

# Synthesis of Non-oxide Ceramic Powders by Carbothermal Reduction of a Combustion Synthesis Precursor

M.L. Qin<sup>\*</sup>, A.M. Chu, H.F. Lu, B.R. Jia, L. Zhang, H.Q. Yin, X.H. Qu

School of Materials Science and Engineering, State Key Laboratory for Advanced Metals and Materials, Beijing Key Laboratory for Powder Metallurgy and Particulate Materials, University of Science and Technology Beijing, Beijing, P. R. China, 100083  
<sup>\*</sup>qinml@mater.ustb.edu.cn,

## ABSTRACT

A novel method of synthesizing non-oxide ceramic powders by the combination of low temperature combustion synthesis (LCS) and carbothermal reduction is introduced in this paper. Firstly, a homogeneous precursor consisting of fine oxide and carbon particles was prepared by the LCS method using a mixed solution. Subsequently, the non-oxide ceramic powders were fabricated by the carbothermal reduction of the LCS precursor. Several kinds of nanosized non-oxide ceramic powders including AlN, TiN, ZrC, and SiC were successfully synthesized by this modified carbothermal reduction route. The advantages of LCS, such as energy saving, easiness and quickness, well-defined chemical compositions, and homogeneous distribution of the elements can be fully taken in this method. Owing to the fact that the carbothermal reduction conditions were improved greatly and the non-oxide ceramics powders with fine particles and uniform distribution were produced at lower temperatures and shorter reaction times.

**Keywords:** Non-oxide ceramic powders, Carbothermal reduction, Low temperature combustion synthesis, Precursors

## 1 INTRODUCTION

Non-oxide ceramics including carbide, nitride, boride, and silicide, and their composites have been applied widely in many fields due to excellent physics and chemical properties [1-11]. The preparation methods of non-oxide ceramics powders include carbothermal reduction (CR) [5-7], direct nitriding or carbonizing of according metal [12, 13], selfpropagating high-temperature synthesis (SHS) [8], and chemical vapor deposition (CVD) [4] et al. Among various methods, the non-oxide ceramic powders prepared by the CR method exhibit high purity, well dispersibility, good sinterability, and the particle size and morphology can be well controlled [9-11]. Moreover, the CR method has already been applied widely in industrialization production due to its low cost and suitable mass production [1-3].

Although the carbothermal reaction mechanisms of preparing non-oxide ceramics powders are varied at present [1-3], many researches indicate that the species, particle size, and mixing homogeneity of starting materials have significant effect on the reaction conditions and properties of the synthesized non-oxide ceramics powders [14-16]. One of the most effective approaches for improving carbothermal reduction conditions and preparing non-oxide ceramics powders with fine granularity is to prepare a homogeneous mixture of oxide and carbon by the chemical method. It is well-known that LCS is one of the most appropriate chemical methods to prepare the oxide-based materials [17-22]. The LCS method exhibits the advantages such as energy saving, easiness and quickness, well-defined chemical compositions, and homogeneous distribution of the elements [17-22].

In present work, the LCS method is modified by adding water-soluble organic carbon source (for example, glucose, sucrose, soluble starch, citric acid et al) to the mixed solution of the aim nitrate (or the soluble material of including target elements and nitric acid) and organic fuel. The uniform mixing of the target elements and organic carbon source on the atomic or molecular level can be successfully achieved in solution. As the combustion reaction takes place, the nitrate and the organic carbon source are transformed into fine oxide and carbon particles respectively by the heat generated in the reaction, and the oxide particles are uniformly dispersed into the carbon matrix which is formed by the dehydration and carbonization of organic carbon source. In this way, a precursor that contains a homogeneous mixture of very fine oxide and carbon particles can be obtained. Several kinds of precursors consisting of fine oxide and carbon particles were firstly prepared by the LCS method using aluminum nitrate, zirconium nitrate, titanium sulfate, silica sol, nitric acid, urea, glucose, etc. as raw materials. Subsequently, the prepared precursors were successfully transformed into several kinds of non-oxide ceramics powders such as AlN, TiN, ZrC, and SiC by the modified CR method.

## 2 EXPERIMENTAL SECTION

All the chemicals are of analytical grade. Although the

procedure is very general, we focus in this first contribution on the synthesis of AlN. In a typical synthesis for the preparation of AlN powders, aluminum nitrate (37.5 g), urea (6 g), and glucose (26.4 g) were dissolved in distilled water (200 ml) in a 2000 ml glass, and subsequently the solution was heated in air on an electrical furnace to prepare the precursor. As the heating continued, the solution swelled accompanying with the release of a lot of gases. The whole process only took several minutes resulting in a porous and foamy mixture of (Al<sub>2</sub>O<sub>3</sub>+C) precursor. The nitridation reaction of the precursor was performed in a tube furnace. The precursor was heated at 1400 °C for 3 h with a 1 L/min flow rate of nitrogen. Similarly, a LCS precursor of (SiO<sub>2</sub>+C) mixture, derived from silicic acid, polyacrylamide, nitric acid, urea, and glucose mixed solution, was maintained at 1500 °C for 3 h with a 0.5 L/min flow rate of argon to obtain SiC powders. Then, a LCS precursor of (TiO<sub>2</sub>+C) mixture, derived from titanium nitrates (prepared by precipitation method using titanium tetrachloride as materials), citric acid, and glucose mixed solution, was heated to 1100 °C for 3 h with a 1 L/min flow rate of nitrogen to prepare TiN powders. Moreover, a LCS precursor of (ZrO<sub>2</sub>+C) mixture, derived from zirconium nitrate, urea, and glucose mixed solution, was heated to 1500 °C for 3 h with a 1 L/min flow rate of argon to prepare ZrC powders. The particle size and morphology of four kinds of precursors exhibit obvious diversity (Fig. 1), which may be ascribed to the nature of materials composition in different solution systems.

X-ray diffraction study of the calcined products was carried out in an X-ray diffractometer using CuK $\alpha$  radiation (XRD, Rigaku, D/max-RB12). XRD results and the MDI Jade software package were used to determine the lattice parameters of the synthesized powders. The particle size and morphology of precursors and calcined products were observed by scanning electron microscopy (SEM, JSM-6301F) and field emission scanning electron microscopy (FE-SEM, JSM-6701F), respectively.

### 3 RESULTS AND DISCUSSION

Fig. 2 shows the typical XRD patterns and FESEM images of four kinds of products. It is obvious in Fig. 2a that the sample, synthesized at 1400 °C, exhibits only the peaks corresponding to AlN, indicating that pure hexagonal AlN (JCPDS card 25-1133) is obtained via the modified CR route. Moreover, the AlN powders exhibit well-dispersed spherical particles with diameter of 50-80 nm. In another run, SiC is obtained successfully by a similar route. Fig. 2b demonstrates the XRD pattern and FESEM image of the SiC product synthesized at 1500 °C. The XRD pattern revealed the presence of  $\beta$ -SiC (JCPDS card 29-1129). A low-intensity peak at about  $2\theta=33.6^\circ$  can be indexed to the stacking faults [23], which is marked with SF. SiC powders are mostly comprised of spherical particles with diameter of 80-120 nm, and contain minor amount of rod-shape crystals with a diameter of 100 nm and a length of up to several micrometers (Fig. 2b). Fig. 2c shows the XRD pattern and FESEM image of TiN powders synthesized at 1100 °C for 3 h. The XRD pattern displays the formation of TiN phase. The lattice parameter is calculated to be  $a=4.241 \text{ \AA}$ , which is in good agreement with cubic TiN (JCPDS card 38-1420,  $a=4.242 \text{ \AA}$ ). The synthesized TiN powders exhibit well-dispersed spherical particles with diameter of 80-100 nm, as shown in Fig. 2c. Furthermore, ZrC has also been synthesized successfully by a similar route. It is obvious in Fig. 2d that the pure-phase of ZrC is observed in the 1500 °C sample. The lattice parameter is calculated to be  $a=4.692 \text{ \AA}$ , which is nearly consistent with cubic ZrC (JCPDS card 35-0784,  $a=4.693 \text{ \AA}$ ). The ZrC powders, synthesized at 1500 °C, consist of well-distributed spherical particles ranging from 80 to 120 nm (Fig. 2d).

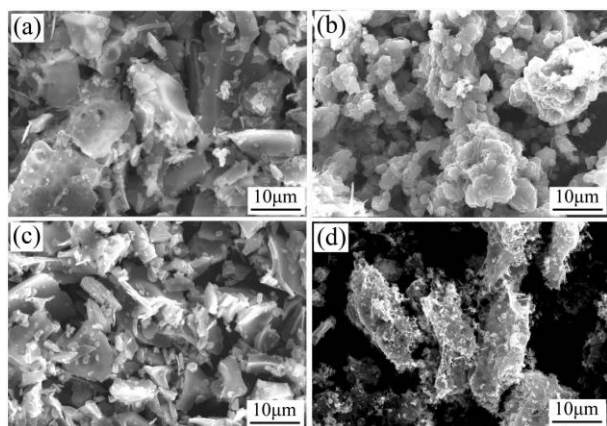


Figure 1: SEM images of precursors: (a) Al<sub>2</sub>O<sub>3</sub>+C; (b) SiO<sub>2</sub>+C; (c) TiO<sub>2</sub>+C; (d) ZrO<sub>2</sub>+C

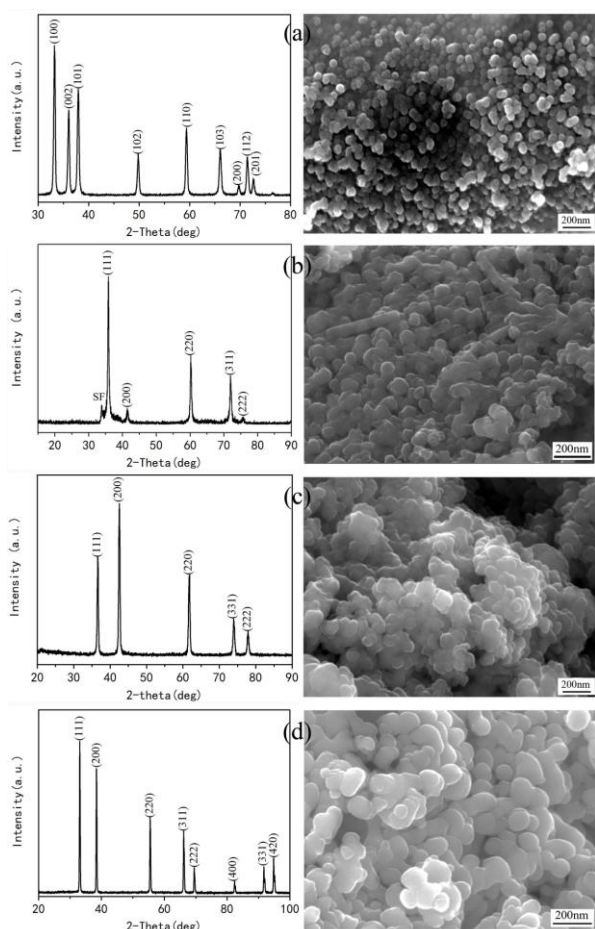


Figure 2: XRD patterns and FESEM images of synthesized products: (a) AlN; (b) SiC; (c) TiN; (d) ZrC

## 4 CONCLUSIONS

A novel preparation method of non-oxide ceramics powders by combining the LCS and CR is presented in this paper. It utilizes adequately the advantages of LCS and CR methods, which can produce non-oxide ceramic powders with high-quality at low cost and in large scale. This work has broadened the applications of the LCS (LCS is usually just used as the method for the synthesis of oxide ceramic powders) and enriched the theory and practice of the combustion synthesis. And this study would be of great importance in promoting the use of LCS method for the synthesis of other nanosized non-oxide ceramics powders such as WC, WN, MoC, MoN, VN, TiB<sub>2</sub>, BN, Si<sub>3</sub>N<sub>4</sub>, and so on.

## ACKNOWLEDGEMENTS

This work is financially supported by National Natural Science Foundation Program of China (50802006) and (51172017), Natural Science Foundation Program of

Beijing (2102028), and the Fundamental Research Funds for the Central Universities.

## REFERENCES

- [1] M. Hnatko, D. Galusek and P. Sajgalik, *J. Eur. Ceram. Soc.* 24, 189, 2004.
- [2] J.M. Gao, H.N. Xiao and H.Q. Du, *Ceram. Int.* 29, 655, 2003.
- [3] H. Preiss, L.M. Berger and D. Schultze, *J. Eur. Ceram. Soc.* 19, 195, 1999.
- [4] J. Wagner, C. Mitterer, M. Penoy, C. Michotte, W. Wallgram and M. Kathrein, *Int. J. Refract. Met. Hard Mater.* 26, 120, 2008.
- [5] E.J. Res, C.D.A. Brady and G.T. Burstein, *Mater. Lett.* 62, 1, 2008.
- [6] L. Baca, N. Stelzer, *J. Eur. Ceram Soc.* 28, 907, 2008.
- [7] L.C. Pathak, A.K. Ray and S. Das, *J. Am. Ceram. Soc.* 82, 257, 1999.
- [8] R.C. Juang, C.C. Chen, J.C. Kuo, T.Y. Huang and Y.Y. Li, *J. Alloys Compd.* 48, 928, 2009.
- [9] M.L. Qin, X.L. Du, Z.X. Li, I.S. Humail and X.H. Qu, *Mater. Res. Bull.* 43, 2954, 2008.
- [10] A. Sinha, T. Mahata and B.P. Sharma, *J. Nucl. Mater.* 301, 165, 2002.
- [11] J.B. Claridge, A.P.E. York, A.J. Brungs and M.L.H. Green, *Chem. Mater.* 12, 132, 2000.
- [12] C.M. Balkas, R.F. Davis, *J. Am. Ceram. Soc.* 79, 2309, 1996.
- [13] A.S. Bolokang, M. Phasha, *Int. J. Refract. Met. Hard Mater.* 28, 610, 2010.
- [14] X.T. Li, X.H. Chen and H.H. Song, *J. Mater. Sci.* 44, 4661, 2009.
- [15] V. Raman, G. Bhatia, S. Bhardwaj, A.K. Srivastva and K.N. Sood, *J. Mater. Sci.* 40, 1521, 2005.
- [16] Y. Zheng, R. Wang and K.M. Wei, *J. Mater. Sci.* 43, 5331, 2008.
- [17] K.C. Patil, J.J. Kingsley, *Mater. Lett.* 11-12, 427, 1988.
- [18] X.Y. Deng, W. Li, B. Liu, Y. Qu, B.X. Xu and H. Zuo, *Mater. Lett.* 64, 1150, 2010.
- [19] T. Aarathi, G. Madras, *Catalysis. Communications.* 9, 630, 2008.
- [20] H. Mohebbi, T. Ebadzadeh and F.A. Hesari, *J. Powder Sources.* 178, 64, 2008.
- [21] J. Kishan, V. Mangam, B.S.B. Reddy, S. Das and K. Das, *J. Alloys. Compd.* 490, 631, 2010.
- [22] R.D. Purohit, B.P. Sharma, K.T. Pillai and A.K. Tyagi, *Mater. Res. Bull.* 36, 2711, 2001.
- [23] K. Okada, H. Kata and K. Nakajima, *J. Am. Ceram Soc.* 77, 1691, 1994.