperatures of the powder mixture are studied. It has been found that with an increase in the pre-heating temperature, the porous structure changes from layered to isotropic one in the NiTi foams, but cavities appear. The USV treatment reduces the number of cavities and increases the maximum pre-heating temperature at which they are not formed. It has been found that the USV treatment reduces the size and volume fraction of precipitates and makes the chemical composition of the NiTi phase more uniform that affects the martensitic transformation. It has been assumed that an increase in the pre-heating temperature compensates the heat transferred from the powder mixture outside the thermal chamber by the titanium waveguide, which increases the length of the reacted zone. This allowed USV to influence the structure formation in the NiTi foams in the same way as it was observed during conventional crystallization of Ti or Al-based alloys.

Keywords: NiTi foams, self-propagating high-temperature synthesis, ultrasonic vibration, pre-heating temperature.

1. Introduction

NiTi shape memory foams are promising materials for bone implants, since they are characterized by high open porosity (50 – 70%) and exhibit shape memory behaviour as observed in cast NiTi shape memory alloys [1]. An average diameter of porous channels is 200 – 500 μm that makes it possible for the bone tissue to grow through the channels and fix the implants inside the body [2]. High open porosity allows one to decrease the elastic modulus from 40 – 70 GPa that is typical for cast NiTi alloys [3] to 3 – 20 GPa that is typical for bone tissue [4]. Moreover, NiTi foams demonstrate superelasticity — the ability to recoverable unelastic deformation that makes the behaviour of implants close to that of bone, which prevents implant destruction [5 – 7].

Self-propagating high-temperature synthesis (SHS) is a cheap and simple way to produce NiTi foams. However, the disadvantage of this technique is the formation of an heterogeneous structure of the alloy [8 –17]. Among the NiTi phases, the Ti_2Ni, Ni_4Ti_3, Ni_3Ti_2 and Ni_3Ti phases may appear during SHS. At the same time, the shape memory behaviour is caused by the thermal elastic martensitic transformation that occurs only in the NiTi phase. The existence of the Ti_2Ni, Ni_4Ti_3, Ni_3Ti_2 and Ni_3Ti precipitates affects the martensitic transformations in NiTi as well as the shape memory behaviour and mechanical properties hence, it influences the functional behaviour of NiTi foams.

One of the important tools for controlling structure formation during the SHS is the pre-heating temperature of the Ti and Ni mixture. The Ti + Ni reaction is characterized by a small reaction enthalpy, hence the SHS reaction can be initiated if the Ti + Ni mixture is pre-heated to a temperature within a certain temperature range. If the pre-heating temperature is less than the minimum value of this interval, then the reaction cannot be initiated. If the pre-heating temperature is greater than maximum value of this interval, then large cavities form inside the porous sample. The pre-heating temperature window depends on the parameters of the Ti + Ni powder mixture, the SHS technique and the heat transfer during SHS [8,11,12 –13,16 –19]. Previously, it was found that the heat transfer of the Ti + Ni mixture during SHS might be changed by the ultrasonic vibrations that were applied to the powder mixture [20]. However, regardless of the change in the USV treatment parameters, SHS was initiated at the same pre-heating temperature (350°C) of the powder mixture [20]. Obviously, pre-heating temperature may affect the structure of the NiTi foams produced by the new SHS + USV technique, but this has not been studied. Thus, the aim of the present paper is to study the influence of the pre-heating temperature and the USV treatment on the structure and martensitic transformation of the NiTi foams produced by SHS.

2. Materials and Methods

Powders of high-purity Ti (catalogue type PTOM-2) and Ni (catalogue type PNK-1L5) with an average grain size of 40 μm were mixed in the composition of Ti-50.0 at.%Ni. The mixture was placed into a quartz tube 30 mm in diameter (mixture green density was 2.4 g/cm^3), installed on a titanium waveguide inside the thermal chamber. The other edge of the wave guide was connected to an US converter outside the thermal chamber. The mixture was heated to various temperature from 350°C to 550°C in an argon atmosphere ($p = 1$ atm) and held for 1 hour to make the temperature inside the powder mixture and the titanium waveguide to be homogeneous (all preheating temperatures did not affect the powder mixture characteristics). Then, the SHS reaction was initiated with a heated tungsten wire (electric current) without USV treatment or under the action of USV with a frequency of 20 kHz and an amplitude of 25 µm. The SHS reaction occurred for 5 seconds, then the sample was held under USV treatment for 180 seconds. After that, the samples were cooled inside the thermal chamber.

Porous samples with a diameter of 30 mm and a length of 30 mm were cut with an electro discharge machine across and along the sample. Cross sections were ground according to the standard procedure using the SiC paper with a size of 60 to 1200 and polished with a diamond suspension with a particle size of 9 to 1 µm. The polished surface was not subjected to etching. The porous structure was studied by optical microscopy. The microstructure and chemical composition of the NiTi foams were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The martensitic transformations were studied by differential scanning calorimetry (DSC).

3. Results and Discussion

Figure 1 shows longitudinal sections of the NiTi samples produced by SHS at various pre-heating temperatures. It is seen that at a pre-heating temperature of 350 – 400°C, the samples were characterized by a layered-porous structure regardless of whether they were produced with or without USV treatment (Fig. 1a, b, f, g). An increase in the pre-heating temperature to 450°C changes the porous structure from layered to isotropic (Fig. 1c, h). However, in the sample produced by SHS without USV, a large cavity was found in the central part of the sample (Fig. 1c), whereas the cavity was not observed in the sample manufactured by SHS + USV (Fig. 1h). An increase in the pre-heating temperature over 450°C leads to the formation of one cavity in the samples produced by SHS + USV (Fig. 1i, j) and many cavities in the samples produced by SHS without USV (Fig. 1d, e).

Thus, an increase in the pre-heating temperature changes the layered porous structure to an isotropic one. The action of USV during SHS widens the pre-heating temperature range at which the isotropic structure can be formed without cavities. The variation in the porous structure from layered to isotropic one was caused by an increase in the pre-heating temperature which changed the regime of the combustion wave propagation from the pulse (self-oscillation) propagation to the stationary one. To manufacture NiTi porous samples by the SHS + USV technique, a mixture of Ti and Ni in a quartz tube was put on the titanium waveguide, one end of which was in the thermal chamber, and the other was outside the chamber at room temperature. At low pre-heating temperatures (350 – 400°C), the contact of the powder mixture with the titanium waveguide influenced the heat distribution and heat transfer in the mixture that led to pulsed propagation of the combustion wave. An increase in the pre-heating temperature compensated the heat transfer by the waveguide, resulting in stationary of the combustion wave and the formation of an isotropic porous structure. However, at a high pre-heating temperature, a larger melt layer formed during SHS and cavities were formed during solidification. At the same time, the action of USV during SHS partially suppressed the formation of cavities, as it was observed during conventional USV assisted crystallization (sonocrystallization) [21 – 24].

Figure 2 shows SEM images of the structure of the samples produced by SHS at pre-heating temperatures of 350 or 450°C (the structure of the samples produced at high temperatures was not studied due to the formation of large cavities). The structure of the sample produced at a pre-heating temperature of 350°C, hardly depended on whether or not SHS was subjected to USV treatment. The Ti_2Ni and Ni_3Ti_2 precipitates were localized in various sites of the NiTi phase and were

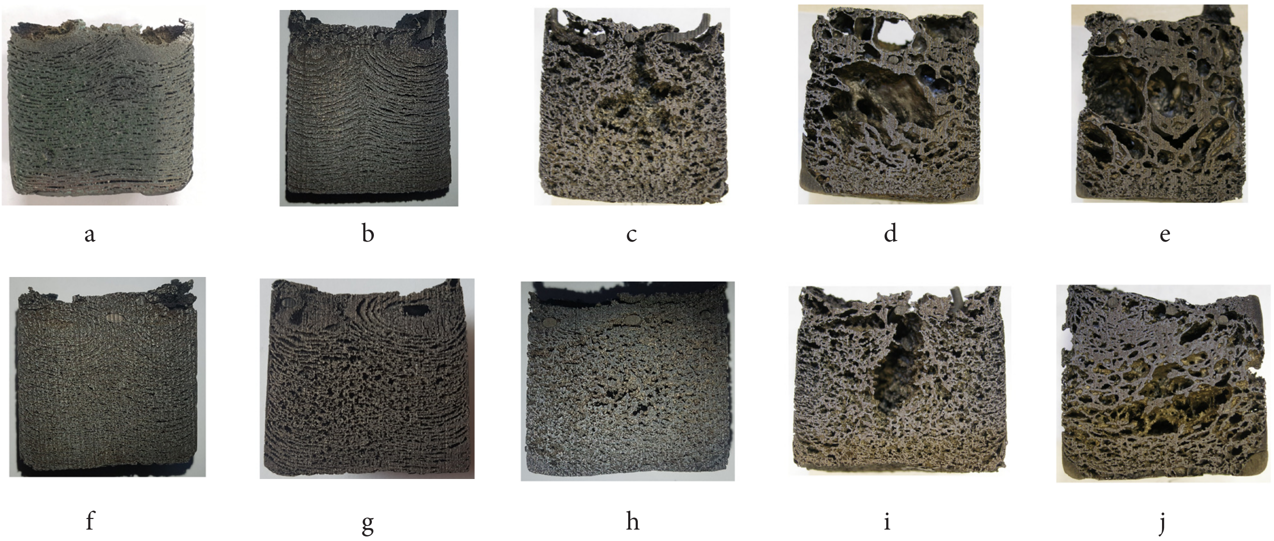
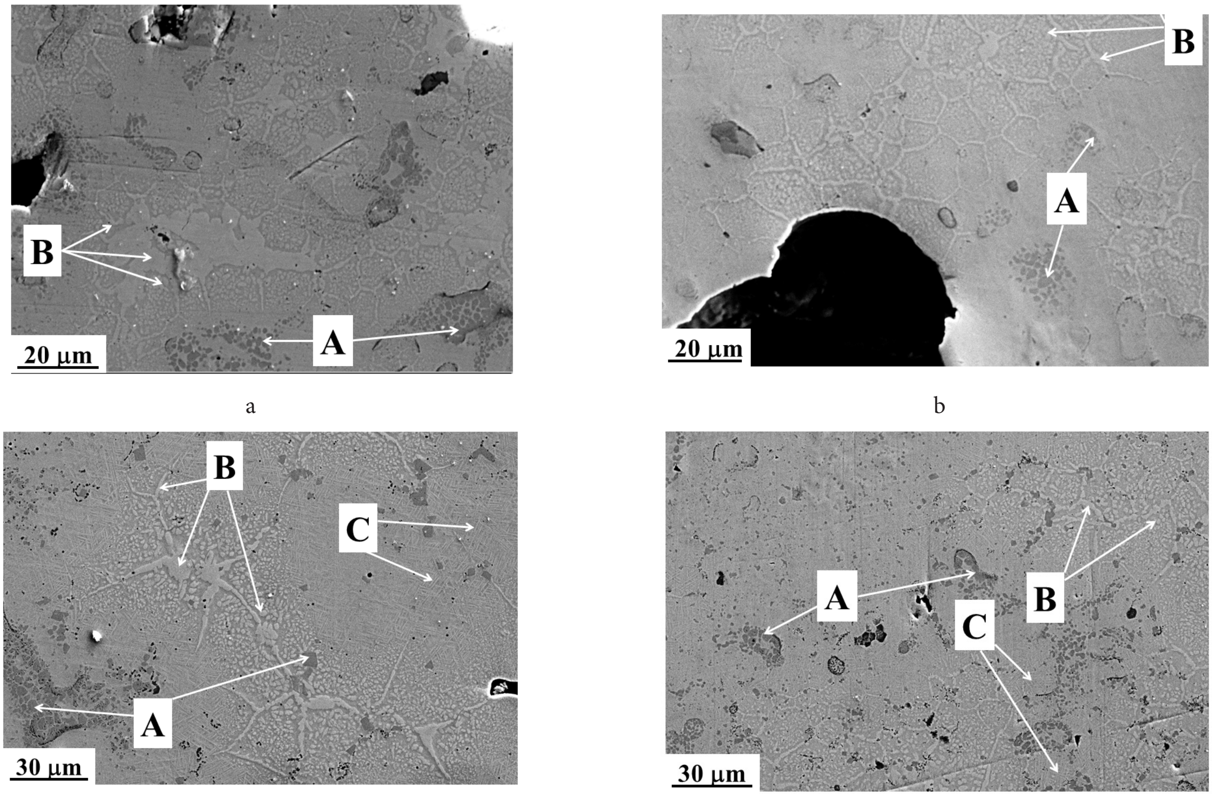


Fig. 1. Longitudinal section of the NiTi samples produced by SHS without USV (a – e) or with USV treatment (f – j). The pre-heating temperature of the mixture was 350°C (a, f), 400°C (b, g), 450°C (c, h), 500°C (d, i), 550°C (e, j). The sample diameter was 30 mm.



a b

c d

Fig. 2. SEM images of the NiTi samples produced by SHS without USV (a, c) or with USV (b, d). The pre-heating temperature was 350°C (a, b) or 450°C (c, d). Ti_2Ni phase — dark grey (marked by A); Ni_3T_2 phase — light grey (marked by B), Ni_4Ti_3 — light grey stripes (marked by C); Ti — dark small dots; NiTi — grey. The presence of all phases was confirmed by X-ray analysis.

characterized by large sizes (Fig. 2 a – b). An increase in the pre-heating temperature to 450°C decreased the volume fraction of the precipitates, but retained the localization of areas with Ti_2Ni and Ni_3Ti_2 precipitates in the NiTi foam produced by SHS without USV. Moreover, a large volume fraction of long Ni_4Ti_3 precipitates is observed (Fig. 2 c). In the sample produced at a pre-heating temperature of 450°C during USV treatment, the size of precipitates and their volume fraction decreased significantly, whereas, the NiTi fraction increased. There were some areas with localization of the Ti_2Ni precipitates, but the distribution of these particles in the whole sample was more uniform (Fig. 2 d). Thus, the USV treatment during SHS at a pre-heating temperature of 450°C significantly suppressed the formation of precipitates, as it was found during conventional crystallization [21 – 24].

The chemical composition of the NiTi phase was studied by EDX in the samples manufactured by SHS at various pre-heating temperatures with or without USV treatment (Table 1). The results of the study showed that in the samples produced at a pre-heating temperature of 350°C, the localization of precipitates led to the NiTi phase characterized by a different concentration of Ti and Ni atoms in different places. In areas with Ti_2Ni precipitates, the TiNi phase was Ti-rich or equiatomic, whereas in areas with Ni_3Ti_2 precipitates, there was the Ni-rich NiTi phase. Due to the heat transfer through the titanium waveguide, the length of the reacted zone decreased. This prevented the alignment of Ti and Ni concentrations in the melted layer and led to the formation of areas with various compositions of NiTi and precipitates. The USV treatment during SHS additionally changed the heat transfer and decreased the length of the reacted zone. This intensified the localization of areas with different chemical compositions of the NiTi phase and precipitates.

Table 1. Minimum (c_{min}), mean (c_{av}) and maximum (c_{max}) values as well as standard deviation (D_c) of the Ni concentration in the porous NiTi samples produced by SHS or SHS + USV at different pre-heating temperatures (T_p) with or without USV.

T_p, °C	Method	c_{min}, at.%	c_{max}, at.%	c_{av}, at.%	D_c, at.%
350	SHS	49.9	52.5	51.1	0.7
350	SHS + USV	48.7	52.9	51.1	1.2
450	SHS	50.8	52.1	51.7	0.6
450	SHS + USV	51.2	52.2	51.8	0.4

In the samples produced at a pre-heating temperature of 450°C, the largest volume of the alloy was occupied by the Ni-rich NiTi phase (Table 1). Due to an increase in the pre-heating temperature, the width of reacted zone increases that helps to align the Ti and Ni concentrations in the melt. This made the chemical composition of the NiTi phase more uniform, as a result, the volume fraction of precipitates and their sizes decreased. Moreover, as the increase in the pre-heating temperature compensated the accelerated heat output through the waveguide, the USV treatment had a chance to affect the phase formation in the reacted zone. As a result, the volume fraction and sizes of precipitates decreased, and the volume fraction of the NiTi phase increased that is very important for the application.

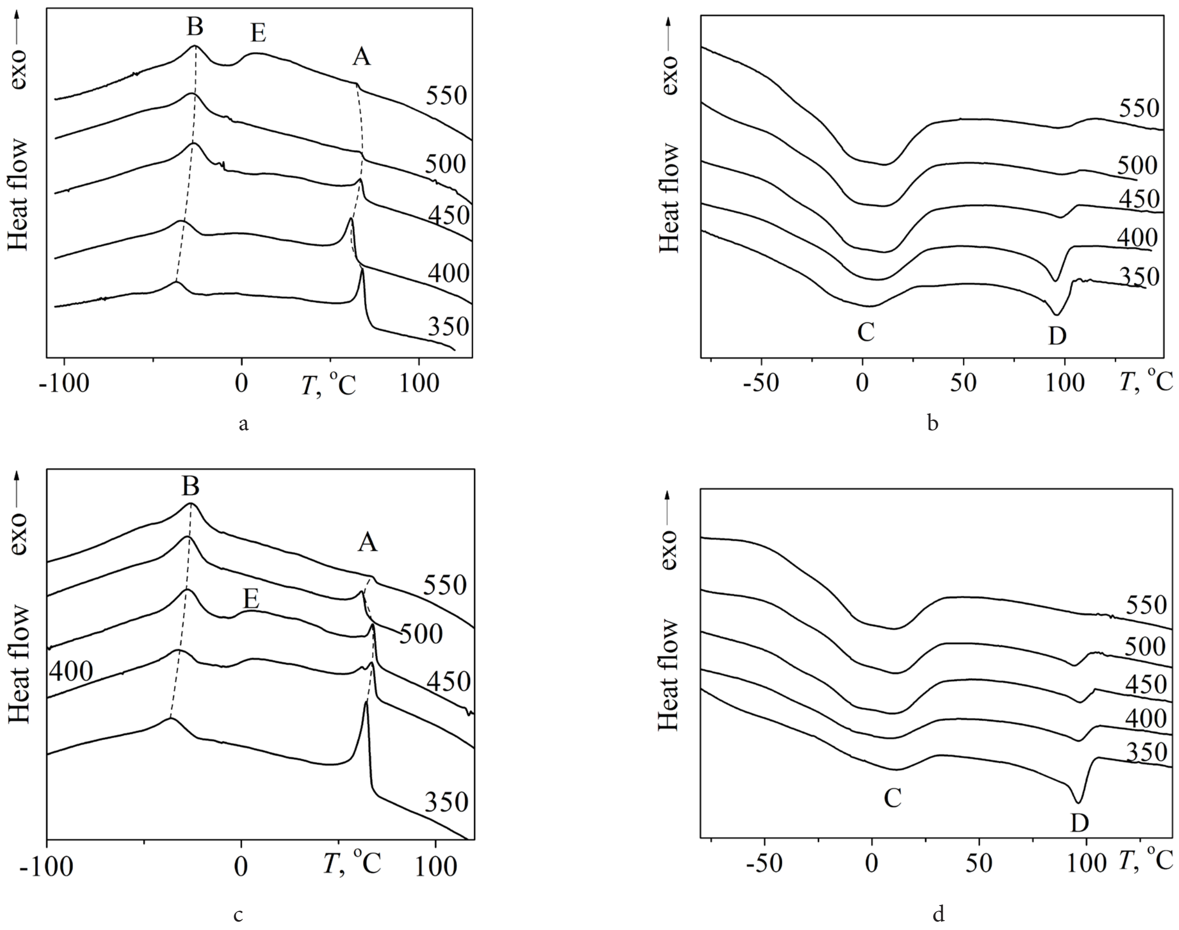


Fig. 3. The calorimetric curves obtained on cooling (a, c) and heating (b, d) of the NiTi foams produced by SHS without USV (a, b) or with USV (c, d) treatment. The pre-heating temperatures are shown near the curves.

The variation in the chemical composition of the NiTi phase and volume fraction and size of precipitates with an increase in the pre-heating temperature should affect the martensitic transformation. Figure 3 shows the calorimetric curves obtained in the NiTi foams produced at various pre-heating temperatures by SHS with or without the USV treatment. Two calorimetric peaks of heat release were found on cooling and two peaks of heat absorption were observed on heating of the samples manufactured at a pre-heating temperature of 350°C. According to [16], high-temperature peaks (A and D) were caused by the $B2\leftrightarrow B19'$ transformation in the NiTi areas with a Ti concentration of 50.0 at.% or more. Low-temperature peaks (B and C) were due to the same transformation occurred in the NiTi phase with a Ni concentration larger than 50.5 at.%. An increase in the pre-heating temperature decreased the intensity of high-temperature peaks both on cooling and heating. The square under the calorimetric peak was proportional to the volume fraction of the alloy undergoing the martensitic transformation. Thus, a decrease in the high-temperature peak intensity showed that the volume fraction of the NiTi phase with a Ti concentration of 50.0 at.% or more decreased on a rise in pre-heating temperature. This correlates to the EDX results described above. If the sample was manufactured at pre-heating temperature of 550°C, an additional peak E was found. One may assume that this peak was attributed to the $B2\rightarrow R$ transformation, however an additional calorimetric study on cooling in an incomplete temperature range and followed heating showed that this peak was caused by the $B2\rightarrow B19'$ transformation. Thus, in this sample, there are areas of the NiTi phase with a Ni concentration larger than 50.5 at.% and less than 50.0 at.%, which leads to the observation of peak E.

In the samples produced by SHS under USV treatment, the intensity of high-temperature peaks was low even at a pre-heating temperature of 400°C. Peak E was found if the pre-heating temperature was in the range 400–450°C, but this peak was not observed if the pre-heating temperature was 500°C or more. Thus, the USV treatment during SHS intensified the alignment of the Ti and Ni concentrations in the NiTi phase that was observed at lower pre-heating temperatures than in the samples produced without USV. This is in a good agreement to the SEM data.

4. Conclusions

The results of the study showed that an increase in the pre-heating temperature compensated the heat output through the waveguide. This changed the regime of combustion wave propagation from pulsed to stationary as a result, the porous structure became isotropic. It was assumed that a rise in the pre-heating temperature increased the width of the reacted zone. If the pre-heating temperature is low, then the reacted zone is short that prevents the alignment of the Ni and Ti elements in NiTi melt layer. As a result, areas with the Ti-rich and Ni-rich NiTi phase appear which undergo martensitic transformation at high and low temperatures. Moreover, secondary phases with various chemical composition are formed that additionally affects the martensitic transformation. If the pre-heating temperature increases, then the reacted zone widens and the distribution of the Ti and Ni elements in the melt becomes more homogeneous. This decreases the volume fraction of the Ti-rich NiTi phase as a result, the NiTi phase undergoes the martensitic transformation at low temperatures. The size and volume fraction of the secondary phase decrease. The higher the pre-heating temperature, the larger the volume fraction of the NiTi phase and the smaller the fraction of secondary phases. However, an increase in the pre-heating temperature leads to the formation of cavities during SHS that makes it impossible to use the NiTi foam. The action of the USV treatment during the SHS increases the pre-heating temperatures at which an isotropic porous structure without cavities is formed, and additionally decreases the volume fraction and size of the precipitates. This allows to fabricate the NiTi foams with more a homogenous structure, which should improve their functional properties.

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