INFLUENCE OF PRECURSOR PREPARATION ON CELL STRUCTURE OF POROUS TI COMPOSITE

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Abstract

Porous titanium carbide (TiC) and TiC/Ti composites were synthesized by self-propagating high-temperature synthesis (SHS). Titanium and carbon powders were blended with various Ti/C blending ratios. The heat of reaction between titanium and carbon was high enough to induce the self-sustaining reaction of TiC formation on condition that some processing parameters (the Ti/C blending ratio and porosity of the precursor) were appropriately selected. The important parameters to control the pore morphology turned out to be an adiabatic combustion temperature and fraction of the metallic (liquid) phase during the SHS reaction. By increasing the Ti/C ratio, the liquid metal phase existed during the reaction, and this allowed the deformation and growth of pores. Preheating the precursor resulted in the higher combustion temperature, which reduced the viscosity of the metallic phase and promoted the growth of pores.

1 Introduction

Titanium alloys and titanium carbide ceramics have attracted a great deal of attention due to their excellent mechanical properties, good corrosion resistance and biocompatibility [1-3]. Porous metals and ceramics have been studied by many researchers for medical purposes (artificial hard-tissue replacements, for example), and it is well-known that porous materials are suitable for surgical implants because the pores permit bone ingress and give a firm bond between the implants and the human bone [4]. The pore size is one of the most important characteristics for the porous implant materials, and an optimum range of the pore size was reported roughly from 200μm to 500μm [1]. The pore morphology and porosity are also important characteristics, which regulate physical properties of the porous materials. Besides from the bio-oriented applications, the porous Ti alloy and TiC ceramic are applicable to tribological purposes and to filtering materials under extremely severe environments (high-temperature or highly corrosive environments).

Porous titanium alloys and TiC ceramic are generally fabricated by a sintering process, but a disadvantage is that this process consumes large amount of energy. In contrast to the conventional sintering process, self-propagating high-temperature synthesis is a cost-effective process that makes use of a large amount of heat of reaction. Fig.1 shows a brief outline of the SHS process of the TiC formation from a precursor consisting of elemental titanium and carbon powders. In the SHS process, only a part of the precursor needs to be heated. Once the temperature at the heated zone reaches to the ignition temperature (T_{ig}) [5], then a TiC formation occurs (reaction zone in Fig.1), and the heat of reaction shown below is released.

$$Ti + C \rightarrow TiC + Q, \quad Q = 186kJ \quad (1)$$

This heat of reaction raises the temperature of the neighboring zone and induces the TiC formation again. Thus the reaction propagates to the other end of the specimen spontaneously. Since the SHS process uses the heat of reaction, only a small amount of energy is required to synthesize ceramics or intermetallics [6-8]. The following three factors are the typical characteristics of the SHS process.

- *simple processing (no special equipment is required)*
- *short-time processing (reaction completes in several seconds)*

- *synthesis of porous materials (initial pores in the compacted powder remain after the reaction)*

The purpose of this work is to synthesize porous TiC/Ti composites with pore sizes below 500μm by the SHS process. In this paper, (1) effects of blending ratio of starting materials (Ti/C) and (2) preheating on possibility of the SHS reaction and pore morphology are dealt with.
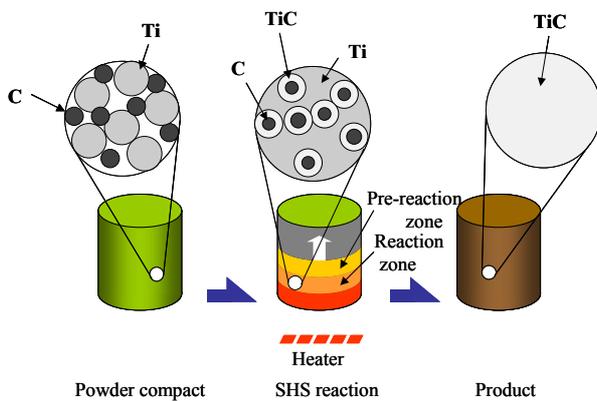
Fig.1. Brief outline of the SHS process for TiC/Ti composite formation

2 Experimental procedure

Starting materials used in this experiment were titanium powder (99.4% pure, size : <45μm) and carbon powder (99.9% pure, size : <5μm). First of all, the starting powders were blended by molar blending ratios (Ti/C) ranging from 1.33 to 2.99. The blended powder was then compressed by a constant pressure (55MPa) to prepare precursors (cylindrical shape : 15mm in diameter, 10mm in height). The precursor was placed in a chamber as shown in Fig.2. The chamber was evacuated by a rotary pump and then backfilled with Ar. The bottom part of the precursor was heated by an ignition heater to induce the TiC formation (Eq.(1)). In some experiments, the precursor was preheated (473K) prior to igniting the SHS reaction. After the reaction, the cross section of the specimen was observed by optical microscopy (OM) and scanning electron microscopy (SEM) and analyzed by an X-ray diffraction (XRD) method. The pore size was evaluated by an image analyzing software.
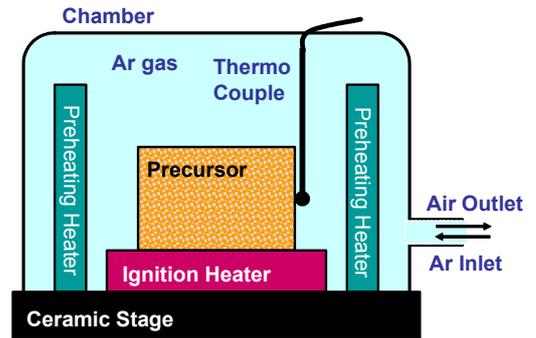
Fig.2. Schematic illustration of the experimental apparatus for SHS process

3 Results

3.1 Self-propagation of the reaction

Table 1 shows the possibility of the SHS reaction with various Ti/C blending ratios (from 1.33 to 2.99). The compacting pressure for preparing the precursor was fixed to 55MPa (porosity of the precursor : 35%). The SHS reaction occurred only when the Ti/C ratio was 1.88 and 2.33. The reaction did not occur when the Ti/C ratio was 1.33, 1.59 and 2.99. This result suggests that there is an adequate range of the Ti/C ratio to induce the SHS reaction. It is well-known that the following two features are important parameters for the possibility of the SHS reaction.

- *Thermal Conductivity : Temperature of the pre-heated zone should be raised to the ignition temperature to allow the self-sustaining reaction. This condition is sometimes difficult to be achieved when the thermal conductivity of the precursor is high.*
- *Heat of Reaction : When a material, which is not involved in the reaction, is blended in the precursor, such a material absorbs the heat of reaction. As a result of the absorption, the temperature of the precursor during the SHS reaction (Combustion Temperature: T_c) is reduced, and the pre-heated zone can not reach to the ignition temperature.*

Since thermal conductivity of carbon is much higher than that of titanium (C: 900 ~ 2000W/m・K, Ti:21.9W/m・K), the precursors with low Ti/C ratios (1.33 and 1.59) conduct more heat than other specimens. Therefore the heat of reaction could not raise the temperature of the heated zone to the ignition temperature. On the other hand, high Ti/C

ratio (2.99) produced an excessive amount of titanium, which could not be involved in the reaction. This excess titanium phase absorbed the heat of reaction and reduced the combustion temperature, which prevented a sufficient increase in the temperature of the heated zone to the ignition temperature.

Table 1. Effect of the Ti/C ratio on the possibility of the SHS reaction

Ti/C ratio	Compacting Pressure (MPa)	Possibility of the Self Propagation
2.99		NO
2.33		Self Propagate
1.88	55	Self Propagate
1.59		NO
1.33		NO

3.2 Ti/C blending ratio

Fig.3 shows the cross section of the specimens after the SHS reaction with the Ti/C ratios of 1.88 and 2.33. As already indicated in the former section, the reaction propagated throughout the specimen successfully with these Ti/C ratios. The bright region and the dark region in Fig.3 are the TiC/Ti composite and pores, respectively. Pores with average diameter of 50μm (Ti/C=1.88) and 100μm (Ti/C=2.33) are identified, which proves that the pore size was affected by the Ti/C blending ratio. Namely, pores became larger by increasing the Ti/C ratio. The mechanisms of pore formation are considered as follows;

- *original pores in the precursor remains after the SHS reaction*
- *diffusion of molten titanium into carbon generates pores where titanium powder was originally located.*
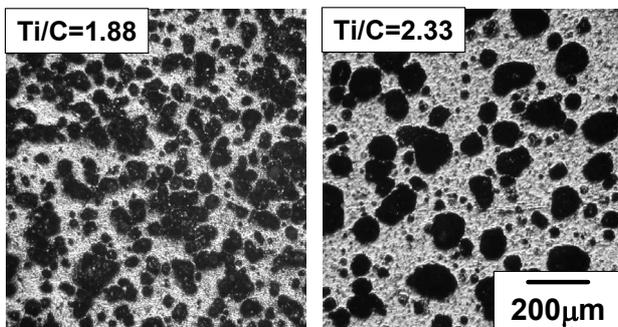
Fig. 3. Cross-sectional view of combustion synthesized specimens (Ti/C molar ratio = 1.88 and 2.33)

Therefore, the excess amount of titanium played an important role in determining the pore morphology. If the combustion temperature exceeded the melting point of titanium, the fluidity of the specimen sharply increased. This allowed the deformation and connection of pores, and also attributed to the growth of the pore size shown in Fig.3.

Fig.4 shows the XRD patterns of these specimens. When the Ti/C ratio was 2.33, the X-ray diffraction peaks of both titanium and TiC were clearly detected at appropriate angular positions, whereas the diffraction peaks of titanium were scarcely detected when the Ti/C ratio was 1.88.
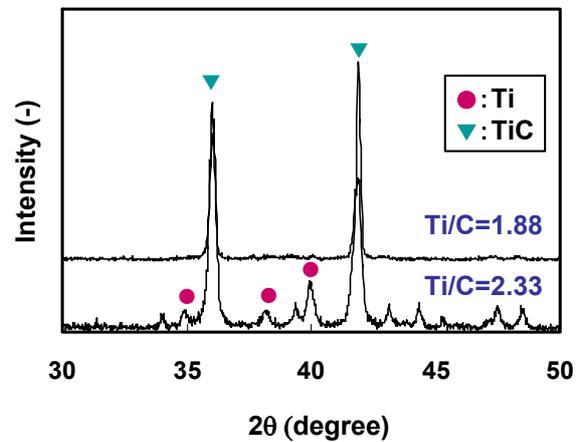
Fig.4. XRD patterns of combustion synthesized specimens (Ti/C ratio = 1.88 and 2.33)

Fig. 5 shows the microscopic cross sections of the two specimens observed by SEM. Both titanium and TiC were observed when Ti/C ratio was 2.33, but only a minute quantity of titanium was observed when the Ti/C ratio was 1.88.

Titanium carbide has a cubic NaCl-type structure which has a wide composition range between $TiC_{0.49}$-$TiC_{0.95}$ [9] and the composition of non-stoichiometric TiC_x can be predicted from the Ti-C phase diagram. The formation of monolithic $TiC_{0.53}$ phase was expected when Ti/C ratio was 1.88, and Fig.4 and 5 proved the formation of nearly monolithic phase. When the Ti/C ratio was 2.33, the formation of $TiC_{0.49}$ and the remaining titanium was expected from the phase diagram, and confirmed experimentally as already indicated in Fig.4 and 5.
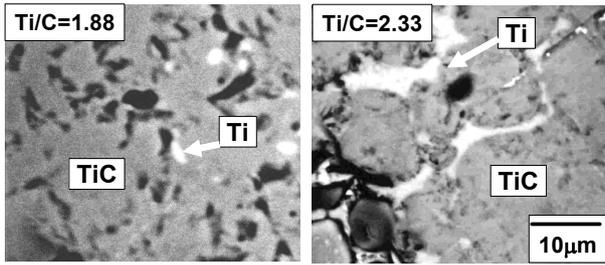
Fig.5 SEM image of combustion synthesized specimens
(Ti/C ratio : 1.88 and 2.33)
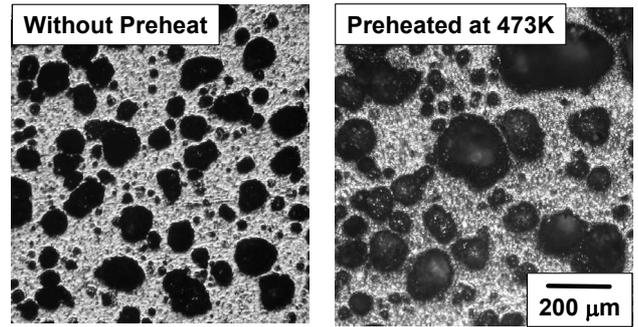
Fig.6 Macroscopic view of combustion synthesized
specimens with and without preheating
(Preheating temperature=473K, Ti/C ratio=2.33)

3.3 Preheating the precursor

Preheating the precursor prior to the SHS reaction was carried out and the effect of preheating on the pore morphology is discussed in this session. The role of preheating was to controll the combustion temperature and the pore morphology. Fig.6 shows the cross section of the specimens (Ti/C=2.33) without preheating and with preheating at 473K. The larger pores (200μm) were formed by preheating the specimen. By preheating the precursor, the combustion temperature (T_c) was raised. The combustion temperature can be calculated thermodynamically by the following equation.

$$\Delta H_f(TiC)+\int_{T_{ig}}^{T_c}\left(C_p(TiC)\right)dT$$
$$+ (\alpha - 1)\cdot\left(\int_{T_{ig}}^{1939} C_p(Ti)\,dT + \Delta H_{melt}(Ti) + \int_{1939}^{T_c} C_p(Ti)\,dT\right)$$
$$= 0$$

$$(2)$$

where ΔH_f denotes the heat of reaction (J/mol), ΔH_{melt} denotes the latent heat of melting (J/mol), C_p denotes the specific heat (J/K・mol), T_0 denotes the initial temperature (K), α denotes the molar Ti/C ratio.

Fig.7 shows the enthalpy data of the reactants (titanium and carbon) and the product (TiC) calculated form Eq.(2). According to the calculation, the combustion temperature is above the melting point of titanium, and it is also understood that the preheating effectively raises the combustion temperature. This means that fluidity of the liquid phase during the SHS reaction becomes higher by preheating the precursor, which promotes the deformation and connection (coarsening) of pores.
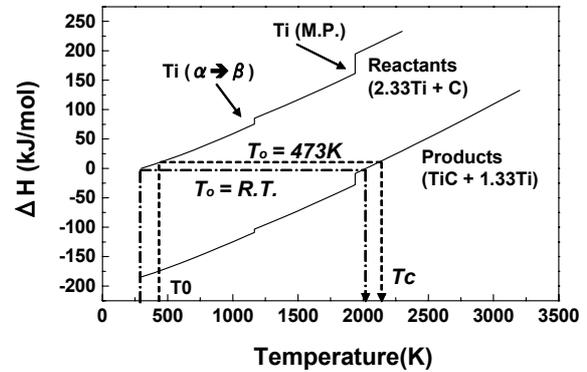
Fig.7 Enthalpy data of the Ti-C system (Ti/C=2.33) for the calculation of the adiabatic combustion temperature.

4. Conclusions

The porous TiC/Ti composite was fabricated by self-propagating high-temperature synthesis. The powder blending ratio and preheating temperature were regarded as important processing parameters to control the SHS reaction and pore morphology. The results obtained by the present work are summarized as follows.

1. The heat of reaction between titanium and carbon was high enough to induce the SHS reaction on condition that the Ti/C blending ratio was appropriately selected (1.88 and 2.33).
2. Low Ti/C ratios (1.33 and 1.59) did not allow the SHS reaction because the thermal conductivity of the precursor was too high to raise the pre-heated zone to the ignition temperature. When the Ti/C ratio was high (2.99), the heat of reaction was absorbed by

the excess amount of titanium. As a result, the heated zone was not heated up to the ignition temperature.

3. The pore size could be varied from 50μm to 100μm by changing the Ti/C blending ratio from 1.88 to 2.33.

4. By preheating the precursor, the combustion temperature was raised and the liquid phase formation also increased, which afterwards attributed to the larger pore formation.

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