Fabrication of cellular NiTi intermetallic compounds

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Self-propagating high temperature synthesis (SHS) has been successfully developed for the fabrication of cellular NiTi intermetallic compounds, which have an open cellular structure with about 60 vol% porosity and more than 95% open-porosity ratio. The SHS reactions lead to the formation of TiNi, Ti_2Ni, Ni_3Ti, and Ni_4Ti_3 intermetallics. The SHS process can be controlled by regulating the preheating temperature, which has effects on the phase amount and the shape as well as macrodistribution of pores in the products.

There is a growing need for fabrication of artificial hard-tissue replacements. The biomaterials industry worldwide has an annual turnover of $2.3 billion in the field of hard-tissue repair and replacement (total of $12 billion). There is currently an increasing growth rate of 7-12% per annum for biomaterials in clinical applications.[1] Several nonmetallic materials have been proposed as candidates for artificial bones and/or teeth, but none has found wide applications. Due to their low reliability, especially in wet environments, materials such as Hydroxyapatite-based biomaterials cannot presently be used for heavy load-bearing applications (like artificial bones or teeth).[2] Metals have been widely used for major load-bearing applications. There are, however, various problems related to normal metallic materials in the human body due to physical properties, corrosion, wear, and/or negative tissue reaction.[3] Appropriate hard-tissue replacement implants should achieve a match of mechanical behavior with the tissue to be replaced.[4]

It is almost certain that cellular materials permit the simultaneous optimization of stiffness, strength, and overall weight in a given application. Cellular materials are naturally load-bearing materials; for example, nature often uses cellular materials such as wood, bone, coral as load-bearing materials. Recently, cellular NiTi intermetallic compound has been acknowledged as a most promising biomaterial for use as artificial bones or teeth roots because of its special pseudoelasticity, which can accommodate the deformation behavior of hard tissue, and its attractive combination of properties such as excellent mechanical properties, good corrosion resistance, biocompatibility, and shape memory effect.[5-6] Moreover, its cellular structure allows the ingrowth of bone tissue and is favorable for the fixation of the implant as well as the transport of body fluids. In addition, by obtaining different porosity and pore sizes through controlling the synthesis conditions, it is easy to adjust the mechanical behavior of cellular NiTi alloys to match that of replaced hard tissue.

The engineering potential of cellular NiTi alloys in medicine is considerable as aforementioned, but its realization requires new and innovative method of design, unfamiliar to traditional engineers. Self-propagating high temperature synthesis (SHS), is used to synthesize many ceramics and intermetallics,[7-11] including NiTi intermetallic compounds. Compared with the conventional process, the SHS method provides advantages with respect to both time- and energy-savings, and easier processing.

The main aim of this study is to synthesize cellular NiTi intermetallic compounds by SHS. By changing pre-heating temperature, we expect to control the SHS process and get products with high-porosity and well distributed pores.

Reactant powders of Ti and Ni were mixed at the equiatomic Ni/Ti composition. The blended powders were pressed into cylindrical pellets with a diameter of 26mm. The relative density of the pellets was about 42% of the theoretical value. The pellets were ignited in a SHS reaction chamber. X-ray diffraction (XRD) was conducted to identify the phases in the products. Optical metallography and scanning electron microscopy (SEM) were performed for microstructural characterization analysis.

Fig. 1 shows an XRD trace for the blended powders. As can be seen, the Ni and Ti powders have been only mechanically blended and no alloying has occurred.

Because of the low exothermic character of

the reactions of Ti and Ni to synthesize Ni-Ti intermetallic compounds by SHS, pre-heating is needed.[12] It is reported that control of the SHS process can be achieved by regulating the pre-heating temperature.[6] In the present study, the effect of pre-heating temperature on the fabrication process is investigated. Fig. 2 shows XRD patterns of SHS-synthesized cellular NiTi intermetallic compounds under different pre-heating temperatures. It can be seen that the SHS process results in the formation of several intermetallic compounds. The dominant phase, B2(NiTi) and B19(NiTi), which are the desired products, are present in every case; by-product phases like Ti_2Ni, Ni_3Ti, and Ni_4Ti_3, can also be observed. With increasing pre-heating temperature, B19(NiTi) increases while B2(NiTi) and Ni_4Ti_3 decrease, and Ni_4Ti_3 vanishes after the pre-heating temperature is increased to 550°C. The following reactions take place during combustion:

$$Ni + Ti \rightarrow NiTi + 67kJ\ mol^{-1} \quad (1)$$
$$Ni + Ti \rightarrow Ti_2Ni + 83kJ\ mol^{-1} \quad (2)$$
$$Ni + Ti \rightarrow Ni_3Ti + 140kJ\ mol^{-1} \quad (3)$$
$$Ni + Ti \rightarrow Ni_4Ti_3 + heat \quad (4)$$

All these four reactions are exothermic in nature with the heat released as indicated. With the reaction heat and the heat provided by pre-heating, combustion becomes self-sustaining. As NiTi, Ti_2Ni and Ni_3Ti are three stable phases while N_4iTi_3 is metastable in NiTi alloys,[13] reactions (1), (2) and (3) always take place and reaction (4) only occurs at pre-heating temperature below 525°C. Thus, NiTi, Ti_2Ni and Ni_3Ti exist in all alloys and Ni_4Ti_3 vanishes at a pre-heating temperature of 550°C.

The pre-heating temperature also has an effect on the shape and macrodistribution of pores in the products. Fig. 3 (a) and (b) show macrographs of sintered products. As can be seen, sintered at pre-heating temperature below 500°C, each product has a regular shape. From Fig. 3 (b), however, one can clearly see evidence of melting at a pre-heating temperature of 525°C or above, causing the products to deform and melt seriously. This results from the heat released and the increase of pre-heating temperature, which means that more external heat input the Ti-Ni reaction system increases the combustion temperature. When the combustion temperature increases over 950°C, Ti_2Ni begins to melt. Obviously, products synthesized at pre-heating temperature below 500°C are the ones desired.

It is necessary to note that clinical success of implants requires the implant to have a structure similar to the tissue to be replaced. Since the hard-tissue like human bone is cellular and liquid-permeable, it is desirable that the implant materials should have a similar open cellular structure. Table I represents the density, porosity, open-porosity and open-porosity ratio obtained under different pre-heating temperatures. It is clear that the effect of pre-heating temperature on porosity and open-pore ratio is not very obvious and the sintered samples have an open cellular structure in each case. Their porosity is about 60 vol.%, and the pores are almost totally interconnected as the open-porosity ratio is above 95%. This high porosity and high open-porosity ratio ensure an open structure of the materials and have the following advantages: primarily, they can achieve a stable interface by mechanical bonds due to direct ingrowth of connective tissue into the implant; secondly, body fluids can penetrate this open structure by capillary effect, which results in better

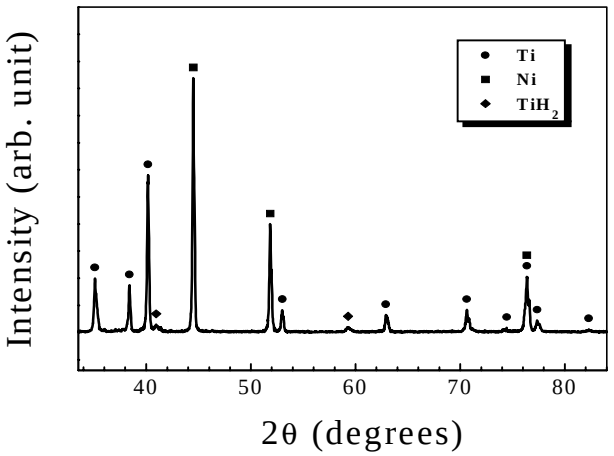

FIG. 1. XRD pattern of the mixed powders before SHS. The TiH_2 is minor and may come from the Ti powders.

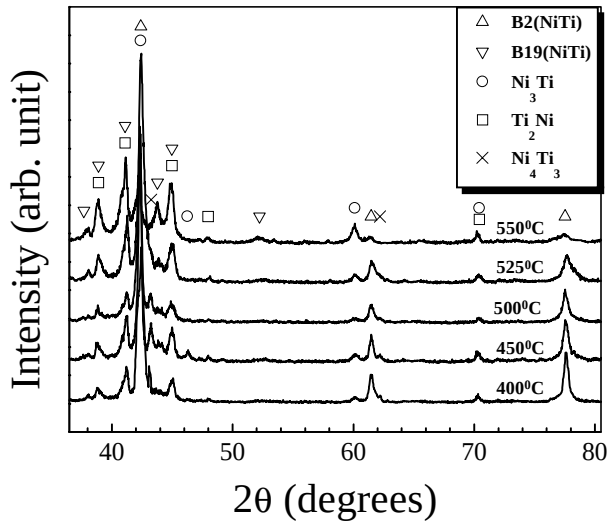

FIG. 2. XRD profiles of the products synthesized at various preheating temperatures.

healing than with fully dense materials. This open cellular structure can also be seen from a representative optical photograph (Fig. 4) and a scanning electron microscopy image (Fig. 5). It can be seen that most pores form a net of channels, well connected to each other. Moreover, there exist a lot of small isolated pores, which are almost spherical in shape and tend to shrink with further sintering. This high porosity and high open-porosity ratio are attributed to the character of the SHS. They can be explained as being caused by (1) the initial porosity of the powder mixture prior to the combustion reaction; (2) the density change upon intermetallic compounds formation from the elemental constituents; and (3) the trapped gases, e. g., Ar, in the pellet, leaving the matrix during combustion, as suggested by Kenneth S. Vecchio *et al.*[14]

In summary, cellular NiTi intermetallic compounds with about 60 vol.% porosity with more than 95% open-porosity ratio have been fabricated successfully by SHS, which shows the advantage

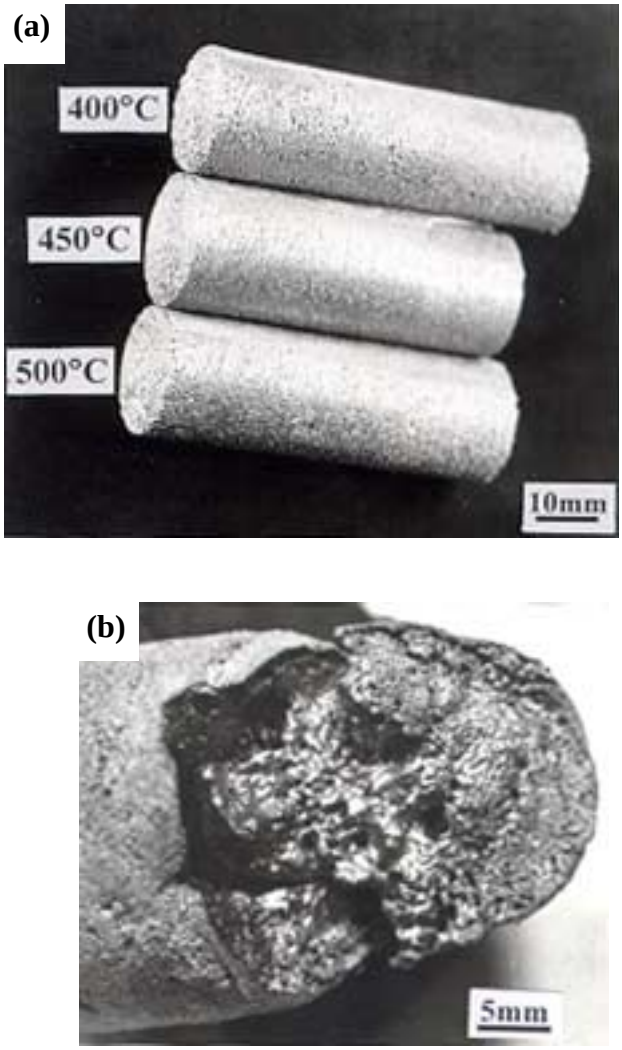

FIG. 3. Macrographs of the products synthesized at different preheating temperatures: (a) below 500°C and (b) at 525°C.

TABLE I. The density, porosity, open porosity, and open-porosity ratio of cellular NiTi intermetallic compounds produced at various preheating temperatures.

Pre-heating temperature (℃)	400	450	500	525	550
Density (g cm^{-3})	2.54	2.70	2.51	2.52	…
Porosity (%)	60.6	58.0	61.1	60.8	…
Open-porosity (%)	58.2	57.2	59.2	58.1	…
Open-porosity ratio (%)	96.0	98.6	96.9	95.6	…

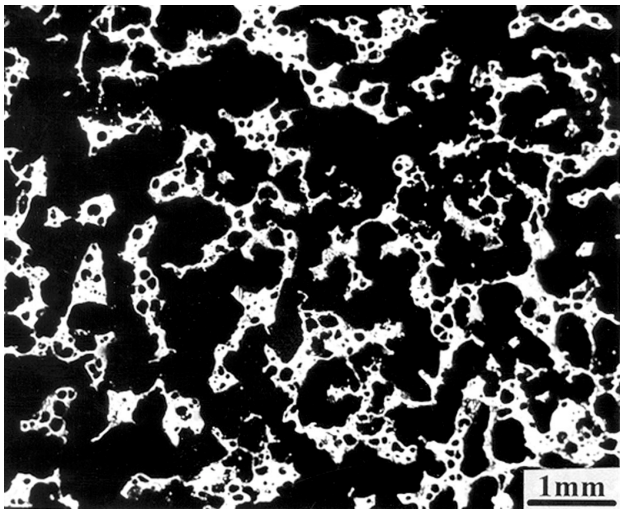

FIG. 4. Optical micrograph of cellular NiTi intermetallic compounds fabricated at pre-heating temperature of 400°C.

FIG. 5. SEM micrograph of cellular NiTi intermetallic compounds synthesized at pre-heating temperature of 500°C.

that both time and energy savings can be made compared to conventional processing. The SHS reaction results in the formation of intermetallics, such as TiNi, Ti_2Ni, Ni_3Ti, and Ni_4Ti_3 in seconds. The SHS process can be controlled by regulating the pre-heating temperature, which influences the phase amount and the macrodistribution of pores in the sintered products but does not change the porosity and open-porosity ratio significantly. More extensive thermodynamic analysis of and kinetic experimentation with the SHS process will be considered in the near future.

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