ELSEVIER

Ceramics International 33 (2007) 379–383

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Combustion synthesis and compaction of Si_3N_4–TiN composite powder

Kh.V. Manukyan [a], S.L. Kharatyan [a,b], G. Blugan [c,*], J. Kuebler [c]

[a] *Department of Chemical Physics, Yerevan State University, 375025 Yerevan, Armenia*
[b] *Laboratory of Kinetics of SHS Processes, A.B. Nalbandyan Institute of Chemical Physics*
National Academy of Sciences of Armenia, 375014 Yerevan, Armenia
[c] *Empa, Materials Science and Technology, Laboratory of High Performance Ceramics, 8600 Duebendorf, Switzerland*

Received 21 June 2005; received in revised form 15 July 2005; accepted 4 October 2005

Abstract

The possibilities for combustion synthesis of TiN–Si_3N_4 composite powders were investigated using different titanium silicides (TiSi, Ti_5Si_3, $TiSi_2$) as initial raw materials. Thermodynamic analysis and relevant experiments have shown that at relatively low nitrogen pressure (up to 5 MPa) Ti_5Si_3 is the most suitable compound for this purpose. Optimum experimental conditions for synthesizing two-phase silicon-free TiN–Si_3N_4 (containing 30–35 wt.% TiN) composite powders with characteristic sizes of approximately 5–10 μm were determined. Compact discs of 50 mm diameter were fabricated using hot pressing technique. Microstructural features of the composite powder and hot pressed samples were investigated, i.e. biaxial flexure strength.

Keywords: B. Composite; C. Strength; D. Si_3N_4; Combustion synthesis

1. Introduction

It is well known that silicon nitride (Si_3N_4) is an excellent structural ceramic material because of its high strength, hardness and Young's modulus, its good thermal shock and creep resistance, low thermal expansion coefficient and high temperature refractoriness, etc. However, two factors that prevent its widespread use are its relatively low fracture toughness in comparison with metals and high cost of processing, because typically diamond machining of components is required. From this point of view the addition of titanium nitride (TiN) can make Si_3N_4 more attractive for a wide range of applications. In fact the combination of individual properties of TiN and Si_3N_4 yields improved electrical and mechanical properties (including fracture toughness), providing wide use of TiN–Si_3N_4 composites [1–6] which are electro discharge machinable.

These composite materials can be prepared in several ways including mechanical alloying of individual components, reaction bonding, etc. The preparation of particulate composite powders by conventional processing technique can generate large agglomerates and hence limits the degree of microstructural homogenity. Production of composites by in situ synthesis methods can reduce costs and the number of process steps and can result in more homogeneous composites.

Recently, a self-propagating high-temperature synthesis (or combustion synthesis) method [7–9] has been applied for in situ synthesizing of a number of refractory materials and composites on their bases, such as Al_2O_3–SiC, Si_3N_4–$MoSi_2$, Si_3N_4–SiC, etc. [10–12]. TiN–Si_3N_4 composites have been combustion synthesized using a mixture of elemental Si and Ti in a nitrogen atmosphere [13,14]. High exothermicity of the nitridation process is frequently accompanied by melting of components in the interaction zone, which complicates nitrogen infiltration from an external medium to the combustion front and results in incompleteness of the reaction. To prevent this undesirable phenomenon usually an inert diluent (mainly TiN and/or Si_3N_4) is introduced into the initial mixture. According to the study of Hillinger and Hlavacek [13] the amount of such diluents is up to 55–70 wt.%. Another approach for synthesizing the above listed composites is based on using initial compositions, containing compounds instead of individual elements. For example TiN–SiC–Si_3N_4 composites were synthesized from a $TiSi_2$–SiC mixture via a combustion reaction under a nitrogen pressure of 130 MPa [15].

---

* Corresponding author. Tel.: +41 44 823 4119; fax: +41 44 823 4150.
E-mail address: gurdial.blugan@empa.ch (G. Blugan).

0272-8842/$32.00
doi:10.1016/j.ceramint.2005.10.006

The current work is aimed at revealing possibilities of one-stage synthesizing of TiN–Si_3N_4 composite powders by using titanium silicides as the initial raw materials for the preparation of hot pressed samples. Particular attention has been given to synthesizing these materials under low (up to 5 MPa) nitrogen pressure, as well as determining strength and microstructural characteristics of hot pressed samples.

2. Experimental

The experiments on combustion synthesis were carried out in a PC-linked constant pressure reactor using a nitrogen (purity 99.7%) atmosphere at pressures ranging between 0.5 and 5 MPa. Cylindrical pellets of 40 mm in diameter and a height of 35–50 mm were used. The following powders were used as raw materials: in-house SHS-derived titanium silicides (Ti_5Si_3, TiSi, $TiSi_2$) [16] with an average particle size of less than 30 μm and silicon nitride (containing 20 wt.% of α-Si_3N_4) with a particle size of less than 15 μm as an inert diluent. A micro-thermocouple technique was used to register the maximum combustion temperature (T_c). The measurements were carried out with tungsten–rhenium thermocouples having a wire diameter of 100 μm. The average value of the combustion velocity (U_c) was determined by signals from an array of thermocouples embedded into the sample. Burned down samples were exposed to X-ray analysis with Cu Kα radiation on a diffractometer DRON-3.0. Chemical analyses were performed to determine the content of nitrogen and free (non-reacted) silicon in the final products. The particle size distributions of the composite powders were measured using a Malvern Mastersizer X analyzer.

The synthesized composite powder was mixed with 3.5 wt.% Y_2O_3 (H.C. Starck, Grade C) and 2.1 wt.% Al_2O_3 (Alcoa, CT3000SG) as sintering additives with isopropyl alcohol in a ball mill using alumina grinding media. After the milling procedure the alcohol was removed by evaporation. Dried and sieved powders were compacted into discs of 50 mm in diameter by uni-axial pressing. These discs were then hot pressed at 1750 °C for 30 min with a pressure of 25 MPa in a low nitrogen atmosphere. Two hot pressed discs were strength tested by the ring on ring biaxial flexure test method (diameter of outer/inner ring was 40/16 mm) at room temperature. Scanning electron microscopy (BS-300 and Vega TS 5136 MM) was used for studying the microstructure of combustion products as well as of the hot pressed samples.

3. Results and discussion

3.1. Thermodynamic calculations

For estimating the feasibility of the combustion synthesis of TiN–Si_3N_4 composites from various titanium silicides ($TiSi_2$, TiSi, Ti_5Si_3), as well as to reveal optimum conditions of reactions proceeding under the combustion mode, thermodynamic analyses were performed. Adiabatic combustion temperatures and possible equilibrium compositions of synthesized products were calculated using ISMAN-THERMO software [17].

Table 1
The parameters characterizing the combustion of titanium silicides in nitrogen atmosphere, $P = 5$ MPa

Silicide	T_{melt} (°C)	T_{ad} (°C)	Equilibrium composition of products
Ti_5Si_3	2130	2267	5TiN, 3Si
TiSi	1570	2084	TiN, 0.8Si, $0.067Si_3N_4$
$TiSi_2$	1500	2084	TiN, 1.3Si, $0.23Si_3N_4$

In Table 1 results of preliminary thermodynamic calculations of adiabatic combustion temperature and equilibrium composition of products are presented for the above listed titanium silicides. In all cases high adiabatic temperatures do not promote silicon nitridation because of Si_3N_4 dissociation ($T_{dis} = 2084$ °C, at 5 MPa), whereas titanium is nitrided completely. Based on these results it can be concluded that under identical conditions $TiSi_2$ is nitrided better than other silicides.

As the analysis has revealed, for infiltration combustion processes, apart from the thermodynamic calculations, the following two factors are very important: (a) the melting point of the silicide selected and, (b) the amount of fusible component (Si) in this compound. From this viewpoint the Ti_5Si_3 silicide fitted best for further investigation. To check this assumption nitridation of all three silicides under combustion mode was performed. These experiments have shown that at the minimum nitrogen pressure (0.5 MPa) only Ti_5Si_3 possess the ability for combustion, while the other silicides burn at higher pressures ($P(N_2) \geq 2$ MPa). On this basis further studies were performed with Ti_5Si_3. For the purpose of reducing the combustion temperature and excluding the dissociation of silicon nitride the initial charge was diluted by a certain amount of Si_3N_4.

Thermodynamic calculations carried out for the $Ti_5Si_3 + nSi_3N_4 + N_2$ system at $P(N_2) = 5$ MPa (where n is the number of Si_3N_4 moles) have shown (Fig. 1) that for $0.5 < n < 3$ the adiabatic temperature (T_{ad}) remains constant up to reaching the dissociation temperature of Si_3N_4. Accordingly the Si_3N_4 concentration grows, and the amount of free silicon decreases. For $n \geq 3$ the T_{ad} tends to decrease and the product is free of silicon. For further optimization of the synthesis conditions the influence of nitrogen pressure on the value of T_{ad} and the equilibrium composition of the final products the $Ti_5Si_3 + 3Si_3N_4$ mixture was selected. As the results of the thermodynamic calculations have shown (Fig. 2), at low nitrogen pressures (up to 5 MPa) free silicon is present in the combustion products too, this disappears at $P \geq 5$ MPa. At the same time, after a small increase up to 2070 °C, the value of T_{ad} remains constant for the pressure interval 5–10 MPa.

3.2. Combustion in the Ti_5Si_3–Si_3N_4–N_2 system

Combustion experiments of $Ti_5Si_3 + nSi_3N_4$ mixtures in a nitrogen atmosphere were performed based on the preliminary thermodynamic calculations. According to the results obtained (Fig. 3) a combustion limit of $n = 4.5$ was obtained. It can be seen that within the $0 \leq n < 4.5$ interval the combustion

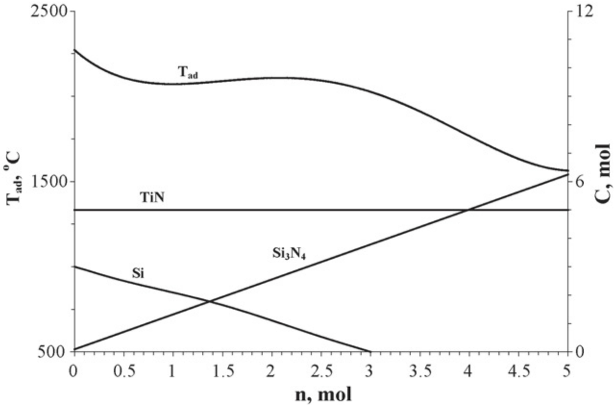

Fig. 1. Adiabatic combustion temperature (T_{ad}) and equilibrium concentration of combustion products for the $Ti_5Si_3 + nSi_3N_4 + N_2$ system at $P = 5$ MPa.

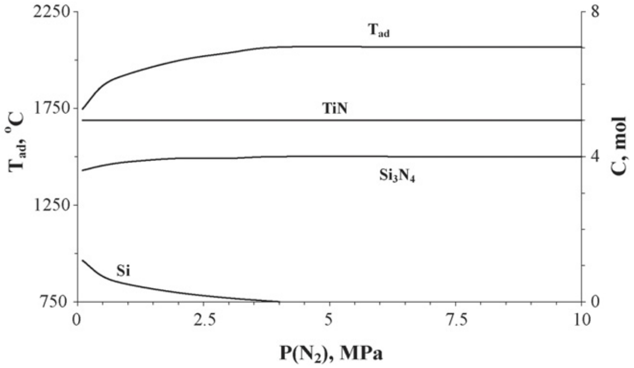

Fig. 2. Adiabatic combustion temperature (T_{ad}) and equilibrium concentration of combustion products vs. nitrogen pressure for the $Ti_5Si_3 + 3Si_3N_4 + N_2$ system.

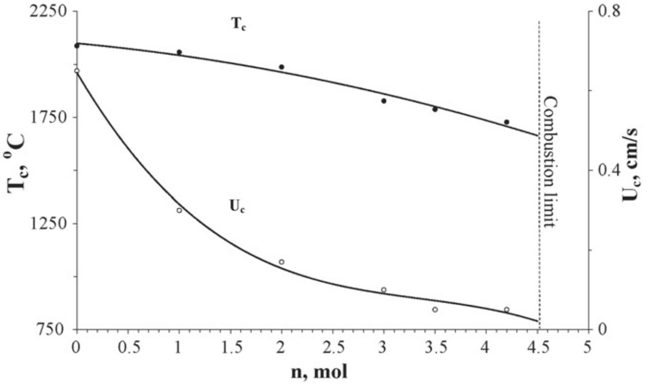

Fig. 3. Combustion temperature (T_c) and velocity (U_c) vs. n value for the $Ti_5Si_3 + nSi_3N_4 + N_2$ system at $P = 50$ MPa.

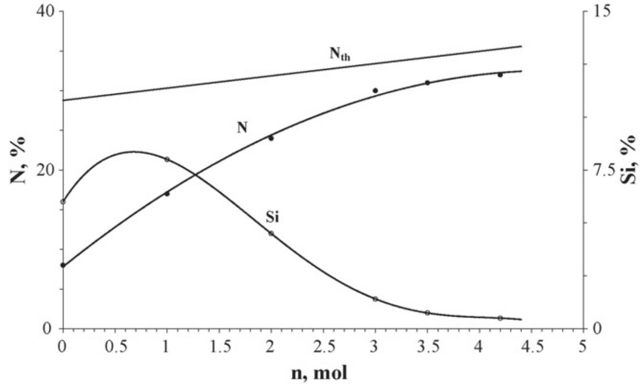

Fig. 4. The theoretical value of bound nitrogen, amount of nitrogen and non-reacted silicon vs. n at combustion of the $Ti_5Si_3 + nSi_3N_4$ mixture in nitrogen atmosphere.

temperature decreases monotonously (from 2084 to 1770 °C), and within the $0 \leq n \leq 3$ interval the combustion velocity is reduced about 6.5 times (from 0.65 down to 0.1 cm/s).

The results of the chemical examinations of burned down samples are presented in Fig. 4. It is obvious that depending on the n value the nitrogen content in the combustion products can change from 8 up to 32 wt.%, and the silicon content is expressed by a curve with an extremum. All burned down samples were exposed to X-ray analysis (Fig. 5).

It can be seen (Fig. 5b) that within the $0 \leq n < 3$ interval these samples contain titanium and silicon nitrides, as well as significant amounts of non-reacted silicon. It should be noted that burning the pure Ti_5Si_3 (diluent-free) in nitrogen yields a product containing titanium nitride, non-reacted silicide, silicon, as well as traces of silicon nitride (Fig. 5a). For n values

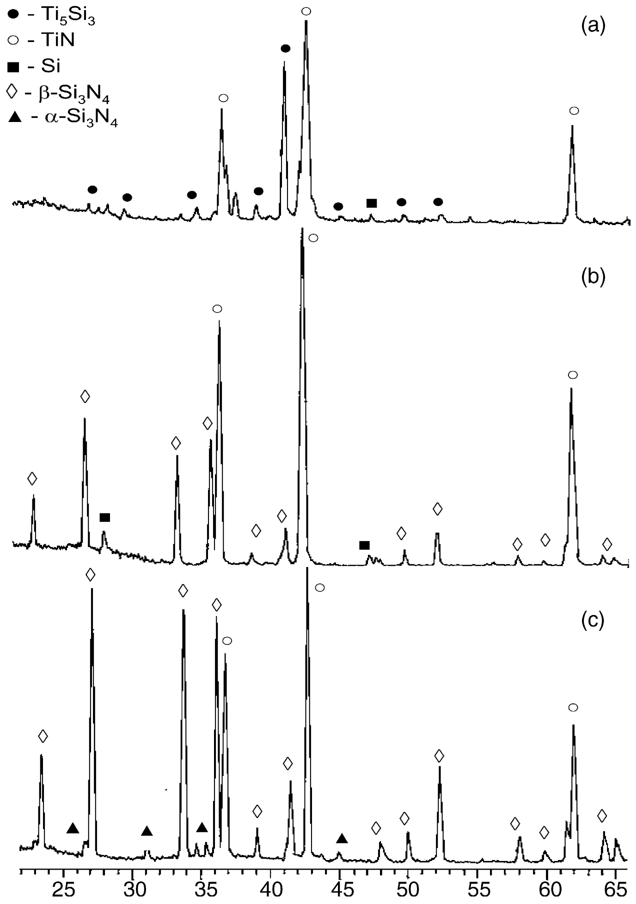

Fig. 5. XRD patterns of combustion products for $Ti_5Si_3 + nSi_3N_4 + N_2$ system at various n: (a) $n = 0$, (b) $n = 1$ and (c) $n = 4.2$, $P = 5$ MPa.

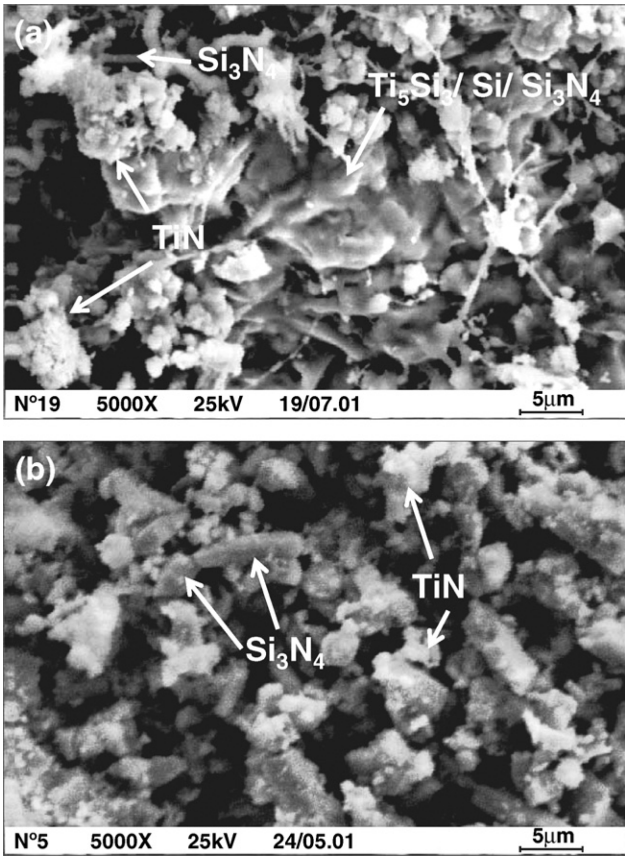

Fig. 6. Microstructural features of combustion products for $Ti_5Si_3 + N_2$ (a) and $Ti_5Si_3 + 4.2Si_3N_4 + N_2$ (b) systems.

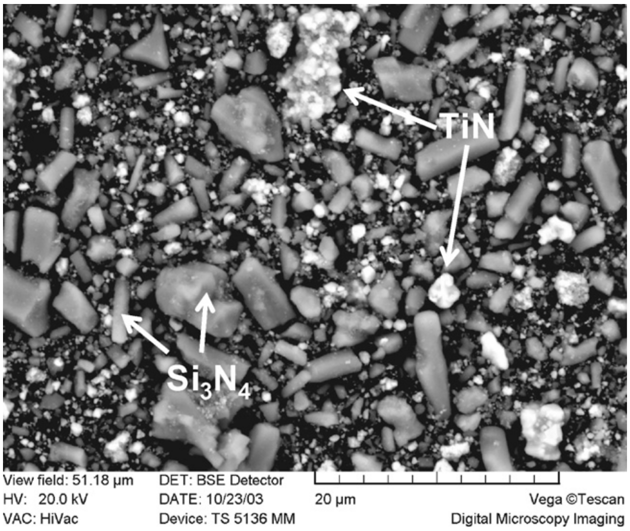

Fig. 8. Microstructure of the 30% TiN–70% Si_3N_4 composite.

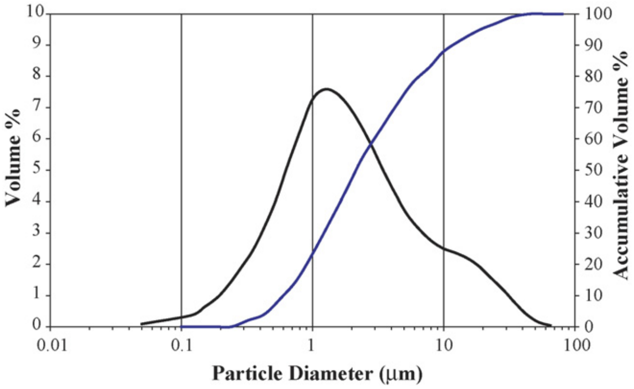

Fig. 9. Particle size distribution of 30% TiN–70% Si_3N_4 composite.

from 3 to 4.5, two-phase Si_3N_4–TiN products were formed. Here both the modifications (α- and β-) of Si_3N_4 were detected (Fig. 5c). Microstructural examinations have illustrated that the products obtained at combustion of pure Ti_5Si_3 contains alloyed segments formed from a melt (Fig. 6a). The products obtained with the use of Si_3N_4 as a diluent are characterized by a more particulate structure (Fig. 6b).

For further optimization of the synthesis conditions, experiments on the combustion of $Ti_5Si_3 + 4.2Si_3N_4$ mixtures at various nitrogen pressures were performed. The results obtained have indicated (Fig. 7) that this mixture does not burn at a nitrogen pressure of less than 2 MPa and within the pressure range of 2–5 MPa the combustion velocity is increased twofold (from 0.024 up to 0.05 cm/s), while the total increase of T_c is about 60 °C. This result points to an unequivocal relation between U_c and the nitrogen initial concentration in the

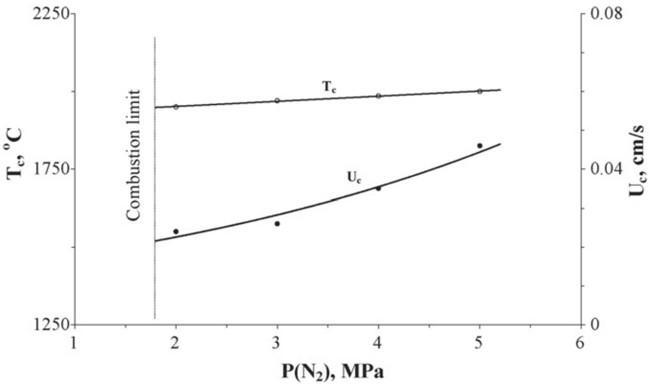

Fig. 7. Combustion temperature (T_c) and velocity (U_c) vs. nitrogen pressure for combustion of the $Ti_5Si_3 + 4.2Si_3N_4$ mixture.

Fig. 10. Fracture pattern of hot pressed disc.

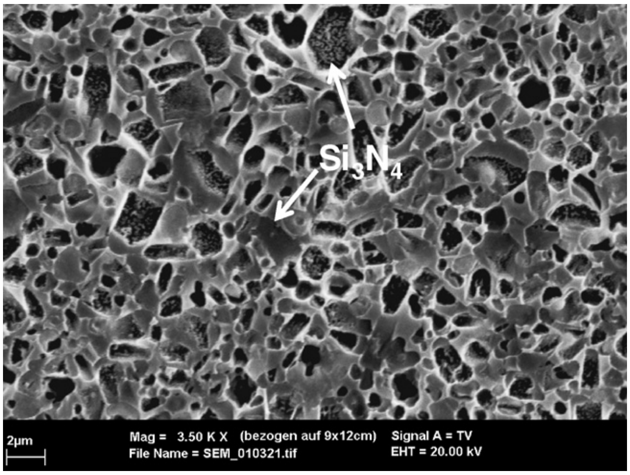

Fig. 11. Microstructure of 30% TiN–70% Si_3N_4 composite sample (TiN grains removed by over etching).

sample's pores. In all cases burned down samples contained two phases: TiN and Si_3N_4.

3.3. Compaction and characteristics of TiN–Si_3N_4 composite

Based on the combustion experiments carried out, composite powders of TiN–Si_3N_4 were synthesized, in which the content of titanium nitride varied between 30 and 35 wt.%. Microstructure examinations have shown (Fig. 8) that the characteristic sizes of the particles obtained are located in two main ranges: from 1 to 5 and from 20 to 30 μm.

The particle size distribution of a 30% TiN–70% Si_3N_4 composite is shown in the Fig. 9. It can be seen from the figure that approximately 25 vol.% of the particles are of submicron size. The diameter of 50 and 90 vol.% of particles is less than 2 and 13 μm, respectively.

Combustion synthesized 30% TiN–70% Si_3N_4 composite powder was compacted by hot pressing in nitrogen atmosphere. The density of the hot pressed samples was 0.97 of the theoretical density. After diamond grinding of the disc surfaces, ring on ring biaxial flexure tests were performed at room temperature. The fracture strengths for the disc were $\sigma_f = 306$ and 320 MPa. The fracture pattern on the tensile surfaces of the hot pressed discs after biaxial flexure testing indicated a medium to high strength (Fig. 10).

For studying microstructural features of compact samples plasma-etching was applied. A typical SEM micrograph is presented in the Fig. 11. It can be seen from the imprints in the glassy phase in Fig. 11 that the average grain has a size of about 2–5 μm and are not of an extremely elongated form (even through most of the grains have been removed within the etching process).

4. Conclusions

This study has successfully demonstrated that Si_3N_4–TiN composite powders without free silicon and having particulate structure can be synthesized from Ti_5Si_3 silicide accordance to accepted combustion laws. Optimum conditions for synthesis of TiN–Si_3N_4 ceramics containing 30–35 wt.% titanium nitride under the relative low nitrogen pressures (from 2 to 5 MPa) have been determined. The combustion synthesized 30% TiN–70% Si_3N_4 composite powders were hot pressed and compact samples were prepared, which had a medium to high biaxial flexural strength.

Acknowledgements

The authors would like to thank Roland Baechtold and Salvatore Fuso at EMPA for preparing SEM images of powders and particle sizing. Further they would like to thank the partial support by the European Community Fund "Copernicus-2" (Contract ICA2-CT-2000-10020).

References

[1] Yu.G. Gogotsi, F. Porz, The oxidation of particulate-reinforced Si_3N_4–TiN composites, Corrosion Sci. 33 (1992) 627–640.
[2] A. Bellosi, S. Guricciardi, A. Tampieri, Development and characterization of electroconductive Si_3N_4–TiN composites, J. Eur. Ceram. Soc. 9 (1992) 83–99.
[3] J.L. Huang, M.T. Lee, H.H. Lu, D.F. Lii, Microstructural, fracture behavior and mechanical properties of TiN/Si_3N_4 composites, Mater. Chem. Phys. 45 (1996) 203–210.
[4] B.T. Lee, Y.J. Yoon, K.H. Lee, Microstructural characterizations of electroconductive Si_3N_4–TiN composites, Mater. Lett. 47 (2001) 71–76.
[5] G. Blugan, J. Janczak-Rusch, J. Kuebler, Properties and fractography of Si_3N_4/TiN ceramic joined to steel with active single layer and double layer braze filler alloys, Acta Mater. 52 (2004) 4579–4588.
[6] G. Blugan, M. Hadad, J. Janczak-Rusch, J. Kuebler, T. Graule, Fractography, microstructure, and mechanical properties of commercial silicon nitride–titanium nitride composites, J. Am. Ceram. Soc. 88 (2005) 926–933.
[7] A.G. Merzhanov, Solid flames: discoveries, concepts, and horizons of cognition, Combust. Sci. Technol. 98 (1994) 307–336.
[8] H.C. Yi, J.J. Moore, Self-propagating high temperature (combustion) synthesis (SHS) of powder-compacted materials, J. Mater. Sci. 25 (1990) 1159–1165 (review).
[9] Z.A. Munir, U. Anselmi-Tamburini, Self-propagating exothermic reactions: the synthesis of high-temperature materials by combustion, Mater. Sci. Rep. 69 (7/8) (1989) 277–365.
[10] D. Kata, J. Lis, R. Pampuch, Combustion synthesis of multiphase powders in the Si–C–N system, Solid State Ionics 101–103 (1997) 65–70.
[11] L.S. Abovyan, H.H. Nersisyan, S.L. Kharatyan, R. Orru, R. Saiu, G. Cao, D. Zedda, Synthesis of alumina–silicon carbide composites by chemically activated self-propagation reaction, Ceram. Int. 27 (2001) 163–169.
[12] S.L. Kharatyan, Kh.V. Manukyan, H.H. Nersisyan, H.L. Khachatryan, Macrokinetic laws of activated combustion during synthesis of composite ceramic powders based on silicon nitride, Int. J. SHS 12 (2003) 19–34.
[13] G. Hillinger, V. Hlavacek, Direct synthesis and sintering of silicon nitride/titanium nitride composite, J. Am. Ceram. Soc. 78 (1995) 495–496.
[14] H. Wanbao, Z. Baolin, Z. Hanrui, L. Wenlan, Combustion synthesis of Si_3N_4–TiN composite powders, Ceram. Int. 8 (2004) 2211–2214.
[15] J.C. Han, G.Q. Chen, S.Y. Du, J.V. Wood, Synthesis of Si_3N_4–TiN–SiC composites by combustion reaction under high nitrogen pressures, J. Eur. Ceram. Soc. 20 (2000) 927–932.
[16] L.S. Abovyan, H.H. Nersisyan, S.L. Kharatyan, The Study of Combustion Laws in Spongy Titanium–Silicon System, Preprint IChPh NAS RA, Yerevan, 1991, p. 30 (in Russian).
[17] A.A. Shiryaev, Thermodynamic of SHS: modern approach, Int. J. SHS 4 (1995) 351–362.