Phase transformation of NiTi alloys during vacuum sintering

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Abstract: The aim of this study is to ascertain the Phase transformation of NiTi alloys during vacuum sintering. NiTi shape memory alloys (SMA) of atomic ratio 1:1 were prepared through press forming and vacuum sintering with the mixture of Ni and Ti powders. Different samples were prepared by changing the sintering time and the sintering temperature. Phase and porosity of the samples were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results show that in the process of sintering $NiTi_2$ and Ni_3Ti phases are formed firstly and then transform into NiTi phase. The quantity of $NiTi_2$ and Ni_3Ti phases gradually decreased but not eliminate completely with increase of sintering time. The porosity of specimen sintering at 900℃ decreases slightly with increase of sintering time. With increase of sintering time the porosity of specimen sintering at 1050℃ decreased firstly and then increased because of generation rich titanium liquid in the process of sintering.

1. Introduction

NiTi shape memory alloy of atomic ratio 1:1 has the advantages of good shape memory effect, superelasticity and biocompatibility, etc.[1]. These outstanding properties allow commercial applications of NiTi SMAs in the fields of biomedicine[1-3], intelligent machine[4.5] and aerospace [6].

The advantages of preparing NiTi alloy by powder metallurgy technology are[7]: (1) the compositions of sintered body are homogenous and esy to control; (2) it is easy to add alloy elements and prepare composite material; (3) it is easy to fulfill near-net-shaped forming of complex components, to reduce the amount of post machining. Thus, powder metallurgy technology has become an important research direction of preparation method of NiTi alloy. Presently, researches in this area mostly focus on preparation of porous NiTi shape memory alloy[8-11], while there are few research reports on preparation of dense NiTi alloy by powder metallurgy technology. There are two problems need to be solved. The first is existence of $NiTi_2$ and Ni_3Ti impurity phases in the sintered compact. The other is that the porosity is high. Understanding the phase and porosity transformation mechanism of NiTi alloys during vacuum sintering is necessary to solve both problems.

For purpose of this paper, it was planned to prepare dense NiTi alloy by powder metallurgy technology, and research the transformation of phase and porosity in sinter process. The research results can provide guidance for further optimizing sintering technology.

2. Experiment

2.1 Sample preparation

The nickel powder (particle size 2.45 um, purity> 99.75%) and titanium powder (particle size 5 um, purity> 99.9%) used in the experiment were commercially available. Weigh them according to equal molar ratio, and then put them into vacuum ball-milling pot together with proper amount of anhydrous ethanol, and then wet-grind them in the planetary ball mill for 12 hours, with milling speed of 340r / min, and ball-to-powder ratio of 15: 1. After finishing the ball milling, we got mixed powder through drying, sieving and prilling.

The green compact was got at the pressing force of 10 ton by four-pillar hydraulic machine. The size of the green compact is 16×16×5 mm. Then put them into vacuum furnace for sintering, at sintering temperature of 900℃ and 1050℃ respectively, for 2h, 4h, 6h and 8h each with the heating rate of 5℃ / min. After sintering, samples were cooled by furnace cooling.

2.2 Sample test

The X-ray diffraction (XRD) analysis was carried out for phase identification. Microstructure was investigated by SEM in a back-scattered electron (BSE) mode. Archimedes method was used to test the density of sample. Porosity was calculated by formula (1)[12].

$$\theta = (1 - \frac{\rho}{\rho_s}) \times 100\% \quad （1）$$

Where ρ is density of the samples, g.cm^{-3}; ρ_s is theoretical density of NiTi alloy, ρ_s=6.45g.cm^{-3}.

3. Results and Discussion

3.1 Phase analysis

Figure 1 is the XRD testing results of NiTi alloy specimens prepared with different sintering time at 900℃. As can be seen from the figure, in addition to B2-NiTi and B19 '- NiTi phases, there are also a lot of NiTi$_2$ and Ni$_3$Ti impurity phases and a little of Ni and Ti elements in the sample sintered for 2 hours. The diffraction peak intensity of NiTi$_2$ and Ni$_3$Ti impurity phases sharply decreases with the increase of sintering time, and become very weak after 6 hours sintering time. NiTi$_2$ and Ni$_3$Ti diffraction peak still exists when increase the sintering time to eight hours. And compared with the sample sintered for 6 hours, there is no further weaken.
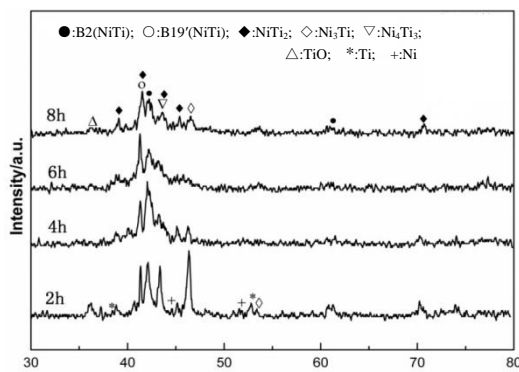
Figure 1. Typical XRD patterns of the samples sintered at 900℃ with different sintering time
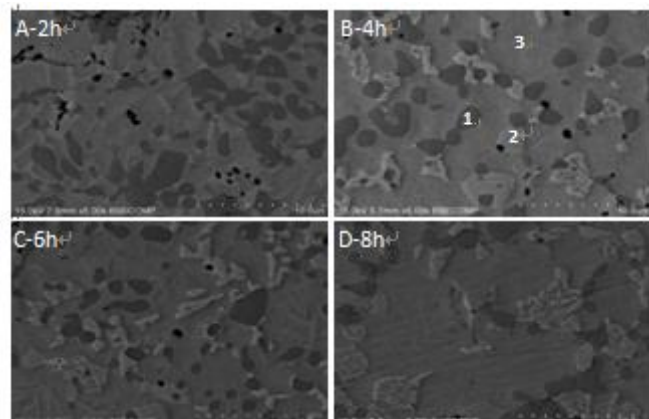
Figure 2. Backscattered electron image of the specimens with different sintering time at 900℃

As can be seen from figure 2, there are three main contrast images in the BSE pictures. The area with different contrast was studied by energy spectrum analysis, and the results are shown in table 1. The dark grey area 1 is NiTi$_2$ phase, the offwhite areas 2 is Ni$_3$Ti phase, the grey area 3 is NiTi phase. And in the picture, black circular area is the pores in the material. NiTi phase increases gradually with the increase of sintering time, and NiTi$_2$ and Ni$_3$Ti impurities content gradually reduce. But the content of NiTi$_2$ and

Ni_3Ti in sample with 6 and 8 hours sintering time are almost same. This shows the $NiTi_2$ and Ni_3Ti impurity phases will not reduce with the increase of sintering time when the sinter time was reduced to a certain degree. So, it does not to completely eliminate the impurity in the organization through long-time sintering. The morphology of $NiTi_2$ in the organization also changed with the increase of sintering time, finally the irregular thick sheet become into small sphere.

Laeng[13]et al. believe that, during the sintering process, NiTi phase is not directly formed from mutual diffusion between Ni and Ti. As the sinter temperature increases, α-Ti is converted to β-Ti[14]at 760-820℃; then Ni diffuses into β-Ti, resulting in the formation of β-Ti(Ni) solid solution; after the β-Ti(Ni) solution is saturated with Ni, reaction between Ni and β-Ti(Ni) begins (β-Ti(Ni)+Ni→$NiTi_2$), followed by the subsequent reaction of $NiTi_2$+Ni→NiTi if the thermodynamics condition allows. At the same time, Ti diffuses into Ni, resulting in a solid solution of Ni(Ti); the continued diffusion of Ti converts the saturated Ni(Ti) solid solution into Ni_3Ti phase, and further leads to the conversion of Ni_3Ti+Ti→NiTi. The above diffusion reaction needs time. Large amount of $NiTi_2$ phase and Ni_3Ti phase can be detected in a test sample after only 2-hour sintering at 900℃. It due to the fact that those initially formed $NiTi_2$ phase and Ni_3Ti phase fail to be completely converted into NiTi phase through the secondary reactions as the sintering time is short. With the increase of sintering time, more and more $NiTi_2$ and Ni_3Ti turned into NiTi phase, which made the content of $NiTi_2$ and Ni_3Ti in tissue reduce, so diffraction peak intensity of $NiTi_2$ and Ni_3Ti impurity phase became weak gradually. However, according to the mutual diffusion mechanism between Ni and Ti, the main reason that $NiTi_2$ and Ni_3Ti in tissue reduced was that $NiTi_2$ and Ni_3Ti respectively occurred reaction with Ni and Ti, which transfer into NiTi phase. With the process of transformation, the number of Ni and Ti became less and less, when simple substance of Ni and Ti ran out, the residual $NiTi_2$ and Ni_3Ti would be remained in tissue, which would not decrease with the extension of sintering time. So even sintering the sample for 8 hours under 900℃, there was still little $NiTi_2$ and Ni_3Ti impurity phase in tissue.

Table1. EDS analysis of phases identified in Fig. 2

	Ni(at%)	Ti(at%)	phase
charcoal grey 1	34.39	65.61	$NiTi_2$
offwhite 2	74.60	26.40	Ni_3Ti
grey 3	48.48	51.52	NiTi

Figure 3 were XRD test results of samples which were sintered for 2 hours under 900℃and 1050℃. It could be found that the diffraction peak intensity of NiTi2 and Ni3Ti of the sample sintered at 1050℃ was weaker. It means that the impurity content of this sample is less. So under the same sintering times, improving sintering temperature could obviously promote the sintering reaction, made the content of $NiTi_2$ and Ni_3Ti impurity phase reduce, and increased the content of B2 and B19' phase.
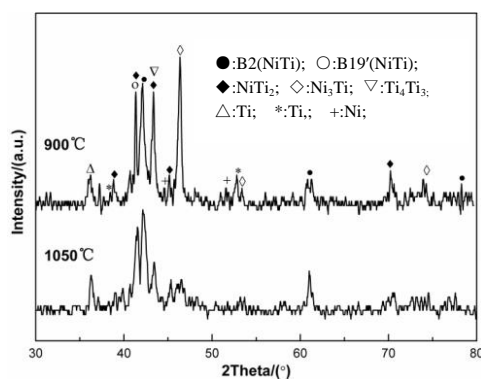
Figure 3. XRD pattern of specimens sintered 2 hours at different sintering temperature
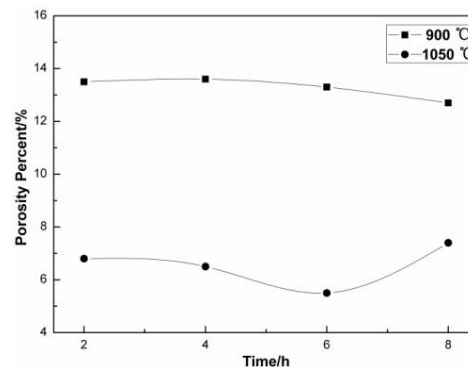
Figure 4. Effect of sintering temperature and time on porosity of NiTi alloy specimens

A transformation of β(Ti)+NiTi$_2$→L (liquid phase) occurs when the temperature reaches 942℃. As the temperature increases to 984℃, residual NiTi2 will be transformed to NiTi+L (liquid phase). Both the generated liquid phase and higher sintering temperature increase diffusion rates of Ti and Ni atom, which facilitates sintering reaction and allows more NiTi$_2$ and Ni$_3$Ti to be transformed into NiTi phase. In addition, thermal explosion reaction occurs when the generated titanium-rich liquid phase contacts the nickel-rich zone, and NiTi phase is formed[14]. Therefore, the diffracted intensity of NiTi$_2$ and Ni$_3$Ti impurity phase achieved in the sample tissue after sintering under 1050℃ for 2 hours is weaker (see Fig. 3), and it means that the content of the impurity phase is less.

It is seen from experimental results that sinter time and sinter temperature has relative evident influence on phase composition of samples. Expanding sinter time and increasing sinter temperature both reduce percentages of impurity phases NiTi$_2$ and Ni$_3$Ti in sample tissues. Compared to the high sintering temperature, longer sintering time is required for the same outcome at low sintering temperature.

3.2 Porosity analysis
The density of the sintered sample was measured based onArchimedes drainage method. Porosity of the sintered sample was calculated by formula (1). The results are demonstrated in Figure 4. It could be observed that the porosity of the samples sintered at 900℃ decreased with the extension of sintering time; nevertheless, the decrease extent was small. The porosity of the samples sintered at 900℃ ranged from 12.7% to 13.6%. Their density ranged from 5.58g.cm^{-3} to 5.63g.cm^{-3}. The theoretical density of the compact NiTi alloy is 6.45g.cm^{-3}. When the sintering temperature was increased to 1050℃, the porosity of the sintered sample decreased at the beginning while increased later with the increase of sinter time. When the sintering time was 6 hours, the density of the sample reached up to the maximum value of 6.10g.cm^{-3}; at this time, the porosity was 5.43%.

Extension of sintering time may lead to two phenomena which will then cause a decrease of alloy's porosity. (1) With extension of sintering time, diffusion between Ti and Ni becomes more sufficient while combination between particles becomes closer, which will make part of original pores diminish o rdisappear [15]; (2) With extension of sintering time, crystal grains will gradually grow bigger. During movement of the grain boundary, a large number of pores which have been swept by the grain boundary will disappear, and porosity will gradually decrease[16]. But when sintering time is prolonged to 8 hours,porosity in the tissue will instead increase. Whitney[14] et al. explained that: when the sintering temperature rises to 942℃, transformation of β(Ti)+NiTi$_2$→L will occur and thus produce Ti-rich liquid phase; when the sintering time is long enough, a large amount of liquid can flow to the Ni-rich area through pores by crystallization and react with it to form intermetallic compound, so that pores will be formed at the original location of liquid phase.

4· Conclusions
Phase and porosity transformation characteristics of NiTi shape memory alloys in the process of vacuum sintering were investigated, the conclusions drawn from this study can be summarized as follows:
1) With increase of sintering time, the content of Ni$_3$Ti and NiTi$_2$ impurity phases decreases, and that of B2 and B19′ increases. Transformation from Ni$_3$Ti and NiTi$_2$ impurity phases to NiTi can be promoted by raising the sintering temperature.
2) The impurity phases of Ni$_3$Ti and NiTi$_2$ cannot be thoroughly eliminated by long-time sintering.
3) With increase of sintering time, the porosity of specimens sintering at 900℃ decreases slightly with increase of sintering time. But the porosity of specimen sintering at 1050℃ decreased firstly and then increased. The reason is that the generation mechanism of NiTi phase change when the sintering temperature reach or exceed 942℃.

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