Characteristics of self-propagating reaction in TiN combustion synthesis

HIROSHI KUDO, OSAMU ODAWARA
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

The characteristics of the combustion synthesis of TiN are investigated through a self-propagating reaction of titanium powder compacts of specific packing density (40% to 60% theoretical one) in the presence of flowing nitrogen gas (0.01 m³ min⁻¹) under atmospheric pressure. It was found that the propagating velocity of the combustion wave became slower with increasing packing density. The conversion ratio of nitrided titanium increased with increasing packing density, and reached about 70% in the case of 60% densely packed compact covered with a quartz tube. However, in the case where nitrogen gas flowed from the centre bottom of the compact, the conversion ratio was almost independent of packing density. It is considered that the predominant factors for achieving higher conversion are the combustion wave velocity and temperature gradient in the high temperatures region behind the combustion front.

1. Introduction
Recently, the combustion synthesis of metal nitriding has been widely investigated [1-4], and titanium nitriding is one of the typical systems used. The process of the combustion reaction of metallic titanium and nitrogen gas system is written as follows

$$Ti + 1/2N_2 = TiN + 336 \, kJ \qquad (1)$$

The maximum adiabatic temperature calculated for the above system is more than 4900 K. Because the melting points of titanium and TiN are 1941 and 3233 K, respectively, the TiN produced and the reactant titanium would be the liquid state if the reaction proceeded to completion. Once the reactant melts, nitrogen gas penetration into the space of the reactant powders and the conversion would be interrupted by the effect of lowering the surface area of the reactant. Therefore, it is considered that the achievable conversion would be less than 40% when reacted under an atmospheric nitrogen gas environment [3].

Although it is considered that high pressures of nitrogen gas cause a high conversion of titanium to titanium nitride [2], 100% conversion could not be achieved, even in such environmental applications, because of melting of metallic titanium in front of the propagating combustion wave and the interruption of further nitrogen penetration.

To achieve perfect conversion, the addition of some diluent was proposed on the basis that the maximum temperature reached with the reaction is lowered, with the heat dispersed in to the diluent [2]. A technique utilizing sodium azide (NaN₃) as a solid source of nitrogen was also proposed for full conversion [3], in which the environmental pressure is sufficient at atmospheric levels. Considering these improvements for efficient conversion, the temperature behind the

combustion wave and the state of nitrogen penetration during the process should be important factors in the combustion synthesis of metal nitrides.

In the present work, in order to clarify the mechanism of the self-propagating reaction in TiN combustion synthesis, the synthesis was performed under 1 atm nitrogen pressure and with various conditions of packing density and reaction environment. The combustion velocity, conversion ratio and the composition of the product were also measured.

2. Experimental procedure
2.1. Reactant sample
Titanium powders used in the present work were of reagent grade with particle size ~40 μm. The powder was compressed to a cylindrical shapes of 25 mm diameter and 30 mm long, the packing densities of which were 40% to 60% theoretical ($4.51 \times 10^3 \, kg \, m^{-3}$).

2.2. Experimental apparatus
The present experiments were carried out in the presence of nitrogen gas at atmospheric pressure under three different conditions: (i) the sample compact was set in a large vessel (300 mm i.d. and 40 mm high) with a flow rate of 0.01 m³ min⁻¹ of nitrogen gas from the side of the vessel bottom; (ii) under condition (i), a quartz tube of 27 mm i.d. and 2 mm thick was set concentrically over the sample compact (see Fig. 1a); and (iii) the position of flowing gas was changed to the centre bottom of the sample compact which was covered with a quartz tube of the same dimensions as that in condition (ii), as shown in Fig. 1b.

2.3. Experimental procedure
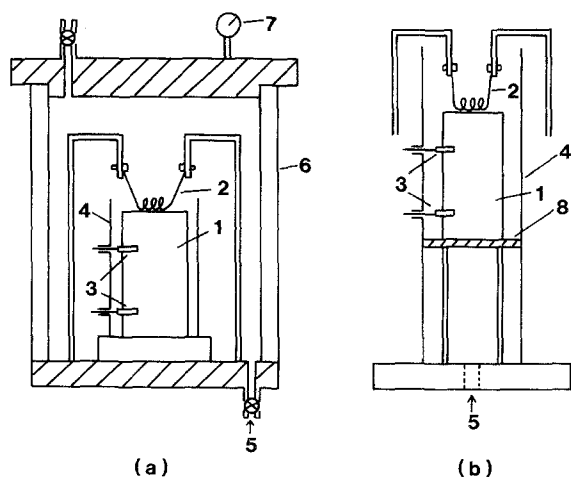The ignition of titanium powder compact was carried

Figure 1 Schematic drawings of the design of the apparatus. 1, sample; 2, tungsten wire for ignition; 3, alumel–chromel thermocouple; 4, quartz tube; 5, nitrogen gas inlet; 6, reaction vessel; 7, pressure gauge; 8, supporting net (stainless steel).

Figure 2 Changes in (a) combustion velocity and (b) conversion ratio related to the packing density of the titanium compacts used. (△) in a large vessel (condition i), (O) covered with a quartz tube (condition ii), (□) in a stream of nitrogen gas (condition iii).

out by electrical heating with a tungsten wire (0.5 mm diameter) attached to the top of the sample. The propagation velocity of the combustion wave was estimated by measuring the time delay in temperature increase between two alumel–chromel thermocouples (0.1 mm diameter, $\sim 50\,\mu\text{sec}\,K^{-1}$ in response) inserted into the sample from the side-wall at an interval of 20 mm, following previous work [5]. The conversion ratio of the products was determined by the difference in weight between the product and the reactant. The distribution and structure of the synthesized TiN was measured by X-ray powder diffraction.

3. Results and discussion

3.1. Combustion velocity and conversion ratio

The changes in the propagation velocity of the combustion wave (combustion velocity) and the titanium nitriding ratio (conversion ratio) with changing packing density of the titanium powder compact are shown in Figs 2a and b, respectively. The value of combustion velocity is almost the same in the present environmental conditions and becomes slower with increasing packing density. In the case of a sample with low packing density, the combustion front was observed to propagate downwards as a parallel wave from the ignited top end plane. On the other hand, it propagated spirally in the case of the samples with packing density more than 55%. This kind of combustion wave propagation is called "spin combustion" [6], and it is considered that the reaction propagation may reach the limits of that self-propagation. With respect to the conversion ratio, although low packing density would mean a high penetration of nitrogen gas around the packed metal powders, resulting in a high achievement of conversion, the present results show the inverse; the conversion ratio became higher with increasing packing density.

Because the slower the combustion velocity, the narrower is a region of heat generation by the reaction, higher heat condensation and longer keeping time at high temperature in the region behind the combustion
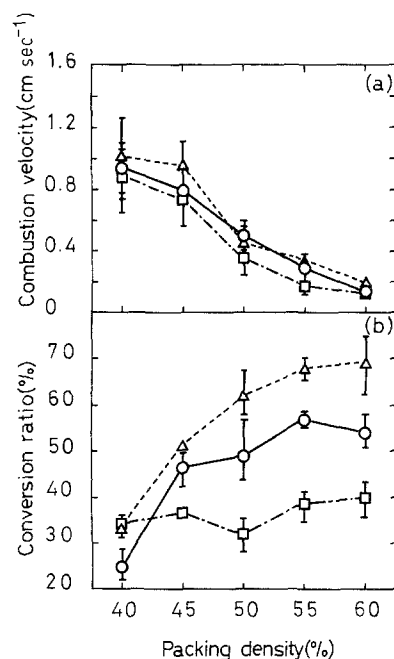
front should be expected in the combustion synthesis of higher packed compacts. Therefore, higher conversion could be obtained for higher packed compacts, i.e. with lower combustion velocity. Although it was considered in the past that the dominant factor in the conversion was the nitrogen gas penetration into the powders which was hindered by the metal melting, the influence of the metal melting must be overcome by inducing a continuous self-propagating reaction with a narrow region of high heat generation as estimated from the present results. Comparing the conversion ratio reached in the quartz tube (condition ii), that is, in some thermal insulating condition, with that done in a large vessel (condition i), the former is seen to be about 5 to 15% higher than the latter because of the high temperature remaining to a greater extent in the powders behind the combustion front. In condition (iii), the conversion ratio is almost independent of packing density and about 30 to 40%.

3.2. Structure and distribution of the products

Fig. 3 shows the photographs of the products obtained with the sample compacts of packing densities 40%, 50% and 60% under condition (i). Although it is difficult to observe the detailed difference in each picture because of obsecure contrast in the mono-colour technique for identifying the gold (TiN) and grey titanium colours, the distribution outlined would be obtained. As shown in Fig. 3a, metallic titanium was mainly distributed around the surface and even the inside of the sample, in the case of 40% packing density. For 50% packed compact, the metallic part is not observed clearly inside the sample and most of it exists at the surface constructing layer (see Fig. 3b). Contrary to these cases, the metallic part is not observed around the surface area but somewhat
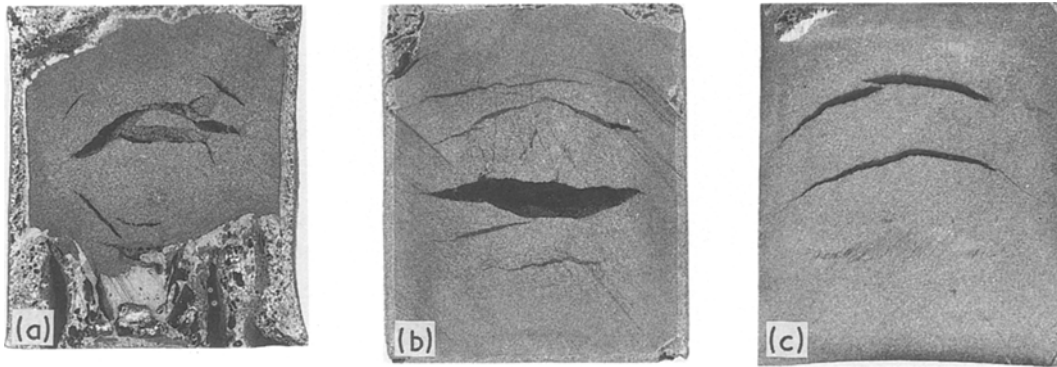
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Figure 3 Cross sections of the products obtained under condition (i) (reaction propagation; downwards from the top): (a) 40%, (b) 50%, (c) 60% packing density of the sample compact.

inside, in the case of combustion synthesis of a 60% packed compact.

These observations may also be discussed considering the combustion wave propagation and the subsequent synthesis at high temperatures. As the heat condensation becomes larger with increasing packing density, as previously mentioned in Section 3.1, the small region behind the combustion front can be maintained at higher temperatures much longer than that of lower packed compacts, causing a smaller temperature gradient around the surface wall of the compact. Therefore, it becomes possible to supply enough heat for synthesis with increasing packing density, while the heat under the large temperature gradient around the surface area can only melt the metal in the case of the lower packed compact. The residual metallic part inside the sample with high packing density is caused not by the propagation behaviour of the combustion wave, but by the lack of penetration of nitrogen under atmospheric pressure.

Because it is considered that the insulating effect of temperature is high in the order of condition (ii) > (i) > (iii) of the present environmental conditions investigated, the conversion in each case is expected to be the different, even if the combustion velocity is almost the same. In Figs 4 and 5, the X-ray powder diffraction patterns of the products obtained for 50% packed compact under the present three environmental conditions are shown for the surface wall and centre areas, respectively. As can be seen from the figures, titanium and TiN are the main components and some trivial amount of Ti_2N exists. For conditions (i) and (ii), metallic titanium is observed at the surface area, and its amount decreased in inside areas. Comparing the peak heights of the titanium and TiN patterns, the conversion under condition (ii) is larger than that under condition (i). This is probably caused by the difference in the temperature insulating effect. In the case of nitrogen gas flowing from the centre of the sample bottom (condition iii), conversion in the surface area is large, and the sample inside is less converted. The nitrogen content around the sample surface is larger than that in other conditions, so that the surface area would be converted to a greater extent. However, as heat release from the surface is large because of the effect of convection following the nitrogen gas flow, the inside could not be converted enough with insufficient heat and nitrogen supplied.
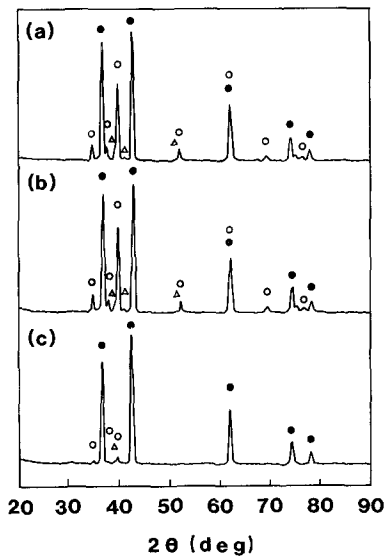

Figure 4 X-ray powder diffraction patterns of the product surface area obtained from the 50% packed compact under the three sets of environmental conditions used. (a) condition (i), (b) condition (ii), (c) condition (iii). (●) TiN, (△) Ti_2N, (○) Ti.
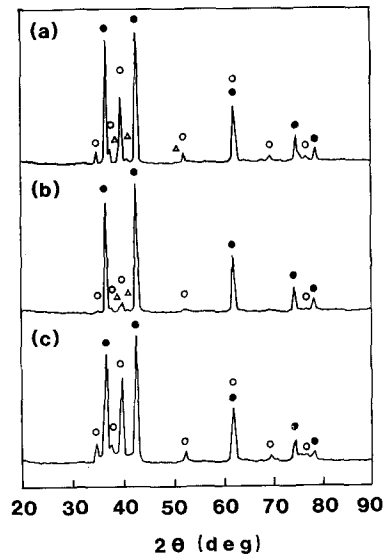

Figure 5 X-ray powder diffraction patterns of the product centre area obtained from the 50% packed compact under the three environmental conditions used. (a) condition (i), (b) condition (ii), (c) condition (iii). (●) TiN, (△) Ti_2N, (○) Ti.

In conclusion, it was confirmed from the present investigation that the predominant factor for the conversion in the combustion synthesis of TiN is not the heat generation which does not produce a molten titanium layer causing hinderance of nitrogen gas penetration into the compact, but is the continuous propagating of a region of heat condensed by the reaction, which gives a long retention time at high temperatures. For the highly efficient conversion of TiN, it is useful to make the combustion velocity slower, resulting in longer holding times of higher temperature region behind the combustion front, and to a decrease in temperature gradient around the sample compact during the propagation of reaction.

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