PREPARATION OF TiNi SHAPE
MEMORY ALLOY POROSINT BY SHS[①]

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ABSTRACT   TiNi shape memory alloy porosint, a promising artificial bone material, was prepared by self-propagating high-temperature synthesis method. It is found that the key technical parameter affecting the porosity, the shape and distribution of the bores in the synthesized product is the pre-heating temperature of green compact. While the pre-heating temperature varies between 523 K and 673 K, the TiNi shape memory alloy porosint with wholly homogeneously distributing bores will be gained. The porosity of the porosint is 70% when the pre-heating temperature is near 673 K, which is maximal under different pre-heating temperatures. The compressive strength of TiNi SMA porosint with a porosity of 70% manufactured by SHS is up to 100 MPa and the percentage recovered is 92%.

Key words   TiNi shape memory alloy   porosint   self-propagating high-temperature synthesis

1   INTRODUCTION

Recently, a novel technique, termed self-propagating high-temperature synthesis (SHS) or combustion synthesis has been used to synthesize many materials, such as ceramics and intermetallic compounds. This technique is concerned with the ignition of a compressed powder mixture, in either air or inert atmosphere, producing a chemical reaction, with sufficient heat release (exothermic reaction) that it becomes self-sustaining. Some material scientists have made studies on the preparation and the microstructure of TiNi shape memory alloys (SMA) synthesized by SHS[1-3]. However, the products synthesized by SHS is porous, and usually can not be used. But the TiNi SMA porosint is a promising artificial bone material. The present paper tries to prepare the TiNi SMA porosint by SHS and analyze the formation mechanism. In addition, the technical condition of producing TiNi SMA porosint by SHS is proposed.

2   EXPERIMENTAL

The features of Ti and Ni particles used in this study are listed in Table 1.

Table 1   Purity and sizes of Ti and Ni particles

Particles	Purity / %	Size / μm	Impurity
Ni	99. 6	$\leqslant$50	Fe, Si, O
Ti	99. 5	$\leqslant$50	Fe, Si, H, O

The Ti and Ni powders in equiatomic stoichiometry were thoroughly mixed and compacted into cylindrical compacts of 20 mm in diameter and 20~ 30 mm in height. The relative density is about 45% theoretical.

Combustion synthesis of Ti-Ni pellets was

carried out inside an SHS equipment under an atmosphere pressure(about 0. 1 MPa) of flowing 99. 98% pure argon. Small holes are drilled in the sides of the compacts to accommodate W-5% Re/ W-26% Re thermocouples used to determine the pellet temperature. In our previous studies, we found the key technical parameter influencing the porosity of the porosint and the distribution of bores is the pre-heating temperature[3]. So we will study the effect of the pre-heating temperature on the porosity of the product. The heating rate is 400 ℃/ min and the pre-heating temperature varies between 0 ℃ and 600 ℃.

We test the porosity of the products under different SHS conditions, analyze the distribution and the inwall configuration of bores in the porosint by Scanning Electron Microscope (SEM) and study the phase constituent of TiNi SMA porosint by X-ray diffraction. The compressive strength and the percentage recovered are determined by a DN-10T type testing machine.

3 RESULTS

3. 1 Effect of pre-heating temperature on combustion temperature (t_c), porosity of porous body and macrodistribution of bores

The calculating formula of the porosity of the porosint is

$$P = (1 - m/(\rho V)) \times 100\%$$

where P is the porosity(%) , m is the mass of the samples, ρ is the theoretical density of TiNi alloy, V is the volume of the samples.

Fig. 1 shows the effect of pre-heating temperature (t_0) on combustion temperature (t_c) and the porosity (P) of the porosint. With increasing pre-heating temperature, which means giving more external heat to the Ti-Ni reaction system, the combustion temperature increases, but the porosity of the porosints increases in the initial stage and reaches an extreme point, then decreases at last. The maximum of porosity is 70% when the pre-heating temperature t_0 is about 400 ℃.

Fig. 2 shows the effect of the pre-heating temperature on the shape and macro-distribution of bores in the products. Figs. 2(a), (b) and (c) show the sections of three typical kinds of porosint with the bores in different shapes respectively, whose pre-heating temperatures have been listed. When the pre-heating temperature is lower than 250 ℃, the bores in the porosints are uniformly distributed and stripe like. It' s clear that the products are to be solid or semisolid state with a low fraction of liquid at the combustion temperature t_c. So the gas in the products
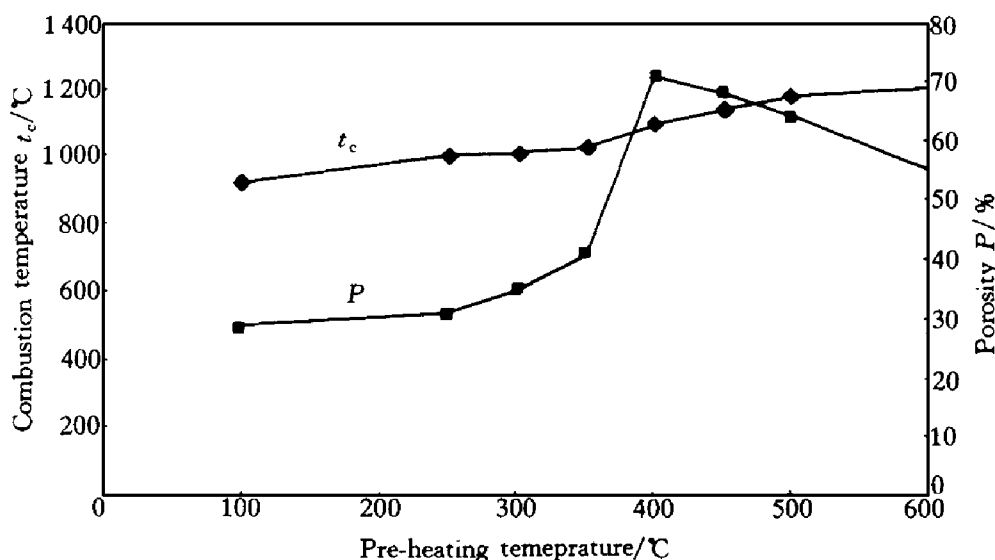

Fig. 1 Effect of pre-heating temperatures t_0 on combustion temperature t_c and porosity P
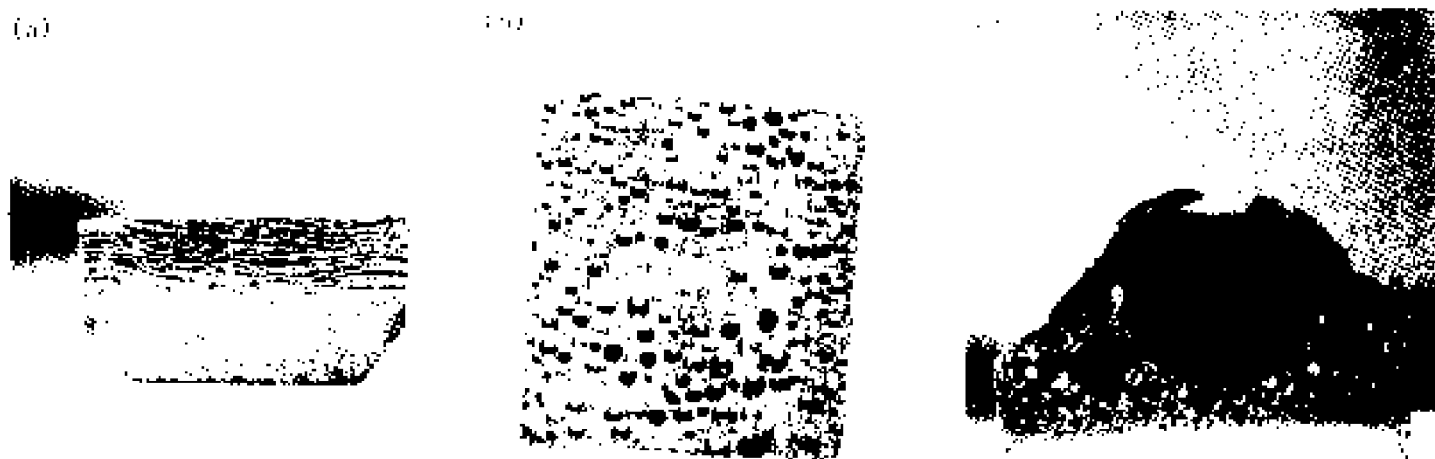
Fig. 2 Distribution of bores in products under different pre-heating temperatures
(a) $-t_0=$ 200 ℃; (b) $-t_0=$ 350 ℃; (c) $-t_0=$ 600 ℃

can not expand sufficiently and the porosity of the porosints is not very high. Owing to its low strength, this kind of porosint is not the one we expect. When the pre-heating temperature varies between 250 ℃ and 400 ℃, the porosints have spherical bores, which distribute homogeneously.

By Scanning Electron Microscope (SEM), we found the inner surfaces of the bores are not smooth and some irregular or spherical particles are mounted on them(Fig. 3). That is to say, the products at the combustion temperature(t_c) is semisolid with a suitable fraction of liquid. At this time the viscosity of the sample decreases, so the gas in the sample can expand sufficiently, which makes the spherical bores appear. With increasing t_0, the combustion temperature t_c increases and the porosity becomes larger. However, the viscosity and the fraction of the solid phase are still to be high so that the gas cavities can not join to be big ones.

When the pre-heating temperature is higher than 400 ℃, the bores in the products are spherical but distribute heterogeneously. They concentrate on the upper part of the samples and their inwalls are smooth. That is to say, the product at t_c is liquid or semisolid with a large fraction of liquid. At this time the viscosity of

the products is so low that the gas goes up and the gas cavities gather on the top of the sample. With the gas going up and outgassing, the porosity decreases. So it's possible that the porosity has its maximal value in Fig. 1. Owing to the fast cooling rate, the products have already been solidified before all the gas is outgassed, which makes the products always have
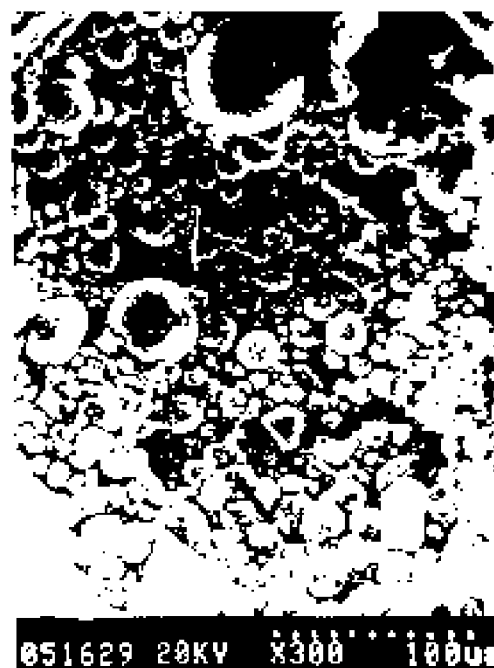

Fig. 3 Inner surface of bores in porosint ($t_0=$ 350 ℃)

some cavities.

3. 2   Compressive strength and percentage recovered of TiNi porosint

The compressive samples with 24 mm in diameter and 22 mm in height were cut from the TiNi porosint with a porosity of 70%. The compressive strength of this porosint is up to 100 MPa, which is very high for the artificial bone materials. The percentage recovered R is calculated by

$$R = \Delta L_r / \Delta L \times 100\%$$

where ΔL is the pre-deformation of the samples, ΔL_r is the value recovered. The compressive sample was pre-deformed ΔL, then put into hot water, whose temperature (50 ℃) is higher than the recovery temperature of NiTi SMA. Testing the value of ΔL_r, we can calculate that the percentage recovered of the porosint with a porosity of 70% is 92%.

4   DISCUSSION

The sample will be porous if a lot of gas has gone out of the reactant and a shrinkage of product occurs during combustion synthesis reaction. There are three kinds of gas origins during combustion reaction: (1) gas absorbed by row powders, (2) gas existing in the bores of the green compact, (3) gas stemming from evaporation of volatile impurities. In addition, a change of the molar volume from a reactant to a product in equiatomic Ti-Ni SMA brings about a shrinkage. Therefore, the product prepared by combustion synthesis will be porous generally.

In order to get a porosint with uniformly distributed gas cavities, two prerequisites are put forward. First, a sample must be semisolid at combustion temperature t_c. From the equilibrium diagram of the Ti-Ni system, we can see that the liquid phase of the equiatomic Ti-Ni intermetallic compound will appear at above 1 310 ℃.

However, the metallography and transmission electron microscope analysis of the sample obtained by combustion synthesis of the green compact of equiatomic Ti-Ni powders indicated that a dendritical and block-like Ti_2Ni phase existed in it[3]. That is to say, the combustion synthesis reaction is a process deviating from equilibrium state. In fact, the liquid phase may be formed in it above 942 ℃. So the sample is in semisolid state at the combustion temperature. During combustion reaction a lot of gas has come into being and intensely expands, which results in the formation of uniformly distributed gas cavities under an appropriate uniform pressure. The expansion of gas compels liquid phase to permeate solid phase and makes the latter further merge.

5   CONCLUSIONS

(1) The preparation of TiNi SMA porosint by SHS is possible.

(2) When the pre-heating temperature varies between 250 ℃ and 400 ℃, the product at t_c is semisolid with a suitable fraction of liquid phase and the TiNi porosint with homogeneously distributing bores are prepared. When the pre-heating temperature is about 400 ℃, the porosity of the porosint reaches the maximal value 70%.

(3) The compressive strength of the TiNi SMA porosint with the porosity 70% is up to 100 MPa and the percentage recovered is 92%.

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