JOURNAL OF MATERIALS SCIENCE **34** (1999) 4469–4473

Combustion synthesis of highly porous ceramics: The TiC-Al_2O_3 system

W. ZHOU, W. B. HU, D. ZHANG
State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University,
Shanghai, 200030, People's Republic of China
E-mail: zw60363@ mail1.sjtu.edu.cn

To make use of the porous nature of the SHS reaction products a novel investigation was made to manufacture the highly porous ceramics with SHS method by adding certain amounts of volatile agents to the green compacts. The interconnected open porosity of the obtained highly porous ceramics can be as high as 83% and the interconnected network open pore microstructure was developed in the obtained highly porous ceramics. Large amounts of micropores were found present in the obtained highly porous ceramics, which is a special and important advantage of manufacturing porous ceramics with SHS method. Also this particular combustion process was studied in detail and it was found that the propagation rates are increased considerably due to the unique green compact structure left by the volatile agents. © *1999 Kluwer Academic Publishers*

1. Introduction

Combustion synthesis, reaction synthesis, or self-propagating high-temperature synthesis (SHS) are methods of producing ceramics, intermetallics, and composite materials that have received a great deal of attention [1–3]. However, the relatively high levels of porosity, e.g., 40–50%, in the reaction products has led to some limitations in the application of this technique for producing advanced materials. For this reason, various densifying techniques have been explored, including hot pressing [4], explosive compaction [5], modified HIP [6], and impact forging [7].

On the other hand, as we know, porous ceramics have found wide applications ranging from heterogeneous catalyst carriers, membranes used for isolating bacteria in bioreactors and environmental filters for hot fuel gases and diesel engine emissions and it is becoming more and more important to our modern technological world. In consideration of this, we are prompted to make highly porous ceramics with SHS method on purpose to make use of the porous nature of the SHS reaction products. Also by doing so we can have the general advantages of combustion synthesis including higher purity of the products and elimination of any high-temperature furnaces. Furthermore, we could avoid the densification process generally needed in the SHS reaction products. Few attempts have been made in this respect except a few former soviet scientist have done some work on it [8, 9]. Nevertheless, the customary SHS reaction products are not satisfactory to be directly used as porous ceramics. There are still some problems to be solved because its total porosity and interconnected open porosity is yet not high enough and the closed porosity of the SHS reaction products makes up a considerable part of the total porosity.

Here a novel application of combustion synthesis is currently being investigated which involves the addition of certain amounts of volatile agents. The volatile agents are added for the aim of further increasing the total porosity and the interconnected porosity of the SHS reaction products. After adding the volatile agents we have obtained a much highly porous SHS reaction products, i.e., the highly porous ceramics, the interconnected open porosity of which could be as high as 83%.

The microstructure and porosity formation of the obtained highly porous ceramics is characterized and compared with that of the normal SHS reaction products. Micro-pore formation is detected in the investigated TiC-Al_2O_3 system, which is a special and important advantage for producing highly porous ceramics with SHS method. In addition, the combustion process involved is studied in conjunction with the unique structure left by the volatile agents and a much faster propagation rate is found and explained.

2. Experimental

This article will discuss the initial observations of the TiC-Al_2O_3 system, using the reaction

$$3TiO_2 + 3C + 4Al = 3TiC + 2Al_2O_3 \qquad (1)$$

Commercially available reactants of TiO_2, Al, and C were used to synthesize TiC-Al_2O_3 porous ceramics. The TiO_2 was reagent-grade rutile, the Al was commercially pure, inert-gas-atomized powder, and the carbon was graphite. The nominal particle sizes of the TiO_2, Al and C were 0.5, 12 and 20 μm, respectively.

The stoichiometric powder mixture were attrition wet-milled in ethanol for 24 h using alumina balls,

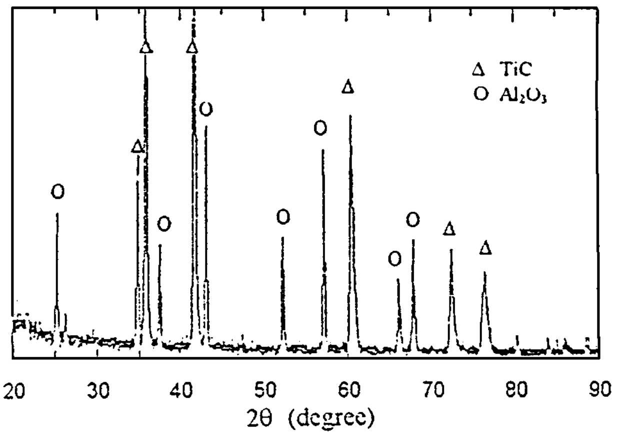


Figure 1 X-ray diffraction patterns of the SHS reaction products (the volatile agents added).

subsequently dried and passed through a 100 μm sieve. Experimental samples were prepared, each having a net reactant mixture of 22 g. Different amounts of volatile agents were added to the samples. The average size of the volatile agents is 150 μm.

Cylindrical compacts approximately 48 mm in diameter were uniaxially pressed at a constant press load of 30 MPa after each sample was evenly blended and screened to 200 μm sieve. For comparison a few samples were also prepared without adding the volatile agents and pressed at different press loads. The green compacts with the volatile agents were stored in air in a drying oven maintained at 75 °C for 24 h to evaporate the volatile agents completely. SHS reaction was ignited in a nitrogen protective atmosphere using the propagating mode with a heated silicon carbide rod located immediately beside the pellet. All the pellets were dried at 150 °C for 60 min prior to ignition. The whole combustion wave propagation process could be observed from an observation window to assess the stability of combustion wave and its rates of propagation were determined using a stopwatch.

The obtained highly porous ceramics and normal reaction products without adding the additives were analyzed by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). The interconnected open porosity and the closed porosity of the reaction products were determined using immersion in water and steam technique.

3. Results and discussion

3.1. X-ray diffraction pattern of the obtained highly porous ceramics

Al_2O_3 and TiC are still the only reaction products as can be clearly seen from the X-ray diffraction patterns in Fig. 1. This result suggests that almost all the volatile agents are excluded from the reaction products in the drying process or in the high temperature synthesis reaction, which is beneficial for producing high-purity porous ceramics.

3.2. Interconnected open porosity and closed porosity of the obtained highly porous ceramics

Fig. 2 shows the effect of addition amounts of volatile agents on the interconnected open porosity and the closed porosity of the reaction products.

According to our experimental observations, the interconnected open porosity of the normal Al_2O_3-TiC reaction products before adding the additives is generally in the range of 35–50%, and the closed pores is approximately 8–13%. However, as shown in Fig. 2 we can see that with the addition volume of the volatile agents exceeding 41% the interconnected open porosity of the reaction products increases sharply until reaching over 80%. On the other hand, the percentage of closed pores is also greatly reduced from approximately 11% to 2–4% and the higher the interconnected open porosity the lower the closed porosity. However, we could notice that there is a rise in the closed porosity when the volume percentage of volatile agents is 41%. The reason may be that when the volume percentage of the volatile agents is not high enough, some of the volatile agent particles are separated by the reactant forming more closed porosity. So we could deduce that the addition volume percentage of the volatile agents must exceed a critical value when we want to increase the interconnected open porosity and reduce the closed porosity of the reaction products in this way. This critical volume percentage is closely related to the size of agent particles and the press load.

3.3. Porosity formation and microstructure characterization

As we understand, there can be four sources of porosity in the combustion reaction products: (a) the initial

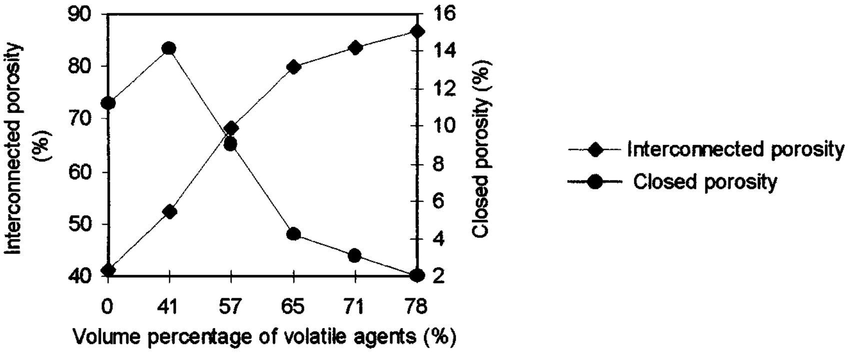


Figure 2 Dependence of the interconnected porosity and closed porosity of SHS reaction products on the volume percentage of volatile agents.

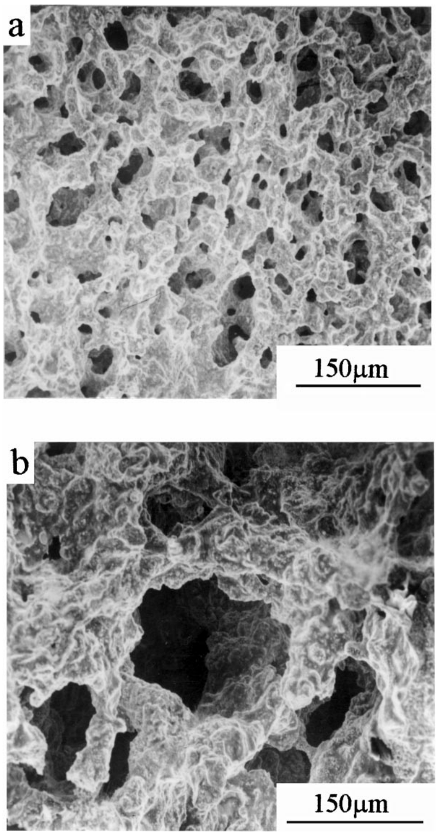


Figure 3 Fractographs of SHS reaction products: (a) without volatile agents; (b) with volatile agents.

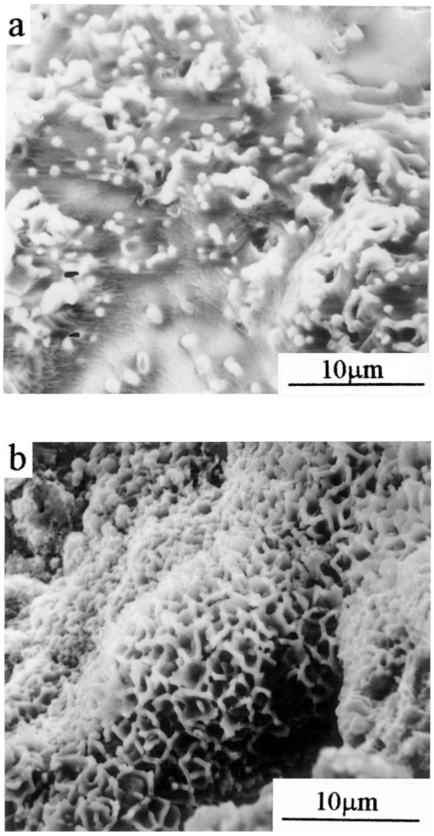


Figure 4 Micro-pores discovered in the reaction products: (a) without volatile agents; (b) with volatile agents.

porosity of the powder mixture prior to the reaction; (b) the shrinkage associated with the reaction (i.e., products that have a higher specific volume than the starting reactants); (c) the formation of gases in conjunction with the reaction, and their subsequent expansion, entrapment, or escape; and (d) the capillary flow of least refractory constituent.

Fig. 3 presents the fractograph morphology of the reaction products. The pore size of the reaction products without adding the volatile agents (25 μm, Fig. 3a) is far less than that of the reaction products with the volatile agents (150 μm, Fig. 3b). Obviously, this difference is caused by the volatile agents. It is known from the experimental procedures that the green compacts were left with large amounts of *in situ* interconnected open pores after the drying process. This part of pores is inherited by the reaction products. Also, part of the reactant volume contraction, evaporation of some volatile inclusions and the initial pores of the pellets all will contribute partly to the total interconnected open porosity of the reaction products. When the reaction products of high interconnected open porosity is needed as in our experiment, it is evident that the *in situ* interconnected open pores left by volatile agents play a dominant role, accounting for most of the total interconnected open porosity, especially when the addition volume of volatile agents is more than the critical volume percentage. The interconnected open pore structure of the obtained highly porous ceramics could clearly be seen from Fig. 3b.

Fig. 4b presents the micro-pores morphology of the obtained highly porous ceramics, which is a special phenomenon of the SHS reaction products in comparison with Fig. 4a. It is believed that these micro-pores are formed when the residue volatile agents and some volatile inclusions are heated to run out of the reaction products through these micro-pore paths during the SHS reaction. The addition of large amounts of volatile agents has introduced much more evaporative impurities and the ready-made interconnected outward pore channels have decreased the pore size notably due to the reduced interior pressure in the combustion process. The size of these micropores is very small, only 1–2 μm, which could increase the specific surface of the obtained porous ceramics greatly and promote the interconnection of the open pores further. The micropore formation of the combustion synthesized highly porous ceramics is significantly advantageous and important for producing porous ceramics which need large specific surface, e.g., catalyst support system or porous electrode.

3.4. Combustion synthesis process

After the evaporating process, the green compacts are left with large amounts of *in situ* pores leading to a very low green relative density, which is 17–37% compared to the normal 50–70% without adding volatile agents. However, the combustion process is still in stable condition under such low green density of the reactant mixture. And it is noteworthy to point out that not only the combustion wave propagation is becoming more stable but also the combustion propagation rate is much faster than that of without adding volatile agents. Fig. 5

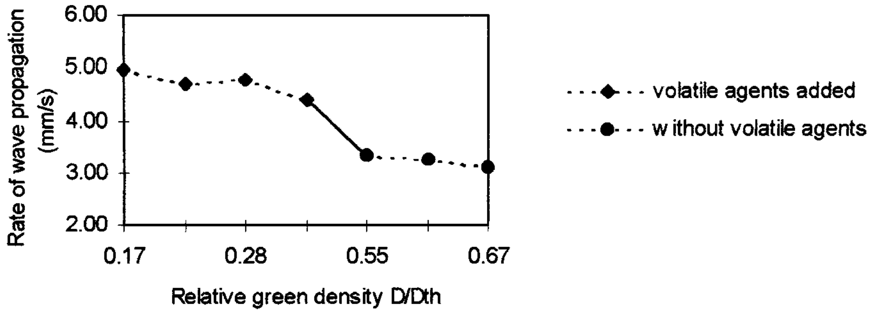


Figure 5 The effect of relative green density on the combustion propagation rate.

presents the influence of relative green density on the combustion propagation rate.

A variety of reactions [10, 11] shows propagation rates decreasing with increasing density (decreasing porosity) at higher densities and generally not being ignible at high densities. At low densities considerable data [12] for reactions in which all (initially) are solid reactants show propagation rates decreasing with decreasing densities and there is a generally pronounced maxima in propagation rates, e.g., at 50–60% of theoretical density [13].

However, this trend is totally different from that of the combustion synthesis here studied. We can see from Fig. 5 that the combustion propagation rate is distinctly faster than that of without adding volatile agents. The former is nearly 150% of the latter and it seems the lower the relative density the higher the combustion propagation rate, at least it is so in our experimental scope. So what are the reasons that could be accounted for this propagation rate enlargement under such low green relative density?

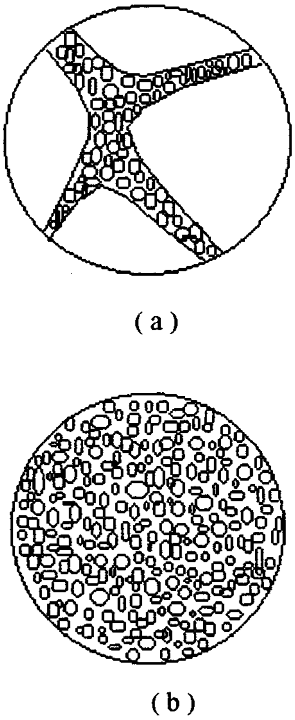
Merzhanov [14] has derived an expression for the rate of propagation of a planar combustion front based upon an elementary model of the process. In this model, he made use of the generalize form of Fourier's [] one-dimensional heat conduction equation.

$$C_\mathrm{p}\frac{\rho\partial T}{\partial t} = \frac{k\partial^2 T}{\partial X^2} + Q\frac{\rho\partial\phi}{\partial t} - \frac{2\alpha}{r}(T - T_0) - \frac{2\varepsilon\sigma_0}{r}\left(T^4 - T_0^4\right) \qquad (2)$$

where C_p is the heat capacity, ρ the density, x the axial distance, T the temperature, T_0 the ambient temperature, ϕ the fraction reacted, t the time, k the thermal conductivity, Q the heat of the reaction, α the heat transfer coefficient, r the sample radius, ε the emissivity coefficient, and σ_0 the Stefan-Boltzmann constant. After a series of simplifying and assuming, he calculated the velocity of a steady state combustion as

$$u^2 = s_n a\frac{C_\mathrm{p}}{Q}\frac{RTc^2}{E}k_0\exp(-E/RTc) \qquad (3)$$

Where u is the propagation wave velocity, a the thermal diffusivity, n the order of the reaction, σ_n a constant which depends upon the order of the reaction (for example: for $n = 0$, $\sigma_n = 2$; for $n = 1$, $\sigma_n \approx 1.1$; for $n = 2$, $\sigma_n \approx 0.73$), T_c the combustion temperature, E the activation energy for the reaction, k_0 a pre-exponential constant. From the above equation we can see the combustion propagation rate is closely related with the thermal conductivity of the reactants. Also Lakshmikantha and Rice [13, 15] have done some work to study the effect of thermal conductivity on the propagation velocity. All these research results suggest that the relative green density of the reactant mixture can have a great influence on the propagation rate by affecting the thermal conductivity of the reactant mixture. And the influence of thermal conductivity is two-fold: if it is too low, the combustion process is hard to propagate for the lack of efficient heat transfer; if it is too high, the thermal loss in the front of the propagation wave will be too big to sustain the reaction. So a balance between having enough particle contact to aid reaction but not too much to lead to excessive thermal loss from the reaction zone is important in modifying the propagation rate. Here we consider that the unique structure of the green compacts left by adding the volatile agents could be accounted for the particular propagation rate enlargement in the combustion process. Fig. 6 is a diagrammatic sketch showing the unique structure of the green compact.



(a)

(b)

Figure 6 Diagrammatic sketch of the green compact structure (a) volatile agents added (b) without volatile agents.

It is easy to understand that the great difference between the two green compact structures is the much higher porosity and pore size left by the volatile agents. By taking into account the entire compact's volume, we have assumed a rather low relative density of the green compacts as in Fig. 5. In fact, from Fig. 6a we can see that after the evaporation of the volatile agents, the reactant mixture agglomerates have a larger relative density than that which is simply calculated in the traditionally adopted method. To get the real relative density of the reactant mixture agglomerates we have to count out the volume taken up by the volatile agents. In light of this detail, we calculated the real relative density of the reactant mixture agglomerates, which is in the range of 61–69%, comparable with that of 56–68% for without adding volatile agents. This result suggests that the thermal conduction of the reactants is not reduced greatly after adding the volatile agents and so we can understand now why the SHS reaction is still stable and can propagate smoothly. But how can the reaction be much faster? We think it is still on account of the unique structure left by the volatile agents. First, the high porosity now could act as an effective insulating device to prevent excessive thermal loss from the reaction zone. Second, as suggested by Bhattacharya [16], for quite large pore sizes the local overall conduction process may even increase beyond that for solid conductivity due to contribution from radiation across the pore surfaces. So, with the unique structure of the green compacts left by the volatile agents, the combustion process enjoys high thermal conduction and low thermal loss at the same time, which give rise to a considerable propagation rate growth.

4. Conclusions

By adding the volatile agents to the green compacts before the SHS reaction we have obtained a much highly Al_2O_3-TiC porous ceramics, the interconnected open porosity of which could be as high as 83%. The network open pore structure is developed in the obtained highly porous ceramics. Large amounts of micro-pores (1–2 μm) is found present in the reaction products, which is a special and important advantage of manufacturing porous ceramics with SHS method. In the combustion synthesis process, the combustion propagation rates are increased considerably due to the unique green compact structure left by the volatile agents. This phenomenon suggests that a different kinetics is involved in the combustion synthesis.

Acknowledgement

This work is supported by the National Natural Science Foundation of People's Republic of China. The contract number is 59501002.

References

1. Z. A. MUNIR, *Ceram. Bull.* **67** (1988) 342.
2. M. FU and J. A. SEKHAR, *Key Engin. Mater.* **108–110** (1995) 19.
3. M. G. LAKSHMIKANTHA and J. A. SEKHAR, *J. Amer. Ceram. Soc.* **77** (1994) 202.
4. S. D. DUNMEAD, Z. A. MUNIR, J. B. HOLT and D. D. KINGMAN, *J. Mater. Sci.* **26** (1991) 2410.
5. B. H. RABIN, G. E. KORTH and R. L. WILLIAMSON, *J. Amer. Ceram. Soc.* **73** (1990) 2156.
6. O. YAMADA, Y. MIYAMOTO and M. KOIZUMI, *ibid.* **70** (1987) C-206–C-208.
7. J. C. LASALVIA, M. A. MEYERS and D. K. KIM, *J. Mater. Synth. Process* **2** (1994) 255.
8. V. N. BLOSHENKO and V. A. BOKIJ, *Inzhenerno-Fizicheskii Zhurnal.* **65** (1993) 466.
9. S. B. BABKIN and V. A. BOKIJ, *Fizika Goreniya iVzryva.* **29** (1993) 67.
10. Z. A. MUNIR and U. ANSELMY-TAMBURNI, *Mater. Sci. Rept.* **3** (1989) 277.
11. J. B. HOLT, D. D. KINGMAN and G. M. BIANCHINI, *Mater. Sci. and Eng.* **71** (1985) 321.
12. S. KUMAR, in dissertations, State University of New York, Buffalo, 1988.
13. W. RICE, *J. Mater. Sci.* **26** (1991) 6533.
14. A. G. MERZHANOV, *Arch. Procesow Spalania* **5** (1974) 17.
15. M. G. LAKSHMIKANTHA, A. BHATTACHARYA and J. A. SEKHAR, *Metall. Trans.* **23A** (1992) 23.
16. A. K. BHATTACHARYA, *J. Mater. Sci.* **27** (1992) 3050.

Received 21 September 1998
and accepted 2 January 1999