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 NiTi₂ and Ni₃Ti phases are formed firstly and then transform into NiTi phase. The quantity of NiTi₂ and Ni₃Ti 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 easy 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 NiTi₂ and Ni₃Ti 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 340 r/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 \( \rho \) is density of the samples, g.cm\(^{-3} \); \( \rho_s \) is theoretical density of NiTi alloy, \( \rho_s = 6.45 \text{g.cm}^{-3} \).

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.

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$_3$Ti in sample with 6 and 8 hours sintering time are almost same. This shows the NiTi$_2$ and Ni$_3$Ti 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°C; 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$_3$Ti phase, and further leads to the conversion of Ni$_3$Ti+Ti→NiTi. The above diffusion reaction needs time. Large amount of NiTi$_2$ phase and Ni$_3$Ti phase can be detected in a test sample after only 2-hour sintering at 900°C. It due to the fact that those initially formed NiTi$_2$ phase and Ni$_3$Ti 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$_3$Ti turned into NiTi phase, which made the content of NiTi$_2$ and Ni$_3$Ti in tissue reduce, so diffraction peak intensity of NiTi$_2$ and Ni$_3$Ti impurity phase became weak gradually. However, according to the mutual diffusion mechanism between Ni and Ti, the main reason that NiTi$_2$ and Ni$_3$Ti in tissue reduced was that NiTi$_2$ and Ni$_3$Ti 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$_3$Ti 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°C, there was still little NiTi$_2$ and Ni$_3$Ti impurity phase in tissue.

|     | Ni(at%) | Ti(at%) | phase  |
|-----|---------|---------|--------|
| charcoal grey 1 | 34.39 | 65.61 | NiTi$_2$ |
| offwhite 2 | 74.60 | 26.40 | Ni$_3$Ti |
| grey 3 | 48.48 | 51.52 | NiTi |

Figure 3 were XRD test results of samples which were sintered for 2 hours under 900°C and 1050°C. It could be found that the diffraction peak intensity of NiTi$_2$ and Ni$_3$Ti of the sample sintered at 1050°C 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$_3$Ti impurity phase reduce, and increased the content of B2 and B19’ phase.
A transformation of $\beta(Ti) + NiTi_2 \rightarrow L$ (liquid phase) occurs when the temperature reaches 942°C. As the temperature increases to 984°C, 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 NiTi2 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°C 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 on Archimedes 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°C decreased with the extension of sintering time; nevertheless, the decrease extent was small. The porosity of the samples sintered at 900°C 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°C, 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 or disappear [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°C, transformation of $\beta(Ti) + NiTi_2 \rightarrow L$ 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°C decreases slightly with increase of sintering time. But the porosity of specimen sintering at 1050°C decreased firstly and then increased. The reason is that the generation mechanism of NiTi phase change when the sintering temperature reach or exceed 942°C.

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References
[1] Fu Tao, Li Hongwei, Wu Feng, Li Wen and Sun Jianmin 2016 Rare Metal Materials and Engineering 45 pp 1128-1131
[2] Kong Xiangque, Jin Xuejun and Liu Jiannan 2016 Journal of Functional Material 47 1007-1011
[3] Bing Hui Dong, Feng Wu, Zafer Alajmi, Chen Zhang, Tao Fu and Yuan Ge 2014 Rare Metal 33 pp 21–27
[4] Zhou Chao, He Zhirong, Liu Lin and Li Xudong 2015 Hot Working Technology 44 pp 7-11
[5] Song Jie, Yin Hesheng, Xu Chengkai, Li Xiaogao, Song Xianyi and Kong Weichuan 2014 Development & Innovation of Machinery & Electrical Products 27 pp 23-25
[6] H.J. Jiang, S. Cao, C.B. Ke, X. Ma and X.P. Zhang 2013 Materials Letters 100 pp 74–77
[7] Gang Chen, Klaus-Dieter Liss and Peng CA 2015 METALLURGICAL AND MATERIALS TRANSACTIONS A 46 pp 5887-5899
[8] Kang Xiaoyu, Li Yanfeng, Yin Xiangqian, Xie Haofeng and Mi Xunjun 2013 Heat Treatment of Metals 38 pp 23-26
[9] C. Bewerse, L.C. Brinson and D.C. Dunand 2016 Acta Materialia 115 pp 83-93
[10] Liu A L, Gao Z Y, Gao L, Cai W and Wu Y 2007 Journal of Alloys and Compounds 437 pp 339-343
[11] Zhao Tengfei, Lu Xin and Qu Xuanhui 2012 Powder Metallurgy Technology 30 pp 300-306
[12] Xu Wei, Shi Xinying, Guan Ruifeng, Zhang Xiping and Zhao Ke 2011 Journal of Medical Biomechanics 26 pp 349-354
[13] Jamaluddin, Zhimeng, Xiaoxue Xu, Sun Xudong, Ru Hongquiang, Liu Yinong 2007 Physica Scripta 129 pp 250-254
[14] M. Whitney, S. F. Corbin and R. B. Gorbet 2008 Acta Materialia 56 pp 559-570
[15] Ma Xuliang, Li Li, Zhu Chengwu, Wang Xiang and Zheng Yufeng 2011 Journal of Materials Engineering 5 pp 6-10
[16] Li Mingwei, Yan Yinhao and Cheng Min 2011 Powder Metallurgy Technology 29 pp 372-379