Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 1871–1876

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Air-exposed combustion synthesis of Al_2O_3 nanofibers in $Al/TiO_2/C$ system

H. Amel-Farzad[a,b,*], J. Vahdati-Khaki[c], A. Haerian[d]

[a]Department of Materials, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran
[b]Department of Materials Engineering, Faculty of Engineering, Bu-Ali Sina University, Hamedan, Iran
[c]Department of Materials and Metallurgical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[d]Department of Mechanical Engineering, Faculty of Engineering, Sadjad Institute of Higher Education, Mashhad, Iran

Received 25 May 2012; received in revised form 12 August 2012; accepted 12 August 2012
Available online 18 August 2012

Abstract

TiC/Al_2O_3 composite was synthesized through air-exposed combustion synthesis using $Al/TiO_2/C$ initial mixture. Al_2O_3 was formed as fibers of submicron/nanometer thickness and several microns length on the external and internal pores. The nanofibers were considered to be synthesized directly through simultaneous oxidation and condensation of air-exposed Al vapor. Bundles of Al_2O_3 nanofibers were synthesized by diluting the stoichiometric system by nano-sized Al–33%Al_2O_3 mixture. The effect was considered as a result of significant increase in Al free surface area, and hence the Al/atmospheric-O_2 reaction front. Metal/gas combustion synthesis was considered as a method for producing metal oxide/nitride nanofibers.

Keywords: Al_2O_3 nanofibers; Combustion synthesis; TiC/Al_2O_3 composite

1. Introduction

Combustion synthesis, also called self-propagating high-temperature synthesis (SHS), is a technique for producing a wide range of materials, mostly ceramics and intermetallics [1]. In this method, the reaction takes place through a highly exothermic reaction similar to wick burning. The reaction is ignited externally. The heat released must be large enough to ignite the reaction in the adjacent points to keep the SHS wave stable. The more negative the enthalpy of formation, the stronger the combustion. It has been empirically proposed that if the maximum adiabatically achievable temperature (T_{ad}) is higher than 1800 K [2] or 2000 K [3], then the SHS wave will be stable. Refusing the heat leakage and also the kinetic parameters such as particles surface contact, T_{ad} can be calculated as

$$\Delta H = \int_{T_0}^{T_{ad}} \sum c_{p,\ products}.dT \quad (1)$$

More recently, salt-added combustion systems of much lower T_{ad} have been reported in the literature, in which, the presence of salt helps the formation of products with very fine particle sizes [4–7]. SHS has recently been optimized for mass production of nanopowders [4–6].

Several cases of formation of fibers and also rods of micron or submicron diameter through SHS have been reported in the literature. Most of these cases are limited to the synthesis of nitrides (mostly Si_3N_4 [8–14] and AlN [15–20]) and oxides (usually Al_2O_3 [21,22]) but not carbides, borides, silicides, etc. Formation of MgO and SiAlON fibers has also been reported [23–26]. Oxide fibers have also been observed even in metal/metal combustion reactions performed in atmospheric air [27]. In this work the widely used TiC/Al_2O_3 composite was produced [28–33]. Regardless of the results discussed in the previous work, this article concentrates on the morphological aspects of the products [34].

*Corresponding author at: Department of Materials Engineering, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran. Tel.: +98 915 507 3285.
E-mail address: hh_amel@yahoo.com (H. Amel-Farzad).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.08.035

Table 1
The purity level of initial components as determined by chemical titration.

Powder	Al	C	TiO_2
Purity (%)	99.65	99.94	99.95

2. Experimental procedure

In this work the following reaction was used to produce the widely used TiC/Al_2O_3 composite [28–33]:

$$3TiO_2 + 4Al + 3C \rightarrow 3TiC + 2Al_2O_3$$

In this system T_{ad} is about 2065 °C, and 100% of the produced Al_2O_3 melts at 2052 °C which keeps the temperature from rising up to about 2580 °C (the indistinctness comes from the approximation of the available thermodynamic data). Additionally, diluting the system with Al and/or Al_2O_3 was studied, which can be presented as

$$3TiO_2 + (4+x)Al + 3C + yAl_2O_3 \rightarrow$$
$$3TiC + (2+y)Al_2O_3 + xAl$$

Table 1 shows the degree of purity of the initial powders determined by chemical titration. The morphologies of the precursor particles are shown in Fig. 1a–c. Prior to SHS, the powders were mixed in a very low energy ball mill for 15 min using several 3 mm diameter balls. An ignition setup, containing a preheating system and electric arc equipment, was assembled and used to stimulate the reactions (Fig. 2). Test samples were cylinders of 6 mm diameter and 15 mm height, with various raw densities.

After SHS, some samples were fractured intentionally for microscopic evaluation of the inner free surfaces as well as the outer ones. EDS results are presented in Figs. 4 and 5. Since fibrous morphology was observed in all the surfaces, the idea was proposed to relate the morphology with the solid/gas reaction. So, an Al/atmospheric-air SHS reaction was designed to evaluate the effect of removing the other components on the final morphology. Similar SEM evaluations were carried out on the products. Various degrees of dilution and also a range of relative raw densities were evaluated, as explained before [14].

3. Observations

It was found out that the combustion was not a case of classical ''solid flame'', but a flame surrounded the sample, especially those diluted with Al (Fig. 3). Additionally, significant sputtering of materials from the burning sample was observed (Fig. 3). SEM micrographs showed fully fibrous microstructures of submicron diameter on all free surfaces, both outer surfaces and internal pores surfaces (Figs. 4–6). EDS results indicated that fibers are alumina. Diluting the stoichiometric mixture with Al_2O_3 made the fibers thicker and straighter (Fig. 5), while, additional Al particles made them thinner (Fig. 6). Diluting the system

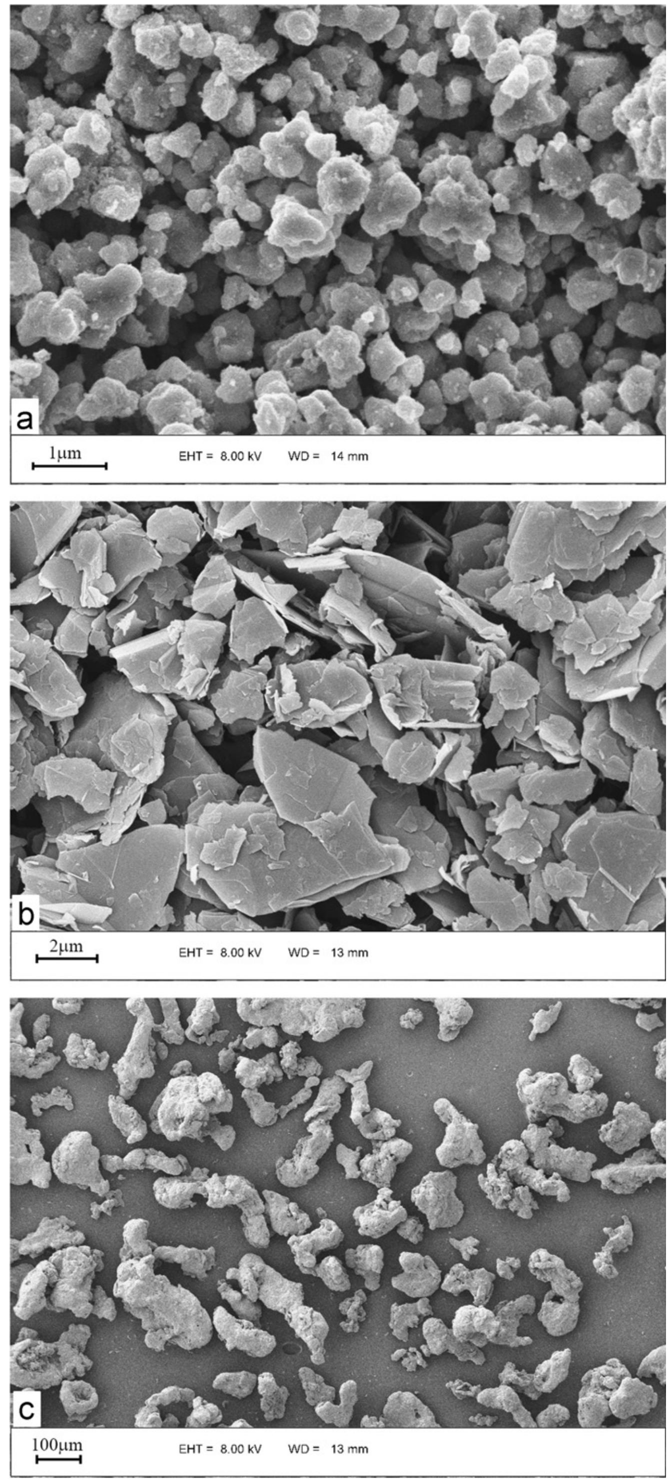

Fig. 1. Initial powders under SEM (a) TiO_2, (b) C and (c) Al.

with severely ball milled Al-33%wtAl_2O_3 mixture (with particle diameter of 100–200 nm) was also assessed in the present work. It was found that increasing the amount of such diluents, caused more intense SHS reaction, which was a rather unexpected result. In this case, bundles of alumina nanofibers a few hundreds of nanometers or less in thickness with several tens of micrometers length and aspect ratio of about 1000 were found (Fig. 7).

4. Discussion

In all other works reporting of the fibrous morphology in the SHS products the combustion has taken place in metal/gas mode [8–27]. Apparently, this is the key for combustion synthesis of ultrafine/nano-sized ceramic fibers. Metal/gas SHS reactions with oxide and nitride products provide some unique possibilities necessary for fibers formation. Firstly, their adiabatic temperature is much higher than those of similar carbides and borides, etc. This is usually higher than the boiling temperature of metallic component of the initial mixture, which makes it evaporate as a result of the reaction in adjacent points. Secondly, oxides or nitrides whiskers can form directly through simultaneous vapor-metal/gas reaction and condensation of the products. Thirdly, the metal/gas reactions provide much larger reaction front area, rather than solid/solid reactions, which can cause the metal to evaporate more easily. The reaction front area is an effective parameter which has always been mentioned in SHS studies of both solid/solid and solid/gas reactions [1,4]. Of course, this phenomenon is much more effective in reactants of nano-sized scale [16]. Even solid/solid reactions are highly intensified using nano-sized particles [27,35].

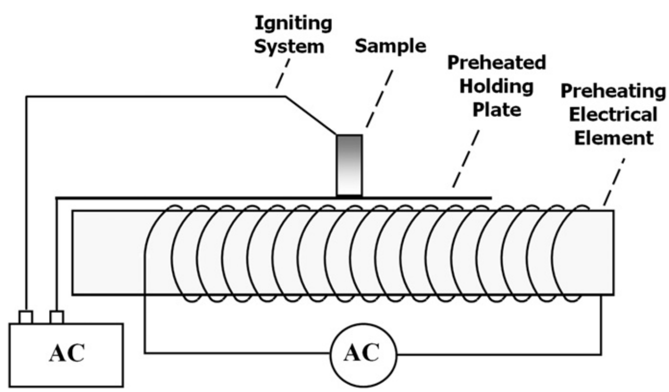

Fig. 2. The air-exposed handmade SHS setup sketch.

Recently, Shi et al. reported the synthesis of AlN through salt assisted Al/N_2 reaction, under 0.25 MPa pressure of N_2 [19]. The morphology of these nanowhiskers was quite similar to those presented in Fig. 4. Similar to the present work, their Al spheres had reacted with N_2 gas and crystallized as AlN nanowhiskers with outwards radial alignment. Their Al particles were finer than those used in this study and some other minor conditions were different. The fibrous morphology was visible in the outer shell of 5–15 μm thickness of the Al particles.

As has been discussed elsewhere, it was found that some of the initial Al/atmospheric-O_2 reaction had replaced Al/TiO_2 reaction [7]. Since the initial Al particles were 2–3 orders of magnitude larger than the other ones, the reaction had to occur on Al particle surfaces and the spaces between them. It was found that as a result of Al/atmospheric-O_2 reaction, the temperature was much higher than the predicted value of 2065 °C. This phenomenon is much more intense especially when diluting the system with ultrafine Al/Al_2O_3 mixture with nanoscale particles and very large specific surface area. This caused Al to evaporate from the free surfaces and subsequently condense directly with fibrous morphology. Similar phenomenon is reported in the article by Hunt et al. which is for air-exposed Ni/Al combustion reaction [27]. They reported that

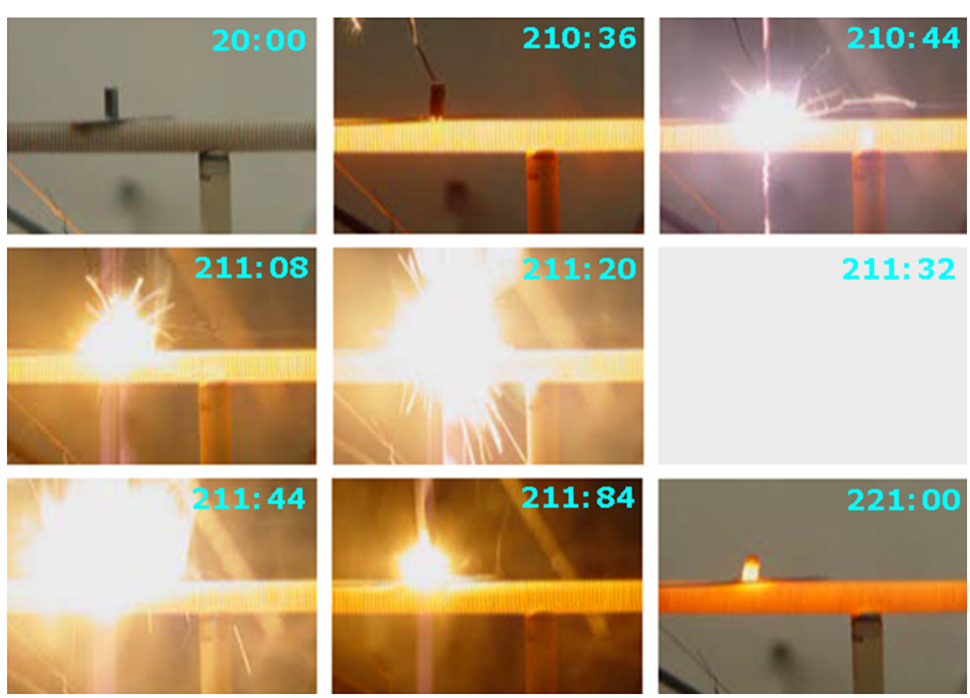

Fig. 3. Successive frames of SHS reaction. The electric arc is clearly seen in the second frame. The solid/gas reaction steps are clear in the subsequent frames.

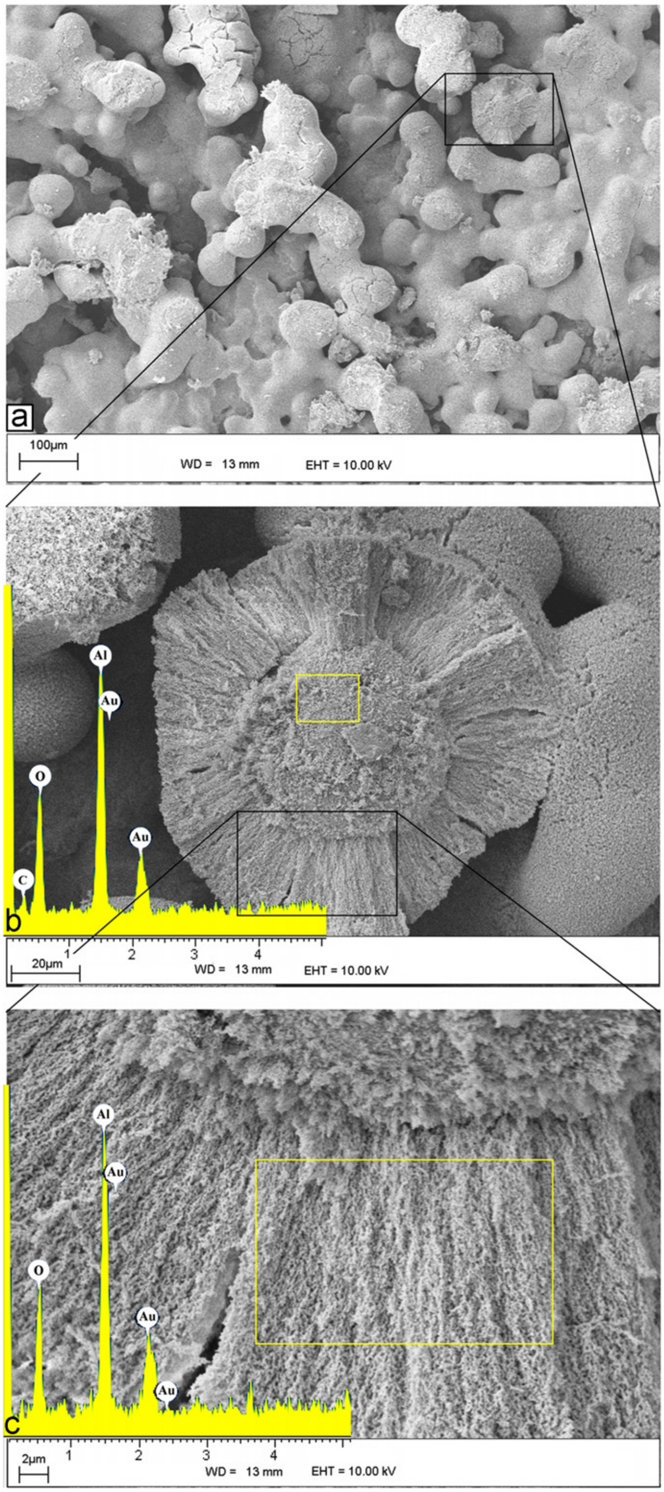

Fig. 4. Air-exposed external surface of the stoichiometric sample under SEM and related EDS results. Compare the particle sizes in (a) with those in Fig. 1c. An unintentionally fractured part is shown in (b) and (c) in higher magnifications, in which Al_2O_3 fibers are more visible. EDS tests are taken from the light-colored rectangular region.

in contrast to microscale Al particles, nanoscale Al particles have reacted with atmospheric O_2 leading to Al_2O_3 nanofibers formation.

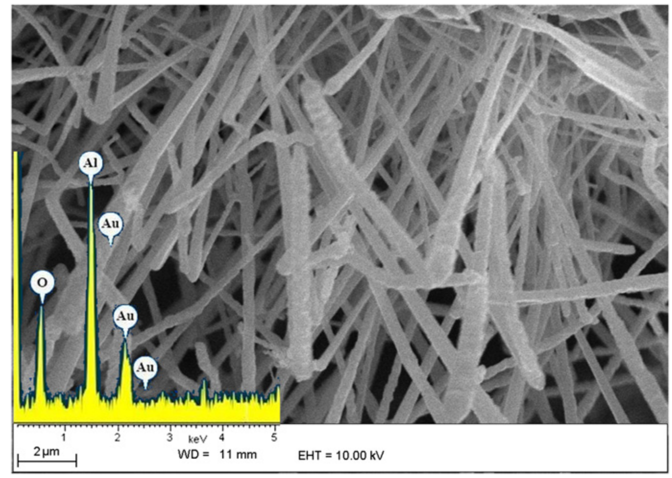

Fig. 5. Al_2O_3 fibers grown inside the pores of an Al_2O_3-diluted sample.

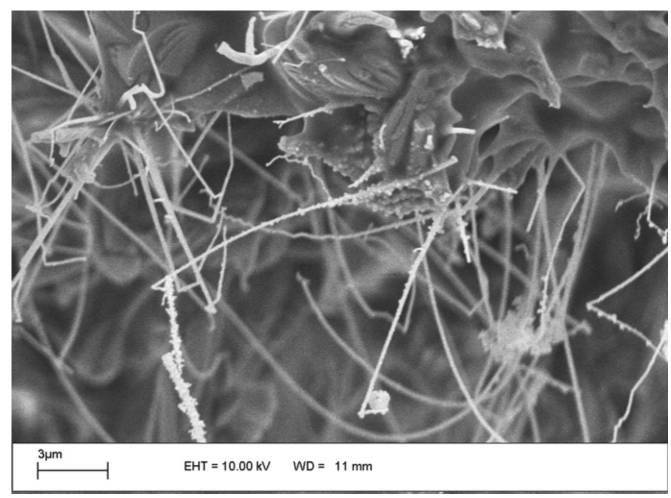

Fig. 6. Al_2O_3 fibers grown inside the pores of an coarse-Al-diluted sample. EDS test could not be carried out.

It should be noted that the presence of fine particles with higher melting temperature (TiC and C) keeps the Al particles from coalescence, which may lead to significant decrease in reaction front area.

In short, metal/gas reactions have all the necessary conditions for synthesis of nanofibers. This probably means that ultrafine/nanometric fibers of most metallic oxides and nitrides with aspect ratio of the order of 1000 can theoretically be combustion synthesized though Metal/O_2 and Metal/N_2 SHS reactions.

5. Conclusion

1. Large amounts of Al_2O_3 nanofibers were fabricated through air-exposed combustion synthesis in Al/TiO_2/C system.
2. It was considered that they formed during Al/atmospheric-O_2 reaction.
3. Diluting the system with highly reactive ultrafine Al particles led to formation of bundles of Al_2O_3 nanofibers.

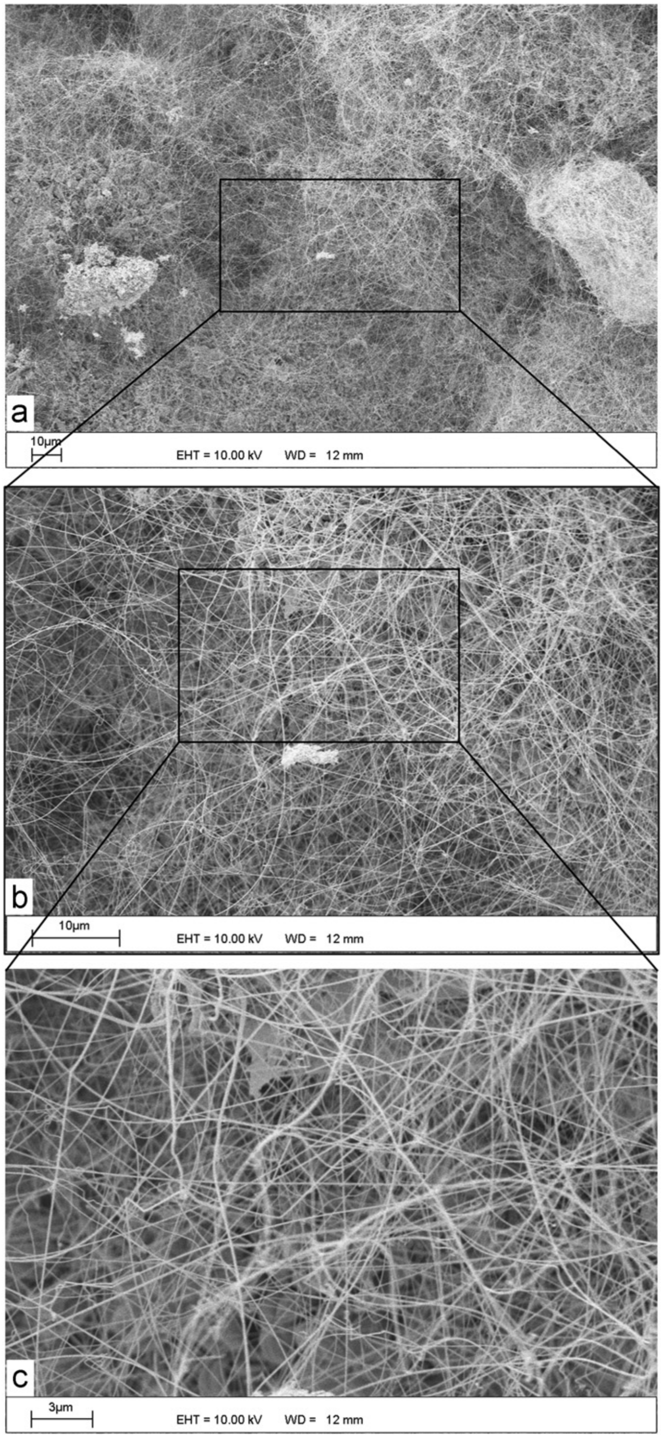

Fig. 7. Bundles of Al_2O_3 nanofibers (more than 100 μm in length and about 100 nm thick, with length/thickness ratio of about 1000) shown in different magnifications. The fibers had grown inside the pores of the sample diluted with ultrafine Al/Al_2O_3 mixture.

Additionally, it can probably be proposed that most metallic oxides and nitrides can theoretically be synthesized though Metal/O_2 and Metal/N_2 SHS reactions.

4. The Al_2O_3 fibers formed in Al_2O_3-diluted samples were much straighter and thicker (over 500 nm) than the fibers in the Al-diluted samples few hundred nanometers or less. Especially, in the samples diluted with ball milled ultrafine Al/Al_2O_3 mixture, bundles of fibers of about such thickness and several tens of microns length were formed, which was essentially considered to be the result of their very large surface area.
5. It is concluded that, the metal/gas combustion reactions can systematically lead to metal oxide/nitride nanofibers with aspect ratio of the order of 1000.

References

[1] Z.A. Munir, U. Anselmi-Tamburini, Self-propagating high-temperature synthesis of hard materials, in: R. Riedel (Ed.), Handbook of Ceramic Hard Materials, Wiley-VCH, 1999, pp. 322–373.
[2] N.P. Novikov, I.P. Borovinskaya, A.G. Merzhanov, Thermodynamic analysis of SHS reactions, in: A.G. Merzhanov (Ed.), Combustion Processes in Chemical Technology and Metallurgy, 1975.
[3] Z.A. Munir, U. Anselmi-Tamburini, Self-propagating exothermic reactions: the synthesis of high-temperature materials by combustion, Materials Science Reports 3 (1989) 277–365.
[4] C.W. Won, H.H. Nersisyan, H.I. Won, J.H. Lee, Refractory metal nanopowders: synthesis and characterization, Current Opinion in Solid State and Materials Science 14 (2010) 53–68.
[5] E.L. Dreizin, Metal-based reactive nanomaterials, Progress in Energy and Combustion Science 35 (2009) 141–167.
[6] H.I. Won, H.H. Nersisyan, Ch.W. Won, A macrokinetic study of the WO_3/Zn reaction diluted with NaCl, Chemical Engineering Journal 153 (2009) 193–198.
[7] J. Wang, Y. Wang, M. Qiao, S. Xie, K. Fan, A novel sol–gel synthetic route to alumina nanofibers via aluminum nitrate and hexamethylenetetramine, Materials Letters 61 (2007) 5074–5077.
[8] J.G. Xu, H.A. Zhang, G.J. Jiang, B.L. Zhang, W.I. Li, SiC whisker reinforced $MoSi_2$ composite prepared by spark plasma sintering from CoSHS-ed powder, Transactions of Nonferrous Metals Society of China 16 (2006) 504–507.
[9] Ch. Dianying, Zh. Baolin, Zh. Hanrui, L. Wenlan, X. Suying, Synthesis of β-Si_3N_4 whiskers by SHS, Materials Research Bulletin 37 (2008) 1481–1485.
[10] H. Wang, J.C. Han, Sh. Du, Effect of nitrogen pressure and oxygen-containing impurities on self-propagating high temperature synthesis of Si_3N_4, Journal of the European Ceramic Society 21 (2001) 297–302.
[11] G. Peng, G. Jiang, H. Zhuang, W. Li, S. Xu, Fabrication of β-Si_3N_4 whiskers by combustion synthesis with $MgSiN_2$ as additives, Materials Research Bulletin 40 (2005) 2139–2143.
[12] W. Li, D. Chen, B. Zhang, H. Zhuang, W. Li, Effect of rare-earth oxide additives on the morphology of combustion synthesized rod-like h-Si_3N_4 crystals, Materials Letters 58 (2004) 2322–2325.
[13] J. Xu, G. Jiang, W. Li, H. Zhuang, B. Zhang, L. Chen, In situ synthesis of SiCW/$MoSi_2$ composite through SPS process, Journal of Alloys and Compounds 462 (2008) 170.
[14] A.V. Gabrielyan, Kh.V. Manukyan, S.L. Kharatyan, Comparative study of combustion laws for Mo–Si–N and W–Si–N ternary systems, Journal of Alloys and Compounds 454 (2008) 394–399.
[15] R. Fu, K. Chen, S. Agathopoulos, J.M.F. Ferreira, Factors which affect the morphology of AlN particles made by self-propagating high-temperature synthesis (SHS), Journal of Crystal Growth 296 (2006) 97–103.
[16] A. Gromov, V. Vereshchagin, Study of aluminum nitride formation by superfine aluminum powder combustion in air, Journal of the European Ceramic Society 24 (2004) 2879–2884.
[17] I.G. Cano, M.A. Rodrıguez, Synthesis of β-silicon nitride by SHS: fiber growth, Scripta Materialia 50 (2004) 383–386.

[18] A. Mukasyan, Combustion synthesis of nitrides: mechanistic studies, Proceedings of the Combustion Institute 30 (2005) 529–2535.
[19] Zh. Shi, M. Radwan, S. Kirihara, Y. Miyamoto, Zh. Jin, Formation and evolution of quasi-aligned AlN nanowhiskers by combustion synthesis, Journal of Alloys and Compounds 476 (2009) 360–365.
[20] H. Wang, J.C. Han, Zh. Li, Sh. Du, Effect of additives on self-propagating high-temperature synthesis of AlN, Journal of European Ceramic Society 21 (2001) 2193–2198.
[21] X. Zhu, T. Zhang, V. Morris, D. Marchant, Combustion synthesis of $NiAl/Al_2O_3$ composites by induction heating, Intermetallics 18 (2010) 1197–1204.
[22] L.S. Abovyan, H.H. Nersisyan, S.L. Kharatyan, R. Orru, G. Cao, The effect of degassing modes on the self-propagating reactions for the SiO_2–Al–C system in the presence of reaction promoters, Ceramics International 29 (2003) 175–182.
[23] S.V. Aydinyan, Zh. Gumruyan, Kh.V. Manukyan, S.L. Kharatyan, Self-sustaining reduction of MoO_3 by the Mg–C mixture, Materials Science and Engineering B 172 (2010) 267–271.
[24] G. Liu, K. Chen, H. Zhou, C. Pereira, S. Quaresma, J.M.F. Ferreira, Preparation of Y-SiAlON rod-like crystals and whiskers by combustion synthesis, Materials Letters 59 (2005) 3955–3958.
[25] C.L. Yeh, F.S. Wu, Y.L. Chen, Effects of α- and β-Si_3N_4 as precursors on combustion synthesis of (α+β)-SiAlON composites, Journal of Alloys and Compounds 509 (2011) 3985–3990.
[26] G. Liu, K. Chen, H. Zhou, K. Ren, Jiangtao Li, C. Pereira, J.M.F. Ferreira, Formation of β-SiAlON micropalings consisting of nanorods during combustion synthesis, Scripta Materialia 55 (2006) 935–938.
[27] E.M. Hunt, K.B. Plantier, M.L. Pantoya, Nano-scale reactants in the self-propagating high-temperature synthesis of nickel aluminide, Acta Materialia 52 (2004) 3183–3191.
[28] J.H. Lee, S.K. Ko, C.W. Won, Combustion characteristics of $TiO_2/Al/C$ system, Materials Research Bulletin 36 (2001) 1157–1167.
[29] Q. Hu, P. Luo, Y. Yan, Influence of an electric field on combustion synthesis process and microstructures of TiC–Al_2O_3–Al composites, Journal of Alloys and Compounds 439 (2007) 132–136.
[30] A. Slocombe, L. Li, Selective laser sintering of TiC-Al_2O_3 composite with self-propagating high-temperature synthesis, Journal of materials Processing Technology 118 (2001) 173–178.
[31] G. Golkar, S.M. Zebarjad, J. Vahdati-Khaki, Role of nano-size TiO_2 particles on the crystallite size of microwave-combustion synthesized Al_2O_3/TiC composite, Journal of Alloys and Compounds 504 (2010) 566–572.
[32] D. Atong, D.E. Clark, Ignition behavior and characteristics of microwave-combustion synthesized Al_2O_3-TiC powders, Ceramics International 30 (2004) 1909–1912.
[33] G. Golkar, S.M. Zebarjad, J. Vahdati-Khaki, Optimizing the ignition behavior of microwave-combustion synthesized Al_2O_3/TiC composite using Taguchi robust design method, Journal of Alloys and Compounds 487 (2009) 751–757.
[34] H. Amel-Farzad, J. Vahdati-Khaki, A. Haerian, A. Youssefi, Combustion wave stability in diluted $TiO_2/Al/C$ system in atmospheric air, Solid State Sciences 10 (2008) 1958–1969.
[35] C. Farley, T. Turnbull, M.L. Pantoya, E.M. Hunt, Self-propagating high-temperature synthesis of nanostructured titanium aluminide alloys with varying porosity, Acta Materialia 59 (2011) 2447–2454.